

Karl W. Böer

Handbook of the Physics of Thin-Film Solar Cells

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ISBN 978-3-642-36747-2

ISBN 978-3-642-36748-9 (eBook)

DOI 10.1007/978-3-642-36748-9

Springer Heidelberg New York Dordrecht London

Library of Congress Control Number: 2014935163

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Printed on acid-free paper

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Foreword

It is an honour to have been asked to prepare this short foreword for Karl Wolfgang Böer's new "*Handbook of the Physics of Thin-Film Solar Cells*". I first met Karl back in 1976 when I visited "Solar One", the first solar powered house that Karl proposed back in 1972. On the same day, I also visited the Institute of Energy Conversion, also founded by Karl at the University of Delaware in 1972. The early work of the Institute focussed on copper sulphide/cadmium sulphide ($\text{Cu}_2\text{S}/\text{CdS}$) thin-film solar cells, the most promising thin-film cells of that era. Karl also served at that time as Chairman of Solar Energy Systems (SES) Inc. formed to commercialise these thin-film cells in conjunction with Shell Oil. These pioneering efforts have paved the way for the next wave of thin-film devices, those based on amorphous silicon, cadmium telluride and copper indium gallium diselenide, each treated in separate chapters at some length in the new Handbook. Karl is obviously in a strong and well-informed position to take on the challenge that preparing such a Handbook presents.

This is not Karl's first Handbook on the present scale. His monumental and influential "*Handbook of Semiconductor Physics*", first published in 1993 and subsequently updated, has clearly earned its place as the most comprehensive treatment of the field by a single author. The present Handbook follows in the tradition of the earlier one, providing in-depth treatment of the material and device physics required to fully understand the technology and operational characteristics of present thin-film solar cells and those that may emerge in the future. In his treatment, Karl brings to bear his decades of experience as both a researcher and educator in this field, as well as an often unique perspective on many of the underlying issues.

The Handbook is a particularly timely contribution given the rapid growth of the photovoltaic industry over the last decade and the technology's now established position as a cost-competitive, sustainable source of future energy on a large scale. The present Handbook will serve as a useful reference for those already in the field wanting to improve their understanding of the underlying materials science issues and also for the growing number of engineers and scientists likely to enter the field over the coming decade.

Bronte, Sydney

Martin Green

Preface

Based on my experience I have selected the parts of basic science that were helpful to my own research of solar cells, specifically on CdS based thin-film cells. As any, even somewhat more comprehensive treatises, a selection was made to include, beyond basic material science and the description of space charge effects, mostly CdS/Cu₂S and CdS/CdTe solar cells. These treatments are more comprehensive, including most recent references. The descriptions are excellent examples for the theoretical analysis of most other thin-film solar cells. The other thin-film solar cells, the CIS-group and amorphous Silicon are discussed in three shorter chapters at the end of this book.

Overall the book is structured to address most aspects of thin-film solar cells, starting from the history of their development and covering all features of these including most recent technologies, commercial viewpoints, and global material resources.

Commercial solar cells are based on materials that are handed to us often more than half a century ago and grown or deposited by conventional methods, doped to produce homo- or hetero-junction and then treated in various ways to improve their performance. All of this has become a routine and the selection of the processes was done often in respect to production economics, with an eye to minimize long term cell degradation. Only a few researchers were involved to search for new ways to make these cells or use totally new materials in the hope for performance improvement or economic production advantages and had to look for more basic material science properties.

This is one of the reasons behind composing this book. The other one is to help for a better understanding of solar cell operation.

In organizing this book I want to provide a toolbox for scientists and engineers for designing new solar cells, improving the conventional ones and understand better their operation. This toolbox needs to cover a wide field from the understanding of the material science aspects of the building blocks and structure of solar cells to the electronic configuration with its influence on the separate parts of the cell, and finally of the solar cell itself, analyzing it and interpreting its performance.

This is a complex field with constantly new developments, and to attempt a comprehensive description is impossible in a reasonable and useful single volume. Therefore a selection was made between basic facts and useful results that have more principle value than going into detail for which a long list of cited literature exists. This excludes more extensive description of analytical tools that are not dealt with in detail here, and many more fields of the rapidly developing science. But the book should give the foundation from which to build further research in the field.

As any selection, this is subjective to the judgment of the author and his specific experience. It will be therefore more detailed in the fields relating to cadmium sulfide and other adjacent fields that have proven helpful in designing my research and relating to the development of a variety of thin film solar cells. Whenever possible within the constraints of this book, important solar cell developments were guidance to select.

At many junctures, possible problems are pointed out in conventional manufacturing processes, or from model analyses that could lead to costly misjudgments and can be avoided by following some of the suggestions listed in this book.

In all, different segments of this book are more helpful to production engineers at the bench, while others may guide researchers into the development of new solar cells. Since it is open ended in which direction further investigation will lead, I have included some small sections of the book in fields that are not relevant to present solar cells, but may stimulate excursion into adjacent fields that provide already a wealth of evidence to stimulate creative advances. Many helpful tables are scattered throughout the text. The literature citations attempt to be more comprehensive, including historical publications of specific and related fields. An extensive subject index and a listing of useful formulae is appended.

In summary, this book is a compendium giving a comprehensive description of the basic physics relevant to the design and the analysis of solar cell materials. It starts from the basics of material science, describing the material and its growth, defect and electrical properties, the basics of its interaction with photons and the involved statistics, proceeding to space charge effects in semiconductors and *pn*-junctions. Most attention is given to analyze homo- and hetero-junction solar cells using various models and applying the field-of-direction analysis for discussing current voltage characteristics, and helping to discover the involvement of high-field effects in solar cells. The comprehensive coverage of the main topics of—and relating to—solar cells with extensive reference to literature helps scientists and engineers at all levels to reach a better understanding and improvement of solar cell properties and their production.

Appreciation: The book is based on four decades of teaching material science and solar cells, and equally important the constant interaction with my students and colleagues. The list is too long, but a very few may be mentioned with appreciation: Ulrich Kümmel, Peter Voss, Gustavo Dussel and Hank Hadley who worked with me early in my carrier. More recently I am especially grateful to many colleagues of the Institute of Energy Conversion (IEC) of the University of Delaware who directed me to recent development with extensive literature especially Bob Birkmeire, the director of IEC and his senior scientists, Steven Hegegedus and Brian McCandless.

I appreciate the dedicated work of Anita Schwarz from the Computer Program of the University of Delaware to facilitate my work in preparing the book. Special thanks are extended to Dieter Palme, a research associate over seven decades for helping me in the many aspects of completing this book. However, my deep gratitude rests with my wife, Renate, who has patiently forgiven me when at times I was a bit absentminded and has continued to encourage me throughout my endeavor.

Naples, USA

Karl W. Böer

Contents

Part I Material Science of Solar Cells Atomic Binding Forces

1	Crystal Bonding	3
1.1	Ionic Bonding	4
1.2	Covalent Bonding	6
1.2.1	Tetrahedrally Bound Elements	11
1.3	Mixed Bonding	11
1.3.1	Tetrahedrally Bonded Binaries	11
1.4	Metallic Bonding (Delocalized Bonding)	14
1.5	Van der Waals Bonding	15
1.6	Hydrogen Bonding	15
1.7	Intermediate Valence Bonding	16
1.8	Other Bonding Considerations	16
1.9	Atomic and Ionic Radii	16
1.9.1	Bond-Length Relaxation in Alloys	19
2	Crystal Structure	23
2.1	Crystal System	24
2.2	The Bravais Lattice	24
2.3	Crystal Classes (The Point Groups)	24
2.4	The Space Groups	26
2.5	Crystallographic Classification	27
2.5.1	Morphology of Crystals	27
2.6	The Reciprocal Lattice	28
2.6.1	Wigner-Seitz Cells and Brillouin Zones	28
2.7	The Semiconductors	29
2.7.1	Element Semiconductors	30
2.7.2	Binary Semiconductors	30
2.7.3	Ternary, Quaternary Semiconductors	32
2.8	Superlattice Structures	35
2.8.1	Superlattices and Brillouin Zones	35

2.8.2	Superlattice Deposition	36
2.8.3	Ultrathin Superlattices	36
2.8.4	Intercalated Compounds	37
2.8.5	Organic Superlattices	37
2.9	Amorphous Structures	38
2.9.1	Glass-Forming Building Blocks	40
2.9.2	Coordination Number and Constraints	41
2.9.3	Short-Range vs. Intermediate-Range Order	41
2.9.4	Network Structures	41
2.9.5	Matrix Glasses; α -Si:H	42
2.10	Quasicrystals	42
3	The Growth of Semiconductors	45
3.1	Nucleation	45
3.2	Growth Habit	46
3.2.1	Single Crystal Growth	46
3.2.2	Crystal Growth Techniques	47
3.3	Recrystallization	48
3.3.1	Slow Recrystallization	48
3.3.2	Stress-Enhanced Crystallization	48
3.3.3	Heating in the Presence of a Flux	49
3.3.4	Local Heating Induced Recrystallization	49
4	Crystal Defects	51
4.1	Defect Classifications	51
4.2	Point Defects	52
4.3	Donors and Acceptors	54
4.3.1	Defect Notation Within the Host Lattice	55
4.3.2	Substitutionals in AB-Compounds	56
4.3.3	Vacancies and Interstitials	56
4.4	Line Defects	57
4.4.1	Edge Dislocations	57
4.4.2	Screw Dislocations	57
4.4.3	The Burgers Vector	58
4.4.4	Dislocations in Compounds	58
4.4.5	Partial Dislocations in Semiconductors	58
4.4.6	Electronic Defect Levels at Dislocations	60
4.4.7	Dislocation Counting	61
4.4.8	Motion and Creation of Dislocations	62
4.4.9	Dislocation Velocity	62
4.4.10	The Frank-Read Source	63
4.4.11	Electroplastic Effects	63
4.4.12	Disclinations	64
4.5	Surface Defects, Planar Faults	64
4.5.1	Stacking Faults	64
4.5.2	Grain Boundaries	65
4.5.3	Metal/Semiconductor Interfaces	69

5	Photochemical Reactions	73
5.1	Defect-Chemical Reactions	73
5.1.1	Photochemistry by Giant Relaxation Oscillators	75
5.1.2	Other Examples	76
5.2	Photochemistry in Silver Halides	76
5.2.1	The Print-Out Effect	77
5.2.2	Film Sensitivity and Sensitization	77
5.3	Time-Dependent Photochemical Reactions	78
5.3.1	Photochemical Degradation	78
5.3.2	The Staebler-Wronski Effect	80
5.3.3	Fast Photochemical Processes	81

Part II Electronic Properties

6	Elements of Band Structure	85
6.1	The Proximity (Chemical) Approach	86
6.1.1	Electronic Structure of Amorphous Semiconductors	87
6.2	The Periodicity Approach	90
6.2.1	The Kronig-Penney Model	92
6.2.2	Periodicity of $E(\mathbf{k})$; Reduced $\mathbf{k}$ -Vector	95
6.3	Newtonian Description of a Quasi-free Electron	96
6.3.1	The Effective Mass	98
6.4	Periodicity vs. Proximity Approach	101
6.4.1	Band-Edge Fuzzing (Deviation from Periodicity)	101
6.4.2	Discrete Defect Level in the Band Gap	102
7	Bands and Band Gaps in Solids	105
7.1	Valence and Conduction Bands	105
7.1.1	Insulators and Semiconductors	107
7.1.2	Electrons and Holes	107
7.1.3	Metals	109
7.1.4	Semimetals and Narrow Gap Semiconductors	110
7.1.5	The Shape of Valence and Conduction Bands in Semiconductors	112
7.1.6	Constant Energy Surface Within the Brillouin Zone	112
7.1.7	The Effective Mass in Real Bands	115
7.1.8	The Conduction Bands	116
7.1.9	The Valence Band	117
7.1.10	Probing Bands with Cyclotron Resonance	122
7.1.11	Measurement of Effective Masses with Cyclotron Resonance	123
7.1.12	The Conduction Band at Higher Energies	125
7.1.13	The Momentum Effective Mass	125
7.1.14	The Effective Mass at Higher Energies	126
7.2	The Band Gap	128
7.2.1	Band Gap Variation	128

7.2.2	Band Gap Bowing	129
7.2.3	Band Gap Dependence on Temperature and Pressure . . .	131
7.2.4	Band Gap Narrowing with Heavy Doping	135
7.2.5	Shift of the Fermi Level into the Band at High Doping Densities	137
7.3	Bands in Superlattices	138
7.3.1	Mini-bands	139
7.3.2	Bands in Ultrathin Superlattices	142
7.3.3	Density of States in Mini-bands	144
7.3.4	Two-, One-, Zero-Dimensional Quantum Well Structures	144
7.3.5	Electronic States in Microcrystallites	145
7.4	Bands in Amorphous Semiconductors	146
7.5	Supercomputer	147
8	Equilibrium Statistics of Semiconductors	149
8.1	The Intrinsic Semiconductor	149
8.1.1	Electron and Hole Densities in Equilibrium	150
8.1.2	Level Distribution Near the Band Edge	150
8.2	Statistical Distribution Functions	153
9	Shallow Level Centers	155
9.1	Hydrogen-Like Defects	156
9.2	Charge Density Distribution, ESR, and ENDOR	159
9.3	The Chemical Identity	159
9.4	Hydrogen-Like Donors in Indirect Band-Gap Semiconductors . . .	161
9.5	Hydrogen-Like Acceptors	163
9.6	Bound and Resonant States	165
9.6.1	Shallow Defects in Compound Semiconductors	166
9.6.2	Higher Charged Coulomb-Attractive Centers	167
9.6.3	Over-Charged Donors or Acceptors	168
9.6.4	Metal-Ion Interstitials	169
10	Deep Level Centers	171
10.1	Mathematical Models of Deep Level Centers	172
10.1.1	Square Well Potential	172
10.2	Coulomb Tail and Deep Center Potential	173
10.3	Theoretical Methods to Analyze Defect Centers	175
10.3.1	Perturbative Methods	176
10.3.2	Cluster Calculation	176
10.3.3	Supercell Technique	176
10.3.4	Green's Function Technique	177
10.3.5	Semiempirical Tight-Binding Approximation	177
10.3.6	Supercomputer Use	177
10.3.7	The Jahn-Teller Effect	178
10.3.8	Crystal Field Theory	178

10.4	Examples of Deep Centers	180
10.4.1	Vacancies in Alkali Halides	180
10.4.2	F-Centers	180
10.4.3	Other Centers in Alkali Halides	183
10.4.4	Vacancies in Covalent Crystals	183
10.4.5	Self-interstitials	184
10.4.6	Antisite Defects	185
10.4.7	Hydrogen in Silicon	185
10.4.8	Substitutional Defects Replacing a Vacancy	186
10.4.9	Impurity and Site Symmetry	187
10.4.10	Isoelectronic Defects	188
10.4.11	Chalcogens in Si	189
10.4.12	Oxygen in GaP	190
10.4.13	Other Deep Defect Centers (<i>EL2</i> , <i>DX</i>)	191
10.5	Negative- <i>U</i> Centers	192
10.5.1	Negative- <i>U</i> in Chalcogenide Glasses	193
10.6	Shallow/Deep Center Instabilities	193
10.6.1	Metastable Lattice Relaxation	194
10.6.2	Transition Metal Impurities	194
10.6.3	Site Character	195
10.6.4	Charge Character	195
10.6.5	The Energy of Levels	198
10.6.6	The Level Spectrum of Various Point Defects	203
11	Defect Associates	207
11.1	Defect Center Pairs	207
11.1.1	Donor-Acceptor Pairs	207
11.1.2	Chalcogen Pairs in Si	210
11.1.3	Hydrogen Pairing in Silicon	210
11.2	Triple and Higher Defect Centers	211
11.3	Defect Clusters Due to Radiation Damage	213
12	Defect States and Band States	217
12.1	Band Tailing	217
12.2	Disorder Effects in Semiconductor Alloys	221
12.3	Impurity Influence, Fundamental Absorption	222
12.4	The Burstein-Moss Effect	223
13	Defects in Amorphous Semiconductors	227
13.1	Band Tails	227
13.2	Classes of Amorphous Semiconductors	229
13.3	Defect Types in Amorphous Semiconductors	229
13.3.1	Strain-Related Defects	230
13.3.2	Under- and Over-Coordinated Defects	231
13.3.3	Dangling and Floating Bonds	231
13.3.4	Deviation from Optimal Bonding Configuration	231

13.3.5	Doping in Semiconducting Glasses	233
13.4	Microcrystalline Boundaries and Voids	233
13.4.1	Recrystallization of Amorphous Si	234
13.5	Spin Density of Defects	234
13.6	Defect Spectrum in Amorphous Semiconductors	234
13.6.1	The Anderson Model	235
13.7	Band Tails and Localization	238
14	Defects in Superlattices	239
14.1	Defects in Compositional Superlattices	239
14.1.1	Isolated Lattice Defects in Superlattices	240
14.1.2	δ -Function Doping	241
14.2	Strained-Layer Superlattices	241
14.2.1	Superlattice-Induced Phase Changes	242
14.3	Doping Superlattices	244
15	Carriers and Their Motion	247
15.1	Carriers Within Their Bands	247
15.2	Sign Conventions	249
15.3	Electronic Conductivity	250
15.4	Joule's Heating	251
15.5	Electron Mobility	251
15.6	Gas-Kinetic Model for Electron Scattering	252
15.6.1	Electron and Hole Drift Current	253
15.7	Momentum and Energy Relaxation	253
15.7.1	The Average Momentum Relaxation Time	253
15.7.2	The Average Energy Relaxation Time	255
15.8	The Mean Free Path of Carriers	256
15.9	Phonon and Electron Drag	256
15.10	The Electric Field	257
15.11	Fields in Graded Band-Gap Semiconductors	259
15.12	Diffusion Currents	260
15.13	Maximum Diffusion Currents	262
15.14	Einstein Relation	262
15.15	The Electrochemical Fields	263
15.15.1	Quasi-Fermi Level	264
15.16	External and Built-in Fields	265
15.16.1	Penalties for a Simple Transport Model	266
15.17	Distributions in Built-in or External Fields	267
15.18	Mobilities in Built-in or External Fields	268
15.19	Summary: Potential Gradients and Currents	269
16	Carrier Transport	271
16.1	Boltzmann Equation	271
16.2	Transport Equations	273
16.3	Thermoelectric Effects	275

16.3.1	The Inhomogeneous Thermoelectric Effect	278
16.3.2	The Isothermal Hall Effect	278
16.3.3	Transverse Magneto-resistance	280
16.3.4	Geometry Factors in Galvanomagnetic Effects	283
16.3.5	Cyclotron Resonance	284
16.4	Carrier Quantum Effects in Magnetic Field	284
16.4.1	Quasi-free Carriers in a Strong Magnetic Field	284
16.5	Diamagnetic and Paramagnetic Electron Resonance	286
16.6	Density of States in Magnetic Fields	288
16.6.1	DeHaas-Type Effects	289
16.7	Magneto-phonon Effects	289
16.8	The Quantized Hall Effect	289
16.8.1	Fractional Quantum Hall Effect	292
17	Carrier Scattering at Low Fields	295
17.1	Types of Scattering Centers	296
17.2	Intravalley Scattering	297
17.3	Electron Scattering with Phonons	297
17.4	Elastic and Inelastic Scattering	298
17.5	Phonon Generation and Annihilation	299
17.6	Longitudinal Acoustic Phonon Scattering	300
17.6.1	Acoustic Phonon Scattering with Piezoelectric Interaction	302
17.7	Optical Phonon Scattering in Nonpolar Compounds	303
17.7.1	Optical Phonon Scattering in Polar Semiconductors	305
17.7.2	Scattering by Intrinsic Point Defects	307
17.8	Scattering by Neutral Lattice Defects	307
17.9	Scattering on Ionic Defects	308
17.10	Coulomb Scattering in Anisotropic Semiconductors	312
17.10.1	Quantum Corrections for Ion Scattering	312
17.11	Carrier-Carrier Scattering	313
18	Carrier Mobility Influenced by Larger Defects	315
18.1	Scattering at Dislocations	315
18.2	Scattering at Defect Clusters	316
18.3	Carrier Influence of Microcrystallite Boundaries	316
18.4	Influence of External Surfaces	318
18.5	Influence of Metal-Semiconductor Boundaries	319
19	Electron at High Fields	321
19.1	Electron Tunneling	321
19.1.1	Tunneling Through Rectangular Barrier	321
19.1.2	Tunneling Through Triangular or Parabolic Barrier	323
19.1.3	Band-to-Band Tunneling	324
19.2	Tunneling in a Three-Dimensional Lattice	325
19.3	Tunneling Currents	325

19.4	Tunneling Spectroscopy	327
19.5	Tunneling with Phonon Assistance	329
19.5.1	Tunneling with Trap Assistance	330
19.6	Tunneling with Photon Assistance (Franz-Keldysh Effect)	330
19.6.1	Influence of the Electric Field on Defect Levels	336
19.7	Field Effects in Superlattices	336
19.8	Ionization via Energetic Particles	337

Part III Photons

20	Basics of Optical Spectroscopy	341
20.1	Phenomenological Theory	342
20.2	Reflection, Transmission, and Absorption	342
20.2.1	Nonabsorbing Dielectrics	343
20.3	Semiconductors with Optical Absorption	344
20.4	The Complex Electrical Conductivity	348
20.4.1	Dielectric Polarization	349
20.5	Measurement of Optical Parameters	349
20.6	Reflectance and Transmissivity in Dielectrics	350
20.7	Reflectance and Transmittance in Semiconductors	353
20.8	Modulation Spectroscopy	358
20.9	Relation to Band-to-Band Transitions	359
21	Photon Interaction with Carriers	361
21.1	Carrier Generation	361
21.2	Photo-Ionization Cross Section	363
21.3	Photo-Ionization Cross Section Measurement	364
21.4	Reaction-Kinetics Evaluation	365
22	Carrier Recombination	367
22.1	Nonradiative Recombination	368
22.2	Capture Cross Section	368
22.2.1	Recombination at Coulomb-Attractive Centers	369
22.2.2	Geminate Recombination	371
22.3	Recombination in Amorphous Semiconductors	372
22.4	Nonradiative Recombination at Deep Centers	372
22.5	Competition Between Radiative and Nonradiative Recombination	374
22.5.1	Nonradiative Multiphonon Recombination	376
22.6	Auger Recombination	376
22.7	Plasmon-Induced Recombination	380
22.8	Statistics of Recombination	380
22.9	Trapping or Recombination	380
22.10	Electron and Hole Traps	380
22.10.1	Recombination Centers	381
22.11	Demarcation Lines	381
22.12	Thermal Equilibrium and Steady State	383

22.12.1 Thermal Equilibrium	383
22.12.2 Steady State	383
22.13 The Hall-Shockley-Read Center	384
23 Kinetics of Electron Distribution in Defects	387
23.1 Changes of Optical Excitation	388
23.2 Rise and Decay of Photoconductivity	388
23.2.1 Rise and Decay of Intrinsic Photoconductivity	389
23.2.2 The Method of Controlled Excitation	393
23.2.3 Photoconduction Time Constants	394
23.2.4 Small Sinusoidal Excitation	395
23.3 Kinetics Influenced by Trap Distribution	396
23.3.1 Ultrafast Photodetectors	397
23.4 Competing Excitation Processes	398
23.5 Optical Quenching	398
23.6 Orientation Relaxation	400
23.7 Changes in Thermal Ionization	400
23.7.1 Thermally Stimulated Luminescence	400
23.8 Thermally Stimulated Currents	403
23.9 Changes in Field Ionization	405
23.9.1 Field-Stimulated Current Curves	405
24 Photoconductivity	407
24.1 Intrinsic Photoconductivity	407
24.2 Extrinsic Photoconductivity	408
24.3 Influence of Traps on Photoconductivity	409
24.3.1 Shallow Traps	410
24.3.2 Trap Distribution	411
24.4 Recombination Centers in Photoconductors	412
24.5 Thermal Ionization of Activators	413
24.6 Sensitization of Photoconductors	415
24.6.1 Superlinearity of Photoconductivity	416
24.7 Photosensitivity and the Gain Factor	416
24.8 Photodetector Figures of Merit	418
24.8.1 Responsivity	418
24.8.2 Detectivity	419
24.9 Frequency Response	420
24.10 Current Continuity	420
24.10.1 Current Continuity in Ambipolar Photoconductors	421
24.11 Persistent Photoconductivity	423
 Part IV Photovoltaics	
25 Creation of Space-Charge Regions in Solids	427
25.1 One Carrier Abrupt Step-Junction	429
25.1.1 Electron Density, Space Charge, and Field Distribution	431
25.1.2 Electrode-Surface Charges	431

25.1.3	Field Distribution	432
25.1.4	Electrostatic and Fermi Potentials	432
25.1.5	Currents	436
25.2	External and Built-in Fields	437
25.2.1	Penalties for a Simple Transport Model	438
25.2.2	Built-in or External Fields	439
25.2.3	Distributions in Built-in or External Fields	439
25.2.4	Mobilities in Built-in or External Fields	440
25.3	Current Rectification	441
25.3.1	Dependence on the Doping Step-Size	442
25.4	Space-Charge Limited Current	444
26	The Schottky Barrier	447
26.1	The Classical Schottky Barrier	447
26.1.1	Schottky Approximation: Field and Potential Distributions	449
26.2	Zero Current Solution of the Electron Distribution	452
26.2.1	Diffusion Potential, Junction Field	452
26.3	Debye Length and Barrier Width	454
26.3.1	The Accuracy of the Schottky Approximation	455
26.3.2	Non-vanishing Currents	455
26.3.3	The Electron Density Distribution	457
26.4	Current–Voltage Characteristics	461
26.5	Modified Schottky Barrier	462
26.5.1	The Schottky Barrier with Current-Dependent Interface Density	463
26.5.2	Metal/Semiconductor Boundary Condition	463
26.5.3	Current–Voltage Characteristic in a Modified Schottky Barrier	465
26.5.4	The Shape Factor	467
26.5.5	Modified Boltzmann Range	467
26.5.6	DRO-Range	468
26.5.7	Electrostatic and Electrochemical Potentials in a Schottky Barrier	470
27	Minority Carriers in Barriers	473
27.1	Carrier Generation and Recombination	474
27.1.1	Thermal Excitation	475
27.1.2	Optical Excitation	476
27.1.3	Field Ionization	478
27.2	Trapping and Recombination	480
27.2.1	Electron and Hole Traps	480
27.2.2	Recombination Centers	481
27.3	Quasi-Fermi Levels, Demarcation Lines	481
27.3.1	Thermal Equilibrium and Steady State	483
27.3.2	Zero Net-Current, Thermal Equilibrium	484

27.3.3	Non-vanishing Current, Steady State	484
27.3.4	Current Continuity	486
27.4	Carrier Lifetimes	488
27.4.1	Large Generation, Optical Excitation	491
28	Minority Carrier Currents	493
28.1	Minority Carrier Currents in the Bulk	494
28.1.1	Thermal Excitation GR-Currents	495
28.1.2	The Diffusion Equation and Its Solution	495
28.1.3	Maximum GR-Currents	498
28.1.4	Pure Generation or Recombination Currents	499
28.2	GR-Current with Surface Recombination	499
28.2.1	Thermal GR-Current with Surface Recombination	500
28.2.2	The Effective Diffusion Velocity	502
28.2.3	Optical Excitation GR-Currents with Surface Recombination	503
28.2.4	Optical Excitation GR-Currents with Recombination at Right and Barrier at Left	503
28.2.5	Currents in Short and Long Devices	506
28.2.6	Collection Efficiency of Minority Carriers	507
28.2.7	Effective Diffusion Velocity for Optical Excitation	509
28.2.8	Optical vs. Thermal Carrier Generation	509
28.3	Drift-Assisted GR-Currents	509
28.3.1	Field-Influence in the Bulk	510
28.3.2	Analytical Solution of Diffusion with Constant Field	510
28.3.3	Drift-Assisted GR-Currents Without Surface Recombination at Right Electrode	511
28.3.4	Total Drift Assisted Minority Carrier Current	513
28.3.5	Justification for the Separation of Injection and Generation Currents	515
29	Schottky Barrier in Two-Carrier Model	517
29.1	Electron and Hole Currents in Barriers	517
29.1.1	Divergence-Free Electron and Hole Currents	518
29.1.2	GR-Currents in Schottky Barrier Devices	519
29.1.3	GR-Currents in the Space-Charge Regions	519
29.1.4	Field Influence in the Barrier Region	522
29.1.5	The Definition of the Carrier Density at the Splicing Boundary	523
29.1.6	Minority Carrier Density at the Metal/Semiconductor Interface	524
29.2	Schottky Barrier with Two Carriers	525
29.2.1	The Governing Set of Equations	525
29.2.2	Example Set of Parameters	526
29.2.3	Boundary Conditions	527
29.2.4	Example Solutions for a Thin Device	528

29.2.5	Carrier Distributions	530
29.2.6	Boltzmann Region for Minority Carriers	530
29.2.7	Demarcation Lines and Shockley-Franck-Read Recombination Centers	533
29.2.8	Currents in the Schottky Barrier	533
29.2.9	Quasi-Fermi Levels and Demarcation Lines	534
29.2.10	Electron and Hole Density Crossings	536
29.2.11	Carrier Inversion Layer with Consequences on the Space Charge	537
29.3	Schottky Barrier Device	538
29.3.1	Medium Width Device, Boundary Conditions	538
29.3.2	General Solution Behavior	538
29.3.3	Schottky Barrier in Wider Device and Violation of the Roosbroek Approximation	539
29.3.4	The Relative Contribution of Divergence-Free and GR-Currents in Schottky Barrier Devices	540
30	pn-Homojunctions	543
30.1	Simplified <i>pn</i> -Junction Model	544
30.1.1	Basic Features of the Simplified Model	544
30.1.2	Simplified Junction Model in Steady State	546
30.1.3	Junction Capacitance	547
30.1.4	The Current–Voltage Characteristic of the Simplified Junction	548
30.1.5	Contribution of the GR-Currents	549
30.1.6	The Diode Quality Factor	550
30.1.7	Relevance to Actual pn-Junctions	551
30.2	Abrupt <i>pn</i> -Junction in Ge	551
30.2.1	Governing Set of Equations and Example Parameters	551
30.2.2	Solution Curves for Thin Germanium <i>pn</i> -Junction	552
30.2.3	The Position of the <i>pn</i> -Junction	553
30.2.4	Junction Field and Potential Distribution	553
30.2.5	Quasi-Fermi Level and Current Distributions in the <i>pn</i> -Junction	555
30.2.6	Boltzmann-, DRO-, and DO-Ranges	556
30.2.7	Carrier Heating in <i>pn</i> -Junctions	557
30.2.8	GR-Currents and Divergence-Free Currents	558
30.2.9	The Current-Voltage Characteristic	560
30.3	Thick <i>pn</i> -Junction Device (Ge)	561
30.3.1	Changes in Current Contributions with Device Thicknes	561
30.3.2	The Quasi-Fermi Levels of the Thicker Device	563
30.4	The Si-Homojunction	565
30.4.1	The Current-Voltage Characteristics	566
30.5	More Complex Homojunctions	567
30.5.1	Linearly Doped Junction	567

30.5.2	High Minority Carrier Injection	568
30.5.3	Series Resistance Limitation	569
30.5.4	Position-Dependent Material Parameters	569
31	The Photovoltaic Effect	571
31.1	Carrier Generation and Recombination with Light	572
31.1.1	Photoconductors	573
31.1.2	Photo-emf and Photocurrents	574
31.1.3	Quasi-equilibrium Approximation	576
31.2	Reaction Kinetic, Balance	576
31.2.1	Trap-Controlled Carrier Densities	579
31.3	Simple Model of the Photodiode	580
31.3.1	Derived Photodiode Parameters	583
31.3.2	Resistive Network Influence on the Diode Characteristics	585
31.4	Device Cooling when Electric Energy is Extracted from Solar Cells Exited with Light	587
31.4.1	Detailed Energy Balance	587
32	The <i>pn</i>-Junction with Light	591
32.1	Open Circuit Conditions	592
32.1.1	Thin, Symmetric Si-Diode with Abrupt Junction	592
32.1.2	Current Distribution in a Symmetric <i>pn</i> -Junction	592
32.1.3	Solution Curves for Symmetric <i>pn</i> -Junction	595
32.1.4	Quasi-Fermi Levels and V_{oc}	596
32.1.5	Influence of Device Thickness	598
32.1.6	Influence of Surface Recombination	599
32.1.7	Influence of Recombination Center Density	599
32.1.8	Influence of the Generation Rate	601
32.1.9	Influence of the Doping Density	602
32.1.10	Parameter Dependence of V_{oc} for Insufficient Minority Carrier Supply	603
32.1.11	Influence of the Energy of the Recombination Center	604
32.2	Thin Asymmetric Si Diodes with Abrupt Junction	606
32.2.1	Recombination Through Charged Recombination Centers	606
32.2.2	Inhomogeneous Optical Excitation	608
32.2.3	Optical Excitation Only in a Thin Front Layer of the Device	608
32.2.4	Thin Asymmetric Junction Design	610
32.2.5	Asymmetric Bulk Thickness	611
32.2.6	Asymmetric Recombination	611
32.2.7	Asymmetric Generation	612
32.2.8	Asymmetric Doping	614
32.2.9	Thick Asymmetric Devices, Si Solar Cells	615
32.3	Non-vanishing Bias	618
32.3.1	Thin Symmetrical <i>pn</i> -Junction Device with Bias	619
32.3.2	Thin Asymmetric Si <i>pn</i> -Junction Device with Bias	621
32.3.3	Si-Solar Cell with Non-vanishing Bias	621

33 The Heterojunction with Light	625
33.1 The Cu ₂ S/CdS Solar Cell	627
33.1.1 The Current-Voltage Characteristics	628
33.1.2 Space Charge Effects in the Heterojunction	630
33.1.3 Influence of Electron Traps in CdS	630
33.1.4 Influence of a Compensated Layer near the Hetero-Interface	633
33.1.5 Influence of a Field-Induced Depletion of Hole Traps	634
33.1.6 Influence of Field Quenching	635
33.1.7 Kinetic Effects of Solar Cell Characteristics	637
33.1.8 Voltage Drop Kinetics Method	638
33.1.9 Influence of Interface Recombination	641
33.1.10 Boundary Condition at the Interface	642
33.1.11 Information from the Exponential A-Factor	642
33.2 Lessons Learned from the CdS/Cu ₂ S Solar Cell	646
34 The CdS/CdTe Solar Cell	649
34.1 Production Methods of the CdS/CdTe Cell	649
34.1.1 Physical Properties of the CdS/CdTe Solar Cell	652
34.1.2 Crystallography	652
34.1.3 Defect Chemistry	652
34.1.4 Processing and Performance	653
34.2 Electrical Properties of the CdS/CdTe Solar Cell	654
34.2.1 Cell Degradation	656
35 CdS/CdTe Analysis and Modeling	659
35.1 Simple Mathematical Models	660
35.2 Model Application	661
36 Basic Physics Discussion of CdS/CdTe	665
36.1 Introduction	666
36.2 Field Distribution in the CdS Side of the Junction	666
36.2.1 High-Field Domain	668
36.2.2 Domain Analysis	668
36.2.3 Direct Experimental Evidence of the High-Field Domain	671
36.2.4 Relevance of the High-Field Domain to the Hetero-Junction	671
36.2.5 Why is Only CdS such an Advantageous Cover-Layer?	672
36.3 Consequences of the Field-Quenching for the Interband Connection	672
36.4 Summary and Conclusions	673
37 Stationary High-Field Domains as Tools	677
37.1 Introduction	678
37.2 Mathematical Analysis (Field-of-Direction-Method)	679

37.3	Determination of the Work Function as Function of the Optical Excitation	681
37.4	Determination of the Field Dependence of the Hall Mobility	681
37.5	Stationary Domains Improve Efficiencies of Solar Cells	681
37.5.1	Virtual Cathode	682
37.6	Anode-Adjacent Domain at Higher Fields	683
37.7	Transition Between the Two Types of Stationary Domains	686
37.7.1	Stabilizing by the Domain in the Pre-breakdown Range	687
37.8	Conditions for Stationary High-Field Domains to Occur	687
37.9	Nonstationary (Moving) High-Field Domains	688
37.10	Summary	689
38	Commercial Use of CdS/CdTe	691
38.1	History of the CdS/CdTe Solar Cell	691
38.2	Why is Cadmium Sulfide the Only Compound?	693
38.3	Economical Aspects of Thin-Film Solar Cells	695
38.4	Cd Toxicity and Te Supply	696
38.5	Larger Recent CdS/CdTe Panel Deployments	697
39	The CdS/CuInSe₂ Solar Cell	699
39.1	Introduction	699
39.2	History	699
39.3	Material Properties	700
39.4	Electronic Properties	701
40	The CdS/Cu(InGa)Se₂ Solar Cells	703
40.1	Introduction	703
40.2	History	703
40.3	Material Properties	704
40.3.1	Structure and Composition	704
40.3.2	Optical Properties and Electronic Structure	705
40.3.3	Electronic Properties	705
40.3.4	Surface and Grain Boundaries	706
40.4	Deposition Methods	707
40.4.1	Substrate Effects	707
40.4.2	Back Contact	708
40.4.3	Deposition Methods	708
40.4.4	Precursor Reaction Processes	709
40.5	Junction and Device Formation Using CdS	710
40.5.1	Interface Effects	711
40.5.2	Transparent Contacts	711
40.5.3	High-Resistance Buffer-Layers	712
40.5.4	Device Completion	712
40.6	Device Operation	713
40.6.1	Light-Generated Current	713
40.6.2	Recombination	715

40.6.3	The Cu(InGa)Se ₂ /CdS Interface	717
40.6.4	Wide and Graded Band-Gap Solar Cells	718
41	Amorphous Silicon Solar Cells	721
41.1	History of Amorphous Silicon Solar Cells	721
41.2	Designs of Modern α -Si:H Solar Cells	722
41.3	α -Si:H-Related Solar Cells	723
41.3.1	Multijunction Solar Cells	723
41.3.2	α -Si:H Followed by a Micro-crystalline Si Layer	723
41.3.3	Staebler–Wronski Effect	723
41.4	Atomic and Electronic Structure of α -Si:H	724
41.4.1	Atomic Structure	724
41.4.2	Defects and Metastability	725
41.4.3	Electronic Density-of-States	726
41.4.4	Band Tails, Band Edges, and Band-Gaps	726
41.4.5	Defects and Gap States	727
41.4.6	Phosphorus Doping Puzzle	727
41.4.7	Alloying and Optical Properties	728
41.4.8	Nanocrystalline Silicon	729
41.5	Depositing Amorphous Silicon	729
41.5.1	Deposition Techniques	729
41.5.2	RF Plasma-Enhanced Chemical Vapor Deposition (RF-PECVD) at 13.56 MHz	729
41.5.3	PECVD at Different Frequencies	730
41.5.4	Hot-Wire Chemical Vapor Deposition	731
41.5.5	Other Deposition Methods	731
41.5.6	Hydrogen Dilution	732
41.5.7	Alloys and Doping	732
41.6	Theory of the α -Si <i>pin</i> Cells	733
41.6.1	Electronic Structure of a <i>pin</i> cell	733
41.6.2	Influence of Thickness on Power Generation	733
41.6.3	Optical Design of α -Si:H and nc-Si:H Solar Cells	734
41.7	Multijunction Solar Cells	736
41.7.1	Advantages of Multi-junction Solar Cells	736
41.7.2	Alloys to Vary the Band Gap	737
41.7.3	Bandgap Grading of α -SiGe <i>i</i> -Layers and of α -SiC	737
41.7.4	α -Si/ α -SiGe Tandem and α -Si/ α -SiGe/ α -SiGe Triple-Junction Solar Cells	738
Appendix A	Important Formulae	739
A.1	General Formulae	739
A.2	Characteristic Lengths in Solids	740
A.3	Effective Masses	740
A.4	Phonons, IR Dispersion, and Thermal Properties	741
A.5	Electron-Lattice Interaction	742
A.6	Optical Properties	743

A.7	Quasi-hydrogen and Deep Well States	744
A.8	Equilibrium Densities, Energies, Velocities	745
A.9	Transport Properties	746
A.10	Characteristic Times and Frequencies	748
A.11	Photoconductivity	749
A.12	Field Effects	750
A.13	Tables of Constants	751
Bibliography		755
Index		869

Abbreviations

List of symbols

A	wave amplitude vector
A	atom A
A	amplitude factor, area, Auger coefficient, Madelung constant acceptor, warped valence band factor
A_a	electron affinity of acceptor
A_E	asymmetry factor for band gap
$A_{\delta F}$	factor quantifying gap narrowing
A_o, A_{oct}	surface area of spherical (octahedral) atomic cavity
a	lattice vector in x direction ($a = a $), acceleration
a	lattice constant for cubic lattice, or in x direction
a_H	Bohr radius of hydrogen atom
a_{qH}	quasi-hydrogen radius
a_ℓ	distance between defects on dislocation line
a_t	distance between traps
a_T	heating rate
B , B_0	magnetic induction, value of
B	atom B
B	amplitude factor, module of compression, exponential tunneling factor, Auger coefficient
$\bar{B}$, B'	warped valence band factors
$B_{\delta e}$	factor quantifying gap narrowing
B_z	Brillouin zone
b	lattice vector in y direction ($b = b $), Burgers vector
b	gap bowing parameter
b/a	ionicity of bonding [Eq. (1.8)]
C	atom C
C	base-centered Bravais lattice, elasticity module, Coulomb-binding energy
C_v, C_p	heat capacity for constant volume or pressure

$\tilde{C}$	warped valence band factor
$C_{\delta e}$	factor quantifying gap narrowing
$\mathbf{c}$	lattice vector in z direction ($c = \mathbf{c} $)
c	light velocity
c_l	elastic constant for longitudinal deformation
c_a, c_c	proportionality constant
$c_c(k), c_n(k)$	coeff. of expansion of eigenfunction of band c or n
c_{cv}	recombination coefficient
c_a	numerical proportionality factor
c_{ik}	capture coefficient for carrier from i^{th} to k^{th} level, adiabatic elastic stiffness constant
c_{ijk}	third order elastic constants
c_{ijkl}	tensor moduli of elastic stiffness
$\mathbf{D}$	electric displacement
D	donor, diffusion constant
D_o	optical deformation potential
D_n, D_p	diffusion coefficient
D_{ik}	diffusion tensor
$D_{\delta p}$	factor quantifying gap narrowing
d	distance between electrodes or dislocations, platelet thickness
d_c	critical thickness for dislocation formation
$\mathbf{E}$	electric field vector in electromagnetic radiation
E	energy, elasticity (Young's) modulus
E_0	Urbach param., unit field in electromag. radiation
E_F	Fermi energy
E_{Fn}, E_{Fp}	quasi-Fermi energy
E_c, E_v	lower conduction and upper valence band edge
E_{qH}	quasi-hydrogen ionization energy
E_g	band gap
$E_{g,\text{exc}}$	gap energy for exciton generation
E_d, E_a, E_t	energy of donor, acceptor, or trap
$\tilde{E}_d, \tilde{E}_a$	distance of donor or acceptor from E_c or E_v
E_{da}	donor-acceptor pair level energy
E_{dd}	energy of deep donors
E_{Dn}, E_{Dp}	demarcation line
E_R, E_r	relaxation energy, energy of recombination centers
E_a	activation energy
E_S, E_{Fr}	Schottky energy, Frenkel energy
E_n	specific subband, energy of n^{th} level
$E_{\delta p}$	factor quantifying gap narrowing
E_i	ionization energy
E_m	blackbody emission
E_μ, E_ν	energy levels for a transition from ν to μ
$\mathcal{E}$	electric field of an electromagnetic wave
e	elementary charge, electron

e^*	static effective charge
$\mathbf{e}, \hat{\mathbf{e}}$	unit electric vector of electromagnetic radiation
e_c, e_s, e_t	Callen, Szigetti, or transverse effective charge
e_i	reduced index strain components (Voigt notation)
e_{ik}	excitation coefficient from i^{th} to k^{th} level, strain components
$\mathbf{F}$	electric field vector
F	field, Helmholtz free energy
F^*	average field from ionized impurities
F, F'	F-center, F'-center
$F_{t,l}$	transversal and longitudinal field
F_l	local field
F_i, F_e	built-in (internal) or external field
F_n	Fermi integral
$\tilde{F}$	Franz-Keldysh function
F_{op}	screening parameter
$\mathcal{F}$	force
f	distribution function (preferably Fermi-Dirac), fractional displacement = $\gamma \bar{u}/a$
f_0	distribution function in equilibrium
f_n, f_p	Fermi function for electrons or holes
f_i	oscillatory strength
$f_{\text{FD}}, f_{\text{BE}}$	Fermi-Dirac or Bose-Einstein distribution function
f_B	Boltzmann distribution function
G	Gibbs free energy, shear modulus, number of states
$\tilde{G}$	Franz-Keldysh function
G_o	photoelectric gain factor
g	density of states, line shape function, Landé g-factor
g, g_n, g_p	generation rate
g_o	optical generation rate
$\mathbf{H}$	Hamiltonian, magnetic field vector
H_s	surface energy
H	Helmholtz free energy (or enthalpy), hexagonal Bravais lattice
H_0	Hamiltonian for unperturbed bands
h	Planck's constant; $\hbar = h/2\pi$, Miller index
$h^\bullet$	hole
I	current, transfer integral, body-centered Bravais lattice
I_d	ionization energy of donor
I, I_L	optical intensity, luminescence intensity
I_n	normalization integral
$J, J_{\mu\nu}$	joint density of states (J_{cv})
j	current density
j_i	diffusion current
j_n, j_p	electron and hole current
$\mathbf{K}$	reciprocal lattice vector, exciton momentum vector
K	mass reaction law constant, electromechanical coupling constant

K_a	anisotropy factor for mobility
$K_{1,2}$	modified Bessel functions
$\mathbf{k}$	momentum (wave) vector (for electrons)
k_x, k_y, k_z	components of momentum vector (= wave number)
k_F	wave number at Fermi level
k	Boltzmann constant, Miller index
$\mathbf{L}$	angular momentum operator
L	sample length, Kane parameter
L_D	Debye length
L_c, L_n, L_p	diffusion length
L_d	drift length
$\hat{\mathbf{L}}$	angular momentum matrix
l	length, angular quantum number, Miller index
l_B	superlattice barrier width
l_i	box dimensions ($i = x, y, z$)
$l_{1,2}$	superlattice layer widths
l_z	width (superlattices or quantum wells)
l_{coh}	coherence length
l_n	<i>Schubweg</i> , drift length
l_ω	fracton localization length
M	mass of atom (ion), Kane parameter
M_i	critical points (M_0, M_1, M_2, M_3)
$\mathbf{M}$	momentum matrix element (M_{ik} for transitions from state i to state k)
M_r	reduced ion mass
M_r^*	effective atomic weight
m	mirror axis, coordination number, Born potential exponent
$\overline{m}$	average coordination number
$\hat{m}$	integral number, shell number, order number, coordination number
$\hat{m}_x, \hat{m}_y, \hat{m}_z$	effective mass-type parameters
m_n, m_p	effective mass of electron or hole
m_l, m_t	longitudinal or transverse effective mass (el)
m_0	rest mass of electron
m^*	effective mass of either electron or hole
$m_{\mu n}, m_{\mu p}$	mobility effective mass
$m_{\text{nds}}, m_{\text{pds}}$	density of state effective mass
m_r	reduced effective mass (exciton)
m_x, m_y, m_z	effective mass in x, y, z directions
m_j	spin quantum number
N	density of atoms or ions or states, valency, Kane parameter
$\mathcal{N}$	number of particles
N_{AM}	critical Anderson-Mott density
N_{Av}	Avogadro's number
N_c, N_v	density of states at cond. and valence band edge

N_{2c}	density of state in two-dimensional structures
N_I	density of ionized lattice defects
N_L	density of lattice atoms
N_S, N_F	density of Schottky or Frenkel defects
N_{sc}	density of scattering centers
N_d, N_a	donor or acceptor density
N_{eff}	effective density of donors (acceptors) = $N_d - N_a$
N_t, N_{tn}, N_{tp}	trap density
N_V	density of vacancies
n_1, n_2, n_3	integer number
n_x, n_y, n_z	integer numbers
n	electron density, principal qu. number, band index
$\hat{n}, \hat{n}_i$	integral number, number of interstitial distances
n_q	running number, quantum number
$\hat{n}_q$	principal quantum number
n_d, n_a	electrons in donors or acceptors
n_i	intrinsic carrier density
n_r	index of refraction (n_{ra} of an external medium)
n_t, n_{tn}, n_{tp}	electron density in traps
n_M	Mott density
n'	electron
$n_{\uparrow}, n_{\downarrow}$	spin occupation number (0, 1)
P	polarization
P _{rc}	momentum matrix element
P_l	angular projection operator
P	primitive Bravais lattice, normal momentum coordinate, optical transition probability, Ehrenreich parameter
P_i	probability for ionization
p	momentum vector
p	momentum ($= mv = \hbar k$), pressure, hole density
p_A	momentum component in direction of electric vector
p_d, p_a	holes in donors or acceptors
p_{phot}	photon momentum
$Q, \Delta Q$	heat of formation, heat flux, Joule heat
Q	configuration coordinate, normal coordinate
q	momentum (wave) vector for phonons
q	wave number for phonons
R	radius vector of atoms or ions
R	resistance, $R = Nk$ gas constant, microcrystallite radius, rhomboedric Bravais lattice, reflectance
R_A	Anderson distance
R_i	coordinates of atoms
R_{ik}	transition rate of carriers from i^{th} to k^{th} level
R_o, R_0	optical reflectivity, reflectance for normal incidence
R_H	Rydberg, Hall constant

r	radius vector, vector in real space
r_e, r_h	radius vector to an electron or hole
<i>r</i>	interatomic distance
<i>r_e</i>	equilibrium distance between atoms
<i>r_{da}</i>	donor-acceptor pair distance
<i>r_i</i>	coordinates of electrons, scattering radius for ions
<i>r_{ij}</i>	distance from <i>i</i> th to <i>j</i> th particle (carrier)
<i>r_o, r₀</i>	optical reflectivity, reflectance for normal incidence
<i>r_r</i>	radiative recombination rate
<i>r_A, r_B</i>	atomic (ionic) radii of atoms (ions) A or B
<i>r_c</i>	Lorentz circle radius
<i>r_{pol}, r_{pl}, r_{ph}</i>	polaron radius (for electrons and holes)
<i>r_n, r_p</i>	recombination rate
<i>r_{qH}</i>	quasi-hydrogen radius
<i>r_{kT}</i>	quasi Bohi radius for $E = kT$
<i>r_s</i>	scattering radius of screened Coulomb center
S	Poynting vector
<i>S</i>	entropy, scattering probability, Huang-Rhys factor
<i>S_c</i>	screening length
<i>S_E</i>	equi-energy surface in momentum space
<i>S_k, S_ω</i>	surface in <i>k</i> space or <i>q</i> space (in energy space)
<i>S_s</i>	structure factor
<i>S_x, S_y, S_z</i>	spin component in <i>x</i> , <i>y</i> , <i>z</i> -direction
S	stress
<i>s</i>	occupation number
<i>s_i</i>	sign matrix (± 1)
<i>s_{ik}</i>	elastic compliance constants
<i>s_n, s_p</i>	capture cross section
<i>s_r</i>	recombination cross section
<i>s_o</i>	optical excitation cross section
<i>s_∞</i>	cross section in gas kinetic model
T	temperature, lattice temperature, transmittance
T	tension, force
T_{ik}	stress tensor
T_e	tunneling probability
<i>T_L</i>	lattice temperature
<i>T_e</i>	electron temperature
<i>T, T_o, T₀</i>	transmissivity, transmittance for normal incidence
<i>T_c</i>	critical temperature for superconductivity
<i>T_m</i>	melting point
t	translational symmetry operation
<i>t</i>	time
<i>t_n, t_p</i>	transit time
<i>U</i>	energy, thermal lattice energy, Hubbard correlation energy, potential energy in exciton Hamiltonian

U_0	matrix element
$\mathbf{u}$	displacement vector
u	amplitude factor of Bloch function, specific internal energy, anion displacem. param., atomic displacem.
u_n	displacement of the n^{th} atom
V	applied voltage (bias), potential, potential energy, vacancy
V_{cc}	central cell potential
V_0	barrier height potential
$\mathcal{V}$	volume
$\mathcal{V}_u$	volume of unit cell
$\mathcal{V}_m$	molar volume
$\mathbf{v}$	velocity vector
v	velocity, light velocity in dielectric medium
v_e, v_n	average electron velocity with field, without field
v_{diff}	diffusion velocity
v_l, v_t	longitudinal or transverse acoustic sound velocity
$v_{\text{rms}}, v_{\text{rms}}^*$	rms velocity of carriers ($v_{\text{rms}}^* = v_{\text{rms}}/\sqrt{6\pi}$)
v_g	group velocity ($= \nabla_q \omega(q) = \nabla_k \omega(k)$)
v_D	drift velocity
v_{Ds}	saturation drift velocity
v_s	sound velocity ($= \omega/q$)
$v_m, \hat{v}_m, v_m^*$	saturation velocities
W	characteristic energy for impact ionization, energy, Debye-Waller factor, statistical probability
$W_{\text{opt,ac}}$	deformation-potential interaction rates
W	heat (energy) current
X	exciton
$x = x_1$	x direction
$y = x_2$	y direction
Z	ionic charge
$Z_{\text{imp}}(r)$	impurity charge function
$z = x_3$	z direction
z	number of ways to realize a defect, coordination number
α	angle between $\mathbf{b}$ and $\mathbf{c}$, fine struct. const., thermal expansion coeff., thermoelectric power, bond binding force const., geometry factor, anisotropy factor
α_α	van der Waals attraction constant
α_β	Wannier function
$\tilde{\alpha}$	impact ionization rate
α_o	optical absorption coefficient (cm^{-1})
α_c	Fröhlich's coupling constant
α_A, α_{L-R}	sound attenuation
α_r	van der Waals repulsion constant
α_S	Seraphin coefficient
$\alpha_\tau = \alpha_0/\tau_m$	normalized optical absorption per τ_m

α_{ik}	transport coefficients
α_v	thermal volume expansion coefficient
β	angle between a and c , force (spring) const., nonlinearity const., hole mobility ratio (μ_l/μ_h), Born repulsion param. (also β'), bond-bending force const.
β, β_n, β_p	exponent for field dependence of μ, μ_n, μ_p
$\tilde{\beta}, \tilde{\beta}_1$	expansion coeff. for warm/hot electron mobility
β_c	compressibility
β_S	Seraphin coefficient
β_E	temperature coefficient of E_g
β_{ik}	transport coefficients
γ	angle between a and b , damping factor, Lindemann parameter, anisotropy factor, adiabatic parameters, penetration depth for Meissner-Ochsenfeld eff., Born repulsion parameter
$\gamma_{1,2,3}$	Luttinger parameters
γ_A, γ_{L-R}	sound attenuation
γ_a	anisotropy factor for $m^*\varepsilon$
γ_o, γ_c	optical auxiliary function
γ_t	tunneling rate
γ_{ik}	transport coefficients
γ_{pc}	photochemical reaction rate
Γ	central point in Brillouin zone, Grüneisen parameter
Γ_G	Gaussian shape factor
Γ'	warped valence band factor
δ	Dirac symbol, fractional charge, small change, dielectric loss: $\tan \delta$, lattice anharmonicity parameter
δ_{ik}	Kronecker Symbol
δ_o	phase shift
$\delta_E, \delta_n, \delta_\mu$	second-order temperature coefficient
δ_i, δ_j	shift of demarcation line
δ_{pc}	photochemical dissociation rate
Δ	displacement, direction along (100), energy gain for Cooper pairs
Δ_0	spin-orbit splitting energy
$\Delta_{1/2}$	half width of line
Δ_1	crystal field splitting
ΔE_B	band width
ΔE_c	collision-broadening band width
ΔE_d	activation energy for variable range hopping
ΔE_i	impurity band width
ΔE_t	thermal activation energy
ΔQ	formation enthalpy
ΔV_b	intergrain barrier potential
$\varepsilon, \tilde{\varepsilon}$	dielectric constant, complex dielectric constant
ε_{ik}	deformation coefficients
ε_0	vacuum dielectric constant

ε_L	dielectric constant due to lattice oscillation
ε^*	effective dielectric constant
$\varepsilon_{\text{st}}, \varepsilon_{\text{opt}}$	static and optical dielectric constant
$\varepsilon', \varepsilon''$	real and imaginary parts of ε
ε_{ik}	dielectric constant tensor
ε_r	reduced dielectric constant
$\varepsilon_{\parallel}, \varepsilon_{\perp}$	dielectric const. $\parallel$ or $\perp$ to optical axis (c -axis)
ϵ	relaxation parameter
Θ	Debye temperature ($= \hbar\omega_0/k$)
Θ_i	Debye temperatures for intervalley phonons
Θ_U	characteristic temperature for Umklapp processes
θ	angle
θ_H	Hall angle
κ	extinction coefficient, isothermal compressibility, thermal conductivity
K_A	Anderson factor
K_c	thermal conductivity for electrons
λ	wavelength, mean free path, trans. matrix element
λ_{ph}	mean free path for phonons
λ_{scr}	screening length
λ_D	Debye-Hückel screening length (Debye length)
λ_{TF}	Thomas-Fermi screening length
λ_{DB}	De Broglie wavelength
Λ	direction along (111)
Λ_{δ}	factor to quantify band-gap narrowing
μ	transition matrix element
μ, μ_0	magnetic susceptibility, permeability of free space
μ_n, μ_p	mobility for electrons or holes
μ_B	Bohr magneton
ν	frequency (in optical spectrum), Poisson ratio
ν_o	optical resonance frequency
ν_p, ν_l, ν_i	attempt-to-escape frequency
ν_s	scattering efficiency
$\nu_D, \nu_{Dd}, \nu_{Da}$	degeneracy factor for the band, donor or acceptor
Ξ_c, Ξ_d, Ξ_s	deformation potential: index d and s for dilatation and shear stress
ξ	alloying composition, correlation coefficient for V fluctuations, reduced energy ($= -(E_c - E_F)/(kT)$)
π	empirical line-shape parameter, Pellier coefficient
Π	Peltier coefficient
ρ	density of the material g/cm^3
ϱ	space-charge density, specific resistivity
σ	symmetry factor, electric conductivity
$\tilde{\sigma}$	complex electric conductivity
$\underline{\sigma}$	Pauli operator matrices, conductivity matrix
σ_n, σ_p	conductivity (for electrons or holes)

σ_{ik}	magnetoconductivity tensor
σ', σ''	real and imaginary part of σ
$\sigma_{\min}$	minimum metallic conductivity
Σ_i	surface charge
τ	characteristic time
τ_e	energy-relaxation time
τ_m	momentum-relaxation time
τ_{sc}	time between collisions
τ_i	intervalley scattering relaxation time
$\tau_{\text{sp}}, \tau_{\text{st}}$	spontaneous and stimulated recombination times
τ_r, τ_{nr}	radiative and nonradiative recombination times
τ_E	dielectric relaxation time
τ_t	transit time
τ_c, τ_n, τ_p	lifetime for carriers, electrons, or holes
τ_o, τ_1	rise and decay time constant
φ	electrochem. potential, wavefunction, gen. function
φ_n, φ_p	quasi-Fermi potentials
ϕ	angle of light beam in respect to reference surface
ϕ, ϕ_λ	photon flux, spectral photon flux
$\phi, \phi_{nq}, \phi_{nq\mathbf{k}}$	envelope function
Φ	wavefunction
χ	susceptibility, electronegativity, dielectric susceptibility
$\chi^{(1)}, \chi^{(2)}, \chi^{(3)}$	susceptibility tensor of i_1 rank
ψ	wavefunction, electrostatic potential ($= -V$)
ψ_o	optical auxiliary function
ψ_n, ψ_p	electrostatic potential for electrons or holes
ψ_{MS}	relative workfunction (metal/semiconductor)
Ψ_i	impurity wave function
Ψ_{MS}	metal-semiconductor workfunction
ω	angular frequency ($= 2\pi\nu$) for phonons
ω_o	resonance frequency
ω_a	evaluating frequency for Kramers-Kronig relation
ω_c	cyclotron resonance frequency
ω_D	Debye frequency
ω_i	atomic oscillation or intervalley phonon frequency
ω_p	plasma frequency
ω_r	breathing-mode frequency
ω_R	Raman frequency
$\omega_{\text{TO}}, \omega_{\text{LO}}$	transverse and longitudinal optical phonon
$\omega_{\text{TA}}, \omega_{\text{LA}}$	transverse and longitudinal acoustic phonons
Ω	solid angle
η	efficiency, tetragonal distortion
η_L	luminescence efficiency
η_t	trap availability factor
ϑ	Sasaki angle

ξ_{ijk}	polarization tensor
<i>Subscripts</i>	
c	carrier (electron or hole)
d	lattice defect
dd	deep level defect
dr, diff	drift, diffusion
exc	exciton
e	equilibrium
f	foreign atom
i, e	internal, extremal
fri	frozen-in
ph	phonon
r	reduced
t	traps
$t, l; T, L$	transverse, longitudinal
th	threshold
n	band index
O	original, basic
o, O	optical
n, p	for electrons or holes
h, l	heavy, light; high, low
l, s	large, small
$i, 1$, or x	in x direction
$k, 2$, or y	in y direction
$l, 3$, or z	in z direction
$\parallel, \perp$	parallel, perpendicular
st, opt	static, optical
ds	density of states
dir, ind	direct, indirect
forb	forbidden
mp	most probable
nq	quantum number
v, c	valence or conduction band
i	interstitial, intrinsic
d, a, t	donor, acceptor, traps
eff	effective
f, s	fast, slow recombination centers
L	luminescence
U	Umklapp process
B, W	barrier, well
perc, hop	percolation, hopping
pol	polaron
0	undisturbed (in thermal equilibrium)
qH	quasi-hydrogen
β	band index

$\pm$ solutions according to sign of square root

Superscripts

' derived variable
 ' negative
 • positive
 $\times$ neutral with respect to the lattice
 * effective
 ^ used for distinction
 (R), (I) real part, imaginary part

Special symbols

i, j, k unit vectors in x, y, z directions
 ∇ ∇ , differential operator $\frac{\partial}{\partial x}\mathbf{i} + \frac{\partial}{\partial y}\mathbf{j} + \frac{\partial}{\partial z}\mathbf{k}$
 Δ difference
 $\sum$ sum
 $\sum'$ sum, except for equal indices
 $\prod$ product
 $[A]$ density of atoms A
 $\langle x \rangle$ average value of x
 $\overline{\tau}$ average of τ
 $\underline{\mu}$ matrix of μ_{ik}
 δE small increment of E
 Re, Im real part, imaginary part
 P principal value
 i $\sqrt{-1}$
 θ, ϕ angle in spherical coordinates
 Ω solid angle
 $\underline{1}$ unity matrix
 $\vec{\mathcal{F}}$ vector of $\mathcal{F}$
 $\mathbf{F}$ vector of F

Part I
Material Science of Solar Cells Atomic
Binding Forces

Chapter 1

Crystal Bonding

Abstract The bonding of atoms is described as function of the electrostatic forces, covalent bonding, mixed bonding van der Waals bonding hydrogen and metallic bonding, and Born repulsion, yielding equilibrium distance and ionic or atomic radii that are tabulated. Repulsive potential softness parameters and Mohs hardness are tabulated. Close packing of ions/atoms determine ordering preferences. Compressibility and Madelung constants, lattice constants and bond length are discussed and tabulated (Table 1.2). Electronegativity, ionicity and effective charges for numerous AB-compounds are listed. Atomic electron density profiles are given.

The bonding of atoms in semiconductors has primary influence of forming the lattice of any solar cell and is accomplished by electrostatic forces and by the tendency of atoms to fill their outer shells. Interatomic attraction is balanced by short-range repulsion due to strong resistance of atoms against interpenetration of core shells. The knowledge of the detail of this interaction is not only of help for selecting most appropriate materials for solar cells but also for judging about the ease of incorporation of desirable crystal defects and avoiding others.

The different types of the bonding of condensed matter (solids) will be reviewed, irrespective of whether they are crystalline or amorphous.

The formation of solids is determined by the interatomic forces and the size of the atoms shaping the crystal lattice. The interatomic forces are composed of a far-reaching attractive and a short-range repulsive component, resulting in an *equilibrium distance* of vanishing forces at an interatomic distance r_e , at which the potential energy shows a minimum (Fig. 1.1). In Binary compounds, this equilibrium distance r_e can be written as the sum of *atomic radii*

$$r_e = r_A + r_B, \quad (1.1)$$

where r_A and r_B are characteristic for the two atoms A and B (Fig. 1.2).

Attractive interatomic forces are predominantly *electrostatic* (e.g., in ionic, metallic, van der Waals, and hydrogen bonding) or are a consequence of sharing valence electrons to fill their outer shells, resulting in *covalent* bonding. Most materials show *mixed bonding*, i.e., at least two of these bond types contribute significantly

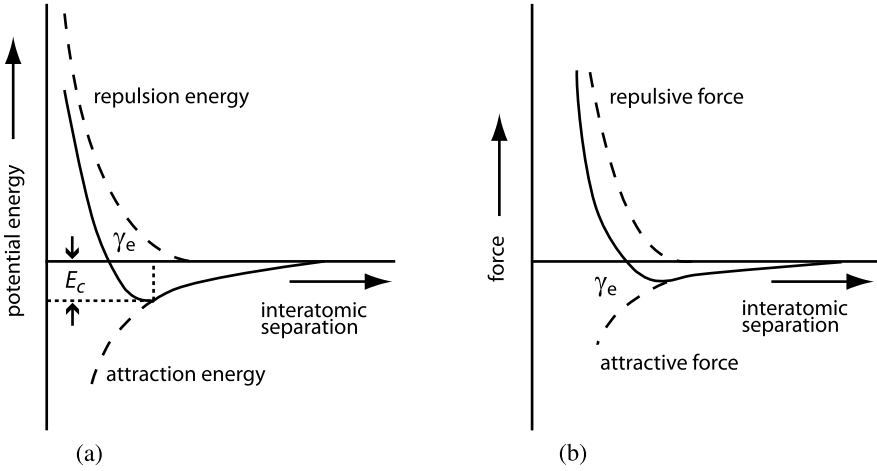


Fig. 1.1 Interaction potential (a) and forces (b) between two atoms; r_e is the equilibrium distance; E_c is the bonding energy at $r = r_e$

to the interatomic interaction. In the better compound semiconductors, the mixed bonding is more covalent and less ionic. In other semiconductors, one of the other types of bonding may contribute, e.g., van der Waals bonding in organic crystals, and metallic bonding in highly conductive semiconductors.

The *repulsive interatomic* forces, called Born forces (see Born and Huang 1954), are caused by a strong resistance of the electronic shells of atoms against interpenetration. The repulsive Born potential is usually modeled with a strong power law¹

$$eV(r) = \frac{\beta}{r^m} \quad \text{with } m \simeq 10, \dots, 12. \quad (1.3)$$

1.1 Ionic Bonding

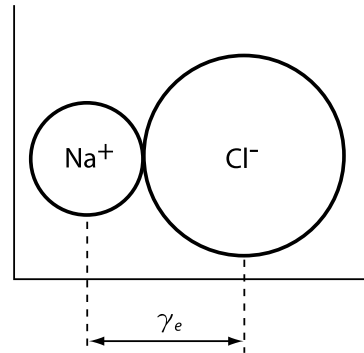
Ionic bonding is caused by Coulomb attraction between ions. Such ions are formed by the tendency of atoms to complete their outer shells. This is most easily accomplished by compounds between elements of group I and group VII of the periodic system of elements; here one electron needs to be exchanged. The bonding is then described by isotropic (radial-symmetric) *nonsaturable* Coulomb forces attracting

¹A better fit for the Born repulsion is obtained by the sum of a power and an exponential law:

$$V_{\text{Born}} = \frac{\beta}{r^m} + \gamma \exp\left(-\frac{r}{r_0}\right). \quad (1.2)$$

r_0 is the *softness parameter*, listed for ions in Table 1.7. For more sophisticated repulsion potentials, see Shanker and Kumar (1987). β is the force constant (see Eq. (1.1)) and m is an empirical exponent. For ionic crystals the exponent m lies between 6 and 10.

Fig. 1.2 Na^+ anion and Cl^- cation shown as hard spheres in actual ratio of radii



as many Na^+ ions as space permits around each Cl^- ion, and vice versa, while maintaining overall neutrality. This results in a closely packed NaCl lattice with a *coordination number* 6 (= number of nearest neighbors).

The energy gain between two ions can be calculated from the potential equation

$$eV = -\frac{e^2}{4\pi\epsilon_0 r} + \frac{\beta}{r^m} \quad \text{for } r = r_e, \quad (1.4)$$

containing Coulomb attraction and Born repulsion. For an equilibrium distance $r_e = r_{\text{Na}^+} + r_{\text{Cl}^-} = 2.8 \text{ \AA}$ results² in a minimum of the potential energy of $eV_{\text{min}} \sim -5 \text{ eV}$ for a typical value of $m = 9$.

In a crystal we must consider *all* neighbors. For example, in an NaCl lattice, six nearest neighbors exert Coulomb attraction in addition to 12 next-nearest neighbors of equal charge exerting Coulomb repulsion, etc. This alternating interaction results in a summation that can be expressed by a proportionality factor A in the Coulomb term of Eq. (1.4), the *Madelung constant* (Madelung 1918).

For the NaCl crystal structure it follows

$$A = \frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{25}{\sqrt{5}} - \cdots + \cdots, \quad (1.5)$$

where each term presents the number of equidistant neighbors in the numerator and the corresponding distance (in lattice units) in the denominator. This series is only slowly converging. Ewald's method (the theta-function method) is powerful and facilitates the numerical evaluation of A. For NaCl, we obtain from (Madelung 1918; Born and Lande 1918):

$$eV = -A \frac{e^2}{4\pi\epsilon_0 r_e} + \frac{\beta'}{r_e^m} \quad (1.6)$$

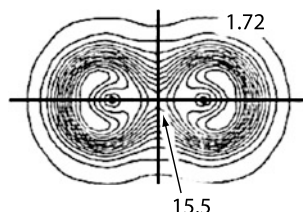
with $A = 1.7476$, a lattice binding energy of $eV_{\text{min}}^A = H^0(\text{NaCl}) = 7.948 \text{ eV}$, compared to an experimental value of 7.934 eV . Here β' and m are empirically obtained

² β can be eliminated from the minimum condition $\{dV/dr|_{r_e} = 0\}$. One obtains $\beta = e^2 r_e^{m-1} / (4\pi\epsilon_0 m)$ and as cohesive energy $eV_{\text{min}} = -e^2(m-1)/(4\pi\epsilon_0 m r_e)$.

Table 1.1 Madelung constant for a number of crystal structures

Crystal structure	Madelung constant
NaCl	1.7476
CsCl	1.7627
Zinc-blende	1.6381
Wurtzite	1.6410
CaF ₂	5.0388
Cu ₂ O	4.1155
TiO ₂ (Rutile)	4.8160

Fig. 1.3 Total charge contour plot of the O₂ molecule (after Cotton and Wilkinson 1979). Copyright Pergamon Press



from the observed lattice constant and compressibility. The Madelung constant is listed for several AB-compounds in Table 1.1 (see Sherman 1932).

The Born-Haber cycle is an empirical process of obtaining the lattice energy, i.e., the binding energy per mole. The process starts with the solid metal and gaseous halogen, and adds the heat of sublimation $W_{\text{subl}}(\text{Na})$ and the dissociation energy $(1/2)W_{\text{diss}}(\text{Cl})$; it further adds the ionization energy $W_{\text{ion}}(\text{Na})$ and the electron affinity $W_{\text{elaff}}(\text{Cl})$ in order to obtain a diluted gas of Na^+ and Cl^- ions; all of these energies can be obtained experimentally. These ions can be brought together from infinity to form the NaCl crystal by gaining the unknown lattice energy $H^0(\text{NaCl})$. This entire sum of processes must equal the heat of formation $W^0(\text{NaCl})$ which can be determined experimentally (Born 1919; Haber 1919):

$$W_{\text{solid}}^0(\text{NaCl}) = \left\{ W_{\text{subl}}(\text{Na}) + W_{\text{ion}}(\text{Na}) + \frac{1}{2} W_{\text{diss}}(\text{Cl}_2) + W_{\text{elaff}}(\text{Cl}) \right\} + H^0(\text{NaCl}). \quad (1.7)$$

A minor correction of an isothermal compression of NaCl from $p = 0$ to $p = 1$ (atm), heating it from $T = 0$ K to room temperature, and an adiabatic expansion of the ion gases to $p = 0$ has been neglected. The corresponding energies almost cancel. The error is $< 1\%$.

1.2 Covalent Bonding

Covalent bonding is caused by two electrons that are shared between two atoms: they form an *electron bridge* as shown in Fig. 1.3 for a diatomic oxygen molecule. This bridge formation can be understood quantum-mechanically by a nonspherical

Table 1.2 Lattice constants (a in Å) and ratio of lattice constants c/a for simple predominantly ionic AB compounds (after Weissmantel and Hamann 1979)^a

NaCl		Structure		CsCl Structure		Zinc-blende		Wurtzite		c/a
AgF	4.93	NaBr	5.973	BaS	6.363	AlP	5.431	AgI	4.589	1.63
AgCl	5.558	NaCl	6.433	CsCl	4.118	AlAs	5.631	AlN	3.110	1.60
AgBr	5.78	PbS	5.935	CsBr	4.296	AlSb	6.142	BeO	2.700	1.63
BaO	5.534	PbSe	6.152	CsI	4.571	BeS	4.86	CdS	4.139	1.62
BaS	6.363	PbTe	6.353	TiI	4.206	BeSe	5.08	CdSe	4.309	1.63
BaSe	6.633	RbF	5.651	TlCl	3.842	BeTe	5.551	GaN	3.186	1.62
BaTe	7.000	RbCl	6.553	TiBr	3.978	CSi	4.357	InN	3.540	1.61
CaO	4.807	RbBr	6.868	TiI	4.198	CdS	5.832	MgTe	4.529	1.62
CaS	5.69	RbI	7.341	NH ₄ Cl	3.874	CdSe	6.052	MnS	3.984	1.62
CaSe	5.992	SnAs	5.692	NH ₄ Br	4.055	CdTe	6.423	MnSc	4.128	1.63
CaTe	6.358	SnTe	6.298	NH ₄ I	4.379	CuF	4.264	TaN	3.056	–
CdO	4.698	SrO	5.156	TiNO ₃	4.31	CuCl	5.417	ZnO	3.249	1.60
KF	5.351	SrS	5.582	CsCN	4.25	CuBr	5.091	ZnS	3.819	1.64
KCl	6.283	SrSe	6.022			GaP	5.447	NH ₄ F	4.399	1.60
KBr	6.599	SrTe	6.483			GaAs	5.646			
KI	7.066	TaC	4.454			GaSb	6.130			
LiF	4.025	TiC	4.329			HgSe	6.082			
LiCl	5.140	TiN	4.244			HgTe	6.373			
LiBr	5.501	TiO	4.244			InAs	6.018			
LiI	6.012	VC	4.158			InSb	6.474			
MgO	4.211	VN	4.137			MnS	5.611			
MgS	5.200	VO	4.108			MnSe	5.832			
MgSe	5.462	ZrC	4.696			ZnS	5.423			
NaF	4.629	ZrN	4.619			ZnSe	5.661			
NaCl	5.693					ZnTe	6.082			

^aFor explanation of the different crystal structures see Chap. 2

electron density distribution extending between the bonded atoms. Examples of such density distributions are shown in Fig. 1.3 for an O₂ molecule and schematically in Fig. 1.4 for a molecule formation with electrons in a $1s$ or $2p$ state, e.g., for H₂ or F₂, respectively.

If an approaching atom of the same element has in its protruding part of the electron density distribution an unpaired electron with antiparallel spin, both eigenfunctions may overlap; the Pauli principle is not violated.

Their combined wave function ($\Psi_+ = \Psi_A + \Psi_B$) yields an increased electron density Ψ^2 in the overlap region (see Fig. 1.5a); the result is an *attractive force* between these two atoms *in the direction of the overlapping eigenfunctions*. This is the state of lowest energy of the two atoms, the *bonding state*.

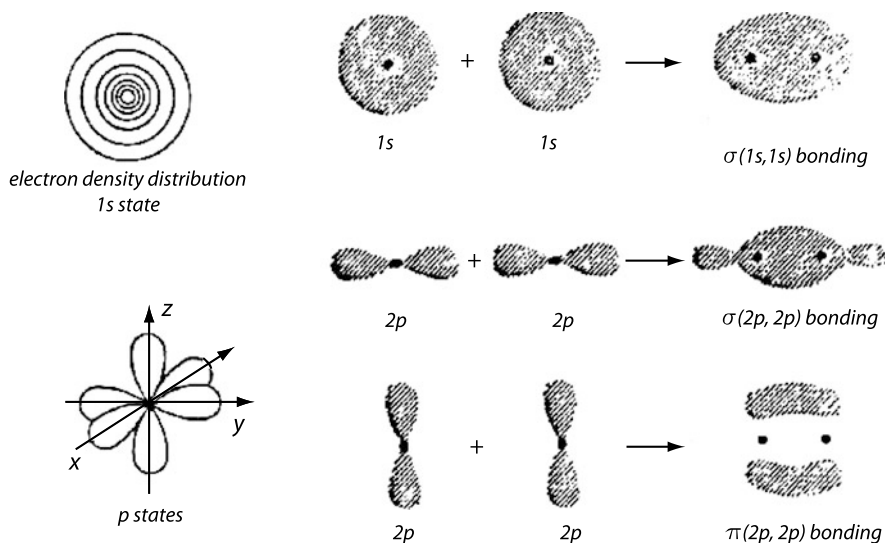
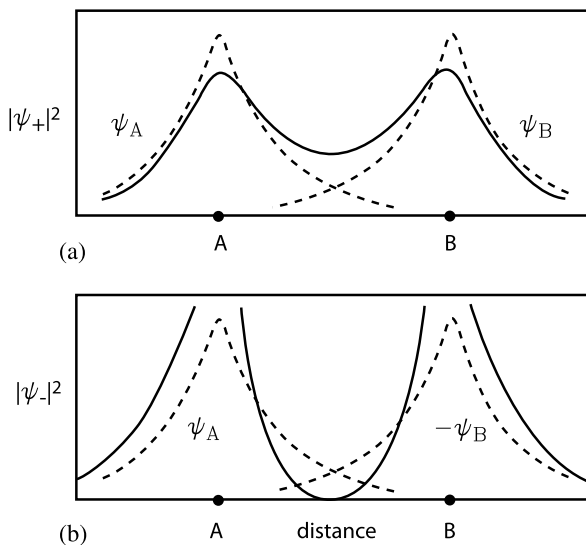


Fig. 1.4 Atomic and molecular electron density distribution for $\sigma(s)$, $\sigma(p)$, and $\pi(p)$ bonding—see Weissmantel and Hamann (1979)

Fig. 1.5 Wavefunctions of one-electron states [*dashed curves*—identical in (a) and (b)] and probability function to find one electron (*solid curves*) in (a), a bonding state, and (b), an antibonding state, showing finite and vanishing electron density at the center between atoms A and B for these two states, respectively [observe the plotting of $-\psi_B$ in (b)]. The picture of these two one-electron states shown here shall not be confused with the two-electron potential given in Fig. 1.6



There is also a state of higher energy, the *antibonding state*, with $\Psi_- = \psi_A - \psi_B$ in which the spin of both electrons is parallel. Here the electrons are repulsed because of the Pauli principle, and the electron clouds cannot penetrate each other; the electron density between both atoms vanishes (Fig. 1.5b). The resulting potential distribution as a function of the interatomic distance between two hydrogen atoms forming an H_2 molecule is given in Fig. 1.6, with both the bonding

Fig. 1.6 Potential energy for the two valence electrons of two covalently bound hydrogen atoms approaching each other; (*upper curve*) antibonding state; (*lower curve*) bonding state; (*middle curve*) from free atom charge distribution bonding. Charge density distributions shown in the insert are for the two covalent states (after Kittel 1986 © John Wiley & Sons, Inc.)

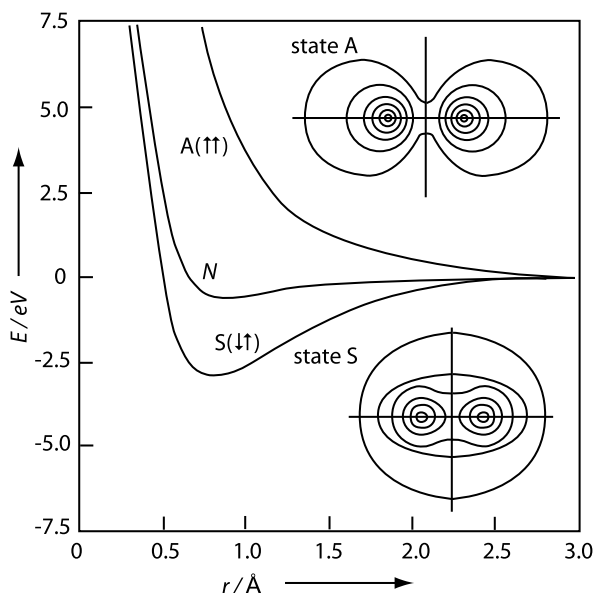


Fig. 1.7 Linear combination (hybridization) of a $1s$ function (spherical) with $3p$ functions (**a**) results in four sp^3 functions (**b**) which extend towards the four tetrahedra axes 1–4, and result in strongly directional bonding with a bond angle of 109.47°

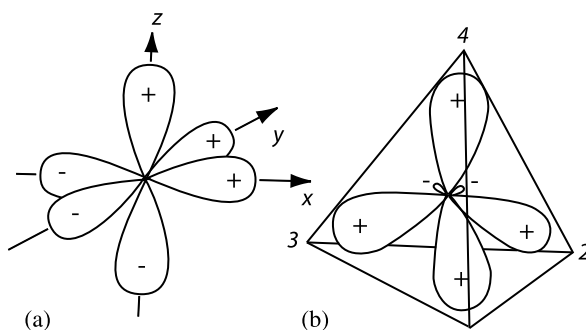


Table 1.3 Bond lengths relevant to organic molecules α -Si and related semiconductors

Bond	Bond length (Å)	Bond	Bond length (Å)
C–C	1.54	Si–Si	2.35
C=C	1.38	Si–H	1.48
C=C	1.42 (graphite)	Ge–Ge	2.45
C≡C	1.21	Ge–H	1.55
C–H	1.09 (sp^3)	C–Si	1.87

(S) and the excited, anti-bonding state (A) shown. The figure also contains as center curve the classical contribution of two H-atoms with a charge density of free atoms: Such bonding is small compared with the covalent bonding shown in Table 1.3.

The bond length (center-to-center distance) between C-atoms in organic molecules decreases with increasing bonding valency as Other bond lengths typical for organic or similar molecules are also listed.

Fig. 1.8 (a) Unit cell of diamond with pairs of electrons indicated between adjacent atoms; (b) electron density profile within the (110) plane (after Dawson 1967)

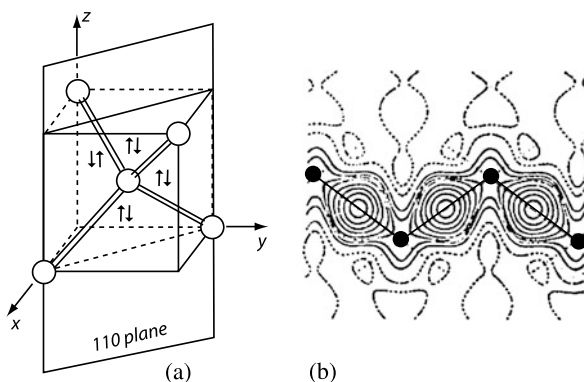
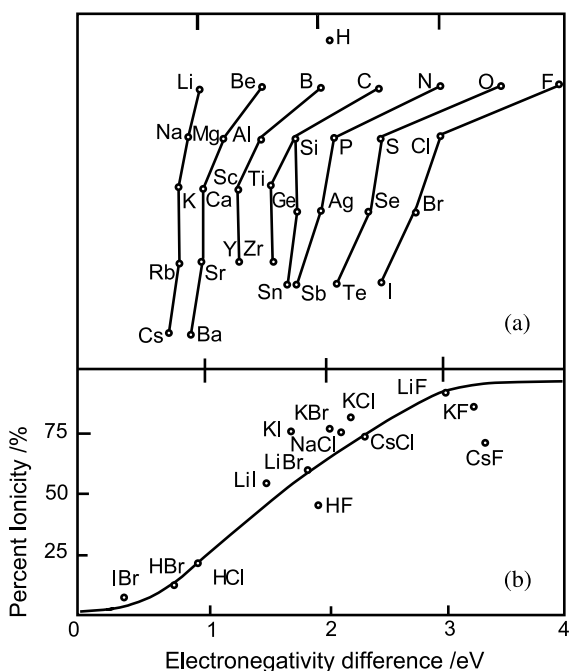


Fig. 1.9 (a) Electronegativity of the elements with groups from the periodic table of elements identified by interconnecting lines; (b) ionicity of alkali halides and halide molecules as a function of the difference in electronegativity (after Pauling 1960)



With additionally missing unpaired electrons in the outer shell, more than one atom of the same kind can be bound to each other. The number of bonded atoms is given by the following valency: monovalent atoms can form only diatomic molecules; divalent atoms, such as S or Se, can form chains; and trivalent atoms, such as As, can form two-dimensional (layered) lattices. Solids are formed from such elements by involving other bonding forces between the molecules, chains, or layers, e.g., van der Waals forces—see Sect. 1.5. Only tetravalent elements can form three-dimensional lattices which are covalently bound (e.g., Si).

1.2.1 Tetrahedrally Bound Elements

Silicon has four electrons in its outer shell. In the ground state of an isolated atom, two of the electrons occupy the s -state and two of them occupy p -states, with a $2s^2 2p^2$ configuration. By investing a certain amount of promotion energy,³ this $s^2 p^2$ -configuration is changed into an sp^3 -configuration, in which an unpaired electron sits in each one of the singly occupied orbitals with tetrahedral geometry (see Fig. 1.7).

From the s -orbital and the three p -orbitals, four linear combinations can be formed, represented as $\sigma_i = 1/2(\varphi_s + \varphi_{px} \pm \varphi_{py} \pm \varphi_{pz})$, depending upon the choice of signs.

This is referred to as *hybridization*, with σ_i as the *hybrid function* responsible for bonding. When we bring together a large number of Si atoms, they arrange themselves so that each of them has four neighbors in tetrahedral geometry as shown in Fig. 1.9. Each atom then forms four electron bridges to its neighbors, in which each one is occupied with two electrons of opposite spin, as shown for the center atom in Fig. 1.8a. Such bridges become evident in a density profile within the (110) plane shown for two adjacent unit cells in Fig. 1.8b.

In contrast to the ionic bond, the covalent bond is angular-dependent, since the protruding atomic *eigenfunctions* extend in well-defined directions. Covalent bonding is therefore a *directional* and *saturable bonding*; the corresponding force is known as a *chemical valence force*, and acts in exactly as many directions as the valency describes.

1.3 Mixed Bonding

Crystals that are bonded partially by ionic and partially by covalent forces are referred to as *mixed-bond crystals*. Most semiconductors have a fraction of covalent and ionic bonding components (see, e.g., Mooser and Pearson 1956).

1.3.1 Tetrahedrally Bonded Binaries

By using the Grimm-Sommerfeld rule (see below) for isoelectronic rows of elements, Welker and Weiss (1954) predicted desirable semiconducting properties for III–V compounds.⁴

³The promotion energy is 4.3, 3.5, and 3.3 eV for C, Si, and α -Sn, respectively. However, when forming bonds by establishing electron bridges to neighboring atoms, a substantially larger energy is gained, therefore resulting in net binding forces. Diamond has the highest cohesive energy in this series, *despite* the fact that its promotion energy is the largest because its sp^3 – sp^3 C–C bonds are the strongest (see Harrison 1980).

⁴Meaning compounds between one element of group III and one element of group V on the periodic system of elements.

Table 1.4 Static effective charges of partially covalent AB-compounds (after Coulson et al. 1962)

Compound	e^*/e	Compound	e^*/e
ZnO	0.60	BN	0.43
		AlN	0.56
		GaN	0.55
		InN	0.58
ZnS	0.47	BP	0.32
CdS	0.49	AlP	0.46
HgS	0.46	GaP	0.45
		InP	0.49
ZnSe	0.47	AlAs	0.47
CdSe	0.49	GaAs	0.46
HgSe	0.46	InAs	0.49
ZnTe	0.45	AlSb	0.44
CdTe	0.47	GaSb	0.43
HgTe	0.49	InSb	0.46

Semiconducting III–V and II–VI compounds are bound in a *mixed bonding*, in which electron bridges exist, i.e., the bonding is directed, but the electron pair forming the bridge sits closer to the anion. This *degree of ionicity* increases for these compounds with an increased difference in electronegativity (Fig. 1.9) from III–V to I–VII compounds and within one class of compounds, e.g., from RbI to LiF—see also Table 1.4. The mixed bonding may be expressed as the sum of the wave functions describing covalent and ionic bonding

$$\psi = a\psi_{\text{cov}} + b\psi_{\text{ion}} \quad (1.8)$$

with the ratio b/a defining the *ionicity* of the bonding. This bonding can also be described as rapidly alternating between that of covalent and ionic. Over an average time period, a fraction of ionicity (b/a) results. The ionicity of the bonding can be described by a static *effective ion charge* e^* , as opposed to a dynamic effective ion charge, which is less by a fraction on the order of b/a than in a purely ionic compound with the charge given by the valency.

The static effective charge for other II–VI and III–V compounds is given in Table 1.4.

The effective charge concept can be confusing if one does not clearly identify the ionic state of the system. For instance, in the case of CdS, a purely ionic state is $\text{Cd}^{++}\text{S}^{--}$, as opposed to the covalent state of $\text{Cd}^{--}\text{S}^{++}$ (which is equivalent to the Si^xSi^x -configuration). In other words, the covalent state is that in which both Cd and S have four valence electrons and are connected to each other by a double bond. This must not be confused with the neutral Cd^xS^x configuration, which is a mixed-bonding state.

Fig. 1.10 Schematic sketch of mixed bonding from nearly perfect covalent (a) in Ge to perfect ionic (d) in KCl it shows diminishing bridge formation and increasing cloud formation of electrons around anions with increasing ionicity (after Ashcroft and Mermin 1976). For instance, in CdS the divalent behavior of Cd and S could result in a doubly charged $\text{Cd}^{++}\text{S}^{--}$ lattice, while measurements of the electric dipole moment indicate an effective charge of 0.49 for CdS

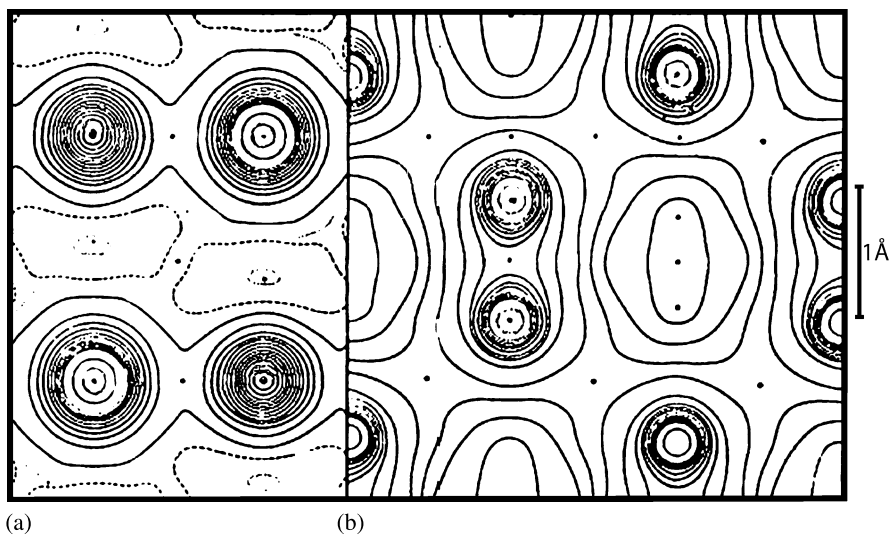
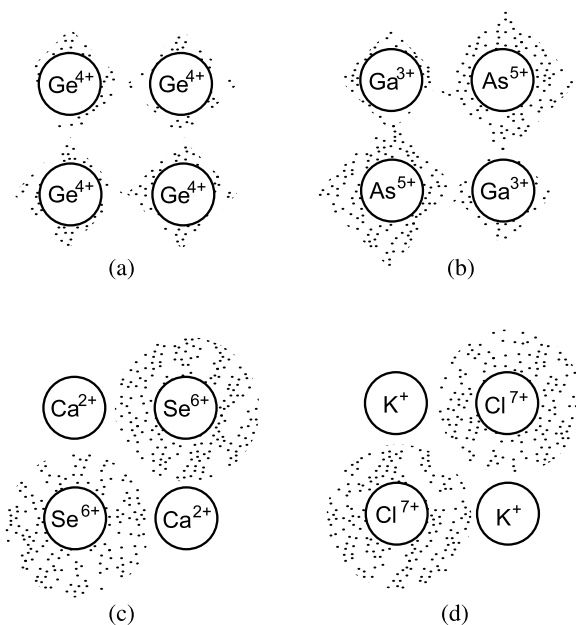


Fig. 1.11 Electron density distribution obtained by Fourier analysis of X-ray diffraction pattern of (a) NaCl and (b) diamond (after Brill et al. 1942)

The expression for the static effective charge (see Coulson et al. 1962) is

$$\frac{e^*}{e} = \frac{N(a/b)^2 - (8 - N)}{1 + (a/b)^2}, \quad (1.9)$$

Table 1.5 Ionic radii r_i and half the nearest-neighbor distances in metals r_m in Å (after Ashcroft and Mermin 1976)

Metal	r_i	r_m	r_m/r_i	Transition			
				Metal	r_i	r_m	r_m/r_i
Li	0.60	1.51	2.52	Cu	0.96	1.28	1.33
Na	0.95	1.83	1.93	Ag	1.26	1.45	1.15
K	1.33	2.26	1.70	Au	1.37	1.44	1.05
Rb	1.48	2.42	1.64				
Cs	1.69	2.62	1.55				

with N as the valency. For $N = 2$, the effective charge vanishes when $a/b = \sqrt{3}$. For $N = 3$ in III–V compounds, e^* vanishes when $a/b = \sqrt{5}/3$, and for group IV semiconductors when $a = b$.

In crystals, low coordination numbers (typically 4) signify a considerable covalent contribution to the bonding.

The different degree of bridge formation in crystals with mixed bonding (Fig. 1.10) can be made visible by a Fourier analysis of X-ray diffraction from which the electron density distribution around each atom can be obtained. This is shown for a mostly ionic crystal in Fig 1.11a and for a mostly covalent crystal in Fig. 1.11b.

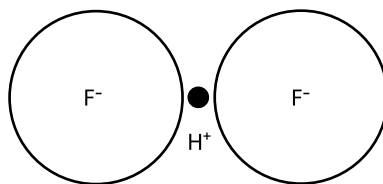
1.4 Metallic Bonding (Delocalized Bonding)

Metallic bonding can be understood as a collective interaction of a mobile electron fluid with metal ions. Metallic bonding occurs when the number of valence electrons is only a small fraction of the coordination number; then neither an ionic nor a covalent bond can be established.

Metallic bonding of simple metals, e.g., alkali metals, can be modeled by assuming that each metal atom has given up its valence electron, forming a lattice of positively charged ions, submerged in a fluid of electrons. Between the repulsive electron–electron and ion–ion interactions and the attractive electron-ion interaction, a net attractive binding energy results, which is *nondirectional and not saturable*, and results in *close-packed structures* with high coordination numbers (8 or 12; Wigner and Seitz 1933), but relatively wide spacing between the submerged metal ions (Table 1.5). Such metals have low binding energies (~ 1 eV/atom) and high compressibility. They are mechanically soft, since the nondirectional lattice-forces exert little resistance against plastic deformation. This makes metals attractive for forming and machining.

In other metals, such as transition group elements, the bonding may be described as due to covalent bonds which rapidly hop from atom pair to atom pair. Again, free electrons are engaged in this resonance-type bonding. These metals have a higher binding energy of ~ 4 to 9 eV/atom and an interatomic distance that is closer to the one given by the sum of ionic radii (Table 1.5). They are substantially harder when

Fig. 1.12 Hydrogen bonding between a positive hydrogen ion (proton) and two ions (coordination number 2)



located in the middle of the transition metal row, e.g., Mo and W (Ashcroft and Mermin 1976).

In semiconductors with a very high density of free carriers, metallic binding forces may contribute a small fraction to the lattice bond, interfering with the predominant covalent bonding and usually weakening it, since these electrons are obtained by ionizing other bonds. Changes in the mechanical strength of the lattice can be observed in photoconductors in which a high density of free carriers can be created by light (Gorid'ko et al. 1961).

For more information, see Ziman (1969) and Harrison (1966).

1.5 Van der Waals Bonding

Noble gas atoms or molecules with saturated covalent bonds can be bound to each other by dipole-dipole interaction (Debye). The dipole is created between the nucleus (nuclei) of the atom (molecule) and the cloud of electrons moving around these nuclei, and forms a fluctuating dipole moment even for a spherically symmetrical atom. The interaction creates very weak, nonsaturable attractive forces. This results in low melting points and soft *molecule crystals*. The bonding energy can be approximated by

$$eV = -\frac{\alpha_a}{r^6} + \frac{\alpha_r}{r^{12}}. \quad (1.10)$$

Van der Waals forces are the main binding forces of organic semiconductors (van der Waals 1873).

1.6 Hydrogen Bonding

Hydrogen bonding (Fig. 1.12) is a type of ionic bonding in which the hydrogen atom has lost its electron to another atom of high electronegativity. The remaining proton establishes a strong Coulomb attraction. This force is not saturable. However, because of the small size of the proton, hydrogen bonding is strongly localized, and spatially no more than two ions have space to be attracted to it. When part of a molecule, the hydrogen bond—although ionic in nature—fixes the direction of the attached atom because of space consideration. It should not, however, be confused with the covalent bonding of hydrogen that occurs at dangling bonds in semiconductors, e.g., at the crystallite interfaces of polycrystalline Si or in amorphous Si:H.

1.7 Intermediate Valence Bonding

An interesting group of semiconductors are *transition metal compounds*. The transition metals have partially filled *inner* $3d$, $4d$, $5d$, or $4f$ shells and a filled outer shell that provides a shielding effect to the valence electrons. In these compounds the crystal field has a reduced effect. Some of these compounds show *intermediate valence bonding*. The resulting unusual properties range from resonant valence exchange transport in copper-oxide compounds (Anderson 1987; Anderson et al. 1987) to giant magnetoresistance and very large magneto-optical effects in rare-earth semiconductors. For a review, see Holtzberg et al. (1980).

1.8 Other Bonding Considerations

Other, more subtle bonding considerations have gained a great deal of interest because of their attractive properties. These are related to magnetic and special dielectric properties, to superconductivity, as well as to other exotic effects.

For instance, dilute semimagnetic semiconductors such as the alloy $\text{Cd}_{1-\zeta}\text{Mn}_\zeta\text{Te}$ (Furdnya 1982, 1986; Brandt and Moshchalkov 1984; Wei and Zunger 1986; Goede and Heitbrodt 1988) show interesting magneto-optical properties. They change from paramagnetic ($\zeta < 0.17$) to antiferromagnetic ($0.6 < \zeta$) to the ferro- or antiferromagnetic behavior of MnTe ; exhibit giant magneto-optical effects and bound magnetic polarons; and offer opportunities for optoelectric devices that are tunable by magnetic fields.

These materials favor specific structures and permit the existence of certain quasi-particles, such as small polarons or Frenkel excitons. These discussions require a substantial amount of understanding of the related physical effects, and are therefore postponed to a more appropriate section of this book (see also Phillips 1973; Harrison 1980; Ehrenreich 1987).

1.9 Atomic and Ionic Radii

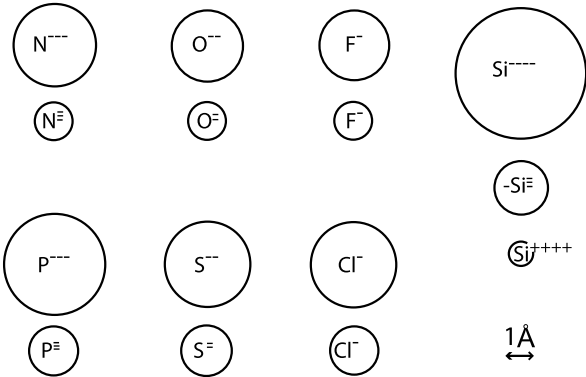
The equilibrium distances between atoms in a crystal define atomic radii when assuming that hard-sphere atoms touching each other. In reality, however, these radii are soft with some variation of the electronic eigenfunctions and, for crystals with significant covalent fraction they depend on the angular atomic arrangement. However, for many crystals the hard-sphere radii are useful for most lattice estimates.

When comparing the lattice constants of chemically similar crystals, such as NaCl , NaBr , KCl , and KBr , one can determine the radii of the involved ions (Na^+ , K^+ , Cl^- , and Br^-) if at least one radius is known independently. Goldschmidt (1927) used the radii of F^- and O^{2-} for calibration. Consequent listings of other ionic radii are therefore referred to as *Goldschmidt radii*. These radii are independent of the compound in which the atoms are incorporated as long as they exhibit

Table 1.6 Covalent (effective ionic charge $e^* = 0$) and standard ionic (identified by $\pm e^*$) radii in Å

e^-	+1	0		+2	0		+3	0	
Li	0.68	1.34	Be	0.30	0.90	B	0.16	0.88	
Na	0.98	1.54	Mg	0.65	1.30	Al	0.45	1.26	
K	1.33	1.96	Ca	0.94	1.74	Sc	0.68		
Cu	0.96		Zn	0.74	1.31	Ga	0.62	1.26	
Rb	1.48		Sr	1.10		Y	0.88		
Ag	1.26		Cd	0.97	1.48	In	0.81	1.44	
Cs	1.67		Ba	1.2		La	1.04		
Au	1.37		Hg	1.10	1.48	Tl	0.95	1.47	
	+4	0	−4	0	−3		0	−2	
C		0.77	2.60	N	0.70	1.71	O	0.73	1.46
Si	0.38	1.17	2.71	P	1.10	2.12	S	1.04	1.90
Ti	0.60			As	1.18	2.22	Se	1.14	2.02
Ge	0.53	1.22	2.72						
Zn	1.77			Sb	1.36	2.45	Te	1.32	2.22
Sn		1.40	2.94						
Ce	0.92			Bi	1.46		Po		2.30
Pb	0.84	1.46							

Fig. 1.13 Scale drawing of rigid sphere atoms with different bonding character (ionic or covalent, identified by the appropriate number of minus signs (*upper row*) or valence lines (*lower row*), respectively)



the same type of bonding. One distinguishes atomic, ionic, metallic, and van der Waals radii. Ionic radii vary with changing valency.

A list of the most important ion and atomic radii is given in Table 1.6. The drastic change in radii with changing bonding force (Mooser and Pearson 1956) is best demonstrated by comparing a few typical examples for some typical elements incorporated in semiconductors (Fig. 1.13). For more estimates of tetrahedral covalent radii, see van Vechten and Phillips (1970).

Table 1.7 Repulsive potential softness parameters (Eq. (1.3)) in Å (after Shanker and Kumar 1987)

Ion	r_0 (th)	r_0 (exp)	Ion	r_0 (th)	r_0 (exp)
Li ⁻	0.069	0.042	F ⁻	0.179	0.215
Na ⁺	0.079	0.090	Cl ⁻	0.238	0.224
K ⁺	0.106	0.108	Br ⁻	0.258	0.254
Rb ⁺	0.115	0.089	I ⁻	0.289	0.315
Cs ⁺	0.130	0.100			

Table 1.8 Change of interatomic distance Δ_m (in Å) for compounds deviating from coordination number $m = 6$

m	Δ_m	m	Δ_m	m	Δ_m	m	Δ_m
1	-0.50	4	-0.11	7	+0.04	10	+0.14
2	-0.31	5	-0.05	8	+0.08	11	+0.17
3	-0.19	6	0	9	+0.11	12	+0.19

The deviation from strict rigidity, i.e., the softness of the ionic spheres, is conventionally considered by using a softness parameter r_0 in the exponential repulsion formula [Eq. (1.3)]. This parameter is listed for a number of ions in Table 1.7.

This softness also results in a change of the standard ionic radii as a function of the number of surrounding atoms. A small correction Δ_m in the interionic distance is listed in Table 1.8. This needs to be considered when crystals with different coordination numbers m , i.e., the number of surrounding atoms, are compared with each other (e.g., CsCl and NaCl).

With increasing atomic number, the atomic (or ionic) radius of homologous elements increases. The cohesive force therefore decreases with increasing atomic (ionic) radii. Thus, compounds formed by the same bonding forces, and crystallizing with similar crystal structure, show a decrease, for example, in hardness,⁵ melting point, and band gap, but an increase in dielectric constant and carrier mobility.

The ratio of ionic radii determines the preferred crystal structure of *ionic* compounds. This is caused by the fact that the energy gain of a crystal is increased with every additional atom that can be added per unit volume. When several possible atomic configurations are considered, the material crystallizes in a modification that maximizes the number of atoms in a given volume. This represents the state of lowest potential energy of the crystal, which is the most stable one. An elemental crystal with isotropic radial interatomic forces will therefore crystallize in a close-packed structure.

⁵This empirical quantity can be defined in several ways (e.g., as Mohs, Vickers, or Brinell *hardness*) and is a macroscopic mechanical representation of the cohesive strength of the lattice. In Table 1.9 the often used Mohs hardness is listed, which orders the listed minerals according to the ability of the higher-numbered one to scratch the lower-numbered minerals.

Table 1.9 Mohs hardness

Material	Chemistry	Lattice type	Hardness
Talc	$\text{Mg}_3\text{H}_2\text{SiO}_{12\text{-aq}}$	Layer lattice	1
Gypsum	$\text{CaSO}_4\cdot\text{H}_2\text{O}$	Layer lattice	2
Iceland spar	CaCO_3	Layer lattice	3
Fluorite	CaF_2	Ion lattice	4
Apatite	$\text{Ca}_5\text{F(PO}_4)_3$	Ion lattice	5
Orthoclase	KAlSi_3O_8	SiO_4 frame	6
Quartz	SiO_2	SiO_4 frame	7
Topaz	$\text{Al}_2\text{F}_2\text{SiO}_4$	Mixed ion-valency lattice	8
Corundum	Al_2O_3	Valency lattice	9
Diamond	C	Valency lattice	10

Table 1.10 Preferred lattice structure for AB-compounds with ionic binding forces (after Goldschmidt 1927)

r_A/r_B	Preferred stable lattice
<0.22	None
$0.22 \dots 0.41$	Zinc-blende or Wurtzite
$0.41 \dots 0.72$	NaCl lattice
>0.72	CsCl lattice

In a binary crystal, the ratio of atomic radii will influence the possible crystal structure. For isotropic nonsaturable interatomic forces, the resulting stable lattices are shown in Table 1.10 for different ratios of the ion radii.

When a substantial amount of covalent bonding forces are involved, the rules to select a stable crystal lattice for a given compound are more complex. Here atomic bond length and bond angles must be considered. Both can now be determined from basic principal density functions calculations. We can then define atomic radii from the turning point of the electron density distribution of each atom, and obtain an angular-dependent internal energy scale from these calculations (Zunger 1981). Using axes constructed from these radii, one obtains well-separated domains in which only one crystal structure is observed for binary compounds (Zunger 1981; Villars and Calvert 1985).

1.9.1 Bond-Length Relaxation in Alloys

The lattice constant of alloys $\text{A}_{1-\xi}\text{B}_\xi\text{C}$ of binary compounds AC and BC interpolates according to the concentration

$$a(\xi) = (1 - \xi)a_{\text{AC}} + \xi a_{\text{BC}} \tag{1.11}$$

Table 1.11 Bond-length of isovalent impurity in given host lattice and bond-length relaxation parameter (after Martins and Zunger 1984)

System	$r_{BC}(AC : B) (\text{\AA})$	ε	System	$r_{BC}(AC : B) (\text{\AA})$	ε
AlP:In	2.480	0.65	InP:Al	2.414	0.73
GaP:In	2.474	0.63	InP:Ga	2.409	0.73
AlAs:In	2.653	0.60	InAs:Al	2.495	0.74
GaAs:In	2.556	0.62	InAs:Ga	2.495	0.73
AlSb:In	2.746	0.61	InSb:Al	2.693	0.75
GaSb:In	2.739	0.60	InSb:Ga	2.683	0.74
AlP:As	2.422	0.65	AlAs:P	2.395	0.67
AlP:Sb	2.542	0.61	AlSb:P	2.444	0.73
AlAs:Sb	2.574	0.60	AlSb:As	2.510	0.71
GaP:As	2.414	0.62	GaAs:P	2.387	0.68
GaP:Sb	2.519	0.57	GaSb:P	2.436	0.73
GaAs:Sb	2.564	0.60	GaSb:As	2.505	0.70
InP:As	2.595	0.67	InAs:P	2.562	0.74
InP:Sb	2.700	0.60	InSb:P	2.597	0.79
InAs:Sb	2.739	0.64	InSb:As	2.667	0.75
ZnS:Se	2.420	0.70	ZnSe:S	2.367	0.78
ZnS:Te	2.539	0.67	ZnTe:S	2.407	0.78
ZnSe:Te	2.584	0.71	ZnTe:Se	2.502	0.74
β -HgS:Se	2.611	0.76	HgSe:S	2.553	0.80
β -HgS:Te	2.716	0.71	HgTe:S	2.579	0.82
HgSe:Te	2.748	0.74	HgTe:Se	2.665	0.80
ZnS:Hg	2.482	0.73	β -HgS:Zn	2.380	0.80
ZnSe:Hg	2.587	0.74	HgSe:Zn	2.494	0.78
ZnTe:Cd	2.755	0.70	CdTe:Zn	2.674	0.78
ZnTe:Hg	2.748	0.69	HgTe:Zn	2.673	0.78
γ -CuCl:Br	2.440	0.81	γ -CuBr:Cl	2.367	0.79
γ -CuCl:I	2.563	0.80	γ -CuI:Cl	2.407	0.76
γ -CuBr:I	2.585	0.79	γ -CuI:Br	2.500	0.76
C:Si	1.665	0.35	Si:C	2.009	0.74
Si:Ge	2.380	0.58	Ge:Si	2.419	0.63
Si:Sn	2.473	0.53	α -Sn:Si	2.645	0.70
Ge:Sn	2.549	0.55	α -Sn:Ge	2.688	0.67

when they crystallize with the same crystal structure (Vegard 1921). However, the bond length between any of the three pairs of atoms is neither a constant, as suggested from the use of constant atomic radii (Pauling 1960), nor a linear interpolation as shown by the dotted line in Fig. 1.14 for total relaxation of the bond of atom B in a different chemical environment AC (or of A in BC).

Fig. 1.14 Variation of bond-length in an $A_{1-\xi}B_{\xi}C$ alloy for rigid atoms ($\varepsilon = 1$), virtual crystal approximation ($\varepsilon = 0$), and experimentally observed relaxation

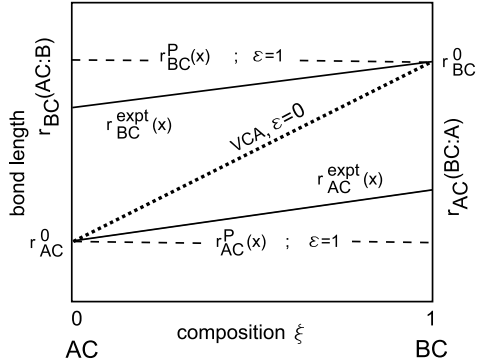


Table 1.12 Bond-length (d), bond-stretching (α) and bond-bending (β) force constants, calculated from elastic constants (after Martin 1970)

Crystal	d (Å)	α (N/m)	β (N/m)	Crystal	d (Å)	α (N/m)	β (N/m)
C	1.545	129.33	84.71	InP	2.541	43.04	6.24
Si	2.352	48.50	13.82	InAs	2.622	35.18	5.49
Ge	2.450	38.67	11.37	InSb	2.805	26.61	4.28
α -Sn	2.810	25.45	6.44	ZnS	2.342	44.92	4.81
SiC	1.888	88.	47.5	ZnSe	2.454	35.24	4.23
AlP	2.367	47.29	9.08	ZnTe	2.637	31.35	4.45
AlAs	2.451	43.05	9.86	CdTe	2.806	29.02	2.44
AlSb	2.656	35.35	6.79	β -HgS	2.534	41.33	2.56
GaP	2.360	47.32	10.46	HgSe	2.634	36.35	2.36
GaAs	2.448	41.19	8.94	HgTe	2.798	27.95	2.57
GaSb	2.640	33.16	7.23	γ -CuCl	2.341	22.9	1.01
				γ -CuBr	2.464	23.1	1.32
				γ -CuI	2.617	22.5	2.05

This nonrigidity of atoms is important when incorporating isovalent impurities into the lattice of a semiconductor (doping) and estimating the resulting deformation of the surrounding lattice. With the bond length r_{BC} within the AC lattice (see Table 1.11), one defines a relaxation parameter

$$\varepsilon = \frac{r_{BC}(AC : B) - r_{AC}^0}{r_{BC}^0 - r_{AC}^0}. \quad (1.12)$$

The superscript 0 indicates the undisturbed pure crystal, the notation AC:B indicates B as doping element with a sufficiently small density incorporated in an AC compound, so that B–B interaction can be neglected.

This relaxation parameter can be estimated from the bond-stretching and bond-bending force constants α and β (see Table 1.12), according to Martins and Zunger (1984),

$$\varepsilon = \frac{1}{1 + \frac{1}{6} \frac{\alpha_{AC}}{\alpha_{BC}} [1 + 10 \frac{\beta_{AC}}{\alpha_{AC}}]}, \quad (1.13)$$

yielding values of ε typically near 0.7—see Table 1.11; that is, isovalent impurity atoms behave more like rigid atoms ($\varepsilon = 1$) than totally relaxed atoms ($\varepsilon = 0$) in a virtual crystal approximation [Eq. (1.11)].

Chapter 2

Crystal Structure

Abstract Symmetry and periodicity determines crystal structure. Crystal systems, Bravais lattices, crystal classes and point groups; space groups, are listed. Schönflies and Herman-Mauguin identification. Crystallographic classification, point lattice, Miller Indices. Morphology of crystals. Reciprocal lattices and relevance. Wigner Seitz cell and Brillouin zones, typical examples are given. Extensive discussion of element, binary and ternary semiconductors. Superlattice structures and Brillouin zones, superlattice deposition. Intercalated compounds including typical properties are presented, organic superlattices with examples are discussed. Extensive discussion of amorphous structures, building blocks; relevance of coordination numbers and constraints. Quasi-crystals.

Many physical properties controlling solar cells depend on the *periodicity* and *symmetry of the lattice* that determines its *crystal structure*. The bonding forces and atomic sizes determine the arrangement of the atoms in crystals in equilibrium and the intrinsic properties of semiconductors. Nonequilibrium states can be frozen-in and determine the structure of amorphous semiconductors and of superlattice. A summary of the basic elements of the crystal structure is presented here since they are often referred to in the literature and it is helpful to have a condensed form presented at the beginning of the book. For a review, see DiBenedetto (1967), Newnham (1975), Brown and Forsyth (1973), Barrett and Massalski (1980), Chemov (1984).

A large variety of semiconductors are discussed that may have potential of future building blocks of solar cells. Their chemical composition and structure is reviewed. The growth of these semiconductors is reported in the following segment of this chapter with helpful description for optimizing.

The structure of a crystalline semiconductor is defined by its smallest three-dimensional building block, the *unit cell*. From these unit cells, the ideal crystal is constructed by three-dimensional repetition. The unit cell usually contains a small number of atoms, from one for a *primitive unit cell*, to a few atoms for non-primitive cells and compound crystals. In molecular crystals, this number can be much larger and is usually a small multiple of the number of molecules forming the crystal. The three-dimensional periodic array of atoms is the *crystal lattice*.

To define a unit cell a three-dimensional *point lattice* is introduced. To this imaginary lattice an atomic *basis* (or *motif*) is added, i.e., one, two, or more atoms in a

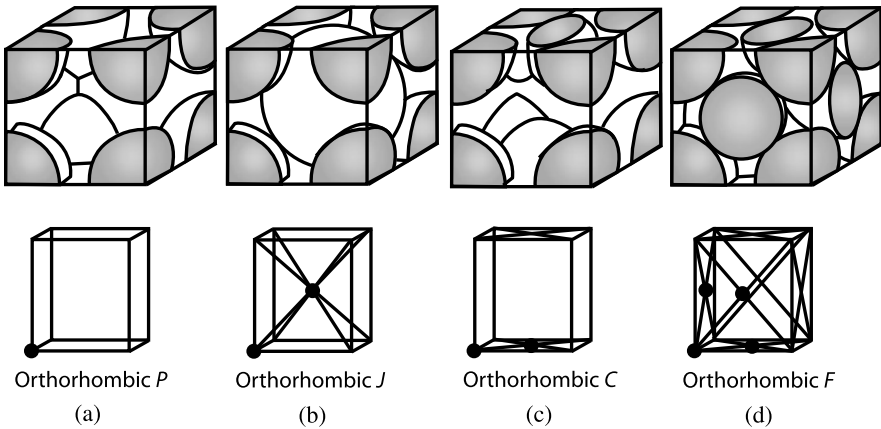


Fig. 2.1 Unit cells of the orthorhombic Bravais lattice. (a) Primitive P ; (b) body-centered I ; (c) base-centered C ; and (d) face-centered F

specific arrangement for each point, in order to arrive at the crystal lattice (Klug and Alexander 1974; Buerger 1956).

2.1 Crystal System

All crystals can be ordered into seven *crystal systems* according to the relative length of their lattice vectors and the angle between these vectors. These crystal systems are listed in Table 2.1, together with other properties identified in the following sections.

2.2 The Bravais Lattice

Several *symmetry operations* can transfer a crystal into itself. All lattices show linear transformation symmetry. A *unit cell* is defined as the smallest parallelepiped that forms the entire crystal when sequentially shifted by a linear transformation. There are 14 different unit cells possible; they form 14 different lattices, called *Bravais lattices*. These are listed in the last column of Table 2.1.

2.3 Crystal Classes (The Point Groups)

The other symmetry operations, excluding any translation, are *rotation*, *reflection* (composed from rotation and inversion on a plane), and *inversion*, i.e., “reflection” at a point. Crystals that are distinguished by one or a combination of these can be divided into 32 different *crystal classes*. These symmetry operations are applied to the *basis* about a *point* of the Bravais lattice and therefore are also called *point groups*.

Table 2.1 Crystal systems, point groups, and Bravais lattices

Crystal systems	Lattice vector relation	Lattice angle relation	Crystal class		Bravais lattices
			Schönflies	Hermann-Mauguin	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$	C_1	1	P
			$\bar{C}_1$	$\bar{1}$	P
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$ $\beta > 90^\circ$	C_2	2	P, C
			$C_{1h} (C_2)$	m	P, C
			C_{2h}	$\frac{2}{m}$	P, C
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	C_{2v}	$2mm$	P, C, F, I
			$D_2 (V)$	222	P, C, F, I
			$D_{2h} (V_h)$	$\frac{2}{m} \frac{2}{m} \frac{2}{m}$	P, C, F, I
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	C_4	4	P, I
			S_4	$\bar{4}$	P, I
			C_{4h}	$\frac{4}{m}$	P, I
			C_{4v}	$4mm$	P, I
			$D_{2d} (V_2)$	$\bar{4}2m$	P, C, F, I
			D_4	422	P, I
			D_{4h}	$\frac{4}{2} \frac{2}{m} \frac{2}{m}$	P, I
Trigonal or rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	C_3	3	C, R
			$S_6 (C_{3i})$	$\bar{3}$	C, R
			C_{3v}	$3m$	H, C, R
			D_3	32	H, C
			D_{3d}	$\bar{3} \frac{2}{m}$	H, C, R
Hexagonal	$a = b \neq c$	$\alpha = \gamma = 90^\circ$ $\beta = 120^\circ$	C_6	6	C
			C_{3h}	$\bar{6}$	C
			C_{6h}	$\frac{6}{m}$	C
			C_{6v}	$6mm$	C
			D_{3h}	$\bar{6}2m$	C, H
			D_6	622	C
			D_{6h}	$\frac{6}{m} \frac{2}{m} \frac{2}{m}$	C
Cubic or isometric	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	T	23	P, F, I
			T_h	$\frac{2}{m} \bar{3}$	P, F, I
			T_d	$\bar{4}3m$	P, F, I
			O	432	P, F, I
			O_h	$\frac{4}{m} \bar{3} \frac{2}{m}$	P, F, I

The symmetry operations are usually identified by their *Schönflies* or *Hermann-Mauguin* symbol.

The Schönflies symbol identifies with capital letters, C, D, T, O the basic symmetry: *cyclic*, *dihedral*, *tetrahedral*, and *octahedral*. A subscript is used to identify

the rotational symmetry, e.g., D_3 has three-fold symmetry. Another index, v, h, d is used for further distinction—see, e.g., Brown and Forsyth (1973).

The Hermann-Mauguin nomenclature indicates the type of symmetry directly from the symbol. It is a combination of numbers (n) and the letter $m:n$ indicates rotational symmetry and $\bar{n}$ denotes either an inversion $\bar{I}$ or a roto-inversion; m indicates a mirror plane parallel to, and $\frac{n}{m}$ perpendicular to, the rotational axis with n -fold symmetry. Repetition of m or other symbols indicates the symmetry about the other orthogonal planes or axes.

All possible combinations of rotation, reflection, and inversion are listed in Table 2.1, with both symbols to identify each of the 32 point groups.

Combining the symmetry operations leading to the point groups with non-primitive translation yields a total of 230 *space groups*.

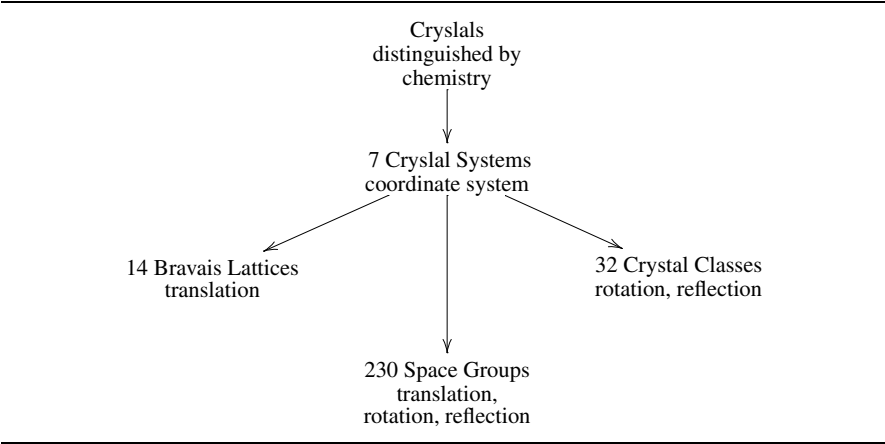
The Schönflies symbol designates the different possibilities, arbitrarily arranged, of combining the symmetry operations by a super-script referring to the point group symbol (e.g., O_h^7 for Si).

In the Hermann-Mauguin symbol, the Bravais lattice identifier is added: A, B, C identify the specific base,¹ P, I, F; R (rhombohedral), and H (hexagonal). In addition, small letters, a, b, c, d , or n are appended to identify specific glide planes—namely, at $\frac{a}{2}, \frac{b}{2}, \frac{c}{2}, \frac{r+s}{4}$ and $\frac{r+s}{2}$, for a, b, c, d , and n , respectively, with r and s standing for any a, b , or c . Typical element semiconductors have O_h symmetry, e.g., diamond O_h^7 (or $Fd\bar{3}m$) for Ge and Si. Other binary semiconductors have C_{4v} (or $4mm$), zincblende T_d^2 (or $F\bar{4}3m$), wurtzite C_{6v}^4 ($P6_3mc$), rock salt O_h^5 (or $Fm\bar{3}m$), and other symmetry.

In summary, crystals are classified according to their lattice symmetry in four different ways, depending on the type of symmetry operation employed. This is shown in Table 2.2.

2.4 The Space Groups

Table 2.2 Crystal classification



¹A is the face spanned between b and c , B between a and c , and C between a and b .

2.5 Crystallographic Classification

A *lattice point* is identified by the coefficients of the lattice vector pointing to it:

$$\mathbf{R}_n = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} \quad (2.1)$$

A lattice point is conventionally given by the three coefficients without brackets:

$$n_1 \ n_2 \ n_3. \quad (2.2)$$

A *lattice direction* is identified by a line pointing in this direction. When this line is shifted parallel so that it passes through the origin, the position of the nearest lattice point on this line, identified by the coefficients of Eq. (2.1) and enclosed in *square brackets*, defines this direction:

$$[n_1 \ n_2 \ n_3].$$

This notation can be reduced by permitting simple fractions; for example, $[2\ 2\ 1]$ may also be written as $[1\ 1\ \frac{1}{2}]$. Negative coefficients are identified by a bar: $[1\ 1\ \bar{1}]$ is a vector pointing diagonally downward to the right.

A *lattice plane* is described by *Miller indices*. These are obtained by taking the three coefficients of the intercepts of this plane with the three axes n_1 , n_2 , and n_3 forming the reciprocals of these coefficients, and clearing the fractions. For example, for a plane that is parallel to c and intersecting the x -axis at $2a$ and the y -axis at $4b$, the fractions are $\frac{1}{2}\ \frac{1}{4}\ \frac{1}{\infty}$. Thus, the Miller indices are $(2\ 1\ 0)$ and are enclosed in parentheses. The general form is $(h\ k\ l)$.

The Miller indices notation is a *reciprocal lattice* representation (see Sect. 1.6). It is useful for the discussion of interference phenomena, which requires the knowledge of distances between equivalent planes. The distance between the $\{h\ k\ l\}$ planes in a cubic system is

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}, \quad (2.3)$$

with a the lattice constant. (See Warren 1969; Zachariasen 1967; von Laue 1960; James 1954 for more details. A recent overview is given by Schultz 1982.)

2.5.1 Morphology of Crystals

When a specific chemical compound crystallizes in different crystal classes, it is called a *polymorph*. When crystals with the same structure are formed by compounds in which only one element is exchanged with a homologous element, they are referred to as *morphotrop*. When similar compounds crystallize in a similar crystal form, they are called *isomorph* when they also have other physical properties in common, such as similar cation to anion radii ratio and similar polarizability.

2.6 The Reciprocal Lattice

The introduction of a reciprocal lattice is advantageous to identify the distance between equivalent lattice planes. This is of help for all kinds of interference phenomena, such as X-ray diffraction, the behavior of electrons when taken as waves, or lattice oscillations. The relevant waves are described by wavefunctions of the type

$$\Phi(\mathbf{k}, \mathbf{r}) = A \exp\{i(\mathbf{k} \cdot \mathbf{r} - \omega t)\} \quad (2.4)$$

where A is the amplitude factor, $\mathbf{r}$ is a vector in real space, and $\mathbf{k}$ is a vector in reciprocal space. Here, $\mathbf{k}$ is referred to as the *wave vector*, or *wavenumber*, if only one relevant dimension is discussed; the wave vector is normal to the wave front and has the magnitude

$$|\mathbf{k}| = \frac{2\pi}{\lambda} \quad (2.5)$$

with λ the wavelength. Since $\mathbf{k} \cdot \mathbf{r}$ is dimensionless, k has the dimension of reciprocal length. $\hbar\mathbf{k}$ has the physical meaning of a momentum.

2.6.1 Wigner-Seitz Cells and Brillouin Zones

The knowledge about the wave behavior can be derived from a unit cell in the reciprocal lattice. A convenient way to introduce this discussion is by examining the *Wigner-Seitz cell* rather than the unit cell itself.

A Wigner-Seitz cell is formed when a lattice point is connected with all equivalent neighbors, and planes are erected normal to and in the center of each of these interconnecting lines. An example is shown in Fig. 2.2, where for the face-centered unit cell ($\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$) the Wigner-Seitz cell is constructed; the plane orthogonal to and intersecting the lattice vector $\mathbf{a}_2$ is visible.

When such a Wigner-Seitz cell is constructed from the unit cell of the reciprocal lattice, the resulting cell is called the *first Brillouin zone*. It is the basic unit for describing lattice oscillations and electronic phenomena.

Most semiconductors crystallize with cubic or hexagonal lattices. The first Brillouin zones of these lattices are given in Fig. 2.3.

Lattice symmetry points can be transformed into the reciprocal lattice and are identified by specific letters. The most important *symmetry points* with their conventional notations are identified in the different Brillouin zones of Fig. 2.2.

Γ is always the center of the zone ($k_x = k_y = k_z = 0$), and X is the intersection of the Brillouin zone surface with any of the main axes (k_x, k_y , or k_z) in any of the cubic lattices. The points Δ , Λ , and Σ , lie halfway between Γ and X , Γ and L , and Γ and K , as shown in Fig. 2.3. The positions of the other symmetry points (H , K , L , etc.) can be seen in Fig. 2.3.

The first Brillouin zone in a primitive orthorhombic lattice extends from $-\frac{\pi}{a}$ to $\frac{\pi}{a}$ in k_x and from $-\frac{\pi}{b}$ to $\frac{\pi}{b}$ in k_y , and from $-\frac{\pi}{c}$ to $\frac{\pi}{c}$ in k_z direction. Since the wave equation is periodic in r and k , all relevant information is contained within the first Brillouin zone.

Fig. 2.2 Face-centered cubic lattice (dashed lines) with primitive parallelepiped, and from it the derived Wigner-Seitz cell in real space, which is equivalent to the Brillouin zone in reciprocal space

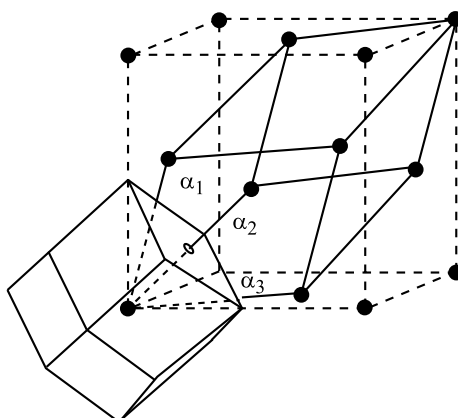
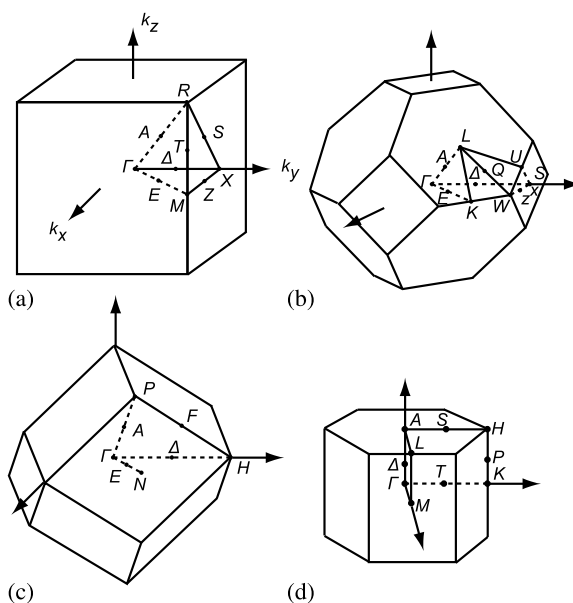


Fig. 2.3 Brillouin zones for the three cubic lattices. (a) Primitive; (b) face-centered; (c) body-centered; and (d) for the primitive hexagonal lattice with important symmetry points and axes



2.7 The Semiconductors

Lattice periodicity is one of the major factors in determining the band structure of semiconductors. The symmetry elements of the lattice are reflected in the corresponding symmetry elements of the bands, from which important information about the electronic structure of a semiconductor is obtained. Therefore the main features of the symmetry of some of the typical semiconductors are summarized below. A comprehensive review of element and compound structures is given by Wells (1984).

Fig. 2.4 Two intertwined tetrahedra with (a) base triangles parallel (dihedral angle 0°), and (b) base triangles rotated by 60°

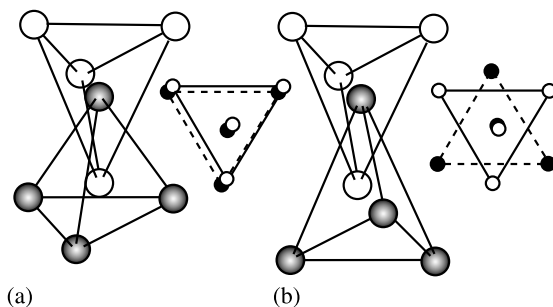


Fig. 2.5 Binary compounds with semiconducting properties



2.7.1 Element Semiconductors

Most of the important crystalline semiconductors are elements (Ge, Si) or binary compounds (III–V or II–VI) (Mooser and Pearson 1956). They form crystals in which each atom is surrounded by four nearest neighbors,² i.e., they have a *coordination number* of 4. The connecting four atoms (*ligands*) surround each atom in the equidistant corners of a tetrahedron. The lattice is formed so that each of the surrounding atoms is again the center atom of an adjacent tetrahedron, as shown for two such tetrahedra in Fig. 2.4. Of the two principal possibilities for arranging two tetrahedra, only one is realized in nature for elemental crystals: the *diamond lattice*, wherein the base triangles of the intertwined tetrahedra are rotated by 60° . Ge and Si are examples. In amorphous elemental semiconductors, however, both possibilities of arranging the tetrahedra are realized—see Sect. 2.9.3.

2.7.2 Binary Semiconductors

Binary III–V and II–VI compounds are formed by both tetrahedral arrangements which are dependent on relative atomic radii and preferred valence angles, although with alternating atoms as nearest neighbors. These compounds can be thought of as an element (IV) semiconductor after replacing alternating atoms with an atom of the adjacent rows of elements (III and V). Similarly, II–VI compounds can be created by using elements from the next-to-adjacent rows—see Fig. 2.5.

²There are other modifications possible. For example, seven for Si, of which four are stable at room temperature and ambient pressure (see Landolt and Börnstein 1982a, 1982b; Landolt and Börnstein 1987). Only Si I and a-Si are included in this book. Si III is face-centered cubic and a semimetal; Si IV is hexagonal diamond and is a medium gap semiconductor (see Besson et al. 1987). Wurtzite lattice (CdS) are constructed from two intertwined hexagonal sublattices of Cd and S.

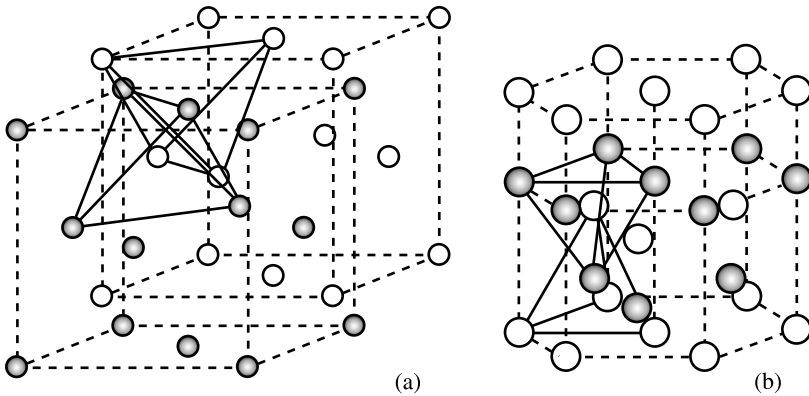


Fig. 2.6 (a) Zincblende lattice (GaAs) constructed from two interpenetrating facecentered sublattices of Ga and As, with a displaced origin at $\frac{a}{4}, \frac{a}{4}, \frac{a}{4}$ with a the edge length of the elementary cube (b)

Aside from these classical AB-compounds, there are others that have interesting semiconducting (specifically thermo-electrical) properties. Examples include the II–V compounds (such as ZnSb, ZnAs, CdSb or CdAs), which have orthorhombic structures. For a review, see Arushanov (1986).

The diamond lattice for AB-compounds results in a *zincblende lattice* shown in Fig. 2.6a. Most III–V compounds, as for instance GaAs, are examples. *Unrotated* interpenetrating tetrahedra, produce the *wurtzite lattice* (Fig. 2.6b) which can also be obtained for a number of AB-compounds. Examples include ZnS and CdS. ZnS can also crystallize in a zincblende modification.

Under certain conditions, alternating layers of wurtzite and zincblende, each several atomic layers thick, are observed. This is called a *polytype*. Usually, the zincblende structure is more stable at lower temperatures and the wurtzite structure appears above a transition temperature (1053 °C in CdS). With rapid cooling the wurtzite structure can be frozen-in. Other structures of binary semiconductors include

- NaCl-type semiconductors, with PbTe as an example;
- Cinnabar (deformed NaCl) structures, with HgS as an example;
- Anti-fluorite silicide structures, with Mg_2Si as an example. These structures can be regarded as derived from the fcc lattice (Fig. 2.6a) with one of the two interstitial positions filled by the second metal atom, similar to the Novotny-Juza compounds (Sect. 2.7.3); and
- A_3B_v -structures, with Cs_3Si as an example.

For a review, see Parthe (1964), Sommer (1968), and Abrikosov et al. (1969).

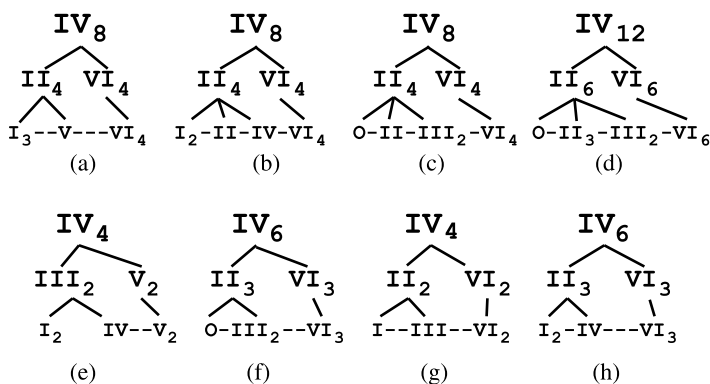


Fig. 2.7 Construction of pseudobinaries (b), ternaries (a, c, d, e) pseudoternaries (g, h), and quaternaries (f) from element (IV) semiconductors (0 represents a vacancy, i.e., a missing atom at a lattice position)

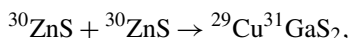
2.7.3 Ternary, Quaternary Semiconductors

Several classes of ternary and quaternary compounds have attractive semiconducting properties. All have tetrahedral structures: each atom is surrounded by four neighbors. Some examples are discussed in the following sections. For a review, see Zunger (1986a, 1986b).

One can conceptually form a wide variety of ternary, quaternary, or higher compounds which have desirable semiconducting properties when one replaces within a tetrahedral lattice, subsequent to the original replacement shown in Fig. 2.5, certain atoms with those from adjacent rows, as given in Fig. 2.7. These examples represent a large number (~ 140) of such compounds and indicate the rules for this type of compound formation. For instance, a II–III₂–VI₄ compound can be formed by replacing 8 atoms of column IV first with 4 atoms each of columns II and VI, and consequently the 4 atoms of column II with one vacancy (0), one atom of column II, and two atoms of column III.

2.7.3.1 Chalcopyrites

Best researched are the *ternary chalcopyrites* I–III–VI₂; they are constructed from two zincblende lattices in which the metal atoms are replaced by an atom from each of the adjacent columns. In a simple example one may think of the two Zn atoms from ZnS as transmuted into Cu and Ga:



with some deformation of the zincblende lattice since the Cu–S and Ga–S bonds have different strengths, and with a unit cell twice the size of that in the ZnS lattice (Fig. 2.8). For a review, see Miller et al. (1981).

Fig. 2.8 (a) ZnS (or GaP) double unit cell; (b) CuGaS₂ (or ZnGeP₂) unit cell

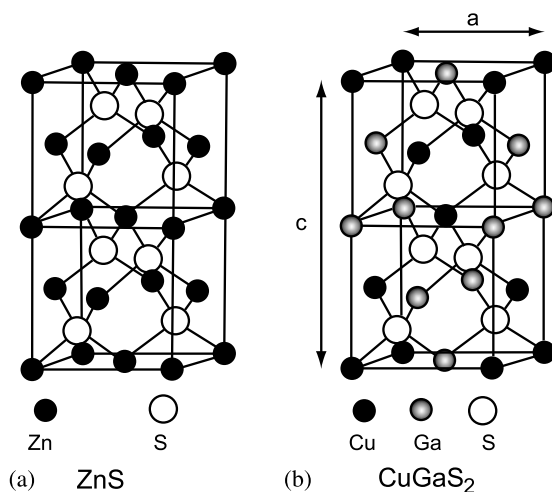
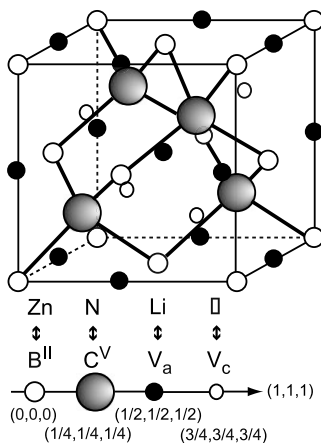
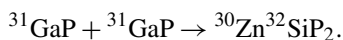


Fig. 2.9 Unit cell of the Novotny-Juza compound



2.7.3.2 Pnictides and ABC₂ Compounds

Other ternaries with good semiconducting properties are the *ternary pnictides* II–IV–V₂ (such as ZnSiP₂) which have the same chalcopyrite structure and, in a similar example, can be constructed from GaP by the transmutation



Still another class with chalcopyrite structure is composed of the I–III–VI₂ compounds, of which CuFeS₂ is representative. (These structures are reviewed by Jaffe and Zunger [1984a](#).)

2.7.3.3 Novotny-Juza Compounds

Interesting variations of this tetrahedral structure (see Parthe 1972) are the *Novotny-Juza compounds*, which are partially filled tetrahedral interstitial I–II–V compounds (e.g., LiZnN). Here the Li atom is inserted into exactly one half of the available interstitial sites of the zincblende lattice (e.g., on V_a or on V_c as shown in Fig. 2.9). A substantial preference for the Li atom to occur at the site closer to the N atom (rather than the site next to the Zn—the lattice energy of this structure is lower by about 1 eV) makes this compound an *ordered* crystal with good electronic properties (Carlson et al. 1985; Kuriyama and Nakamura 1987; Bacewicz and Ciszek 1988)). It should be noted, however, that the Zn atom is fourfold coordinated with N atoms, while the N atom is fourfold coordinated with Zn and fourfold coordinated with Li; therefore, it has eight nearest neighbors.

2.7.3.4 The Adamantine $A_nB_{4-n}C_4$ and Derived Vacancy Structures

Examples of this class of $A_nB_nC_4$ structures with $n = 1$ or 3, such as A_3BC_4 or AB_2C_4 , are the famatinites (e.g., Cu_3SbS_4 or $InGa_3As_4$) or lazarevicites (e.g., Cu_3AsS_4). With $n = 2$ this class reduces to ABC_2 (e.g., $CuGaAs_2$ or $GaAlAs_2$), and with $n = 4$ it reduces to the zincblende (ZnS) lattice. The layered sublattices can be ordered (e.g., in $CuGaAs_2$) or disordered (alloyed) as in $GaAlAs_2$, and are discussed in the following section. All of these compounds follow the octet ($8 - N$) rule; they are fourfold coordinated (each cation is surrounded by four anions and vice versa).

The $8 - N$ rule determines how many shared electrons are needed to satisfy perfect covalent bonding for any atom with N valency electrons, e.g., 1 for Cl with $N = 7$, and 2 for S with $N = 6$, or 4 for Si with $N = 4$, requiring single, chain-like, or tetrahedral bonding, respectively.

Deviations from the $A_nB_{4-n}C_4$ composition may occur when including ordered vacancy compounds into this group, such as II–III₂–VI₄ compounds (e.g., $CuIn_2Se_4$) in which one of the II or III atoms is removed in an ordered fashion, resulting in defect famatinites or defect stannites.

An instructive generic overview of the different structures of tetragonal ternaries or pseudoternaries is given by Bernard and Zunger (1988) (Fig. 2.7). See also Shay and Wernick (1974), Miller et al. (1981), and the conference proceedings on ternary and multinary compounds.

2.7.3.5 Pseudoternary Compounds

Finally, one may consider *pseudoternary compounds* in which one of the components is replaced by an *alloy* of two homologous elements. For example, Ga replaced by a mixture of Al and Ga in GaAs yields $Al_xGa_{1-x}As$; replacement of As by P and As yields GaP_xAs_{1-x} . These pseudoternary compounds contain alloys of isovalent atoms in one of the sublattices.

When the two alloying elements are sufficiently different in size, preference for *ordering* exists for stoichiometric composition in the sublattice of this alloy. Substantial *band gap bowing* gives a helpful indication of predicting candidates for this ordering of stoichiometric compounds. Examples include GaInP_2 , which shows strong bowing, where the Ga and In atoms are periodically ordered (Srivastava et al. 1985), Ga_3InP_4 , or GaIn_3P_4 with similar chalcopyrite-type structures. Here again, the coordination number is four; each atom is surrounded by four nearest neighbors, although they are not necessarily of the same element.

A different class of such compounds is obtained when alloying with non-isovalent atoms, such as $\text{Si}+\text{GaAs}$.

The desire to obtain semiconductors with specific properties that are better suited for designing new and improved devices has focused major interest on synthesizing new semiconducting materials as discussed above, or using sophisticated growth methods to be discussed below, aided by theoretical analyses to predict potentially interesting target materials (see Ehrenreich 1987).

2.8 Superlattice Structures

Periodic alternation of one or a few monolayers of semiconductor A and B produces a composite semiconductor called a *superlattice*. Material A could stand for Ge or GaAs, and B for Si or AlAs. A wide variety of other materials including alloys of such semiconductors and organic layers can be used.

The width of each layer could be a few Angstroms in ultrathin superlattices to a few hundred Angstroms. In the first case, one may regard the resulting material as a new artificial compound (Isu et al. 1987); in the second case, the properties of the superlattice approach those of layers of the bulk material. Superlattices in the range between these extremes show interesting new properties.

2.8.1 Superlattices and Brillouin Zones

The introduction of a new superlattice periodicity has a profound influence on the structure of the Brillouin zones. In addition to the periodicity within each of the layers with lattice constant a , there is superlattice periodicity with lattice constant l .

Consequently, within the first Brillouin zone of dimension π/a , a mini-Brillouin zone of dimension π/l will appear. Since l is usually much larger than a , e.g., $l = 10a$ for a periodic deposition of 10 mono-layers of each material, the dimensions of the mini-Brillouin zone is only a small fraction (a/l) of the Brillouin zone and is located at its center with Γ coinciding. Such a mini-zone is of more than academic interest, since the superlattice is composed of alternating layers of different materials. Therefore, reflections of waves, e.g., excitons or electrons, can occur at the boundary between these materials. The related dispersion spectrum becomes

substantially modified, with boundaries at the surface of such mini-zones. It is this mini-Brillouin zone structure that makes such superlattices especially interesting; this will become clearer in later discussions throughout the book. A more detailed discussion of the mini-zones is inherently coupled with corresponding new properties, and is therefore postponed to the appropriate sections.

2.8.2 Superlattice Deposition

With modern deposition techniques (e.g., vapor phase epitaxy), one is able to deposit onto a planar substrate (e.g., onto a cleaved single crystal of appropriate surface orientation) monolayer after monolayer of the same or a different material. [For a review of the deposition techniques using *molecular beam epitaxy*, see Ploog (1980), Joyce (1985), Gossard (1986), Kelly and Kelly (1985), and for those using *metal-organic vapor phase epitaxy*, see Dapkus (1984) and Richter (1986).] More recently, interest has been stimulated in lateral superlattices.

2.8.3 Ultrathin Superlattices

Single or up to a few atomic layer sequential depositions can be accomplished (Gossard 1986; Petroff et al. 1979) even between materials with substantial lattice mismatch, e.g., Si and Ge, GaAs and InAs. The thickness of each layer must be thinner than the critical length beyond which dislocations can be created. This critical length decreases with increasing lattice mismatch, and is on the order of 25 Å for a mismatch of 4 %.

In ultrathin superlattices, the transition range between a true superlattice and an artificial new compound is reached. This opens an interesting field for synthesizing a large variety of compounds that may not otherwise grow by ordinary chemical reaction using conventional crystallization techniques.

Ultrathin superlattices of isovalent semiconductors are chemically unstable with respect to the segregation. Alloy formation does not require nucleation necessary for crystal growth of the segregated phases. Therefore, alloy formation of GaAs–AlAs is the dominant degradation mechanism. Recrystallization is usually frozen-in at room temperature.

Superlattices with low lattice mismatch, however, are also unstable with respect to alloy formation, e.g., to $\text{Ga}_{1-x}\text{Al}_x\text{As}$. In contrast, the alloy formation of semiconductors with large mismatch lies above that for ultrathin superlattices and they are more stable (Wood and Zunger 1988).

Several of these ultrathin superlattices can be grown under certain growth conditions *spontaneously* as an ordered compound, without artificially imposing layer-by-layer deposition. For instance, $(\text{GaAs})_1(\text{AlAs})_1$ grown near 840 K by Petroff et al. (1978) and Kuan et al. (1985), $(\text{InAs})_1(\text{GaAs})_1$ grown by Kuan et al. (1987),

(GaAs)₁(GaSb)₁ grown by Jen et al. (1986), (InP)_n(GaP)_n grown by Gomyo et al. (1987), and (InAs)₁(GaAs)₃ + (InAs)₃(GaAs)₁ grown by Nakayama and Fujita (1985). All of these lattices grow as ordered compounds of the A_nB_{4-n}C₄-type.

2.8.4 Intercalated Compounds

In crystals, such as graphite, which show a two-dimensional lattice structure, layers of other materials can be inserted between each single or multiple layer to form new compounds with unusual properties. This insertion of layers can be achieved easily by simply dipping graphite into molten metals, such as Li at 200–400 °C. After immersion, the *intercalation* starts at the edges and proceeds into the bulk by rapid diffusion. Such interlayers can be, for example, halogens or alkali metals. Examples include KC₈ or LiC₆, compounds which are transparent (yellow) and show anisotropic conductivity and low-temperature superconductivity.

In the process of intercalation, the metal atom is ionized while the graphite layer becomes negatively charged. When immersed in an oxidizing liquid, the driving force to oxidize Li can be strong enough to reverse the reaction. This reversible process is attractive in the design of high-density rechargeable batteries when providing electrochemical driving forces.

Other layer-like lattices can also be intercalated easily. An example is TaS₂. Many of these compounds have extremely high diffusivity of the intercalating atoms. Some of them show a very large electrical anisotropy. For a review, see Whittingham and Jacobson (1982).

2.8.5 Organic Superlattices

Well known are the *Langmuir-Blodgett films* (Langmuir 1920; Blodgett 1935), which are monomolecular films of highly anisotropic organic molecules, such as alkanolic acids and their salts which form long hydrophobic chains. One end of the chain terminates in a hydrophobic acid group. Densely packed monomolecular layers can be obtained while floating on a water surface; by proper manipulation, these layers can be picked up, layer by layer (Fig. 2.10), onto an appropriate substrate, thereby producing a highly ordered superlattice structure; up to 10³ such layers on top of each other have been produced. The ease in composing superlattices with a large variety of compositions makes these layers attractive for exploring a number of technical applications including electro-optical and microelectronic devices. For reviews, see Roberts (1985) and Agarwal (1988).

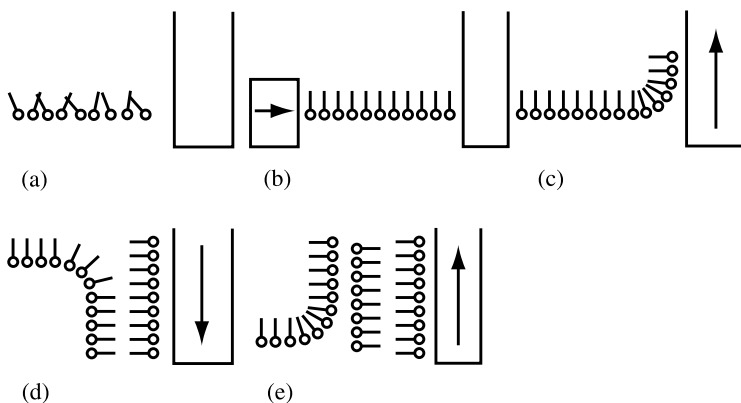


Fig. 2.10 Langmuir-Blodgett technique to produce multilayer films of amphiphilic, i.e., either hydrophilic or hydrophobic molecules from a water surface in a head-to-head and tail-to-tail mode. (a) Monolayer on top of water surface; (b) monolayer compressed and ordered; (c) monolayer picked-up by glass slide moving upward; (d) second monolayer deposited by dipping of glass slide; and (e) third monolayer picked-up by glass slide moving upward

2.9 Amorphous Structures

Although there is no macroscopic structure³ in amorphous semiconductors (*glasses* for brevity), there is a well-determined *microscopic order* in atomic dimensions, which for nearest and next-nearest neighbors is usually nearly identical to the order in the crystalline state of the same material. The *long-range order*, however, is absent (see Phillips 1980).

In many respects, the glass can be seen as a supercooled liquid. When cooling from a melt, glass-forming materials undergo two transition temperatures: T_1 , where it becomes possible to pull filaments (honey-like consistency); and T_g , where form-elasticity is established.

Glass can be formed into any arbitrary shape when its viscosity has reached $10^{15} p$, and its atomic rearrangement time is $\sim 10^5$ s. Only T_g is used for a glass as the transition temperature and is identified in Fig. 2.11 (for a review see Jackie 1986).

When plotting certain properties of a semiconductor—such as its specific density, the electrical conductivity, and many others as a function of the temperature—a jump and break in slopes are observed at the melting temperature T_m when crystallization occurs. Such a jump is absent when cooling proceeds sufficiently fast and an amorphous structure is frozen-in.

Fast cooling (quenching) for typical glasses is already achieved with a cooling rate < 1 deg/s, while many solids, including metals, become frozen-in liquids and

³The surface of glasses, even at very high magnification, does not show any characteristic structure; after fracture, glasses show no preferred cleavage planes whatsoever.

Fig. 2.11 Schematics of the dependence of the reciprocal density as a function of the temperature for a crystal (lower curve with a break at melting) and for a glass (upper curve without a break and the transformation point for form-elasticity identified). T_f to permit pulling filaments is not well identifiable in this diagram; it lies between T_g and T_m

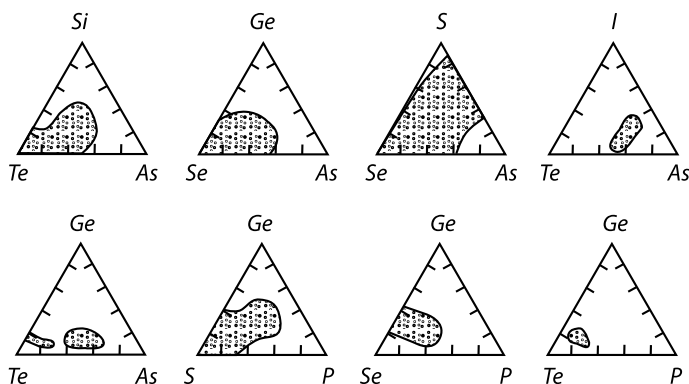
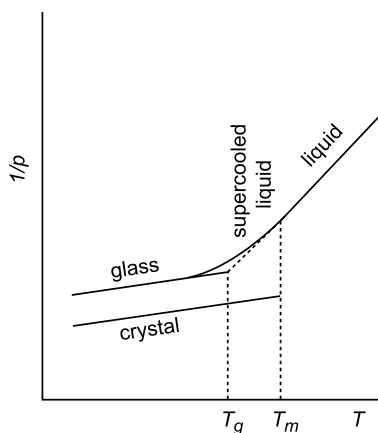


Fig. 2.12 Approximate glass-forming (shaded) regions in a few ternary semiconductor alloy systems; a point within this triangle represents an alloy of the three components of a composition given by the normal to each side of the triangle (after Mott and Davis 1979)

remain amorphous at room temperature when this rate is $\sim 10^7$ deg/s, which can be achieved by *splat cooling* on fast rotating disks.

Near a transition temperature $T_g < T_m$, the slope gradually changes and, for $T < T_g$, the curves in Fig. 2.11 for a glass and a crystal of the same material run essentially parallel to each other.

Materials that have a large fraction of covalent bonding show a tendency for glass formation. Here the liquid becomes significantly more viscous before crystallization takes place. The glass formation composition range is shown for some ternary compounds in Fig. 2.12. In this range, while still liquid, cross-linking of many atoms has already taken place, and the principal building blocks (see below) of the glass are established; however, they cannot adjust with sufficient rigor to produce long-range periodicity.

The resulting amorphous structure is composed of principal building blocks that join each other with slight deviation from the preferred inter-atomic angle and dis-

tance (*frustration*) and consequent relaxation of these relations within the building blocks. In contrast, during crystallization, such building blocks break up easily so that a larger crystallite can grow by sequentially adding atoms rather than entire building blocks. During glass formation, there is usually little tendency to form *dangling bonds*, i.e., bonds not extending between two atoms.

The structural analysis of an amorphous semiconductor can therefore be divided into two parts: the principal atomic building blocks, and the arrangement of these blocks to form the glass.

2.9.1 Glass-Forming Building Blocks

Atomic semiconductors are discussed easily, since all of the neighbors are equivalent. Perfect crystalline order with tetrahedral binding (fourfold coordination) requires the formation of six-member rings. Polk (1971) introduced *odd-numbered rings* (5 or 7), and thereby formed glasses with an otherwise tetrahedrally coordinated arrangement of atoms around these building blocks. Odd-numbered rings were confirmed in α -S (Pantelides 1987) and in a -C (Gallagher 1988).

Comparing crystalline (c) and amorphous (α) structures of the same element (e.g., Ge), one sees that first- and second-neighbor distances (2.45 vs. 2.46 and 4.02 vs. 4.00 Å for c -Ge vs. a -Ge, respectively) are surprisingly similar, as is the *average* bond angle (109.5 vs. 108.5°).

There is, however, a *spread* of $\pm 10^\circ$ in the bond angle for other amorphous structure, resulting in an *average coordination number* of 3.7 rather than 4 for c -Ge (Etherington et al. 1982). The lower effective coordination number indicates a principal building block structure that is slightly less filled but without vacancies, which are ill-defined in amorphous structures. Hard sphere models, which would assist in defining sufficient space between the spheres as vacancies, must be used with caution since covalent structures can relax interatomic lattice spacing when relaxing bond angles (Waire et al. 1971).

Binary compounds are more difficult to arrange in such a fashion, since odd-member rings cannot be formed in an AB sequence without requiring at least one AA or BB sequence. Random network models, however, can also be made with larger *even-numbered rings*. Zachariasen (1932) suggested the first one for SiO₂-type glasses.

Many covalent polyatomic binary compounds containing chalcogenes, easily form semiconducting glasses such as As₂S₃, As₂Se₃, or Ge _{x} Te _{y} . The principal building blocks obey the $8 - N$ rule.

In some of the amorphous chalcogen compounds is the nearest neighbor distance shorter and the coordination number lower than in the corresponding crystalline compounds (Bienenstock 1985). The large variety of possible Ge _{x} Te _{y} building blocks that still fulfill the $8 - N$ rule, created by replacing Ge–Ge with Ge–Te or Te–Te bonds, is the reason that glasses of a continuous composition from pure Ge to pure Te can be formed (Boolchand 1985).

2.9.2 Coordination Number and Constraints

In crystalline covalent semiconductors, the coordination number is given by the $8 - N$ rule. For compounds one can define an *average coordination number*, drawing a shell in the atomic distribution function around an arbitrary atom. These shells contain at nearest neighbor distance a maximum of $m = 4$ atoms for GaAs, $m = 3$ for GeTe (also for As), and $m = 2$ for a linear lattice such as Se. The average coordination number is $m = 2.7$ for GeTe₂, and $m = 2.4$ for As₂Se₃. There are $m/2$ constraints per atom in a crystal with respect to bond length, since two atoms share a bond. This can easily be fulfilled if $m/2 < 3$, since each atom can shift with respect to its neighbor in three dimensions. There are also $m(m - 1)/2$ constraints with respect to the bond angle, since it is defined by three atoms.

Si- and GaAs-type semiconductors are *over-constrained*: a large internal strain prevents any significant deviation from its ordered, crystalline state. But Se, with $m = 2$, is *under-constrained*: it provides a large amount of freedom for deviation from uniformity in bond length and angle; therefore, it easily forms amorphous structures. As₂Se₃, needs only minor alloying to cause m to drop below 2.4, and therefore also forms a glass easily. A glass-forming tendency is rather sensitive to a lowering of m (Ovshinsky 1976a, 1976b, Adler 1985; Phillips 1980).

2.9.3 Short-Range vs. Intermediate-Range Order

The principal building blocks are also described as *intermediate-range order*. These blocks are composed of subunits, identified by the *short-range order* of a few atoms and characterized by bond lengths, bond angles (next-nearest neighbor distances), and site geometry. Intermediate-range order describes *third neighbor distances*, *dihedral angles*, atomic ring structures, and *local topology*. It distinguishes for tetra-, tri-, and divalent bonding truly three-dimensional (tetrahedral), two-dimensional (layer-like), and one-dimensional (chain-like) structures, respectively.

2.9.4 Network Structures

The entire glass can be composed of a *network-like structure* from elements of intermediate-range order, or as a *matrix-like structure*, which is preferable for elemental semiconductors.

Network glasses are constructed from principal building blocks with *long-range disorder* added. Such disorder can be introduced in several ways by statistical variation of interatomic distances and bond angles.

Requirements for creating such a network were given by Bell and Dean (1972) and applied to α -SiO₂, α -GeO₂, and α -BeF₂. When starting from an Si(O_{1/2})₄ unit, one proceeds with a covalent random network, connecting to it other Si(O_{1/2})₄ units with twofold oxygen coordination, while requiring that:

- the bond angle of Si atoms must not deviate more than $\pm 10^\circ$ from the ideal value of 109.47° ;
- all tetrahedra are corner-connected;
- the bond angles of O atoms may spread by $\pm 25^\circ$ from the ideal value of 150° ;
- there is equal probability for all dihedral angles;
- there is no correlation between bond angles at O atoms and dihedral angle; and
- there is complete space filling.

Modifications of these instructions yield slightly different networks. The relation to the dihedral angle (e.g., assuming some correlation) is an example of such modification.

A relatively simple infinite aperiodic network structure is called a *Bethe lattice* (Bethe 1935; Peierls 1935, see also Runnels 1967). Another kind of network structure is the *fractal structure*, in which void spaces between more densely filled regions can be identified (see Mandelbrot 1981).

2.9.5 Matrix Glasses; α -Si:H

Of special interest to solar cells is α -Si:H. Here in an atomic amorphous semiconductor the requirements for a fourfold coordination are relaxed and thereby creating dangling bonds. These bonds could attract monovalent elements such as H or F. Alternatively, the tetravalent host atom could be replaced with an element of lower valency such as N or O.

When foreign atoms are introduced in a density that is large enough so that their interaction can no longer be neglected, we call this process an *alloy formation*; as such, we may include homologous elements (e.g., C in α -Si). In all such cases, we then satisfy the $8 - N$ -rule but achieve a greater degree of flexibility in constructing the amorphous *host matrix*, a reason why such alloys are easily formed.

In addition, we may include into such a host matrix more than one kind of atom, and thereby create more complex alloys, e.g., forming α -Si:O:H or α -Si:N:H.

For a theoretical analysis of the various possibilities of incorporating foreign atoms (e.g., in SiH, SiH₂, or SiH₃ configurations), it is useful to consider larger *atomic clusters* from this network. Such clusters contain nearest, next-nearest, and higher-order neighbors from the alloyed atom. α -Si:H contains hydrogen without substantially changing the dihedral angle. It is incorporated by decorating defects with hydrogen, thereby forming SiH or SiH₂ units (Menelle and Bellissent 1986) eliminating dangling bonds. α -Si:H has a coordination number of ~ 3.7 , and may be described as a mixture of fourfold and threefold coordinated atoms.

2.10 Quasicrystals

Materials with an order between crystalline and amorphous are called *quasicrystals* (Nelson 1986). In contrast to a crystal, which is formed by a *periodic repetition*

of one unit cell, these quasicrystals can be assembled by an aperiodic repetition *of two different unit cells*. One or both of these unit cells may have fivefold symmetry as first shown by Shechtman et al. (1984). This symmetry is forbidden for crystals since it cannot fill space without overlap or voids.

Quasicrystals have no long-range order (Sokoloff 1985) even though there is no variation of bond length or bond angle: all atoms fit into one of the two *unit cells* (Kramer and Neri 1984; Levine and Steinhardt 1984; Cahn et al. 1986; Henley 1987; Steinhardt 1987). Similar quasicrystalline behavior can be modeled with specific (Fibonacci) sequences of superlattices (Todd et al. 1986) (see the following section).

In two dimensions, the arrangement of tiles into a completely filled pattern provides an instructive example. While only three types of regular polygons (namely triangles, squares and hexagons) can fill a given flat surface by themselves, the use of two types allows many other tile shapes, including one with fivefold symmetry, to fill the same surface completely (Penrose tiling: Penrose 1974; Nelson 1986).

Chapter 3

The Growth of Semiconductors

Abstract The growth of crystals through transport, diffusion and attachment of each particle, as well as dissipation of heat is discussed. Nucleation and growth habit, are discussed Typical growth techniques from vapor, melt, and chemical reactions are exemplified. Recrystallization, including means of purification are given, stress and flux enhanced crystallization and local heating is discussed.

The growth of a semiconductor is determined by four processes:

- transport of atomic particles to the surface
- diffusion of the particles across the surface
- attachment of each particle at a preferred surface site
- dissipation of heat developed during growth.

Each of these processes has a specific time constant which can be altered by the experimental conditions. Depending on these conditions, a wide variety of growth habits, morphologies, and degrees of order will ensue, with often decisive consequences on the performance of solar cells based on such growth that can rarely corrected sufficiently. It is therefore important to be aware of consequences that may be directed by economical factors, forcing a compromise between these and performance.

3.1 Nucleation

Any growth starts from a nucleus or crystal seed. It takes place when a state in which the atomic particles are close enough to each other at a temperature below the melting point so that an ordered arrangement of these atoms is energetically preferred. A few atoms in an ordered state,¹ are in a lower energy state and tend to grow when this nucleus is of an overcritical size. The surface tension of a statistically formed nucleus assists in growth by keeping atoms with the nucleus. Interplay between volume and surface energy defines a critical size above which regular growth starts.

¹Even after melting, many nuclei are not broken down and can act as growth centers when the temperature is lowered below the melting point T_m .

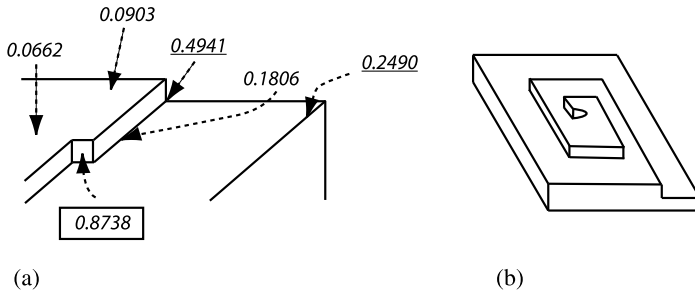


Fig. 3.1 (a) Surface of a cubic alkali halide with atomic step and bonding energies at the various indicated sites. (b) Spiral growth around a screw dislocation in a cubic material

3.2 Growth Habit

When the transport to the surface is slower than the diffusion across the surface, the growth from a nucleus is ordered and a microcrystallite is formed. When such growth occurs from one nucleus (seed) only, a *single crystal* will grow. Growth from statistically formed nuclei results in *polycrystals*.

When the transport to the surface surpasses the diffusion velocity at the surface, i.e., when the viscosity of the material near the surface is too large, the atomic particles do not have time to find their proper, ordered position before more arriving atoms block their movement and freeze in a highly disordered state, creating an *amorphous solid*.

Such growth occurs more easily when the atomic building blocks are larger molecules, or are formed by covalent forces in which, aside from space filling, well-defined angle relations must be fulfilled.

3.2.1 Single Crystal Growth

Crystal growth can easily be understood in an ionic crystal (e.g., an alkali halide). The energy gained by attracting an ion pair on the surface of a crystallite depends on the position at the surface, that is on the number of attracting neighbors and is lowest on a flat surface and highest at an inner edge (Fig. 3.1a). Near the melting point, where the balance between absorption and desorption of ions is only slightly shifted in favor of absorption, the *sticking* of ion pairs will be most persistent at inner corners with a bonding energy $= 0.8738e^2/r$, as shown in Fig. 3.1a; hence, growth will be fastest here. Thereby, all inner corners and inner edges will rapidly disappear, leaving only ideal, flat surfaces. Growth perpendicular to such surfaces has to await nucleation of a two dimensional seed; this then becomes the growth rate limiting process.

A screw dislocation provides atomic steps which cannot be outgrown. Continued absorption of atoms at such steps² results in *spiral growth* (Fig. 3.1b). Fast spiral growth around a screw dislocation results in a whisker growth (Levitt 1970; Kit-tel 1986). Such whiskers have a mechanical strength which is orders of magnitude larger than that of bulk crystals and approaches the theoretical maximum cohesion strength. Here, the central screw dislocation prohibits slips of lattice planes which otherwise would ease mechanical deformation.

3.2.2 Crystal Growth Techniques

Techniques to grow single crystals are numerous, such as:

- vapor phase
- melt
- solution
- chemical reactions.

The *growth from the vapor phase* can proceed by evaporation *in vacuo*, in an inert atmosphere, or in a reacting atmosphere, the latter, e.g., to maintain stoichiometry of a dissociating compound, or to synthesize the desired compound.

Spontaneous nucleation is observed by sublimation of CdS, forming platelets, or by seeding. Vapor phase deposition onto an identical or similar lattice, called *epitaxy*, is well known. Vapor phase epitaxy may involve atomic or molecular beams *in vacuo* (*molecular beam epitaxy*), or may involve dissociation of an evaporated compound, e.g., an organometallic compound, with one of the components condensing.

Single crystal *growth from the melt* requires careful seeding, which can involve dipping of a cooled seed from the top surface and consequent slow pulling (*Czochralski method*). Here, heat removal through the grown crystal is the limiting process of the growth rate.

Another method uses an anisotropic growth rate, e.g., it is largest in c-direction of certain semiconductors. When random crystallization starts in a narrow tip at the bottom of a vessel, crystals aligned with their c-axis in the direction of the axis of the tip capillary will outgrow crystallites with other orientations and will act as an oriented seed for the melt in the wider, upper part of the vessel (*Bridgeman technique*).

Crystallization from a solution using water or organic solvents is usually started by evaporating part of the solvent, or by lowering of the temperature, thereby achieving *supersaturation*. Many other solvents can also be used, including liquid metals

²When grown from an evaporation source, spiral growth is preferred with a substrate perpendicular to the source (e.g. CdS). This requires that the source remains stationary to produce large crystallites, and makes continuous growth on a band disadvantageous as it tends to produce small crystallites in various orientations.

or other molten solids which show phase segregation before both components, the solvent and the dissolved material, solidify.

A wide variety of *chemical reactions* can assist the crystal growth process. These reactions, however, must proceed slowly enough to avoid incorporation of undesired reaction by-products, or to disturb the heat removal during crystallization. For this, we may use highly diluted reaction partners with consequent evaporation during a spray deposition of a fine mist onto a heated condensation plate.

Another method involves gels containing the reaction partners and permitting only a slow interdiffusion to slow down the chemical reaction.

In all, there is a wide variety of crystal growth methods. Often, a specific material requires its own individually designed growth technique to obtain single crystals of the desired quality, with few general rules applicable. Many reviews are available to describe this subject in detail, e.g., Buckley (1951), Laudise (1970), Goodman (1978), Holden and Morrison (1982), Pamplin (1980), and Brice (1986).

3.3 Recrystallization

In many methods of deposition compromises are made by first obtaining polycrystalline materials of a wide variety of crystallite sizes. Growth of these microcrystallites can be achieved by

- Simple heating to an appropriate temperature below the melting point
- Heating with helping stress to enhance crystallization
- Heating in the presence of a “flux” that eases partial temporary dissolution
- Local heating that helps propagating fronts of ordered crystal growth

Each one of these methods has a large variety of application, only a few of them are given here as examples.

3.3.1 *Slow Recrystallization*

In order to facilitate and economize growth, often the molten material has been filled into an appropriate form of minimal interdiffusion with the melt and similar expansion coefficient and slowly cooled without specific seeding. A typical example is polycrystalline silicon that has been cooled in large forms and later cut into slices, similar to Czochralski grown Si.

3.3.2 *Stress-Enhanced Crystallization*

The stress can be introduced directionally by bending a substrate onto which the material is evaporated, or by (depositing) evaporating a foreign atomic layer that

causes local stress starting from the surface, to begin recrystallization. An example for the later is the Kakhenberg method in which a thin layer of copper is evaporated on polycrystalline CdS and heated to a few hundred degrees *in vacuo* to start recrystallization.

3.3.3 Heating in the Presence of a Flux

This method has a large variety of modifications, all characterized that the flux material is applied sparsely, typically from the surface and permitted to diffuse into the crystallites by partially dissolving and immediately crystallizing these again in a more ordered form.

A typical example are many II/VI compounds, e.g. CdS which recrystallizes easily in the presence of cuprous chloride. The consequent incorporation of some copper in the CdS is often benign or even a desirable dopant because of its limited solubility and its ability to increase the photoconductivity of CdS.

3.3.4 Local Heating Induced Recrystallization

Well-known is the method of zone melting that is often used for purification, in which a thin molten zone is slowly moved along a cylinder axis of the material. Since the solubility of impurities is usually different in the melt and in the solid crystal, one achieves segregation of such impurities either at the front or back-end of the molten zone. With repetitive succession of such *zone rectification* can obtain a highly purified single crystal in the middle fraction.

Chapter 4

Crystal Defects

Abstract The growth of crystals through transport, diffusion and attachment of each particle, as well as dissipation of heat is discussed. Nucleation and growth habit, are discussed Typical growth techniques from vapor, melt, and chemical reactions are exemplified. Recrystallization, including means of purification are given, stress and flux enhanced crystallization and local heating is discussed.

A large variety of crystal defects determine the electronic properties of semiconductors. Some of these act as donors or acceptors that are essential for the operation of a solar cell as they produce the *pn*-junction. Others are recombination centers that limit the life time of minority carries, hence the efficiency of these cells. Still others are responsible for carrier scattering or recombination; some of them trap carriers and influence the space charge that determines the carrier transport. A better knowledge of the diversity of these defects helps to improve the solar cell performance. Typical examples of these defect are discussed here. Crystal boundaries A better knowledge of the diversity of these defects helps to improve their performance. Crystal boundaries are discussed as a special class of crystal defects. All of this will come handy to refresh our knowledge and expand it with the given literature. Some tables may be helpful references.

4.1 Defect Classifications

One distinguishes:

- point defects, such as single atoms or vacancies in an otherwise near-ideal lattice;
- line defects (dislocations);
- surface defects relating to external or internal crystal surfaces; and
- volume defects, relating to small, three-dimensional inclusions (precipitates) or defect associates.

These defects are enumerated in the following sections.

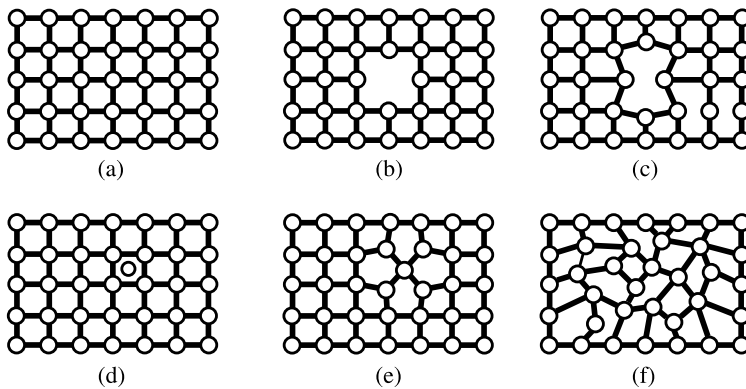


Fig. 4.1 (a) Two-dimensional representation of cubic lattice and some of its defects; (b) ideal vacancy; (c) relaxed vacancy; (d) ideal interstitial; (e) interstitialcy, i.e., interstitial atom forming bridges between adjacent host atoms; and (f) extended interstitial with substantial lattice relaxation beyond nearest neighbors

4.2 Point Defects

Point defects are the main class of defects that act as donors or acceptors, or, when their energy levels are farther separated from the bands, as traps or recombination centers. They are also important as scattering centers, especially when charged with respect to the host lattice. We distinguish:

- A. Intrinsic (native) lattice defects, such as:
 - a. vacancies (a missing lattice atom, Fig. 4.1b),
 - b. interstitials (an additional host atom within the lattice, Fig. 4.1d), and
 - c. antisite defects in compound semiconductors, e.g., in an AB compound where an A atom occupies a B site.
- B. Impurities located at
 - a. substitutional lattice site, or at an
 - b. interstitial site.
- C. The lattice surrounding of such a defect shows some degree of relaxation, such as:
 - a. neighbor position relaxation (Fig. 4.1c) and other special cases, including
 - b. split interstitials (the *interstitialcy*) in which a host atom is replaced by two symmetrically displaced atoms.
- D. Small defect associates are also counted as point defects such as:
 - a. defect pairs- α , divacancies, β . Impurity associated with an intrinsic defect, γ two impurities associated with each other;
 - b. higher defect associates, containing α . Three defects or β more defects in close proximity.

Large varieties of defects are distinguished according to their

E. Geometrical arrangement with respect to each other

- a. forming an anisotropic center, or
- b. forming distant pairs, distinguished by their distance within the lattice while still interacting.

Finally, all defects containing an impurity are distinguished by their

F. chemical identity, which relates to the

- a. defect center and to the
- b. host lattice.

It is often more appropriate to identify the chemical identity with respect to the host lattice and to distinguish.

G. host-related defects, identified as

- a. isovalent impurities (from the same column of the periodic system—also called isoelectronic);
- b. isocoric impurities¹ (from the same row of the periodic table, i.e., having the same core);
- c. substitutionals with $z = \pm 1$ (z is the chemical valency);
- d. substitutionals with $z = \pm 2$ or more;
- e. amphoteric defects,² in which the sign of z can change;
- f. transition metals, identified as a separate group because of their outer shell screening, giving more individuality to the defect and mostly yielding deeper levels.

The distinctions given above will become the major guidelines for the decision of which

H. approximations are best suited for a theoretical analysis to describe the defect with sufficient accuracy, such as

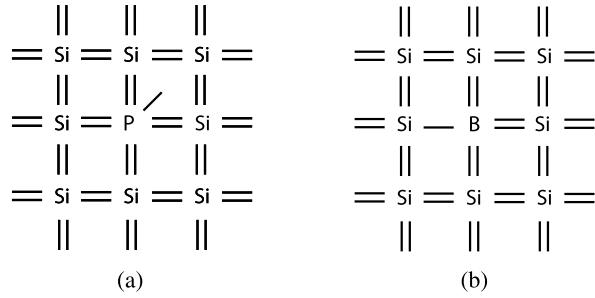
- a. an effective mass treatment, suited for shallow defects, or
- b. other approximations involving the core potential (deep centers), and including
- c. substantial lattice relaxation.

This list is not complete, but shows the great abundance of defects present in real crystals. Each of these contributes to the wealth of electronic *eigenstates*, most of them as levels in the band gap. Only a small fraction of the defects is presently unambiguously identified, therefore only a few examples are discussed

¹An isocoric P in a Si lattice can be thought of as “created” by adding to a lattice atom a proton, i.e., a point charge, and an extra electron (the donor electron, Sect. 4.2), thereby creating the most ideal hydrogen-like defect. Any other hydrogen-like donor, e.g., As or Sb in Si, is of different size, causing more lattice deformation and a substantially different core potential 1 .

²That is, a defect that can act as a donor or acceptor depending on the chemical potential of the lattice (influenced, e.g., by optical excitation or other doping, by compensation).

Fig. 4.2 Substitutional phosphorus P as donor and boron B as acceptor, shown in subfigures (a) and (b), within a covalently bound Si lattice with extra or missing electron (line) to complete bonding at the P or B atom respectively



with confidence below (Lannoo and Bourgoin 1981). For experimental methods of defect identification see Bourgoin and Lannoo (1983).

Levels in the gap are most directly observed by optical absorption or luminescence with or without external fields, to provide information on the transitions between two levels, or involving photoconductivity to provide information about transitions between the levels and one of the bands. More recently, biased junctions have been used for positive identification with the shift of quasi-Fermi levels and thereby the defect center occupation. In the following section, a short review is presented of the most important, electronically active point defects of semiconductors, and on their charge character with respect to the crystal lattice.

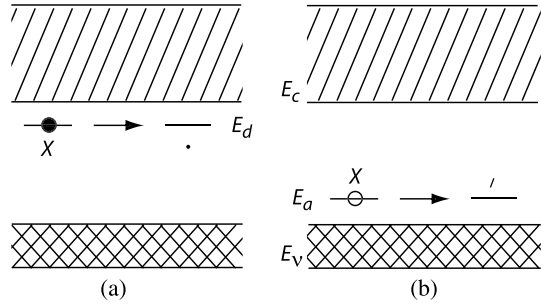
4.3 Donors and Acceptors

Foreign atoms which substitute for an intrinsic lattice atom are most easily described when they are from an adjacent column of the periodic system of elements with respect to the replaced atom, e.g., a boron or phosphorus atom replacing a silicon atom in a silicon crystal.

The pentavalent Phosphorous atom has one extra electron in its outer shell than the host (Fig. 4.2a). A substitutional P atom replacing one Si atom of the lattice, the extra electron is loosely bound and can easily be emitted into the conduction band by thermal ionization. The P acts as a *donor* in the Si crystal; it produces a level close to the conduction band, as shown in Fig. 4.3a. The energies E_d and E_a are assigned to the un-ionized donor and acceptor.

In a similar fashion, the incorporation of a B atom on an Si site causes the deficiency of an electron (Fig. 4.2b) and can be regarded as a hole, bound to a B atom. The hole can be replaced by an electron from the valence band. In the hole picture, the B atom becomes ionized (Fig. 4.3b); it produces a free hole and acts as an *acceptor*, with a level close to the valence band.

Fig. 4.3 Band model of a typical semiconductor with a donor (a) and an acceptor (b), indicating the relative charge character with and without charge carrier (*prime* ['] negative, *dot* • positive, and a *cross* $\times$ as neutral, relative to the surrounding lattice)



4.3.1 Defect Notation Within the Host Lattice

When the donor is ionized, it becomes positively charged. The change in charge character plays an important role in later discussions on carrier capture and scattering. Such charge relations can be followed easily in a chemical representation: the “reaction” between a donor (D) and an electron (e) can be written as



where x , $\bullet$, and $'$ represent neutral, positive, and negative charge with respect to the lattice. This notation is referred to as *Kröger-Vink notation*,³ and it will be used consistently in this book—see Hayes and Stoneham (1984). To be more descriptive with respect to the chemical nature of the defect, one writes



which indicates the atomic defect (P) substituting an Si atom as the subscript. In general, point defects are identified by the symbol of the defect, with the lattice site on which the defect is located as a subscript. For example, a chlorine vacancy (V) in a NaCl lattice is identified as V_{Cl} a potassium ion replacing a sodium ion in the same lattice as K_{Na} , and a copper interstitial as Cu_I .

In a similar fashion, the recharging of an acceptor is described by



or



where h^* represents a hole in the valence band.

³The notation of charges with respect to the neutral lattice was introduced by Kröger, Vink, and Schottky (see Schottky and Stöckmann 1954). This notation should not be confused with the charge identification used in an ionic lattice, e.g., Na^+Cl^- . Inclusion of a Cd^{++} instead of a Na^+ ion makes the cadmium ion singly positively charged with respect to the neutral lattice; hence it is identified here as Cd_{Na}^* when referenced specifically as a lattice defect.

4.3.2 Substitutionals in AB-Compounds

Substitutionals in an AB-host lattice act similarly to substitutionals in element semi-conductors, except one distinguishes whether an anion or a cation is being replaced. For instance, replacement of a divalent Cd ion in a CdS crystal by a trivalent In ion, denoted by In_{Cd}^x , yields:



This results in a shallow donor, as does the replacement of a sulfur ion from group VI with a halogen ion from group VII. On the other hand, the replacement of Cd with an alkali-metal ion, or of S with a group V element like P or As, produces an acceptor. However, the incorporation of one type of defect (in CdS the incorporation of donors) is often easier than for the oppositely charged defect (acceptors in CdS), rendering the material preferably *n*- or *p*-type (CdS is *n*-type). Intrinsic compensation (see Sect. 4.3) is one reason for this preference. An interesting case occurs for some trivalent compounds. For example, in GaAs, the replacement of Ga with the tetravalent Si results in



acting as shallow donor, while the same Si, replacing a trivalent As ion,



results in a shallow acceptor. Depending on the growth condition, one or the other is preferred, and the material becomes either *n*- or *p*-type.

4.3.3 Vacancies and Interstitials

Vacancies and interstitials are denoted in a similar fashion. Metal-ion interstitials usually act as donors example, in CdS,



Metal-ion vacancies act as acceptors:



Nonmetal-ion vacancies usually act as donors:



A first and rather simplified judgment as to whether the defect more readily becomes positively or negatively charged is easily rendered in ionic compounds. Semiconductors with mixed bonding character can also be judged by following the $8 - N$

rule. The rule maintains that elements tend to complete their outer shell by sharing electrons with neighbor atoms; surplus electrons are donated to the lattice; and missing electrons are attracted from elsewhere in the lattice. Interstitial metal ions tend to donate their valence electron(s), consequently reducing their radius, and cause less lattice deformation. Other, more complex aspects of point defects will be discussed in the following chapters. Now a short overview of line defects is given.

4.4 Line Defects

In the previous sections, *point defects* were discussed, i.e., defects that are located at a given atom in the lattice and involve their immediate surroundings. In this section we introduce one-dimensional *line defects* called *dislocations*, which often extend throughout the entire lattice. There are two main types of dislocations:

- edge dislocations and
- screw dislocations.

Other ways to distinguish dislocations will be discussed below—see Read (1953), Weertman and Weertman (1960), or Cottrell (1964); for theoretical analyses, see Nabarro (1967), and Hirth and Lothe (1968).

Dislocations have a major influence on certain types of crystal growth and on electron transport, and are therefore discussed here—see Friedel (1964), and Hull (1975). Other important influences include mechanical deformation (yield strength) and the formation of grain boundaries.

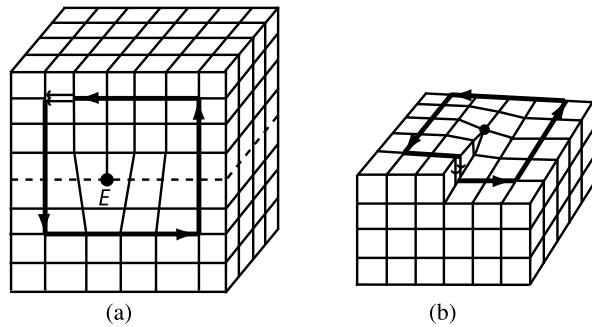
4.4.1 Edge Dislocations

Edge dislocations (Taylor 1934; Orowan 1934) are formed by an extra lattice plane inserted into a part of a crystal as shown in Fig. 4.4a. The dislocation line extends along the terminating edge of the inserted plane. Such dislocations are produced when a crystal is exposed to nonuniform mechanical stress large enough to result in plastic deformation along a *glide plane*. In Fig. 4.4a {001} plane is indicated. Another preferred glide plane in cubic crystals is the {110} plane.

4.4.2 Screw Dislocations

A *screw dislocation* (Burgers 1939—Fig. 4.4b) shows a step at the outer surface, while only a slight lattice deformation exists surrounding the dislocation within the crystal. The screw dislocation is important for crystal growth (Frank 1949a) since adherence of atoms is substantially enhanced at an inside surface edge. A screw dislocation continuously maintains such an edge during growth by forming a growth spiral (Fig. 4.5).

Fig. 4.4 (a) Additional plane partially inserted into a simple cubic crystal, resulting in an edge dislocation E . The glide plane is indicated by a dashed line. (b) (Left-handed) screw dislocation in a simple cubic crystal producing a step at the crystal surfaces. The Burgers vector is identified by a double lined arrow



4.4.3 The Burgers Vector

Dislocations are identified by their *Burgers vector*. The Burgers vector are defined by constructing a polygon with an equal number of lattice steps on each side of the polygon. The path is closed in a perfect crystal. However, it is no longer closed when this path surrounds a dislocation. The lattice vector needed for completion of the polygon is the Burgers vector—see Fig. 4.4. For an edge dislocation, the Burgers vector is orthogonal to the dislocation line; for a screw dislocation, it is parallel to the dislocation line. When the Burgers vector is at an angle $0 < \theta < 90^\circ$ to the dislocation line such dislocation is called a *mixed dislocation*, an example of which is shown in Fig. 4.5.

4.4.4 Dislocations in Compounds

In a binary (AB) compound, edge dislocations in the $[110]$ direction are energetically favored, but require *two* extra (110) planes: an a and a b plane as shown in Fig. 4.4a. These adjacent planes can split into two separate ones (*partial dislocations*), as shown in Fig. 4.6b. The separation of planes maintains the correct AB-sequence above and below the dislocation line, except for a jump of composition between both partial dislocations. Such partial dislocations have a lower energy than the unit edge dislocation and therefore are favored. In more complex crystals, more than two extra planes are required to restore periodic order. Therefore, the Burgers vector becomes larger the more complex the crystal structure is.

4.4.5 Partial Dislocations in Semiconductors

The preferred slip plane in tetragonal bond semiconductors is the $\{111\}$ plane which could lie either between the closely spaced planes, called *glide set*, or between the wider spaced planes, called *shuffle set* (Ba or bB in Fig. 4.6). These are 60° dislocations (Shockley 1953).

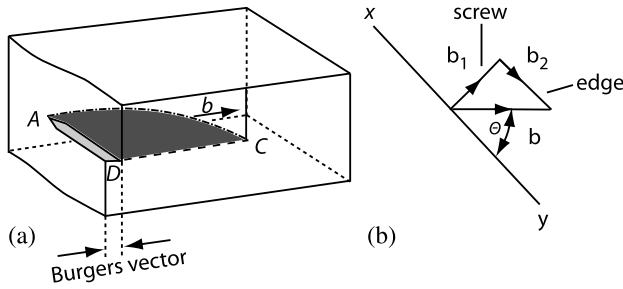


Fig. 4.5 (a) Mixed dislocation, with pure screw at A and pure edge at C. (b) Burgers vector $\mathbf{b}$ involves an edge ($\mathbf{b}_2$) and a screw ($\mathbf{b}_1$) component

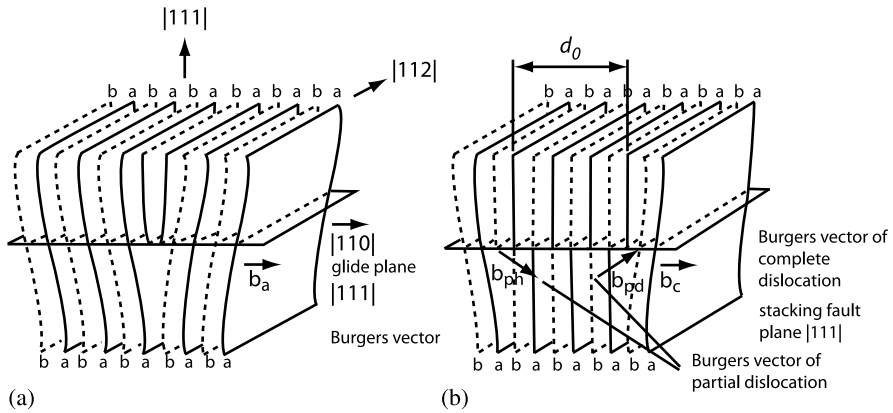


Fig. 4.6 (a): Unit edge dislocation in an AB-compound in the $[110]$ direction of a face-centered cubic crystal. (b): Extended dislocation of the same compound of two Shockley partial dislocations separated by a stacking fault (plane b continues as plane a etc. above the partial dislocation plane)

Along such dislocations a row of dangling bonds appears, as shown in a perspective view in Fig. 4.7. Dangling bonds are expected to effectively trap electrons with major influence on electrical properties (Labusch and Schroter 1980). However, reconstruction of the dislocation core eliminates most of these dangling bonds with substantial reduction of the electrical influence of such dislocations (Hirsch 1985).

The 60° dislocation consists of two partials (a 30° and a 90° partial), each of which is capable of reconstruction. Figure 4.6b shows the reconstruction of the 30° glide partial; whereas Fig. 4.8a shows dangling bonds along a 90° glide partial, and Fig. 4.8b its reconstructed core.

The 90° glide partial shows an interesting alternative of bonding which has the same energy. In the transition region, a dangling bond is created. Such a defect is also referred to as an *antiphase defect*, and can move as a *soliton* along the reconstructed glide partial (Heggie and Jones 1983). For more detail, see the literature cited in Hirsch (1985).

Fig. 4.7 60° dislocation on a shuffle plane of an Si crystal with a row of dangling bonds (after Schroter 1979).

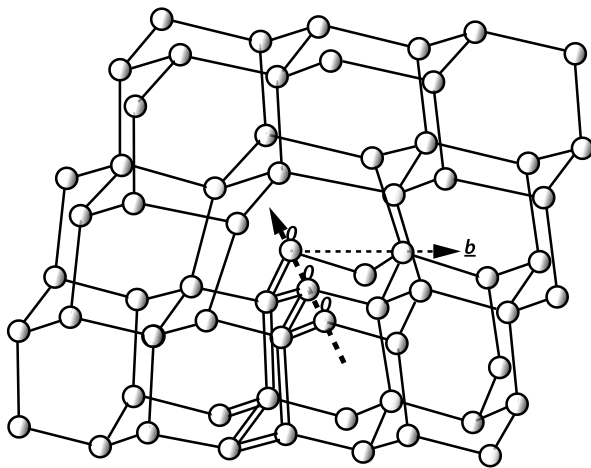
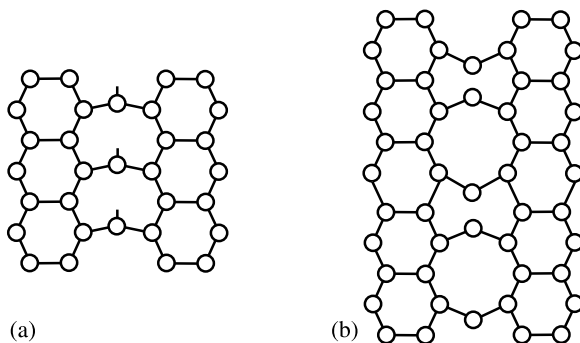


Fig. 4.8 (a) 30° glide partial dislocation in Si shown in an (111) plane; (b) reconstructed (after Jones 1981)



4.4.6 Electronic Defect Levels at Dislocations

Dangling bond states are electronic defect states within the band gap. Non-reconstructed dislocations result in a half-filled defect band in the band gap (Shockley 1953). Their presence affects the carrier density; for instance, plastic deformation on *n*-type Ge can render the material *p*-type (Labusch and Schroter 1980).

Core reconstruction reduces the density of dangling bonds dramatically and the remaining ones act as isolated deep level point defects. In addition, the lattice deformation near the reconstructed core causes defect levels in the band gap closer to the band edges.

Electron paramagnetic resonance and its angular dependence yield information about the density and orientation of defects with unpaired spins, i.e., dangling bonds. Experiments with plastically deformed Si at 650°C indicate that only 0.2, ..., 2 % of the available sites are not reconstructed, and have unpaired spins at dangling bond centers (Weber and Alexander 1983). Kinks, curved dislocations, or other special features, such as jogs or nodes, are the suspected sites of the remaining dangling bonds (Osip'yan 1983).

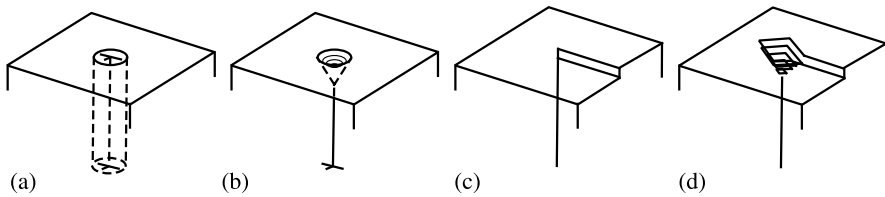


Fig. 4.9 Formation of etch pits at the surface surrounding an edge (**a**, **b**) and a screw dislocation (**c**, **d**)

Deep level transient spectroscopy (DLTS) indicates that filling of deep levels at dislocations, which lie in closer proximity to each other, produces a Coulomb barrier. This impedes consequent trapping of adjacent centers and can be recognized in the DLTS signal (Koeder et al. 1982). Acceptor levels at $E_c - E_a \approx -0.35$ and 0.54 eV, and a donor level at $E_d - E_v \approx 0.4$ eV, have been detected in plastically deformed Si (Kimerling and Patel 1979; Weber and Alexander 1983).

Luminescence and photoconductivity measurements yield additional information about deep levels associated with (mostly reconstructed) dislocations, kinks, jogs, etc. For a review, see Weber and Alexander (1983), Mergel and Labusch (1982), and Suezawa and Sumino (1983).

A unique identification of specific dislocation-related defects is difficult: with deformation at elevated temperatures, other defects and defect associates are formed, the signatures of which cannot easily be separated.

4.4.7 Dislocation Counting

Dislocations can be made visible by several methods (Hull 1975). One of the easiest is via surface etching, i.e., removing parts of the lattice surrounding the dislocation, which are under stress and therefore dissolve more easily. The surface etching method is shown schematically in Fig. 4.9. Since most of the dislocations extend throughout the entire crystal, we obtain their density by counting the *etch pits* at the surface. The best Si crystals contain less than 1 etch pit/cm². Typical commercial semiconductors have a dislocation density of $10^2 \cdots 10^4$ etch pits/cm².

Other methods which involve the direct observation of dislocations include: transmission electron microscopy of thin layer EBIC,⁴ relating to their electronic properties; reflection or transmission imaging, relating to mechanical stress of the surrounding; X-ray diffraction; tunneling; and field ion microscopy. Indirect observation is possible by using *decoration*, which uses precipitates along dislocation lines to increase contrast and also to permit light microscopic observation (Hull, 1969).

⁴Electron-beam-induced conductivity, used in a scanning electron microscope (Heydenreich et al. 1981).

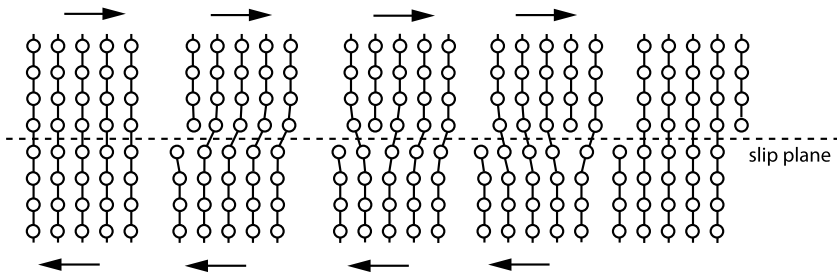


Fig. 4.10 Glide motion of an edge dislocation along a slip plane

4.4.8 Motion and Creation of Dislocations

All dislocations can move conservatively if the motion is parallel to the Burgers vector, or, more generally, when the dislocation moves within its slip plane. Such motion is called *glide*, shown in a two-dimensional representation in Fig. 4.10, and is the essential part in a plastic deformation of a crystal.

The motion of an edge dislocation normal to both its Burgers vector and its dislocation line is called *climb*. It is non-conservative, meaning it causes a change of the height of the inserted plane, i.e., atoms must move to or from the dislocation core (dislocation line).

A gliding dislocation that encounters an obstacle—such as another crossing dislocation, a vacancy, a foreign atom, or other crystal defects—can become pinned at such an obstacle, i.e., the obstacle hinders dislocation movement. In this example the dislocation must “climb over” the obstacle in order to continue moving. Both, glide and climb are important in plastic deformation of crystals—see Cottrell (1958), or Hirth and Lothe (1968).

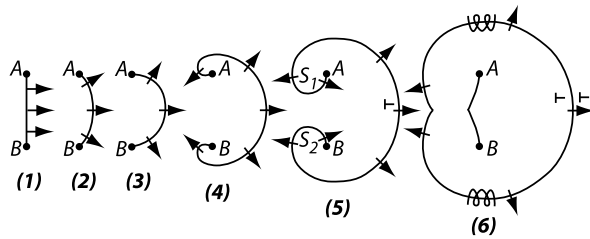
4.4.9 Dislocation Velocity

When a shear stress is exerted parallel to the Burgers vector of an edge dislocation, it is unlikely that the entire dislocation moves step by step as shown in Fig. 4.10.

When drawing the edge dislocation in a plane normal to that shown in Fig. 4.10, we see a more probable sequence of events, in which part of the dislocation moves one lattice spacing and connects to the remaining part with kinks. This type of movement is most probable when some pinning of the original dislocation occurs along its length.

The dislocation velocity is then determined by the nucleation rate and motion of double kinks, as well as by the interaction of such kinks with localized lattice. Such interaction is known to depend on the electrical charge of these defects, and is influenced by the position of the Fermi- (or quasi-Fermi) level (Patel and Chaudhuri 1966). For instance, the velocity of dislocations under otherwise identical conditions

Fig. 4.11 (1) Frank-Read source with progressively growing dislocation loop (2)–(5) and separation (6) to repeat this process (1)–(6)



is ≈ 50 times larger in *n*-type than in *p*-type Ge. Other deep level centers, e.g., oxygen, cause pinning of the dislocation.

This dislocation motion is more complicated when partial dislocations need to be considered. Generation of double kinks in the two partials may be correlated (Wessel and Alexander 1977).

Some partials (e.g., with a Burgers vector inclined to a stacking fault) cannot glide; these are called *sessile* (Frank 1949a, 1949b). Other dislocations which can move easily are called *glissile*.

4.4.10 The Frank-Read Source

The application of sufficient shear stress produces additional dislocations from a dislocation pinned at the two ends (*Frank-Read source*—Frank and Read 1950), and forced to bow by mechanical deformation perpendicular to the direction of the dislocation (Fig. 4.11). In this way *dislocation loops* can be formed sequentially, and the process repeats itself periodically as long as the stress persists (see Read 1953).

4.4.11 Electroplastic Effects

Edge dislocations in covalent semiconductors are partially charged, since in addition to some remaining dangling bonds, the stress field surrounding the dislocation creates traps for carriers, and the termination of an extra layer in an ionic crystal carries an inherent charge (Petrenko and Whitworth 1980). The movement of such a dislocation is therefore influenced by other charges.

The charge density per unit length of the dislocation can be changed when carriers are injected or optically generated. In addition, other defect centers can be recharged. Thereby, the ability of dislocations to climb is changed. Usually, this results in an increase of the mechanical strength, i.e., in its resistance to plastic deformation; photo quenching in contrast causes a decrease in mechanical strength—see Osip'yan et al. (1986). This effect is referred to as the *electroplastic effect* and also, depending on how the change in carrier density is induced, as the *photoplastic effect* or the *cathodoplastic effect*. These effects are rather pronounced in II–VI compounds, and were first observed by Osip'yan and Savchenko (1968) in CdS.

The spectral distribution of the photoplastic effect is nearly identical to that of the photoconductivity, indicating a direct relation to the electron density in the conduction band. Further related to this is an increased density of charged defects, which tends to pin the dislocation movement. A change in their charge *distribution* is also a possible mechanism for pinning of dislocations, thereby decreasing the plasticity.

4.4.12 Disclinations

While dislocations are related to symmetries in translation, *disclinations* are related to symmetries of rotation. Both types of defects are sources of internal strain.

Disclinations can be used to describe frustrated systems resulting in curved lattice regions which are common in amorphous or organic semiconductors. For more information, see the review of Kleman (1985) and the original literature cited therein.

4.5 Surface Defects, Planar Faults

There are several types of two-dimensional defects:

- stacking faults,
- low angle grain boundaries,
- twin boundaries,
- crystallite boundaries,
- hetero-boundaries,
- strained layer systems,
- surfaces (ideal and with absorption or chemisorption layers), and
- metal/semiconductor boundaries.

These defects have a significant influence on the electrical properties of real semiconductors. Most of this influence is caused by defect levels at the boundaries (surfaces), which are usually charged and attract compensating charges in the adjacent crystal volume (*space charges*).

In spite of their importance, however, these defects are mentioned briefly here; they deal with profound inhomogeneities which are covered later in this book.

4.5.1 Stacking Faults

Stacking faults are the least disordered types of interface defects. They occur by alternating between *wurtzite* and *zincblende* structures: to form the lattice from atomic layers stacked on top of each other in the *c*-direction, we start from a hexagonal (“close packed”) layer (A), and deposit the next identical layer (B) offset and turned

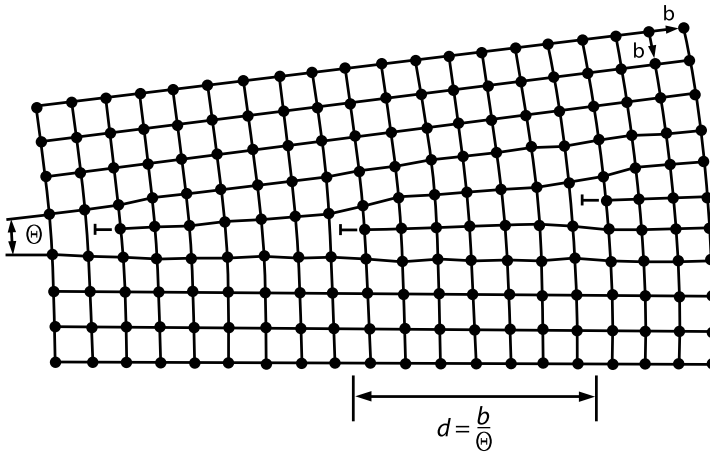


Fig. 4.12 Low-angle grain boundary with an array of edge dislocations separated by seven lattice planes

by 60° to touch each second interspace at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$. For the deposition of a similarly offset third layer, we have the choice of turning it back by 60° to the original position (A), resulting in a wurtzite lattice, or turning it forward by another 60° to offset it from the bottom layer by 120° (C), resulting in a zincblende lattice. The layer sequence ABABAB therefore characterizes wurtzite; the layer sequence ABCABC characterizes zincblende. A sequence ABABABCAB consequently identifies a *stacking fault*. A thin slice of a stacking fault can be seen as being imbedded between two partial dislocations, i.e., the boundary of a stacking fault is a partial dislocation—see Nabarro (1967).

ZnS and SiC are examples for materials that show such stacking faults. There can be a long-range periodicity in these stacking faults, up to a few hundred Å in SiC, which produces so-called *polytype structures*.

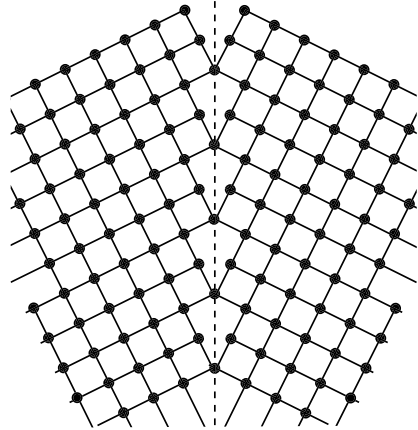
4.5.2 Grain Boundaries

One distinguishes several types of grain boundaries, the more important ones will be discussed in the following sections.

4.5.2.1 Low-Angle Grain Boundaries

Low-angle grain boundaries show a very small tilt between two regular crystallites and can be regarded as an array of dislocations (Burgers 1940; Bragg 1940), as shown in Fig. 4.12.

Fig. 4.13 Twin grain boundary in the (112) surface of a cubic crystal



The angle between the two grains (at most a few degrees) is given by

$$\Theta = b/d \quad (4.11)$$

where b is the length of the Burgers vector and d is the dislocation spacing.

4.5.2.2 Large-Angle Grain Boundaries

Twin boundaries are special angle boundaries between two identical crystallites. The least disturbed twin boundary is that of a stacking fault, as discussed in Sect. 4.5.1, by proceeding from an AB sequence to a BC sequence.

Other twin boundaries are under an angle at which each second (or third) atom falls onto a lattice site as shown in Fig. 4.13. It can therefore be regarded as an array of vacancy lines similar to an array of edge dislocations in low-angle grain boundaries.

Other crystallite boundaries may occur under a wide variety of angles and may incorporate at the interface a variety of disorders, including vacancies, dislocations, and liquid-like structures with a high degree of local stress.

Grain boundaries can have a major influence on semiconducting properties by trapping carriers and creating compensating space charge layers. Some of the effects related to carrier mobility will be discussed later in this book.

4.5.2.3 Heteroboundaries

The heteroboundary between two crystals of different composition is of technical importance for heterojunction devices. It is characterized by a mismatch in several

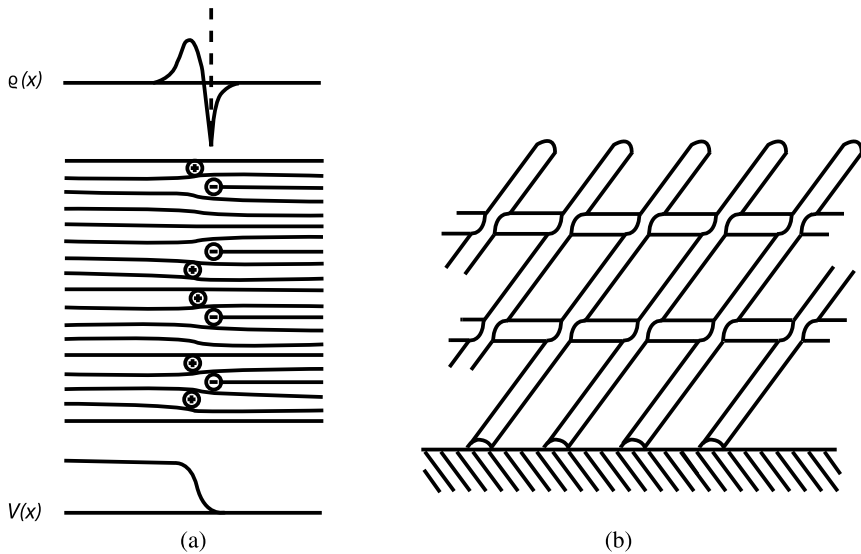


Fig. 4.14 (a) Mismatch dislocations with compensating space charges, resulting in a space charge double layer and potential step. (b) Spatial distribution of the space charge double layer surrounding the dislocation network in the form of half cylinders (after Böer 1983)

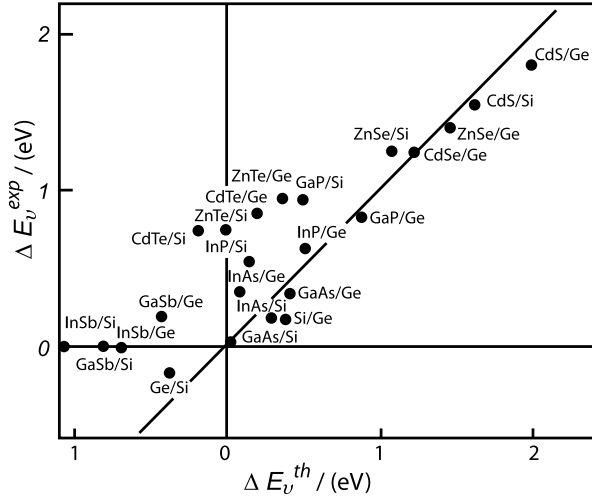
parameters, most importantly the lattice constant, the *electron affinity*⁵ (see Bauer et al. 1983), and the energy gap.

The mismatch of expansion coefficients is of interest when a device is produced at temperatures substantially different from room temperature, or is exposed to temperature cycling during operation. It causes curling of thin layer laminates or may generate major interface defects; in extreme cases, it results in delamination.

The lattice mismatch is accommodated through a network of dislocations (Fig. 4.14b). The strain produced by the mismatch is only partially relieved by the mismatch dislocation network. The remaining strain decreases linearly with the distance from the heterojunction, and depends on the hetero geometry. Usually, it results in an opposite strain at the outer surfaces. This can best be seen for a lattice mismatch in one direction within the interface plane. It results in a bending of the crystal, with a neutral plane near its center. It has compression and expansion at the hetero-interface and the surface, respectively.

⁵The electron affinity of a semiconductor is defined as the energy difference from the lower edge of the conduction band to the vacuum level, i.e., the energy gained when an electron is brought from infinity into the bulk of a crystal, resting at E_c . It should be distinguished from the electron affinity of an atom, which is equal to the energy gained when an electron is brought from infinity to attach to an atom and forms an anion.

Fig. 4.15 Experimental values for the jump of the valence band of various heterojunctions obtained from photoemission (ΔE_v^{exp}), compared with the calculation from the Harrison model (ΔE_v^{th}). Best agreement is obtained for junctions with high degree of lattice match (after Bauer et al. 1983)



The mismatch dislocation network is usually charged and compensated by a space charge region, resulting in a potential step. This step is typically on the order of $0.1 \cdots 0.5$ eV (Böer 1983) as shown in Fig. 4.14a.

The compensating space charge is located close to each dislocation line, surrounding it in the form of a half-cylinder. The closeness is caused by the high density (small Debye length). The half, rather than full, cylinder is caused by the different probabilities of incorporating compensating defects in the different semiconductors and different dielectric constants.

In addition, there is a potential step caused by the difference in electron affinities and modified by the actual dipole moment at the crystal interface (Kraemer 1975; Harrison 1977). The dipole moment varies with changing crystallographic directions of this interface.

The difference in electron affinities is considered to be the major contribution in causing the step in the conduction band at the interface (Anderson 1962). Such linearization, however, can give misleading results. When considering the crystallographic direction of the interface and mismatch dislocation network, additional changes in step height by ± 0.5 eV can be encountered. The difference between electron affinities can be obtained experimentally from photoemission measurements, where the threshold energy directly yields the difference from the top of the valence band to the vacuum level (4.12).

In Fig. 4.15 the jumps of the valence bands of various heterojunctions are given, and are compared with the prediction of the Harrison model, using linear combination of atomic orbitals. There is reasonable agreement for couples with low lattice mismatch, but only fair agreement is observed and a deviation of up to 1 eV for semiconductor couples with larger lattice mismatches. For a review see Katnani and Margaritondo (1983).

Table 4.1 Photoelectrically determined workfunction of metals in eV (preferred values after Michaelson 1972)

Metal	Workfunction	Metal	Workfunction	Metal	Workfunction
Ag (100)	4.75	Ga	4.5	Sb	4.08
(111)	4.81	Hg	4.53	Sr	2.35
Al	4.08	In	3.8	Ta	4.19
Au	4.82	Ir	5.3	Th	3.35
Be	3.92	Mg	3.68	Ti	4.45
Bi	4.24	Mn	3.76	Tl	3.36
C	4.81	Mo	4.3	U	3.63
Ca	2.71	Ni	5.01	V	3.77
Cd	4.07	Os	4.55	W (001)	4.52
Cm	4.4	Pb	4.14	(110)	4.58
Co	4.2	Pd	4.79	(111)	4.39
Cr	4.37	Pt	5.32	(112)	4.65
Cs	1.81	Rb	2.16	(211)	4.50
Fe α	4.70	Rh	4.57	(310)	4.35
β	4.62	Sn β	4.50	Zn (0001)	4.26
γ	4.68	γ	4.38	Zr	4.21

4.5.3 Metal/Semiconductor Interfaces

Metal/semiconductor interfaces are special types of heterojunctions. The electrical properties of all large-area *metal contacts* are determined by this interface; in point contacts, high-field tunneling effects dominate the electrical behavior. The most important parameter of a metal/semiconductor interface is its *relative workfunction* Ψ_{MS} often referred to as the *barrier height* or *contact potential*,⁶ which determines the electron density at this interface:

$$n(x_{MS}) = N_c \exp(\Psi_{MS}/kT) \quad (4.12)$$

where N_c is the effective level density at the band edge of the semiconductor.

Like the difference in electron affinities in a heterojunction, there are many factors which determine the barrier height Ψ_{MS} , such as the chemical nature of metal and semiconductor and the actual structure of the interface. In first approximation,

⁶The contact potential can be measured when both materials are facing each other in vacuum at a temperature sufficient for some electron emission. The material with lower workfunction will emit more electrons, consequently charging the higher workfunction material until the current between both materials vanishes. The relative potential difference, so established between the two materials, is the *contact potential* φ . The workfunction is the energy from the Fermi level to the vacuum level; the electron affinity is the energy from the conduction band edge to the vacuum level. The former is used in connection with metals, the latter preferably in connection with semiconductors.

Fig. 4.16 Barrier height of a few metals on some semiconductors plotted as a function of the interface heat of reaction, indicating the complexity of the involved processes [after Brillson (1978)]

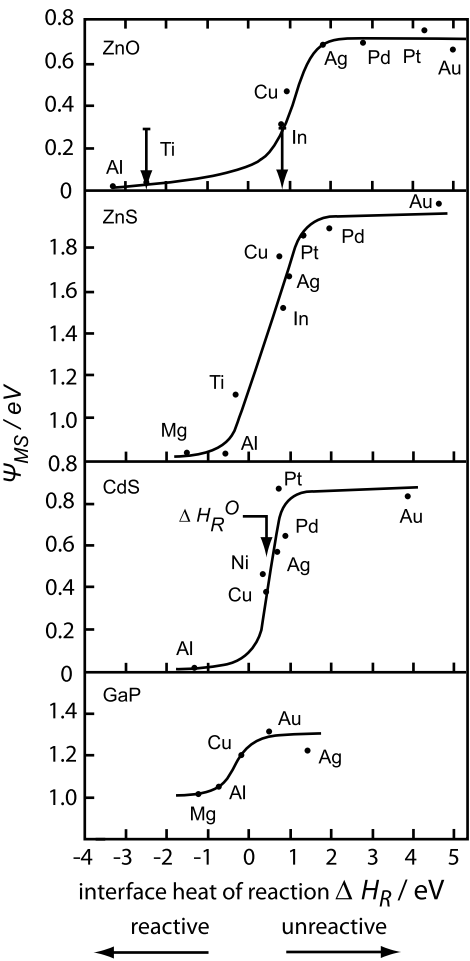


Table 4.2 Intrinsic workfunction of semiconductors in eV (after Zunger 1986a, 1986b; and Smith 1949). @John Wiley & Sons, Inc.

Material	Workfunction	Material	Workfunction
Si	5.2	ZnS	7.5
Ge	4.5	ZnSe	6.82
		ZnTe	
GaP (110)	5.9...6.01	CdS	5.76
GaAs (110)	5.49...5.56	CdSe	7.26
InP (110)	5.69...5.85	CdTe	6.62

Ψ_{MS} is the difference between the workfunctions of the metal (see Table 4.1) and the semiconductor (see Table 4.2). which determines the electron exit from these materials into the vacuum. It is, however, modified by the actual double layer at

the crystallographic interface. Chemical reaction and crystallographic ordering of the interface region, as well as the pinning of the Fermi level by interface defects (Spicer et al. 1980a), have a significant effect on ψ_{MS} . The barrier height of a few metals on some semiconductors is shown in Fig. 4.16.

Space charge effects near the metal/semiconductor contact influence the carrier transport in this region to a large degree. For further studies, see Spenke (1958), Henisch (1957), Rhoderick (1978), and Sharma (1984).

Chapter 5

Photochemical Reactions

Abstract Defect chemical reaction are exemplified, initiated by light, causing device degradation. Involving motion of atomic defects, ionization, polarization, favored position are given. Pair formation, initiation by giant oscillation relaxation are shown. Examples in alkali halides, photochemistry in silver halides, latent picture, development, and fixation of picture are given as examples. Print-out effect. Film sensitivity and sensitization is discussed. Time-dependent photochemical reaction, photochemical degradation of photoconductivity, and the Staebler-Wronski effect. Fast photochemical processes are given.

Defect-chemical reactions that are induced by light usually cause degradation of solar cell performances. Some of these changes are metastable and can be annealed out in the dark. A large variety of photochemical reaction with different degrees of performance changes and examples are presented here to give some guidance for solar cell designs with better life expectancy.

Solar cell degradation is typically caused by a change in the diffusion length of minority carriers that depend on the defect structure that in turn is changed by the illumination. The diffusion length is significantly influenced by the *minority carrier lifetime*, controlled by recombination and by *carrier mobility* that is influenced by carrier scattering.

Light induced changes can be initiated by recharging of defects with consequent lattice relaxation. A large variety of these defects can influence the quasi-Fermi level distribution, the knowledge of which is essential for the understanding of the performance of solar cells. Therefore they will be more extensively discussed in this chapter.

5.1 Defect-Chemical Reactions

Photochemical reactions involve the movement of atomic defects into a new, stable (rarely) or metastable position. Only a few of them are currently related to cell degradation, but many others given here may provide essential background information for a more detailed understanding. Such motion of atomic defects can be

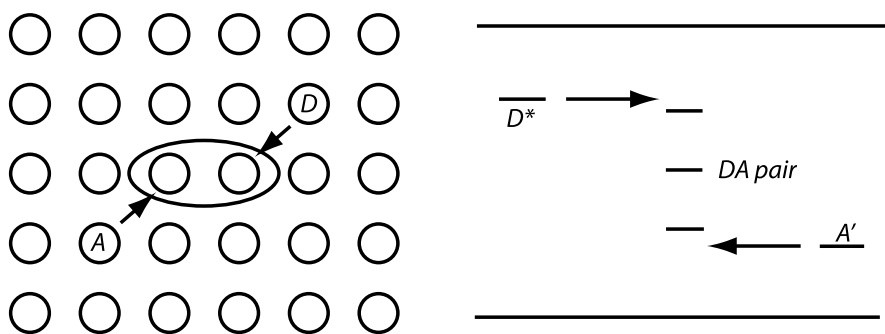


Fig. 5.1 Ionized donors and acceptors moving together and creating a donor-acceptor pair, which acts as a recombination center (level drawn schematically)

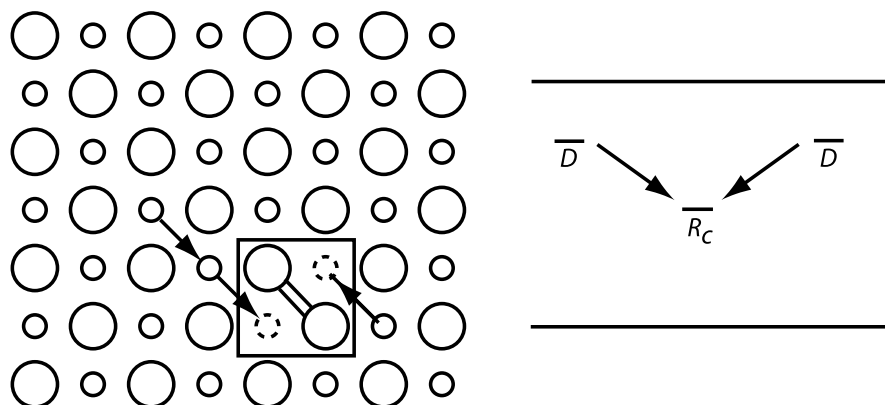


Fig. 5.2 Two cation vacancies moving together, trapping two holes and creating an anion molecule that acts as a recombination center (R_C)

described as the reaction between two defects, induced by ionizing at least one of the partners, thus creating a favorable polarization for an atomic movement into the new position.

It also requires a sufficient temperature, or local heating, i.e., by a photo-induced giant oscillations

An example is the charging of a donor and an acceptor in close proximity. They become Coulomb-attractive, and may move closer to each other and form a *donor-acceptor pair* (Fig. 5.1), which is sufficiently bound to resist separation at the given temperature.

Another example is the pair formation of cation vacancies, which is facilitated when these vacancies are ionized, i.e., a hole is trapped in each. When moving together, the two adjacent anions are neutralized and represent a strongly bound *covalent molecule*—Fig. 5.2. The cluster of the four lattice defects, two vacancies

and the two-anion molecule, can be regarded as a new center with an increased scattering and recombination cross section.

Yet another example is the dissociation of a defect-associate after it is ionized, with the ionization facilitating such dissociation.

When a newly created defects act as a recombination center, the lifetime of photo generated carriers (in photoconductors) or minority carriers (in solar cells), hence the *photoconductivity* or the solar efficiency, respectively, decreases.

In addition, some of the donors or acceptors may disappear, resulting in an increase of distance of the Fermi level from the respective bands, hence the *darkconductivity* decreases.

With cessation of the optical excitation, the photochemical-reaction products tend to dissociate again, hence reversing the photochemical-reaction. At sufficient temperatures, this reversal can be completed, returning the photoconductor to its original state—see Sect. 5.3.

5.1.1 Photochemistry by Giant Relaxation Oscillators

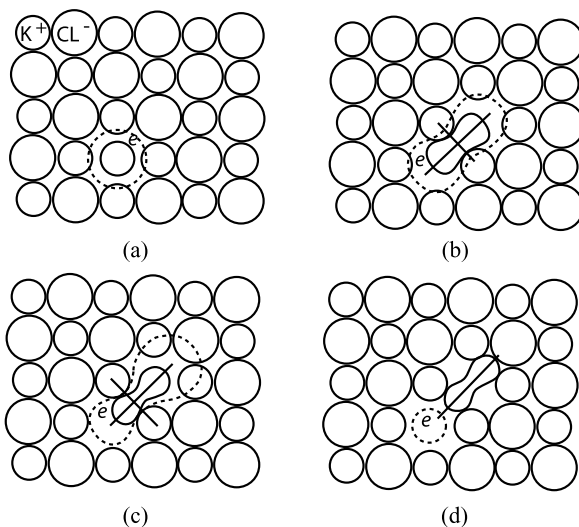
An example of how such defects can be created locally was suggested by Henry and Lang (1977), who have shown that the recharging of a deep center after trapping a carrier causes violent oscillations of the defect before relaxation by dissipation of phonons. Such oscillations can be regarded as strong local heating and can lead to a jump of the defect atom into a new metastable position with a different electronic character, i.e., the creation of a photochemical reaction product. These F- and R-centers can be formed at temperatures far below room temperature, and require thermal activation energies for relaxation between 0.02 and 0.2 eV, depending on the specific alkali halide where the first experiments were performed (Itoh 1982).

In this example the exciton in an alkali halide has a very large electron-lattice coupling. The exciton can be trapped at a halogen lattice site, which in turn can relax to form a halogen molecule. Contracting and moving it to the adjacent *single* halogen site where it forms an R-center. The electron from the original exciton becomes attached to the newly created adjacent vacancy and forms an F-center. This sequence of processes is shown in Fig. 5.3. Evidence of such simultaneous formation is provided by kinetic experiments (see Sect. 5.3.3), as reviewed by Itoh (1982). See also Stoneham (1979).

Photochemical reactions were observed very early by Poole in the 40's with a strong change of the optical absorption spectrum of alkali halides.

Direct optical evidence in typical solar cell materials of relaxation-induced giant oscillations is more difficult to obtain because of the smaller band gap. But a wide variety of defects can form photochemical-reaction products in other semiconductors. Here recombination centers can be formed with an initiation energy much below a threshold at which an *impacting* electron can cause the *ballistic* creation of such lattice defects. It can also take place at relatively low temperatures, depending on the shape of the configuration diagram.

Fig. 5.3 Creation of an F-center with adjacent R-center (a Frenkel pair) starting from (a) a free exciton, via (b) a relaxed, self-trapped exciton, via (c) an intermediate stage to the Frenkel pair, with (d) an anion vacancy adjacent to an anion interstitial, here in symmetrical configuration as a halogen molecule on a halogen lattice site (after Itoh 1982)



The creation of other photochemical reaction centers can be eased within high-field regions, for instance in space charge regions of hetero-junctions. Here with optical excitation new centers can be formed that will influence the potential distributions and thereby the cell characteristics.

5.1.2 Other Examples

Photochemical reactions can be used to change the optical absorption of transparent glasses. If absorption in a wide wavelength range is desired as the result of exposure to light, e.g., for self-darkening sunglasses, scattering on larger colloids is employed. Such colloids can be formed, for instance, by incorporating silver-halide-(AgCl) enriched particles in oxide glasses, doped with Cu^+ . During exposure to UV-light, Cu^+ acts as a hole trap, forming Cu^{++} ions which in turn stimulate silver interstitial diffusion to form silver colloids with consequent increased visible light absorption. In the absence of UV light, thermal fading restores full transparency at room temperature. There is a wide variety of photo chromatic processes that can be used commercially (see Armistead and Stookey 1964).

5.2 Photochemistry in Silver Halides

Seemingly unrelated to solar cells are the photochemical processes in silver halides. However, light-induced copper nucleation with consequent Cu-nodule growth in copper sulfide that causes degradation in $\text{CdS}/\text{Cu}_x\text{S}$ solar cells, gives an example for a related phenomenon. Similar silver halides They are well researched over more

than a century, and may give some indications of some process similarities when translated to similar solar cells, and to many other materials with lesser pronounced photochemical degradation. The silver halides are applied in the photographic process, which can be divided into three steps:

- the formation of the latent picture
- the development, and
- the fixation of the picture.

Silver-bromide grains are usually imbedded in a gelatin film for photography.

A *latent picture* is formed when a grain is exposed to a minimum of ~ 10 photons, creating free electrons. When one of these electrons is trapped by a silver atom, e.g., at a negatively charged Ag_2S center at the surface that attracts highly mobile interstitial silver ion, the newly created center has a deeper level and can attract a second electron, charging this center again, and attracting another silver ion to form a dimer, Ag_2 . Such a dimer is stable but not yet developable; it is called a *subimage*. The process with alternating electron capture and interstitial ion attraction repeats itself as long as free electrons are available, creating a cluster of silver atoms.

For the following *development*, the photographic film is exposed to a moderately reducing agent. Clusters of four or more silver atoms act as quasi-electrodes with catalytic reduction, when receiving electrons from the developer, causing growth of the silver cluster (Jaenicke 1972) which continues to grow. When stopping the developing process at an appropriate time, a wide range of gradation in grain darkening proportional to the initial light exposure can be achieved.

The *fixation* process dissolves all remaining AgBr and thereby stabilizes the developed picture. For reviews, see Brown (1976), James (1977), and Hamilton (1988).

5.2.1 The Print-Out Effect

When AgBr grains or single crystals are exposed to a larger dose of light, increasingly more silver nuclei are formed, and grow visibly as random spots. During this process Br_2 is released.

The motion of Ag to the Ag_n nuclei proceeds via interstitials. Dislocations and grain boundaries assist in providing the space for Ag_n nuclei growth.

5.2.2 Film Sensitivity and Sensitization

The sensitivity of a photographic film is determined by a number of effects:

- grain size and shape;
- creation of a free electron from a photon in the spectral range of interest;

- diffusion of this electron to a nucleation site for latent image-cluster formation in competition with deep trapping and recombination with mobile holes (Mitchell 1958); and
- critical size of the latent image cluster to permit growth during exposure to the developing agent.

The grain *size* influences directly the film sensitivity, since the same number of photons is sufficient to produce a latent image cluster, independent of grain size. One cluster is enough to turn the entire grain into metallic silver. The speed of a photographic film is therefore proportional to d^3 , where d is the grain diameter.

The *diffusion of the free electron* to a nucleation site depends on its mobility, typically $50 \text{ cm}^2/\text{V s}$ at room temperature, on intermediate trapping, and recombination. For good films, the collection efficiency is typically $\sim 50 \%$.

The *critical size of a latent image cluster* that can be developed is on the order of 4 to 7 atoms, and requires 8 to 14 photons for its creation.

Its size can be reduced by *sensitization*, e.g., by surface treatment, resulting in a deposit of gold ions, or by the formation of Ag_2S (inadvertently done by incorporating the AgBr grains in sulphur-containing gelatin—see Keevert and Gokhale 1987).

Some further sensitization can be achieved by a treatment in a reducing atmosphere (H_2) prior to exposure. Here, the threshold for creating developable clusters can be reduced to $2 \cdots 3$ photons.

The *spectral range* can be extended by absorbing organic dyes that permit an electron transfer to the AgBr ; best quantum efficiencies exceed 80% . See James (1977).

A shift of the absorption edge toward longer wavelength in AgBr is achieved by alloying with AgI , typically at the $1 \cdots 10 \%$ range. For further information, see Hamilton (1988) and Mitchell (1989).

5.3 Time-Dependent Photochemical Reactions

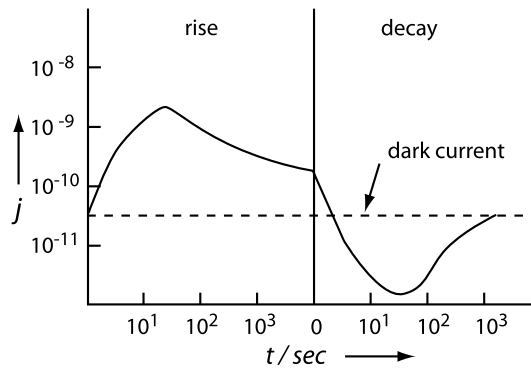
A large group of photochemical reactions relates to a slow degradation of photoelectric properties during optical excitation, such as the Staebler-Wronski effect in $\alpha\text{-Si:H}$ or $\alpha\text{-Si:F}$ (Staebler and Wronski 1977b or Hamakawa 1989) or the slow decrease of photoconductivity in CdS (Böer et al. 1954; Borchardt 1962).

Many other degradation effects, observed after exposure to sunlight, are identified as those caused by similar photochemical reactions, e.g., the chaffing of ZnO -based white paint (Hauffe 1955).

5.3.1 Photochemical Degradation

The kinetic analysis of photochemical reactions in CdS is an instructive example. It reveals the slow production of recombination centers with light, and the annealing of such centers in the dark (Fig. 5.4).

Fig. 5.4 Rise and decay of the photocurrent for CdS at 100 °C, including photochemical reactions causing a nonmonotonic behavior (after Böer et al. 1954)



The photocurrent first increases after light is switched on, with a rise time given by the filling of electron traps. In addition, recombination centers are formed by photochemical reaction with a much slower reaction time. Consequently, the current goes through a maximum and decreases slowly until it reaches a steady-state (Fig. 5.4).

When the light is switched off, the current first decays with the electronic decay time, but undershoots below the original dark current, indicating that some donors were eliminated with the photochemical formation of recombination centers. With sufficient waiting in the dark, these recombination centers are annihilated, and the original density of donors is restored; consequently, the current returns to its original dark current (Fig. 5.4).

The two processes involved here are the redistribution of electrons over the bands and traps, and the photochemical formation of recombination centers; both have substantially different time constants and therefore are easily separated in the described kinetic experiment.

The general behavior can be described mathematically by assuming a creation of recombination centers with a density N_r proportional to the density of electrons, and an annihilation proportional to N_r (Böer et al. 1954):

$$\frac{dN_r}{dt} = \gamma_{pc}n - \delta_{pc}N_r. \quad (5.1)$$

The dissociation parameter δ_{pc} depends exponentially on the temperature:

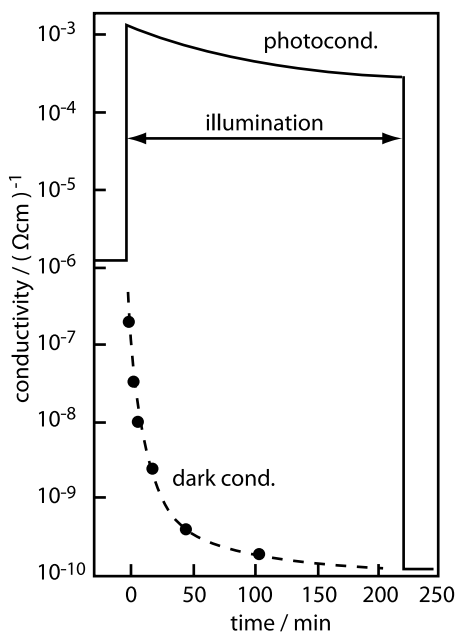
$$\delta_{pc} = \delta_{pc0} \exp\left(-\frac{E_{pc}}{kT}\right); \quad (5.2)$$

the photochemical activation energy E_{pc} is observed to be typically on the order of 1 eV for CdS. E_{pc} depends on the doping elements (Borchardt 1962).

The photoconductivity can be described with a reaction-kinetic model, including such recombination centers and optical as well as thermal generation rates—this includes the dark conductivity. The simplest of these models is given by

$$\frac{dn}{dt} = g_{th} + g_0 - c_{cr}nN_r - c_{cr}n^2. \quad (5.3)$$

Fig. 5.5 Photo- and dark conductivity of undoped α -Si:H at 300 K as a function of the time of illumination with 200 mW/cm² tungsten light (after Staebler and Wronski 1977a, 1977b)



When augmented by traps and other recombination centers, the model becomes more realistic.

5.3.2 The Staebler-Wronski Effect

Similar photochemical reactions, as described in Sects. 5.1.1 and 5.3.1 for CdS, are observed in α -Si:H Staebler and Wronski 1977a, 1977b when it is exposed to prolonged illumination at sufficient intensity (sunlight) and temperature (300 K), as shown in Fig. 5.5. Parallel with the reduction in photocarrier lifetime, the dark conductivity, shown as the dashed curve in Fig. 5.5, and band-tail luminescence decrease and an increase in unpaired spin density and sub band-gap optical absorption is observed (Staebler and Wronski 1977b; Dersch et al. 1981; Moddel et al. 1980). The centers created by photochemical reaction also anneal out during heat treatment in the dark (Han and Fritzsche 1983).

Despite a large body of experimental evidence, the photochemical reaction products in α -Si:H are not yet unambiguously identified. Three proposals are currently considered: that of *weak bond breaking* (Pankove and Berkeyheiser 1980; Stutzmann 1987); an *intimate charge transfer pair* with negative-U character (Adler 1983); and the creation of pairs of dangling and floating bonds (Panitz 1978).

The first process involves the breaking of weak Si–Si bonds in the α -Si matrix with the possible motion of hydrogen to the dangling bond, thereby hindering bond healing.

Fig. 5.6 Creation of the F-center absorption in KCl as a function of the time-delay after excitation with a 266 nm light pulse (after Bradford et al. 1975). Insert shows the observed spectral distribution

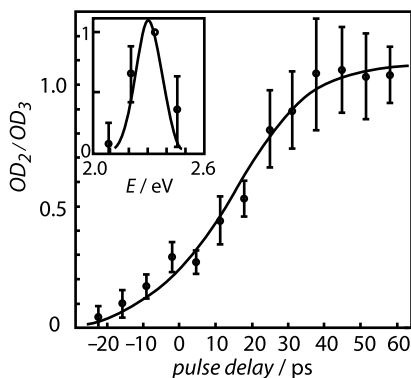
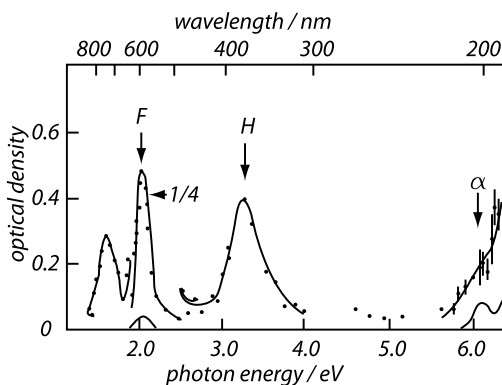


Fig. 5.7 Transient optical absorption spectrum of KBr at 8 K measured 50 ns after excitation by an electron pulse, showing the created F- and H-absorption. A few minutes later, most of the induced absorption has disappeared except for a small F- and α -remnant at ~ 2 and ~ 6 eV (after Kondo et al. 1972)



The second process assumes the trapping of photogenerated electrons at sp^2 -donors and of holes at p^3 -acceptors, which causes a change in the bonding configuration by creating a pair of sp^3 -dangling bonds.

The third process: With highly mobile floating they can react with Si:H bonds and create interstitial hydrogen: $FB + Si = H_i + SiSi$. Interstitial hydrogen can also be used to anneal dangling bonds: $H_i + DB = SiH_0$.

For reviews, see Pantelides (1988) and Hamakawa (1989).

5.3.3 Fast Photochemical Processes

The fast processes are seemingly irrelevant for solar cells. But in cell production the cells are often exposed to high energy radiation, including laser light and gas discharges.

Even though some of the produced defects may anneal out very fast, but others may find a place in their neighborhood where they can lock in and provide important defects to influence cell performance.

Electronically induced photochemical processes in which a lattice ion only needs one step to a new metastable position can proceed very fast, typically in nano- or even picoseconds. As an example, the previously discussed formation of F- and R-centers in alkali halides is given. As shown by Bradford et al. (1975), F-centers can be created in KCl by light pulses at 266 nm within ~ 10 ps (see Fig. 5.6).

Higher excited states of the F-center are the precursors of the F–H-center pair formation (Williams 1978a; Stoneham 1979; Itoh 1982). Excitation with a nanosecond electron pulse forms F- and R-centers within 50 ns after the electron pulse (Kondo et al. 1972). This pair is annihilated within a few minutes after cessation of the excitation—see Fig. 5.7.

Part II

Electronic Properties

Chapter 6

Elements of Band Structure

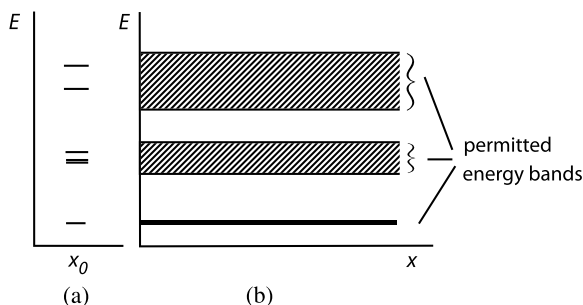
Abstract Origin of electron bands from atomic proximity, or from atomic periodicity in a crystal lattice are indicated. The proximity approach retains chemical atom identity. Atomic level splitting is tabulated and tunneling for electron transfer is discussed. Electronic structure of amorphous semiconductors are identified. Computed eigenvalue spectrum; Periodicity approach; Schrödinger equation for electron wave; $\mathbf{k}$ -vector; electron momentum; de Broglie wavelength; value; electron eigenstates; Bloch function; plane wave; Kronig-Penney Potential; explicit mathematics of band model; $E(\mathbf{k})$ diagram; reduced $\mathbf{k}$ -vector; Newtonian description of quasi-free electrons; Kinetic electron energy; effective mass discussion; Comparison of periodicity vs. proximity approach; Band edge fuzzing of amorphous semiconductors; Discrete levels in band gap; plausibility approach.

Characteristic for much of the electronic behavior in solids is the existence of energy bands, separated by band gaps. Electronic transitions in energy and in space are the basic processes of interest in semiconductor physics. The transition in energy is responsible for the large variety of excitation and de-excitation (i.e., recombination) processes; the transition in space must be considered for carrier transport. Both are characterized by quantum-mechanical features: the spectrum of electronic energy states, called *eigenstates*, the distribution of electrons over these states, and the forces that cause changes in this distribution.

First, the general principles will be discussed that yield the spectrum of energy states typical for the solid semiconductor. It is possible to obtain the main features of this spectrum using two apparently different models. The first model starts from individual atoms and its immediate neighborhood, and expands with less and less attention to the atomistic structure the further one extends from the origin; this approach is referred to as the proximity or chemical approach. The second model is at first view rather insensitive to the detailed properties of individual atoms, but considers the long-range periodicity of a crystalline lattice; this is the periodicity approach. Both yield similar qualitative results: energy spectra that show broad, permitted ranges of energy interspersed with forbidden ranges which, in space, extend as *bands* throughout the entire semiconductor.

The first approach is successfully used for amorphous semiconductors; and both approaches have been used for crystals. In this chapter, both of these approaches

Fig. 6.1 (a) Splitting of eigenstates when two atoms have approached each other. (b) Simple band model of a many-atom crystal



will be discussed, pointing to common features, and expose some of the differences in the results. This discussion will start from a rather heuristic description and will introduce sequentially more sophisticated elements.

6.1 The Proximity (Chemical) Approach

In a very primitive model, the exchange of electrons between two atoms can be made plausible by considering the splitting of eigenstates of degenerate oscillators, i.e., oscillator states having the same eigenfrequency when they become coupled with each other; the energy splitting is a measure of the exchange frequency of the electrons between the two atoms. The addition of more atoms of the same kind at increased distances splits the energy levels into more levels which span a range of energies. If the levels are spaced closely enough, *Heisenberg's uncertainty principle* no longer permits distinction between the individual levels.¹ In this case, one obtains an *allowed energy range* in a large enough cluster of atoms, instead of a discrete energy level spectrum of a single atom or an aggregate of a few atoms—see Fig. 6.5. Since outer shell electrons can be exchanged more easily, the energy ranges created from these valence electrons will be wider than the ranges created from the shielded inner electrons. The latter will more closely resemble the discrete eigenstates of isolated atoms. Since the same atoms behave alike, this allowed energy range extends throughout the crystal. In two dimensions (x, E) one therefore draws *allowed energy bands* separated by *forbidden zones* (Fig. 6.1).

In Fig. 6.1 the total electron energy is drawn disregarding the potential energy that an electron experiences when separated from an individual atom, which is shown in Fig. 6.2 for a single atom (dashed curve) and for a small one-dimensional

¹Applying $\Delta E \Delta t$ and relating ΔE to the time an electron resides at a sufficiently high energy level E_{ilr} (later identified as belonging to an upper band), an uncertainty of ΔE results. The time Δt is related to scattering (see Sect. 15.6); the electron is removed from this level after $\lambda/v_{\text{rms}} \cong 10^{-12}$ s, yielding an uncertainty of $\cong 1$ meV, which is on the same order as the splitting provided by only 10^4 atoms (assuming a band width of $\cong 1$ eV) and an equidistant splitting of 1 level per added atom that is, within a crystallite of <100 Å diameter. With larger crystallites the splitting is even closer and results in a level continuum.

Fig. 6.2 Potential energy of an electron in an atom (dashed curve) and an atomic cluster (solid curve)

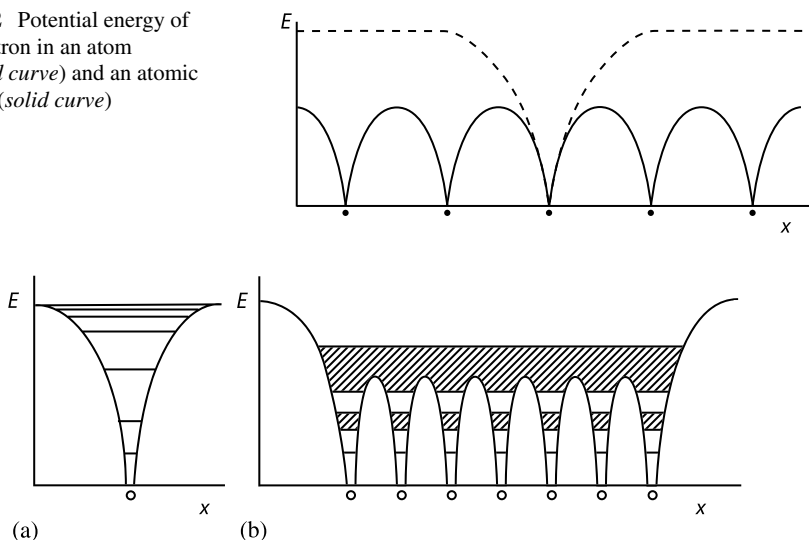


Fig. 6.3 Potential energy and eigenstates of electrons in (a) an atom and (b) a small crystal

cluster (solid curve). The band model emphasizes the *collective* behavior, i.e., the *sharing* of the electron among the atoms of the cluster. The potential distribution picture, on the other hand, emphasizes the *localization* of an electron within each potential funnel. Both pictures are valid: the band picture is more relevant for higher bands, while the potential picture is more relevant for lower (core) levels.

When the band picture is overlaid on the picture of the individual potentials of many adjacent atoms (Fig. 6.3), we recognize that the semi-classical approach, in which electrons may only move above potential barriers, is inappropriate, since bands which indicate electronic exchange exist well below the crest of the barriers. *Tunneling* through such barriers, i.e., a *quantum-mechanical* exchange, is the reason for the electron transfer.

This heuristic approach will now be expanded to make bands “plausible” in a more appropriate quantum-mechanical analysis. The analysis will be applied first to a cluster of atoms that form the building block of an amorphous semiconductor, and then to a periodic lattice.

6.1.1 Electronic Structure of Amorphous Semiconductors

The electron energy depends sensitively on the interatomic distance and bond angle, as shown for a simple H_2 and an H_2O molecule in Fig. 6.4. The bonding and anti-bonding curves reflect anti-parallel and parallel spin of the electrons in the H molecule, respectively.

The electronic structure of a solid can be obtained by starting from an arbitrary atom and including more and more neighbors in an appropriate configuration; the

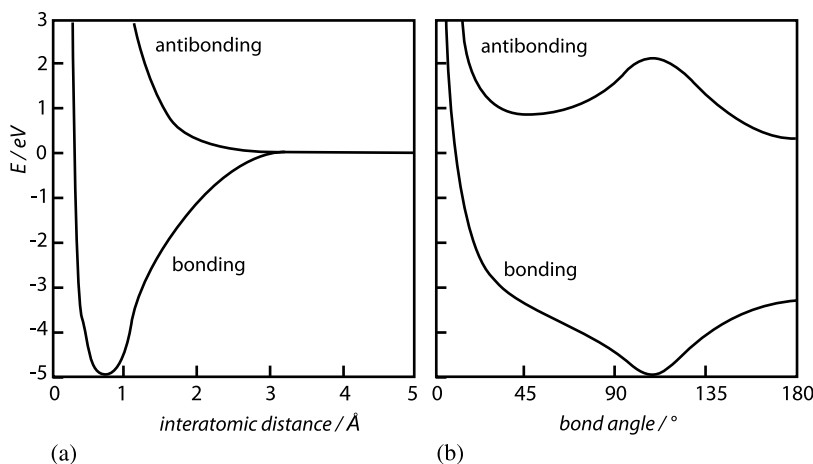
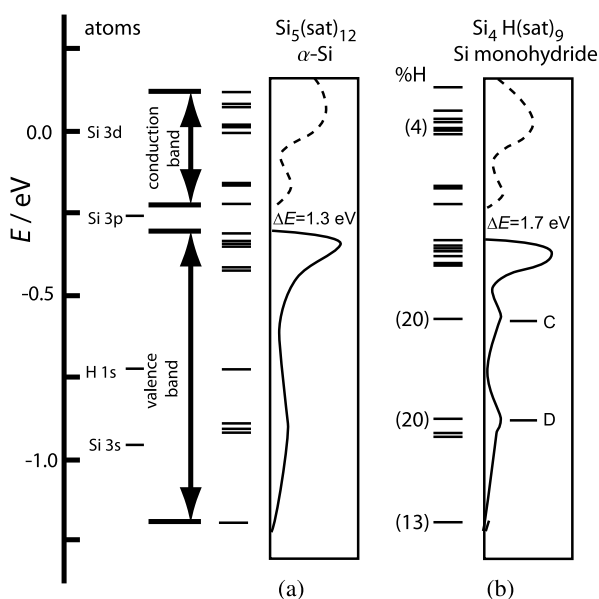


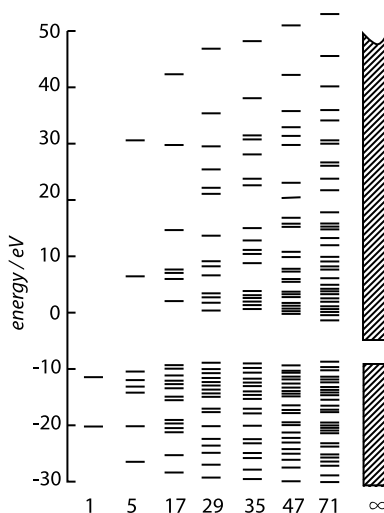
Fig. 6.4 Electron energy as a function of: (a) the interatomic distance of a hydrogen molecule; and of (b) the bond angle in H_2O (after Adler 1985)

Fig. 6.5 Electron energy level distribution for bonding (valence band) and anti-bonding (conduction band) states of a 17-atom cluster and optical density of states (see Sect. 7.1) for (a) α -Si, and (b) α -Si:H (after Johnson 1985). The agreement with the experimental band gap of such a small cluster is spurious, however, and should not be over-evaluated. The calculated band gap depends substantially on the boundary conditions



eigenfunctions of such a cluster are determined by solving its Schrödinger equation. This is referred to as a *tight-binding approach*. Solutions can be obtained numerically, using reasonable approximations (Reitz 1955; Heine 1980; Slater and Johnson 1972—see also Chap. 8). The analysis can be described as that for a large molecule of, say, 20–50 atoms and delivers a spectrum of *energy eigenvalues* that, when the cluster is large enough, presents a valuable estimate of the upper bands.

Fig. 6.6 Energy of one-electron molecular orbitals or diamond cluster size (numbers at clusters with successively increase in bottom of graph), compared to the band structure calculated with the same parameters (after Watkins and Messmer 1973)



The several Si atoms which form such a cluster produce the typical sp^3 -bonding and anti-bonding states that are formed when the atoms are close enough—see Sect. 2.2 and Fig. 2.7. For a small cluster of Si atoms in an “amorphous configuration” (Chap. 8), we calculate an eigenvalue spectrum (Fig. 6.5a) and see that the proximity to other Si atoms significantly changes and splits the atomic levels (shown on the left). They are split by a large amount and are distributed unevenly in energy. A much larger number of atoms, however, is required to create a truly band-like level distribution.

This spectrum changes significantly when hydrogen is added to this cluster, which forms a bridging hydrogen structure (Ovshinsky and Adler 1978). It removes states from the gap of α -Si and thereby increases the band gap from 1.3 eV for α -Si to 1.7 eV for the technically more interesting, hydrogenated α -Si:H as shown by Eberhart et al. (1982).

When more atoms of the same kind are incorporated within such a cluster, more levels appear *within* the two bands, i.e., within the range of bonding and anti-bonding states. These bands have been labeled in Fig. 6.5 as the conduction and valence bands for the benefit of the experienced reader. Such level distribution is shown for diamond C in a 35-atom molecule in Fig. 6.5, and for a successively larger cluster in Fig. 6.6.

The finite cluster approach always overestimates the band gap energy, since, by necessity, this approach omits states present which are far removed from the center that corresponds to the Γ -point of the Brillouin zone and, in direct band gap materials (Sect. 7.2) lie near the edges of the band gap.

From these examples, we can deduce that some information about the energy width of the upper energy bands and the band gap can be obtained from clusters containing only $\cong 50$ atoms in an appropriate configuration. That is, the outer atoms must be kept artificially at positions they would attain when interacting with the surrounding atoms within a much larger amorphous network of atoms.

The level distribution within a band, however, is poorly represented by such a small cluster. The incorporation of many more atoms presents major computational problems for amorphous semi conductors; however, this problem becomes exceedingly simple in a periodic lattice of a crystalline semiconductor. For more reading, see Adler (1985).

6.2 The Periodicity Approach

The behavior of electrons in a semiconductor can be approximated by assuming that they are nearly *free electrons*, but interact with the *periodic potential* that simulates the lattice. In order to distinguish the influence of this periodic potential, one should first recall the behavior of a free electron *in vacuo*. This is determined by the solution of the *Schrödinger-equation* (see Appendix A.2):

$$\nabla^2 \psi + \frac{2m_0}{\hbar^2} E \psi = 0, \quad (6.1)$$

which can be described by an *electron wave*

$$\psi(\mathbf{r}) = A \exp(\pm i \mathbf{k} \cdot \mathbf{r}) \quad (6.2)$$

with A as an amplitude factor. The *wave vector* $\mathbf{k}$ relates to electron momentum and energy as

$$\mathbf{k} = \frac{m_0 \mathbf{v}}{\hbar} = \frac{\mathbf{p}}{\hbar}; \quad E = \frac{m_0}{2} v^2 = \frac{p^2}{2m_0} = \frac{\hbar^2 k^2}{2m_0}, \quad (6.3)$$

or, more accurately, to the expectation value of the momentum given by

$$\langle \mathbf{p} \rangle = \int_{-\infty}^{\infty} \psi \frac{\hbar}{i} \nabla \psi^* d\mathbf{r} = \hbar \mathbf{k} \int_{-\infty}^{\infty} \psi \psi^* d\mathbf{r} = \hbar \mathbf{k}. \quad (6.4)$$

The wave vector $\mathbf{k}$ is the reduced wave vector-see the discussion later in this section and Fig. 6.12.

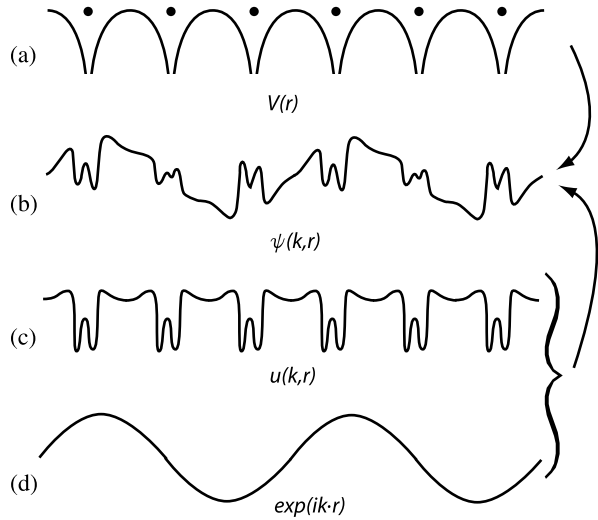
Hence, $E(\mathbf{p})$ or $E(\mathbf{k})$ is described by a three-dimensional paraboloid (by a parabola in one relevant coordinate) with one electronic parameter, the *electron rest mass*.

Equation (6.2) represents an electron wave with a wavelength, the *de Broglie wavelength*,² of

$$\lambda_{\text{DB}} = \frac{2\pi}{k} = \frac{h}{|p|} = \frac{h}{m_0 v} = 7.27 \frac{1}{v(\text{cm/s})} \text{ (cm)} \quad (6.5)$$

²The de Broglie wavelength is on the same order of magnitude as the uncertainty distance obtained from Heisenberg's uncertainty principle $\Delta x \leq \hbar \Delta p$, which has the same form as λ_{DB} . This yields uncertainty distances of $\cong 10 \text{ \AA}$ for thermal (free) electrons at room temperature.

Fig. 6.7 A schematic representation of electronic eigenstates in t crystal. (a) The potential plotted along a row of atoms; (b) A Bloch function; the state itself is complex but only the real part is shown. The Bloch function is composed of the product of (c) $u_k(\mathbf{r})$, which has the periodicity of the lattice; and (d) a plane electron wave, the real part of which is shown to construct the electron wave function (after Harrison 1970)



or, when introducing the electron energy from Eq. (6.3),

$$\lambda_{\text{DB}} = \frac{h}{\sqrt{2m_0 E}} = 12.26 \frac{1}{\sqrt{E(\text{eV})}} (\text{\AA}). \quad (6.6)$$

An electron in the lattice, i.e., when it is exposed to a periodic potential, no longer behaves like a free particle: it experiences interference from the lattice potential when, with increasing electron energy, its de Broglie wavelength becomes comparable to the lattice constant. The ensuing *Bragg reflections* prohibit a further acceleration of the electron, described later in more detail. This simple discussion also indicates the existence of a finite energy range, the energy band in a semiconductor. Near the band edges the electron behaves to some extent like a free electron, i.e., like a classical particle. The quantum-mechanical nature becomes evident when it gains energy in an electric field or is forced to occupy higher states. At energies of 4 eV, the de Broglie wavelength is $\cong 6 \text{\AA}$, i.e., small enough to permit interference effects within the periodic potential of the lattice.

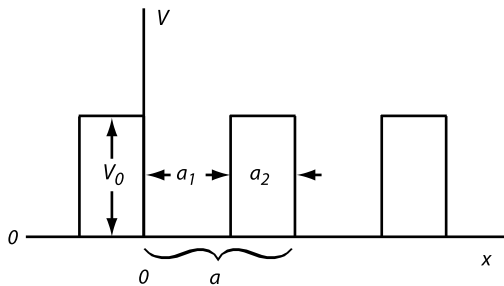
This plausibility argument can be substantiated by describing the electron with a wave equation, the Schrödinger equation, and by introducing into the Schrödinger equation a periodic potential $V(\mathbf{r})$,

$$\nabla^2 \psi + \frac{2m_0}{\hbar^2} (E(\mathbf{k}) - V(\mathbf{r})) \psi = 0. \quad (6.7)$$

The solutions of this Schrödinger equation are so-called *Bloch-functions* which can be expressed as a linear combination of waves

$$\psi_n(\mathbf{k}, \mathbf{r}) = u_n(\mathbf{k}, \mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}), \quad (6.8)$$

Fig. 6.8 Kronig-Penney potential with V_0 the barrier height, a_1 and a_2 the well and barrier widths



with n as the band index specifying a certain band. The waves are plane waves with a space-dependent amplitude factor $u_n(\mathbf{k}, \mathbf{r})$, which shows lattice periodicity (Bloch's theorem, 1928; see Sect. 7).

A one-dimensional schematic representation is given in Fig. 6.7 to indicate the relationship between the lattice potential $V(\mathbf{r})$ and the Bloch function $\psi_n(\mathbf{k}, \mathbf{r})$, which contains $u_n(\mathbf{k}, \mathbf{r})$ and the plane wave function of the electron $\exp(i\mathbf{k} \cdot \mathbf{r})$ (Harrison 1970), to construct the electron wave function.

Inserting Eq. (6.8) into Eq. (6.7), we obtain the result that solutions exist only for certain ranges of the electron energy $E_n(\mathbf{k})$, which are interspersed with energy ranges in which real solutions do not exist. This confirms the previously obtained results: namely, that the energy spectrum in a solid consists of alternating allowed and forbidden energy ranges (energy bands). The periodic potential approach, however, gives additional information that can be demonstrated readily in a simple one-dimensional (x) model.

6.2.1 The Kronig-Penney Model

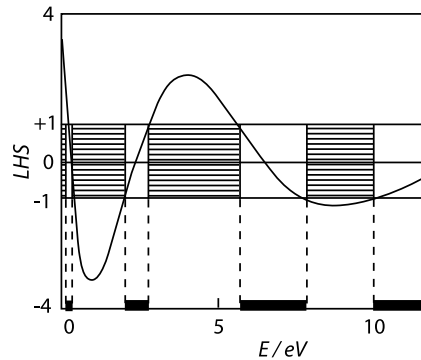
An enormously simplified periodic potential $V(x)$ is sufficient for introduction into Eq. (6.9) to show the typical behavior. This is the Kronig-Penney potential (Kronig and Penney 1931),³ which is shown in Fig. 6.8. Since the discussion of this behavior is rather transparent, it will be used here to introduce the reader to the basic features of the band model.

Introducing (6.8) into Eq. (6.7) for one relevant dimension, we see that $u(x)$ must satisfy

$$\frac{d^2 u}{dx^2} + 2ik \frac{du}{dx} - \left(k^2 - \frac{2m_0[E - V(x)]}{\hbar^2} \right) u = 0. \quad (6.9)$$

³In one dimension, there are other periodic potentials for which the Schrödinger equation can be integrated explicitly. $V(x) = -V_0 \operatorname{sech}^2(\gamma'x)$ is one such potential, which yields solutions in terms of hypergeometric functions (see Mills and Montroll 1970). The results are quite similar to the Kronig-Penney potential discussed later.

Fig. 6.9 Left-hand side (LHS) of Eq. (6.12) as a function of E (contained in α and β), computed for $a_1 = 6 \text{ \AA}$, $a_2 = 1.2 \text{ \AA}$, and $V_0 = 10 \text{ eV}$



We can split Eq. (6.9) after the introduction of the Kronig-Penney potential into two differential equations: one for the bottom of the well, and one for the top of the barrier with a potential $V = V_0$. The solutions in each part can be expressed as the sum of two waves:

$$\begin{aligned} u_1(x) &= A \exp[i(\alpha - k)x] + B \exp[-i(\alpha + k)x] \quad \text{for } 0 < x < a_1 \\ u_2(x) &= C \exp[i(\beta - k)x] + D \exp[-i(\beta + k)x] \quad \text{for } -a_2 < x < 0 \end{aligned} \quad (6.10)$$

where α and β are the k -values for a free electron *in vacuo*, for $V = 0$,

$$\alpha = \sqrt{\frac{2m_0 E}{\hbar^2}} \quad \text{and} \quad \beta = \sqrt{\frac{2m_0(V_0 - E)}{\hbar^2}}. \quad (6.11)$$

and for a constant barrier potential V_0 , respectively.

The integration constants can be determined by the continuity requirements of $u(x)$ and its first derivatives at $x = a_1$ and $x = a_2$, which yield⁴

$$-\frac{\alpha^2 - \beta^2}{2\alpha\beta} \sin(\alpha a_1) \sinh(\beta a_2) + \cos(\alpha a_1) \cosh(\beta a_2) = \cos(ka). \quad (6.12)$$

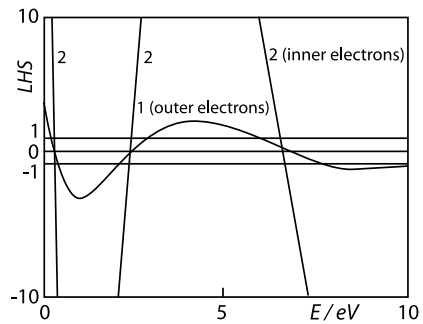
Equation (6.12) provides the *dispersion relation* $E(\mathbf{k})$; (E is contained in α and β).

The dispersion relation is the key to many discussions of electronic properties in solids. Since the wavenumber k is proportional to the electron momentum (Eq. (6.3)), the dispersion equation relates the electron energy to mass and velocity, both of which are essential for understanding of the specific behavior of electrons in a semiconductor. This will be explained in detail in several of the following sections.

⁴For $E > V_0$, the square root in β becomes imaginary. Introducing $\gamma \pm \sqrt{[2m_0(E - V_0)/\hbar^2]}$, and with $\sinh(i\gamma) = i \sin(\gamma)$ and $\cosh(i\lambda) = i \cos(\gamma)$, we obtain for higher electron energies a similar equation:

$$-\frac{\gamma^2 + \alpha^2}{2\alpha\gamma} \sin(\gamma a_2) \sin(\alpha a_1) + \cos(\gamma a_2) \cos(\alpha a_1) = \cos(ka).$$

Fig. 6.10 LHS as in Fig. 6.9, but for two different values of the parameter V_0 (10 eV for curve 1 and 40 eV for curve 2—other parameters as in Fig. 6.9), indicating the reduced width of the permitted bands for higher potential barriers (i.e., for inner electrons that are more tightly bound)



Equation (6.12) reveals that a sequence of allowed energy ranges is interspersed with forbidden energy ranges: energy gaps are formed when the left-hand side (LHS) of Eq. (6.12) exceeds ± 1 , which are the limiting values of the equation's right-hand side. In Fig. 6.9 the hatched ranges show the energy gaps; no solution of the Schrödinger equation can be found here for real values of k . This picture describes a situation between a free electron *in vacuo*, where all energies are permitted, and an electron bound to an isolated atom, where the permitted energy ranges shrink to a set of discrete energy *levels*. The height and width of the potential barriers and wells (a_1 , a_2 , and V_0) determine whether an electron behaves more like an electron bound to a single atom (large a_2/a_1 and V_0) or more like a free electron *in vacuo* (small a_2 and V_0); see Fig. 6.10 in the latter example the permitted ranges extend over a wider energy range.

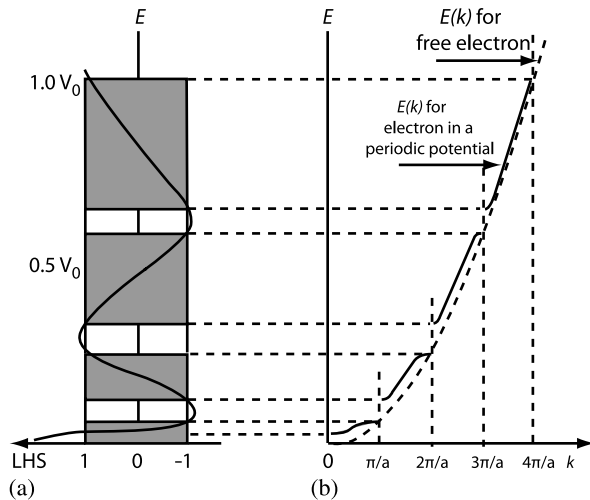
More information can be deduced from the $E(\mathbf{k})$ behavior within each of the permitted energy ranges shown in Fig. 6.11. At the bottom of the first permitted energy range, $E(\mathbf{k})$ is nearly parabolic.

Then E moves with increasing k through an inflection point, and, at the top of this range, becomes nearly parabolic again, but with a negative curvature.

Compared to the parabola of the free electron, the lower part of the $E(\mathbf{k})$ curve is raised. At the upper edge of the first allowed range, i.e., at $k = \pm\pi/a$, the curve coincides again with the free electron parabola. The next permitted band starts after a jump in E from E_1 to E_2 at $k = \pm\pi/a$, and has a similar $E(\mathbf{k})$ behavior as the first energy band, except that the curvatures are larger at the bottom and top of the band. The top is reached at $k = \pm\pi/a$, where again a jump of E occurs, from E_a to E_4 , etc. (Fig. 6.11). This behavior continues for higher bands with broader allowed bands and narrower band gaps. Figure 6.11 also contains $E(\mathbf{k})$ for the free electron (Eq. (6.3)), which is parabolic in the entire $E(\mathbf{k})$ range.

This qualitative behavior is independent of the actual shape of the periodic potential as long as it has sufficient amplitude. Although periodicity of $V(x)$ is a necessary-but not sufficient-condition for energy bands with interspersed forbidden gaps, it so happens that in solids, for inner shell electrons, the potential barriers are sufficiently high to cause rather narrow, lower bands. Electrons at sufficiently high energies occupy wider bands and behave more like free electrons: they can move

Fig. 6.11 (a) As Fig. 6.9, however, for a larger a_1/a_2 ratio. (b) $E(\mathbf{k})$ for a free electron (parabola) and for a Kronig-Penney potential in an extended wavenumber (k) representation



readily through the lattice. They will, however, be subject to interference with the periodic lattice potential.

When analyzing the effect of a three-dimensional periodic potential and using a real lattice potential, the actual $E(\mathbf{k})$ behavior becomes more complex; however, it still maintains the basic features of energy bands interspersed with band gaps. The gaps, however, disappear from higher bands because of an overlap of permitted bands.

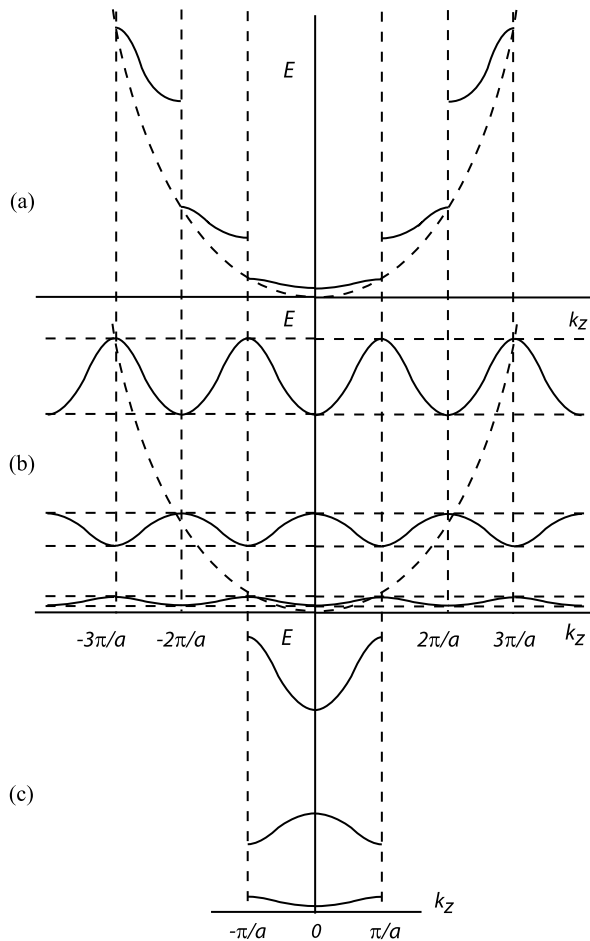
This fundamental behavior is the basis for the electronic behavior of semiconductors, and is described in more detail in many textbooks of solid state physics, e.g., (Anderson 1963; Ashcroft and Mermin 1976; Bube 1992; Callaway 1976; Fletcher 1971; Harrison 1980; Haug 1972; Kittel 1986), and Ziman (1972).

6.2.2 Periodicity of $E(\mathbf{k})$; Reduced $\mathbf{k}$ -Vector

A general feature of the solutions of the Schrödinger equation is the periodicity of $E(\mathbf{k})$, given in Fig. 6.12b. This figure shows the periodicity in $\mathbf{k}$ with a period length of $k_x a = 2\pi$. This means that a shift of the solution $E(k_x)$ by $2\pi/a$ in k_x represents the same behavior. This is indicated in Fig. 6.12 which contains as Fig. 6.12a copy of Fig. 6.11, and shows explicitly the periodicity in Fig. 6.12b. Any full segment of the periodic representation is a reduced $\mathbf{k}$ -vector representation. It is shown within the first Brillouin zone in Fig. 6.12c; i.e., within $-\pi/a < \mathbf{k} < \pi/a$.

The reduced $E(\mathbf{k})$ shows an alternating sign of the curvature at the edge of each band at $k = 0$. It is positive for the first band, negative for the second, etc. This interesting peculiarity occurs in real crystals in a somewhat similar fashion, although is more complex because of a multiplicity of bands.

Fig. 6.12 Comparison between: (a) extended wavenumber k ; (b) periodic, and (c) reduced wavenumber representations of $E(\mathbf{k})$



It is instructive to look at an enlarged detail of Fig. 6.12 as shown in Fig. 6.13d. This figure can be constructed from two parabolas of free electrons, shifted by $2\frac{\pi}{a}$ —a situation that can be thought of by inserting a lattice into the vacuum, although with vanishing lattice potential. The electron in each reference system is described by its corresponding parabola (subfigure b). When interacting through a periodic perturbation potential of amplitude U_0 , the crossing of both $E(\mathbf{k})$ parabolas is eliminated and a splitting occurs with a gap of the order of $12|U_0|$, as shown in subfigures c and d.

6.3 Newtonian Description of a Quasi-free Electron

In many discussions about electron behavior in solids, a classical particle picture is used rather than the quantum mechanical one of a wave packet. It is often more

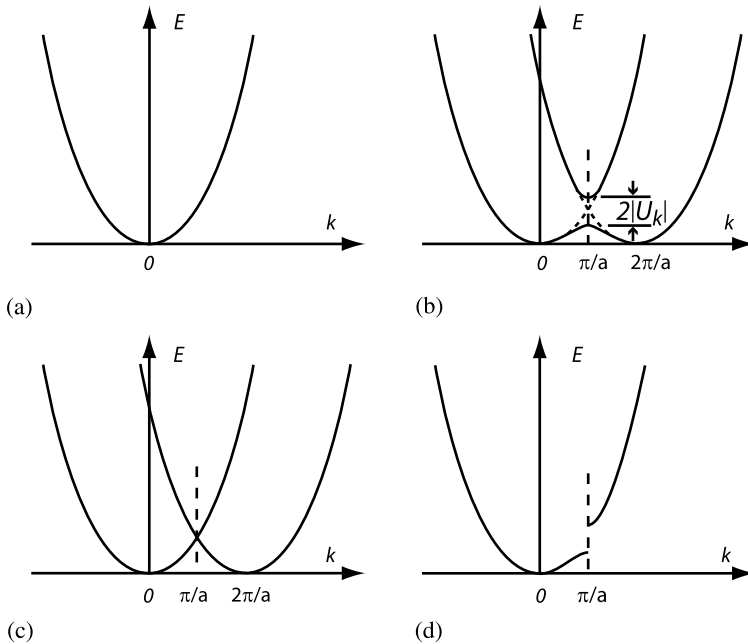


Fig. 6.13 $E(\mathbf{k})$ for (a) free electron. (b) Splitting of $E(\mathbf{k})$ when a small periodic field is introduced. (c) Free electron in empty lattice. (d) $E(\mathbf{k})$ of the original parabola, disturbed by the periodic potential perturbation (compare with Fig. 6.1a)

intuitive. Electrons behave like little balls, “sliding down” a potential hill, and “scattering” upon collision with an atomic lattice defect.

It is justified by using Bohr’s *correspondence principle* near the bottom of the conduction band (the band in which electron conduction takes place). However, since not all of the electron behavior can be described by this model, as explained in the previous section, we can account for the modification by incorporating (see below) the information obtained from its dual nature as a wave into one of its classical parameters—its mass.

An electron, regarded as a classical (Newtonian) particle, has a momentum

$$p = m_0 v \quad \text{and a kinetic energy} \quad E = \frac{m_0}{2} v^2 = \frac{p^2}{2m_0}. \quad (6.13)$$

Relativistic effects are excluded here (i.e., $v \ll c$ is assumed): the electron mass is its rest mass m_0 . The velocity of such a particle changes with time in response to an acting force $\mathcal{F}$ (*Newton’s second law*):

$$\frac{dp}{dt} = m_0 \frac{dv}{dt} = \mathcal{F}. \quad (6.14)$$

On the other hand, an electron *in vacuo*, regarded as a wave, has a momentum

$$p = \hbar k \quad \text{and an energy} \quad E = \frac{p^2}{2m_0} = \frac{\hbar^2 k^2}{2m_0}. \quad (6.15)$$

When exposed to a force, such as that supplied by an electric field $\mathcal{F}$, and with $\mathcal{F} = -eE$, its momentum increases accordingly:

$$\frac{dp}{dt} = \hbar \frac{dk}{dt} = \mathcal{F}. \quad (6.16)$$

When the electron is described as a wave packet, its velocity is the group velocity.⁵

$$v_g = \frac{d\omega}{dk} = \frac{1}{\hbar} \frac{dE}{dk}. \quad (6.17)$$

Applying Newton's law to such an electron wave packet [in a relation similar to Eq. (6.14)],

$$m_0 \frac{dv_g}{dt} = \mathcal{F}, \quad (6.18)$$

and with

$$\frac{dv_g}{dt} = \frac{1}{\hbar} \frac{d}{dt} \left(\frac{dE}{dk} \right) = \frac{1}{\hbar} \frac{d^2 E}{dk^2} \frac{dk}{dt} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} \mathcal{F}, \quad (6.19)$$

we see by comparison with Eq. (6.18) that the factor preceding $\mathcal{F}$ has the dimension of an inverse mass. This factor is proportional to the curvature of $E(\mathbf{k})$. A moving electron is represented by a moving wave packet $\psi = \frac{1}{2\delta k} \int_{k-\delta k}^{k+\delta k} u(x, k) \exp i(kx - \omega t) dk$ which quickly spreads out over time. It has its maximum at a position $\bar{x} = \frac{1}{\hbar} \frac{\partial E}{\partial k} t_1$ yielding for the group velocity, i.e., the velocity of the maximum of this wave packet $v_g = \frac{\partial \bar{x}}{\partial t} = \frac{1}{\hbar} \frac{\partial E}{\partial k}$. With $E = \hbar\omega$, we obtain $v_g = \frac{d\omega}{dk}$.

6.3.1 The Effective Mass

If we want to retain the Newtonian behavior, we have to replace the electron mass m_0 in Eq. (6.18) with the *effective electron mass* when comparing Eqs. (6.18)

⁵In an infinite crystal the electron (when not interacting with a localized defect) is not localized and is described by a simple wavefunction (i.e., having one wavelength and the same amplitude throughout the crystal). The probability of finding it is the same throughout the crystal ($\propto \Psi^2$). When localized, the electron is represented by a superposition of several wavefunctions of slightly different wavelengths. The superposition of these wavefunctions is referred to as a *wave packet*.

and (6.19):⁶

$$m_n = \frac{\hbar^2}{\frac{d^2 E}{dk^2}}. \quad (6.20)$$

This effective mass contains the peculiarities of the interaction of the electron with the lattice (the subscript n distinguishes this mass from the rest mass). However, a possibly important part caused by the adiabatic approximation is missing. The influence of this part can be described by a different effective mass—the *polaron mass*.

From Fig. 6.11, we see that the effective electron mass at the lower edge of the third band, here assumed to harbor free electrons, is smaller than the rest mass of a free electron, since the curvature of $E(\mathbf{k})$ is larger here. At higher energies within the band this curvature decreases, changes sign, and, at the upper edge of the band, becomes negative (as shown in Fig. 6.14). Consequently, the effective electron mass increases, becomes infinite near the center of an allowed band, and changes sign there. Coming from negative infinity, the effective electron mass returns to a finite but negative value which, at the top of the band, is on the same order of magnitude as at the bottom of the band (Figs. 6.12 and 6.14).

This behavior is repeated in the next band, except that the sign sequence is exchanged. Here the effective mass is negative at $k = 0$; however, the effective electron mass is always positive at the bottom of any band and negative at the top. For lower bands, i.e., narrower bands, the value of the effective mass becomes larger at the band edge.

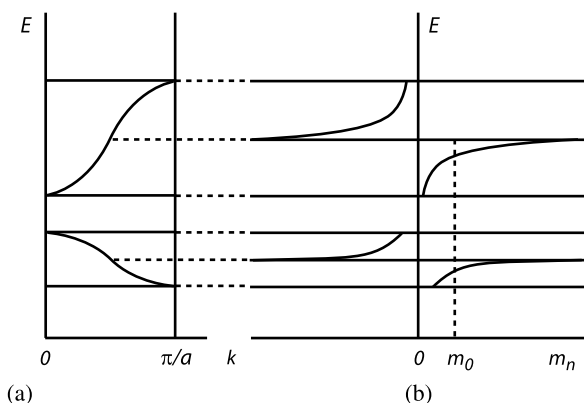
When electrons accelerate substantially above the lower edge of the band in sufficiently high fields, the de Broglie wavelength of the electron becomes smaller and comparable to the interatomic lattice spacing.

Here, *interference effects* of the electron wave with the periodic lattice potential become important: Bragg reflection becomes more prevalent, while more and more frequency components of the wave packet are reflected. Therefore, further acceleration will become more difficult to achieve; in the Newtonian model, the effective mass of the electron increases until, near the center of the band, further acceleration stops. When the energy of the electron is raised above the center of the band, the electron will *decelerate* in the direction of the electric field until it reaches the top of the band, where it will come to a standstill. The electron wave has then reached a perfect diffraction condition.⁷ It can be described as a *standing wave*, composed of incoming and refracted waves of exactly the same amplitude.

⁶For the electron behavior, only *expectation values* can be given. In order to maintain Newton's second law, we continue to use $\hbar k$ [Eq. (6.15)], which is no longer an electron momentum. It is well-defined within the crystal and is referred to as *crystal momentum*. We then separate the electron properties from those of the crystal by using $d^2 E / dk^2$ to define its *effective mass*.

⁷In theory, the electron will continue to accelerate in the opposite direction to the field and lose energy, thereby descending in the band, and the above-described process will proceed in the reverse direction until the electron has reached the lower band edge, where the entire process repeats itself. This oscillating behavior is called the *Bloch oscillation*. Long before the oscillation can be

Fig. 6.14 (a) Typical $E(\mathbf{k})$ for two simple bands, and (b) derived effective *electron* masses within these permitted energy bands. [Actually, one determines $m_n(k)$; this graph is turned 90° to show its relation to the band model shown at the left]



With some caution we may describe the “recoil” of the lattice as being responsible for absorbing an increasing fraction of the electron momentum when it is accelerated. The total momentum is thus still conserved, and Newton’s law is fulfilled. When an electron wave impinges on a thin crystal layer in an energy range in which the crystal is partially transparent for the electron, such momentum transfer can be measured directly by changing the electron energy so that diffraction occurs and part of the electron beam is reflected.

This qualitative relationship also holds for more realistic periodic potentials, although the quantitative relationship depends on many other factors. Each of the bands usually consists of several branches which often overlap one another and may show additional extrema (saddle points) in the first Brillouin zone, making the dependence of the effective mass on the electron energy more complicated. Near the band edge (for electrons), only one—perhaps degenerate— $E(\mathbf{k})$ branch is present in typical semiconductors, so that the above description holds rather well. This branch can be split, for example, by crystal anisotropy or electric or magnetic fields.

In summarizing the much more involved behavior of an electron in such a realistic band, we may wonder if we gained a more intuitive picture using the particle model. If we recognize, however, that the electron will mostly reside close to the bottom of the band, usually within a few kT , the model is then quite helpful for an analysis of a number of basic processes. The electron will behave here like a particle with a constant effective mass; the value of this effective mass depends on the actual lattice potential, i.e., on the chemical and crystallographic nature of the material because these determine the shape of $E(\mathbf{k})$.

completed, however, scattering interrupts the process. Whether in rare cases (e.g., in narrow minibands of superlattices or ultrapure semiconductors at low temperatures) such Bloch oscillations are observable, and whether they are theoretically justifiable in more advanced models (Krieger and Iafrate 1986) is still controversial. In three-dimensional lattices, other bands overlap and transitions into these bands complicate the picture.

6.4 Periodicity vs. Proximity Approach

The proximity of a sufficient number of atoms and the periodic lattice structure of a crystal, both lead to allowed energy bands interspaced by band gaps. We may use one or the other picture to obtain further information about the band structure.

The periodic lattice structure approach is more suited for obtaining the specific $E(\mathbf{k})$ structure of the inner part of the band (near $k = 0$) which cannot be obtained from the proximity approach. It reflects the symmetry of the lattice and permits one to obtain the results in the most economical fashion. Its results, however, are restricted to periodic lattices, i.e., to crystals. This refers specifically to interference phenomena involving diffraction from further-than nearest and next-nearest neighbor distances. These distances, however, can still be discerned in the x-ray diffraction of amorphous semi conductors, and therefore may also be expected to influence electronbehavior further away from $k = 0$.

The proximity approach can be used to obtain some information about the inside of the bands for first orientation. However, the inadvertent inclusion of artificial states at the surface of the cluster and the requirement for an extremely large cluster size to provide band states close to the band edges have been the handicaps of this approach.

A supershell approach is sometimes used to avoid some of the shortcomings of the periodic lattice and proximity approaches. This approach takes a cluster of sufficient size and repeats it *periodically* until the entire crystal volume is filled. In this fashion the mathematical methods developed for studying periodic lattices can be used, while certain elements of an amorphous structure are included in the cluster. The error due to the forced adjustment of each cluster can be minimized by increasing the size of the cluster.

Many of these results are important for understanding the behavior of metals (e.g., overlapping bands), but will not be discussed here. Other results relate to semiconductors, including semiconductor-metal transitions. Some heuristic examples of near-band edge properties are given below.

6.4.1 Band-Edge Fuzzing (Deviation from Periodicity)

The ideal periodicity of a crystal lattice can be modified for a number of reasons, among them lattice oscillations or displaced lattice atoms. An amorphous semiconductor, for example, may be described by having frozen-in large fluctuations of the interatomic distances and bond angles. In some respects such structures are “almost crystalline,” but with slightly changing lattice parameters. A lattice with a different lattice constant causes a different $E(\mathbf{k})$ with a different width of all lowed bands and gaps. Therefore, we expect variations of the band edges in time and space.⁸

⁸This concept must be used with caution, since $\mathbf{k}$ is a good quantum number only when electrons can move without scattering over at least several lattice distances. That is certainly not the case

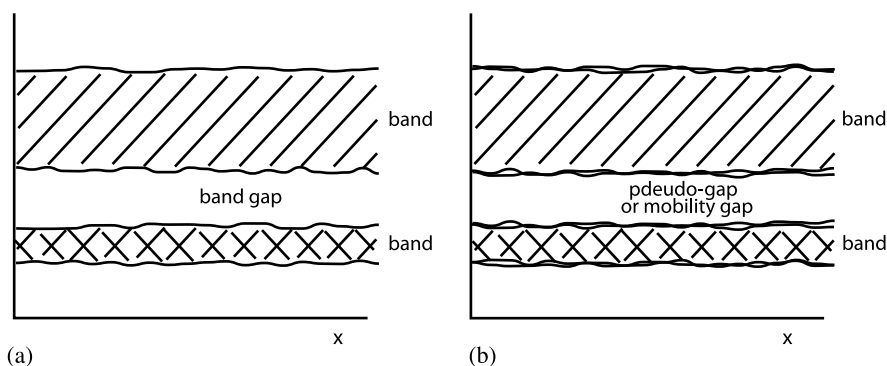
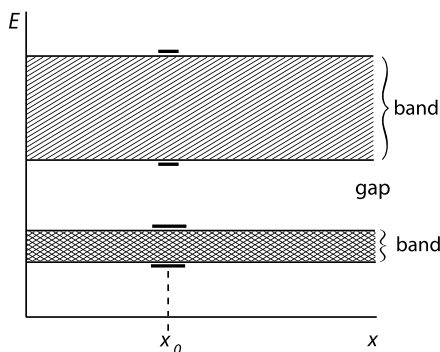


Fig. 6.15 (a) Perturbed and (b) fuzzed-out band edges in a crystal with phonons and in an amorphous semiconductor

Fig. 6.16 Simple intrinsic (i.e., chemically identical to the atoms of the crystal) atomic interstitial in an idealized lattice



Rather than being perfectly straight, the band edge becomes perturbed. Over a time average, the band edge appears to be fuzzed-out (Fig. 6.15).

6.4.2 Discrete Defect Level in the Band Gap

When the deviation from the ideal lattice structure is sufficiently large, the eigenstate of a disordered atom may lie within the band gap. A plausibility argument may be obtained from the proximity model.

Assume an extra atom is incorporated in an *interstitial site* of the lattice). This extra atom is much closer to its neighbors; the exchange frequency is substantially larger than that for the nearest neighbors which yield the largest exchange frequency

in most amorphous semiconductor s near the “band edge”. However, at higher energies further inside the band, there is some evidence that the mean free path is much larger than the interatomic distance even in amorphous semiconductors. In bringing the two approaches together, the argument presented here lacks rigor and has plausibility only in terms of correspondence.

in an ideal lattice (equivalent to the band edges). Thus the eigenstates of this interstitial atom, here an intrinsic point defect, and *its* nearest neighbors lie outside of the allowed bands of the ideal lattice, i.e., within the band gaps (Fig. 6.16).

Energy states within the gap are *localized* at the position of this lattice defect (x_0 in Fig. 6.16), and play an important role in localizing (*trapping*) electrons in real crystals and in amorphous semiconductors. It also becomes reasonable to expect an energy distribution of such localized (*trap*) levels in the gap near the band edge, when taking into consideration that in crystalline and amorphous semiconductors a wide variety of lattice imperfections and lattice parameter variations are observed.

Chapter 7

Bands and Band Gaps in Solids

Abstract The distinction between valence and conduction bands is discussed. Insulators, semiconductors, metals. Electrons and holes definition. Effective mass; sign convention of charge, mass and mobility. Semi-metals and narrow gap semiconductors. Band parameters for typical semiconductors, table. Constant energy surfaces in Brillouin zones. Effective mass in real bands, in conduction and valence bands for various semiconductors, table. Band gaps and higher bands in typical semiconductors, tables. Hole effective mass and valence band splitting for typical semiconductors, splitting, table. Probing of bands and measuring effective masses with cyclotron resonance is discussed. Distinction of momentum effective mass, and effective mass at higher energies is given the band gap discussion, diagram for different types of semiconductors. Band gap variation with temperature and pressure, with alloy composition; gap bending, table of bowing parameters. Direct and indirect band gap discussion and table. Gap narrowing with heavy doping, shift of Fermi level into gap. Bands in superlattices. Mini bands, electron transport. Bands in ultrathin superlattices. Density of states in mini bands. One- two- and zero-dimensional quantum wells. Electronic states in micro crystallites. Bands in amorphous semiconductors. Use of supercomputers is indicated.

Valence and conduction bands and the band gap in between these bands are the key for all semiconducting properties. The change of these bands with changing external parameters or chemical composition provides the insight into the electronic behavior of solids. Here a description is given of the most important bands in semiconductors, the valence and conduction bands and their dependence on various material and external parameters.

7.1 Valence and Conduction Bands

A set of bands (subbands), created by the splitting and hybridization (see below) of the ground state of valence electrons, taken together are referred to as the *valence band*. The number of states contained in this band is given by the multiplicity of its atomic state (typically 4 for sp^3 -hybridization), multiplied by the number of atoms

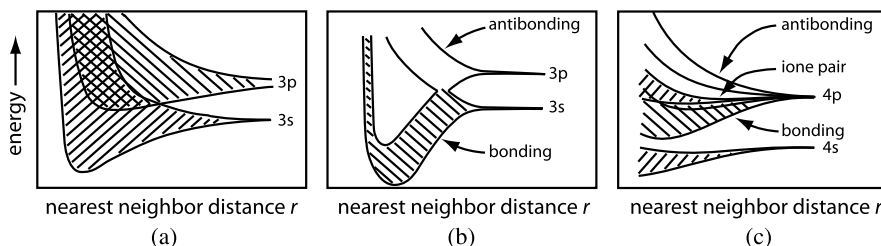


Fig. 7.1 Electronic energy distribution for a crystal as a function of the interatomic distance. (a) Overlap of s - and p -bands in main group metals. (b) sp^3 -hybridization in covalent tetravalent elements for $r \cong r_x$; r_x is the crossover distance. (c) Lone pair semiconductors such as Se

creating this band, e.g., the number of atoms in an entire ideal crystal. In real crystals this number is reduced since the electron scattering limits the coherence length of the electron wave (i.e., the length in which quantum-mechanical interaction can take place). With a mean free path λ , the number of atoms responsible for the band level splitting is of the order of $(\lambda/a)^3$ for a primitive cubic lattice with lattice constant a . Each of these levels is broadened by collision broadening.

The formation of such bands is often shown as it evolves from the spectrum of isolated atoms when they are brought together to form the crystal lattice. Their levels split with decreasing interatomic distance, as shown in Fig. 7.1 and discussed in Sect. 6.1. There are several possibilities for the energy and electron distribution over these levels, depending on the crystal bonding and structure. Three relatively simple examples are given in Fig. 7.1.

Subfigure (a) shows the splitting and *overlap* of the s - and p -bands of a main group metal. The atomic states remain nearly unchanged when the atoms approach each other (here s - and p -bands do not mix) to form a metal.

Subfigure (b) shows the splitting for a covalent (tetravalent) crystal, e.g., for a *thatogen*, such as C (diamond) or Si. Near the crossover point, a *hybridization* into sp^3 -states occurs, providing four sp^3 -states for the lower band and four sp^3 -states for the upper band. A *band gap* appears between these two hybrid bands—see Sects. 7.2.

Subfigure (c) shows the lone pair configuration typical for higher valency atoms, e.g., a *pnictogen*, such as P or As, or a *chalcogen*, such as Se or Te,¹ where some electrons in the p -state do not participate in the bonding states. This is the case for $N > 4$, since anti-bonding states always increase more in energy than bonding states decrease when atoms approach each other (see Fig. 7.1c). Therefore, a *pair* of electrons when non-bonded (*lone pair*) has lower energy than when split into one bonding state electron and one anti-bonding state electron; only a total of four electrons can occupy all of the bonding orbitals.

Bands obtained from such splitting, which are completely or partially filled with valence electrons, are called *valence bands*.

¹AB-compounds containing these elements are referred to as pnictides or chalcogenides.

7.1.1 Insulators and Semiconductors

In a covalent monatomic crystal the four valence electrons fill each of the levels in the valence band. In such a totally filled valence band, electronic conduction is impossible, since electrons can only move by an exchange: for every electron moving in one direction, exactly one electron must move in the opposite direction; there is no free momentum space (*Pauli principle*) for a net electron transport.² Diamond is an example of a simple crystal with tetravalent atoms and a totally filled valence band. It is therefore an *insulator*.

The band above the valence band has the same number of states, but contains no electrons with vanishing excitation. It is an *empty band*.

In materials in which this band is relatively close to the valence band (i.e., in materials with a narrow band gap between these bands, such as germanium with a band gap of $E_g = 0.64$ eV), thermal excitation at room temperature will bring a number of electrons into this upper band and partially fill it, although to a very small fraction of the total level density. These electrons can easily gain energy from an external electric field as there are enough free levels available adjacent to each of these electrons; a *net electron transport* (see next section) in the direction of the electric field can take place. Electronic conduction occurs; therefore, this band is referred to as the *conduction band*. Germanium acts as an insulator for vanishing excitation and as a conductor with sufficient thermal excitation: it is called a *semiconductor*, and is distinguished from an insulator by a somewhat narrower band gap.

This description of electronic transport in a partially filled band needs a more precise discussion, which will be given in Chap. 8. A heuristic description is supplied below.

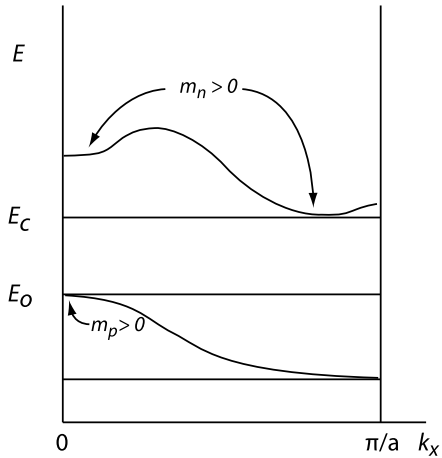
7.1.2 Electrons and Holes

When an electron is lifted from the valence band into the conduction band, an empty state is simultaneously created in the valence band. Just as the electron can move in the conduction band, so can the empty state in the valence band. Since it is surrounded by electrons, which can move into the empty state, the empty state moves in the opposite direction of the electron.

The valence band behavior somewhat resembles the filling of theater seats on the parquet. When all these seats are filled, people still can move, but only by exchanging seats. When the balcony (the conduction band) is opened, some people from the front of the parquet may move up to occupy seats in the balcony, leaving their empty seats below. Consequently, people in the parquet may move toward the stage, giving the impression that empty seats move in the opposite direction. However, only

²In a quantum-mechanical picture any $E(k)$ state represents a certain mass and velocity. In a filled band, all of them add up to zero.

Fig. 7.2 $E(k)$ for a simple valence and conduction band; signs of the effective masses of holes and electrons are indicated



people are moving toward the stage, following the force of attraction. Chairs remain fixed to the floor; their *state* of being empty or filled is moving.

The situation is somewhat similar in a semiconductor: only electrons are moving, not atoms or ions. Ionic conductivity is neglected here. Thus an empty state deserves its own name: a hole. It behaves much like an electron with an effective mass similar in value to the electron mass and not the mass of an ion.

As shown earlier, the electron within the conduction band is free to move when considering its mass as an effective mass. To distinguish it from an electron in vacuo, it is also referred to as a *Bloch electron*. The holes are also free to move. Both contribute to the electrical conductivity and are therefore called *carriers* (of this current).

Electrons tend to occupy the lowest energy states; that is, they fill a band from the bottom up and occupy states near the bottom of the conduction band designated as E_c . Holes will consequently, like soap bubbles in water, bubble toward its upper surface: they will collect at the upper edge of the valence band designated as E_v .

When an electron is accelerated in the direction of a mechanical force, for instance, by accelerating the semiconductor in the Tolman experiment, the hole is accelerated in the opposite direction. Therefore, its effective mass m_p has the sign opposite to the mass of an electron:

$$m_p = -\frac{\hbar^2}{\frac{\partial^2 E}{\partial k^2}|_{E_v}} \quad \text{and} \quad m_n = +\frac{\hbar^2}{\frac{\partial^2 E}{\partial k^2}|_{E_c}} \quad (7.1)$$

this is illustrated in Fig. 7.2. At the top of the valence band, $E(k)$ has a *negative* curvature that results in a *negative effective* mass for *electrons*. However, since the effective mass of the hole has the opposite sign as the electron (Eq. (7.1)), its effective mass is *positive* here, as is the effective mass of an electron at the bottom of the conduction band:

$$m_p(E_v) > 0 \quad m_n(E_c) > 0. \quad (7.2)$$

Table 7.1 Typical properties of electrons and holes

	Charge	Near	m^*	$\partial^2 E / \partial k^2$	Mobility	$j_{n,p}(F)$
Electrons	$-e$	E_c	$+m_n$	positive	$-\mu_n$	positive
Holes	$+e$	E_v	$+m_p$	negative	$+\mu_p$	positive

Finally, the charge of an electron is negative³ by convention; therefore, the charge of a hole (i.e., of an atom with a missing electron) is positive. This permits the distinction between a particle flux under the influence of an electric field $\mathbf{t}$ and the electric current caused by electrons and holes. The particle flux proceeds in opposite directions: electrons move in the direction of the electric field, and holes move against it. However,⁴ both electron and hole currents have the same sign and are therefore additive. Table 7.1 summarizes the typical properties of electrons and holes in a semiconductor.

7.1.3 Metals

In *monovalent metals*, the valence band is only partially filled; 50 % of the s -states are occupied. Therefore, electronic conduction takes place even with vanishing excitation.

Divalent metals show allowed eigenvalues in the range of the overlap between s - and p -bands⁵—see Fig. 7.1a. In this range, therefore, only about 25 % of the two s - and the six p -states are filled, and thus electronic conduction occurs at vanishing excitation.

Trivalent metals have about 63 % of their states in the overlapping s - and p -bands unoccupied. In *transition metals*, inner shell electrons occupy partially filled d -bands.

All metals are thus distinguished from semiconductors by their substantial fraction of free states in the highest partially occupied band with vanishing excitation. This band is therefore both a valence band, containing the valence electrons, and a conduction band where all *metallic conduction* takes place.

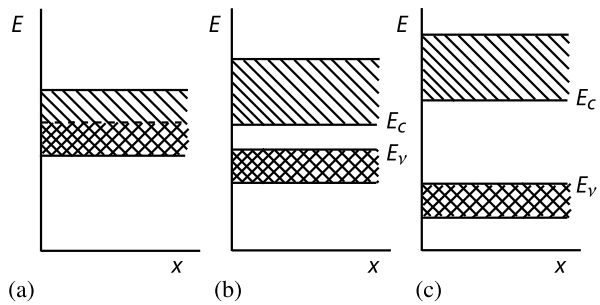
This simple model for distinguishing nonmetals from metals by the complete or incomplete filling of bands is due to Wilson (1931). The model is still valid for most

³A positive charge was arbitrarily related to the charge of a glass rod, rubbed with silk (by Benjamin Franklin); this charge was not caused by an added electron as it became known later, but by a missing electron on the glass rod. This electron was removed by the silk.

⁴In this and all chapters dealing with electrical conductivity, the electric field is identified as F and the energy as E .

⁵The difference between metals, where the overlap range is allowed, and semiconductors, where the overlap range is forbidden (band gap), depends on *Wigner's rules* (Wigner 1959), which state that eigenstates belonging to different symmetry groups of the Hamiltonian cannot mix (metals). In semiconductors they do mix, yielding sp^3 -hybridization for Si.

Fig. 7.3 Empty (*hatched*) and filled (*cross-hatched*) states in the upper bands of (a) a metal; (b) a semiconductor; and (c) an insulator. The energies at the top of the valence band and the bottom of the conduction band are identified as E_v and E_c , respectively



cases, except where magnetic properties or strong binding properties (polarons) interfere, as, for example, in NiO.

7.1.4 Semimetals and Narrow Gap Semiconductors

Metals that show a very small overlap of conduction and valence band exhibit weak electronic conduction. The density of states near the Fermi level (see Fig. 7.3) (see Sect. 7.1.1) is very small and only the relatively few electrons there control the conduction. Only these electrons can be scattered. For reviews, see Ziman (1969), or Cracknell and Wong (1973). These materials are termed *semimetals*; examples are graphite and bismuth.

On the other hand, semiconductors with very small band gaps show *relatively* high conductivity to other semiconductors. By some alloying, application of pressure, or even at elevated temperature, the band gap can vanish, turning such semiconductors into metals.

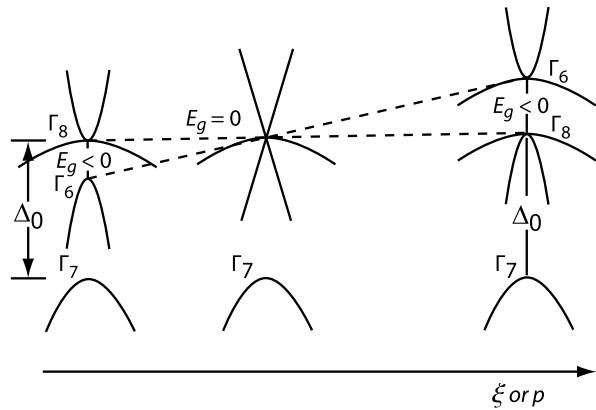
Examples include gray tin with a gap of 0–0.08 eV (suggested by magneto-optical experiments; Pidgeon 1969), and lead chalcogenides, and their alloys with other II–VI compounds, or with SnTe and mercury chalcogenides. For a review, see Tsidilkovski et al. (1985).

The lead chalcogenides are characterized by a small band gap with a maximum of the valence band and a minimum of the conduction band at the L -point rather than the Γ -point for most other direct gap semiconductors with E_g and m_n as shown in Table 7.2. Alloyed with CdTe ($E_g = 1.5$ eV), the band gap varies with composition, but can dip below zero (to -0.1 eV) because of bowing (see Sect. 7.2.1) for an alloy of PbTe containing a few percent Cd (Schmit and Stelzer 1973). A typical change of the $E(\mathbf{k})$ behavior near the Γ -point is shown in Fig. 7.4 for $\text{Hg}_{1-\zeta}\text{Cd}_\zeta\text{Te}$ as a function of the hydrostatic pressure or the composition (Kane 1979). The band gap can be expressed by an empirical relation (Hansen et al. 1982)

$$E_g(\zeta, T) = -0.302 + 1.93\zeta + 5.35 \cdot 10^{-4}(1 - 2\zeta)T - 0.81\zeta^2 + 0.832\zeta^3 \text{ (eV)} \quad (7.3)$$

Table 7.2 Band parameters for lead chalcogenides

Material	T (K)	E_g (eV)	$m_{n\parallel}$	$m_{n\perp}$
PbS	290	0.41	0.11	0.11
	77	0.31		
	4	0.29		
PbSe	290	0.27	0.05	0.08
	77	0.17		
	4	0.15		
PbTe	290	0.32	0.025	0.22
	77	0.22		
	4	0.19		

Fig. 7.4 Conduction and valence bands of $\text{Hg}_{1-\zeta}\text{Cd}\zeta\text{Te}$ as a function of pressure or composition (schematic)

for $0 < \zeta < 1$ and $4.2 < T < 300$ K. The gap also changes linearly with pressure, with a pressure coefficient of 10^{-2} eV/kbar.

Another interesting property is observed when alloying PbTe and SnTe. The L_6^+ and L_6^- bands are inverted; the L_6^- band is the conduction band in PbTe, while it is the valence band in SnTe, and vice versa for the L_6^+ band. In an alloy of $\text{Pb}_{1-\zeta}\text{Sn}\zeta\text{Te}$ $\zeta = 0.62$, both bands touch at 300 K. For $\zeta > 0.62$, the alloy becomes a metal (see Fig. 7.5). Such materials are also referred to as *gapless semiconductors* when the top of the valence band touches the bottom of the conduction band.

These examples demonstrate the possibility of designing very narrow band gap materials or semimetals by alloying two narrow band gap semiconductors with each other (see Fig. 7.6). The density of states in semimetals at the Fermi level is very small compared to that of a metal. In gapless semiconductors, it is zero (see Fig. 7.4 at $\zeta = 0.16$ for $T = 0$ K).

A special case of a gapless semiconductor occurs when tailing band states overlap with the conduction band (Fig. 7.6c). Tailing states are band states which extend into the band gap due to the disturbed neighborhood of lattice defects.

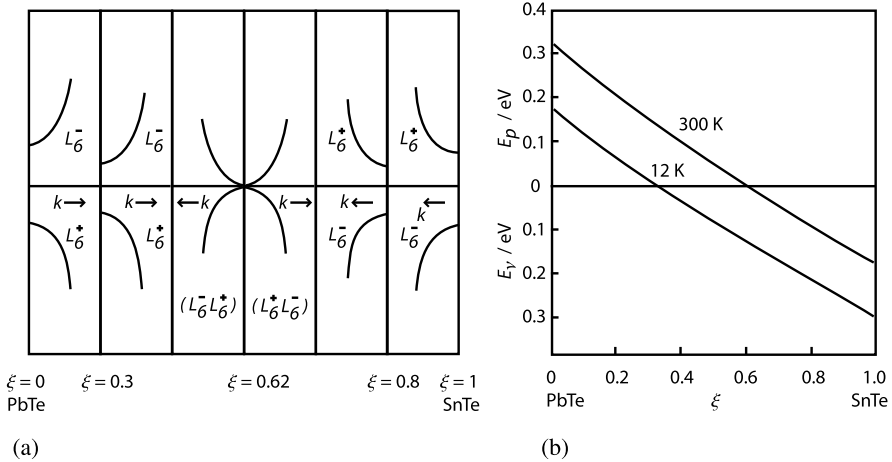
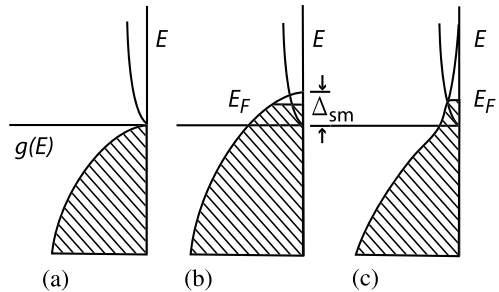


Fig. 7.5 (a) Conduction and valence bands in a schematic $E(\mathbf{k})$ representation of $\text{Pb}_{1-\xi}\text{Sn}_\xi\text{Te}$ for different alloy ratios ξ . (b) Band gap as a function of alloy ratio for $T = 12$ and 300 K (after Dinunock 1971)

Fig. 7.6 Density of states of valence and conduction bands with electron filling indicated for: (a) gapless semiconductor; (b) semimetal; and (c) gapless semiconductor with overlapping tail states



7.1.5 The Shape of Valence and Conduction Bands in Semiconductors

The shape of valence and conduction bands is given by the three-dimensional dispersion relation $E(\mathbf{k})$, and is of interest for semi-conducting properties in the energy range near the bottom of the conduction band (near E_c) and near the top of the valence band (s) (near E_v).

7.1.6 Constant Energy Surface Within the Brillouin Zone

The shape of these bands can be visualized from a constant energy surface near the bottom of the conduction band or the top of the valence band. This surface can

Fig. 7.7 Equi-energy surface for small electron energies within the first Brillouin zone for a primitive cubic lattice

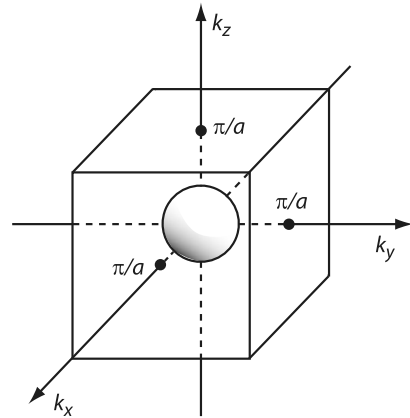
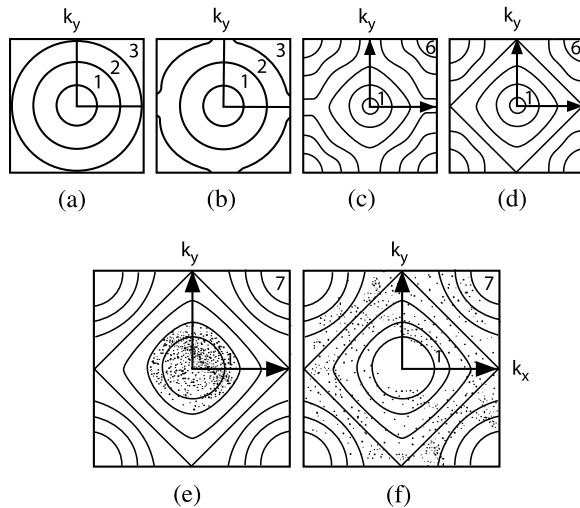


Fig. 7.8 Two-dimensional cut through a family of equi-energy surfaces for a primitive cubic crystal with increasing binding potential from (a)–(d). Filling with electrons is indicated by shading in (e) and (f). Spherical surfaces indicate quasi-free behavior of electrons. Deviations from the sphere indicate substantial lattice influence

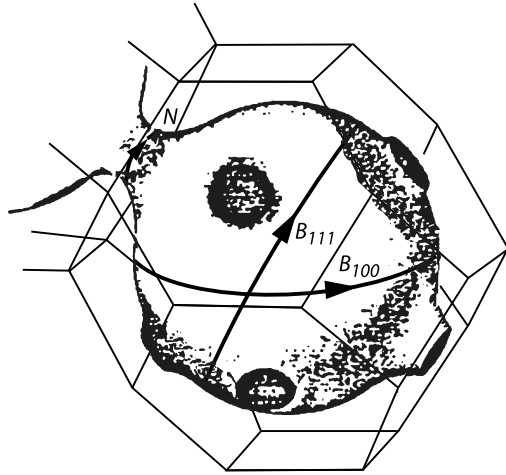


be identified by sequentially filling the band.⁶ Electrons that populate states within $E(\mathbf{k})$ up to a certain energy E_1 [i.e., to the corresponding $k_1(E_1)$] are contained in a small sphere in the center of the zone (Fig. 7.7) that grows parabolically in radius with increasing degree of filling—that is, with an increasing value of k . $k(E)$ is single-valued and monotonic within each band.

When starting from the center, $E(\mathbf{k}_1)$ becomes progressively more deformed with higher energy (higher k). A two-dimensional representation (Fig. 7.8) demonstrates more clearly some typical shapes of *equal energy surfaces* in a simple cubic

⁶Each band contains a large number of energy levels. Increasing numbers of electrons first fill the levels at the lowest energy (for $T = 0$) and then successively higher and higher energies. This process is referred to as band filling.

Fig. 7.9 Equi-energy surface at the Fermi level (Fermi surface) of a face-centered cubic metal, with contacts to the adjacent Fermi surfaces through the center of the hexagonal surfaces of the Brillouin surfaces. Three extreme orbits for electrons along the Fermi surface are identified by B_{111} , B_{100} , and N (after Pippard 1965)



lattice. Subfigures (a)–(d) are distinguished by increasing binding forces, showing increasingly more deviation from circles.

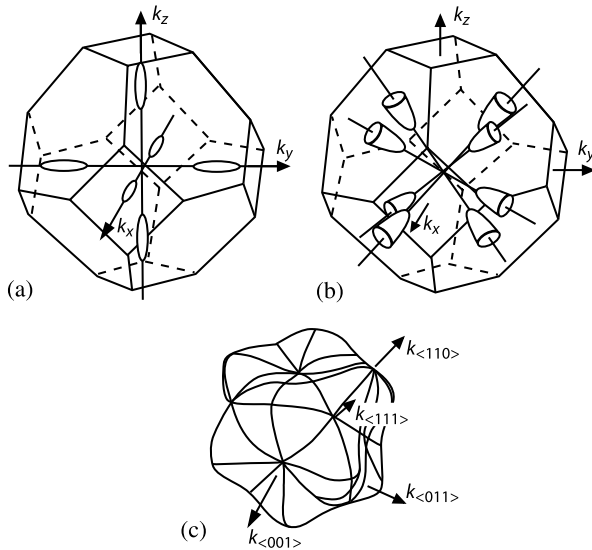
A similar development is observed near the top of the valence band: when it becomes filled with holes, the upper part of the Brillouin zone becomes depleted down to a certain energy E'_1 with the effect of rounding down the sharp edges of the Brillouin zone. Depending on the density of electrons within the band, a large fraction of the Brillouin zone is filled. Figure 7.9 illustrates such a Brillouin zone with a partially filled valence band of a metal. This figure also shows the connection to another neighboring zone. The periodicity of $E(\mathbf{k})$ is indicated at the upper left of Fig. 7.9. The zones are of the same order, first Brillouin zones. Higher Brillouin zones are not relevant to the discussion of semiconducting properties in contrast to the one-dimensional $E(\mathbf{k})$ representation of Fig. 7.12, where several curves in the first Brillouin zones are shown, in the k -space representation only one such equivalent surface can be drawn without confusion. It is the valence band in Figs. 7.8e and 7.9, and 7.10c, and the conduction band in Figs. 7.7 and 7.10a and b.

In semiconductors, the equi-energy surfaces close to the top of the valence band (nearly full Brillouin zone) and at the bottom of the conduction band (nearly empty Brillouin zone) are of interest for the electron transport. They are shown in Fig. 7.10 for Ge and Si.

Figure 7.10a shows for Si six small ellipsoids in the (100) direction which are centered at $\pm 0.8k_x$, $\pm 0.8k_y$, and $\pm 0.8k_z$. Figure 7.10b indicates for Ge in the (111) direction eight ellipsoids which are centered at the L -points (see Fig. 7.8). There are four such L minima per Brillouin zone. Other semiconductors having their lowest minima outside the Γ -point are GaP and AlSb. Most other semiconductors have their lowest conduction band minimum at (000).

Figure 7.10c shows the warped equi-energy surface, near the upper edge of the valence band for heavy holes (see Sect. 7.1.5) in Si and Ge. This equi-energy surface fills almost the entire Brillouin zone. Its shape is shown without the surrounding Brillouin zone in nearly the same scale as in Figs. 7.10a and b.

Fig. 7.10 Brillouin zone of (a) Si and (b) Ge with equi-energy surfaces near the conduction band edge and (c) equi-energy surface of the valence band for heavy holes in Si or Ge near the upper band edge (after McKelvey 1966; Seeger 1973)



The filling of the valence band with holes is greatly exaggerated; otherwise, the Brillouin zone with a flat outer surface and only slightly rounded edges would show. The *shape of these equi-energy surfaces* is intimately related to the three-dimensional shape of the bands ($E(\mathbf{k})$). The anisotropy is evident from Fig. 7.10.

The influence of this anisotropic $E_n(\mathbf{k})$ behavior, is discussed by analyzing the anisotropy of the effective mass in more detail.

7.1.7 The Effective Mass in Real Bands

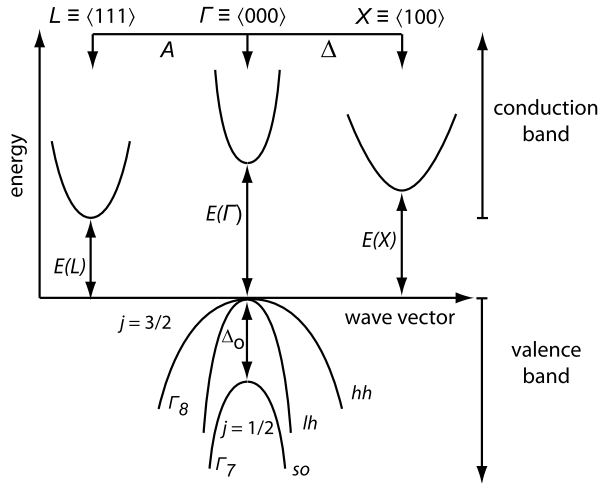
In Sect. 6.2.2 the effective mass is defined as proportional to the inverse of the second derivative of $E(\mathbf{k})$, i.e., of the curvature of $E(\mathbf{k})$.

The anisotropy of $E(\mathbf{k})$ in an actual crystal makes the introduction of a tensor relation for the effective mass necessary:

$$m_n = \underline{\mathbf{m}}_{ik}^* = \left(\frac{\hbar^2}{\frac{\partial^2 E}{\partial k_i \partial k_k}} \right). \quad (7.4)$$

This tensor ellipsoid, when transformed to main axes, contains usually only very few non-vanishing components. We will identify these below for some of the more important semiconductors. Figure 7.11 shows the important minima of typical conduction bands and maxima of the valence bands. In most semiconductors, the relevant conduction band minimum lies at the Γ -point (direct gap), or at or near the L - or X -point (indirect gap). The energies of these minima are listed in Table 7.3. The

Fig. 7.11 Simplified band structure of typical semiconductors near the most important extrema of valence and conduction bands



relevant maxima of the valence band are at the Γ -point. Their energies are listed in Table 7.5.

First the shape of the conduction and valence bands near the band edge will be discussed, and thereby providing simple expressions for the respective effective masses.

7.1.8 The Conduction Bands

The relationship of $E(\mathbf{k})$ in the vicinity of the conduction band minima near the band edge can be described as

The conduction band at Γ :

$$E = (\hbar^2/(2m_0))(\mathbf{k} - \mathbf{q}_0)^2. \quad (7.5)$$

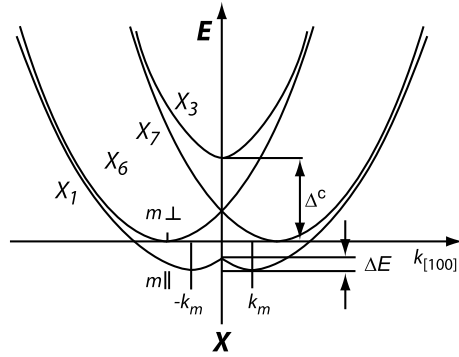
And the satellite conduction band:

$$E_c(\mathbf{k}) = \frac{\hbar^2}{2} \left(\frac{(k_x - k_{0x})^2}{m_{\parallel}} + \frac{(k_y - k_{0y})^2 + (k_z - k_{0z})^2}{m_{\perp}} \right) \quad (7.6)$$

relating $E(\mathbf{k})$ directly to the corresponding effective masses.

Satellite minima of $E(\mathbf{k})$ at $k_0 \neq 0$ show ellipticity, such as those of the indirect gap semiconductors Ge, Si, and GaP; so do the higher satellite minima of others III–IV compounds, such as, e.g., GaAs. For symmetry reasons, these ellipsoids are ellipsoids of revolution about the main axes; hence, we distinguish only two effective masses, parallel and orthogonal to these axes $m_{\parallel}$, and $m_{\perp}$, respectively [Eq. (7.6)]. The main axes of these ellipsoids of revolution lie in (100) direction for Si and in (111) direction for Ge.

Fig. 7.12 Camel's back conduction band in GaP along the Δ -axes near the Brillouin zone boundary at X . Dashed and solid curves for diamond and zinc-blende structures, respectively



Another example is the camel's back conduction band of some III–V compound semiconductors (see Fig. 7.12); it can be described by

$$E(\mathbf{k}) = \frac{\hbar^2 k_{\parallel}^2}{2m_{\parallel}} + \frac{\hbar^2 k_{\perp}^2}{2m_{\perp}} - \sqrt{\left(\frac{\Delta^c}{2}\right)^2 + \Delta_0^c \frac{\hbar^2 k_{\parallel}^2}{2m_{\parallel}}} \quad (7.7)$$

where $k_{\parallel}$, $m_{\parallel}$ and $k_{\perp}$, $m_{\perp}$ are the components parallel and perpendicular to $[100]$, and Δ_0^c describes the non-parabolicity; ΔE and Δ^c are identified in Fig. 7.12.

The energies of the conduction band minima and the corresponding effective masses are listed in Table 7.3. Band gaps of some higher compound semiconductors are listed in Table 7.4.

7.1.9 The Valence Band

The valence band develops from the twofold degenerate s -states and the sixfold degenerate p -states of an atom forming sp^3 -hybrids. Without spin-orbit interaction it breaks into two bands at $k = 0$ (Γ_1 and Γ_{25} as shown in Fig. 6.7). With spin-orbit interaction, the upper edge Γ_{25} breaks into two sets of bands: one set with a total momentum of $3/2$ is fourfold degenerate at $\mathbf{k} = 0$; this degeneracy can be removed in anisotropic crystals with crystal field coupling, for example, in hexagonal CdS.

The other set is twofold degenerate with $j = 1/2$ and shifted by the spin-orbit splitting energy Δ_0 (Figs. 6.8 and 7.11); it is referred to as the *spin-orbit split-off band* “so” with an effective mass m_{50} .

For $k \neq 0$ the degeneracy of the upper band is removed. Here, the band splits into two bands, each of which is twofold degenerate. The one with lower curvature is the *heavy hole band* “hh” with an effective mass m_h ; the other with larger curvature is the *light hole band* “lh” with an effective mass m_l . The valence band energies at a number of symmetry points are given in Table 7.5 for some typical semiconductors. Near the Γ -point ($k = 0$) the Hamiltonian describing the three sets of upper valence

Table 7.3 Electron effective masses in units of m_0 , conduction bands in eV (at 0 K) with characteristic point and band numbers identified and camel's back parameters in eV (Δ^c and Δ_0^c)

Crystal	1. Indir. Gap	$m_{n\parallel}$	$m_{n\perp}$	2. Direct Gap	m_n	3. Gap	m_{nU}	$m_{n\perp}$	Δ^c	Δ_0^c or ΔE
Si	(X_1) 1.16	0.191	0.916	(Γ_2) 4.19		(K_3) 1.70				
Ge	(L_6) 0.76	1.57	0.081	(Γ_7) 0.898	0.038					
GaP	(Δ_1) 2.35	0.91	0.25	(Γ_1) 2.895	0.093	(L_1) 2.64			(Δ) 0.355	(Δ) 0.433 (Δ_0^c)
GaAs	(L_6) 1.82	1.9	0.075	(Γ_6) 1.519	0.067	(X_6) 2.03	1.8	0.257	(X) 0.304	(X) 0.009 (ΔE)
GaSb	(L_6) 1.22	0.95	0.11	(Γ_6) 0.86	0.041	(X_6) 1.72	1.2	0.250	(X) 0.178	(X) 0.025 (ΔE)
InP	(L_6) 2.19			(Γ_6) 1.50	0.077	(X_6) 2.44				
InAs	(L_6) 1.53			(Γ_6) 0.37	0.024	(X_6) 2.28				
InSb	(L_6) 1.03	0.09		(Γ_6) 0.25	0.0136	(X_6) 1.71				
ZnS _{culb}				(Γ_6) 3.78	0.34					
ZnS _{hex}				(Γ_1) 3.91	0.28					
ZnSe	(L_6) 3.96			(Γ_6) 2.82	0.16	(X_6) 4.57				
ZnTe				(Γ_6) 2.394	0.122					
CdS				(Γ_6) 2.583	0.21					
CdSe				(Γ_7) 1.829	0.112					
CeTe	(L_6) 2.82			(Γ_6) 1.475	0.096	(X_6) 3.48				

Table 7.4 Band gaps of some higher compound semiconductors

Crystal	Indirect	E_g	Direct	E_g
Mg ₂ Si	$\Gamma_{15} \rightarrow X_1$	0.6	$\Gamma_{12} \rightarrow \Gamma_1$	2.17
Mg ₂ Ge	$\Gamma_{15} \rightarrow X_3$	0.74	$\Gamma_{15} \rightarrow \Gamma_1$	1.64
Mg ₂ Sn	$\Gamma_{15} \rightarrow X_3$	0.36	$\Gamma_{15} \rightarrow \Gamma_1$	1.2
β -LiSb ^a	$\Gamma_{15} \rightarrow X_1$	0.74	$\Gamma_{15} \rightarrow \Gamma_1$	2.2
K ₃ Sb ^a	$\Gamma_{15} \rightarrow X_1$	1.39	$\Gamma_{15} \rightarrow \Gamma_1$	0.56
Cs ₃ Sb ^a	$\Gamma_{15} \rightarrow X_1$	1.75	$\Gamma_{15} \rightarrow \Gamma_1$	1.02

^aCalculated by Wei and Zunger (1986)

Table 7.5 Upper (except Γ_6) valence bands in eV in typical semiconductors

Semiconductor	Γ -related		Maxima	L -related	X -related
Si	$(\Gamma_1) - 12.5$	$\Gamma_{25} = (\Gamma_8)0$	$(\Gamma_7) - 0.044$	$(L_3) - 2.82$	$(X_4) - 6.27$
Ge	$(\Gamma_6) - 12.7$	$(\Gamma_8)0$	$(\Gamma_7) - 0.29$	$(L_{6,5}) - 1.43$	$(X_5) - 3.29$
GaP	$(\Gamma_1) - 13.0$	$\Gamma_{15} = (\Gamma_8)0$	$(\Gamma_7) - 0.08$	$(L_3) - 1.1$	$(X_5) - 2.7$
GaAs	$(\Gamma_7) - 12.6$	$(\Gamma_8)0$	$(\Gamma_7) - 0.35$	$(L_{4,5}) - 1.2$	$(X_7) - 2.87$
GaSb	$(\Gamma_6) - 12.0$	$(\Gamma_8)0$	$(\Gamma_7) - 0.756$	$(L_{4,5}) - 1.1$	$(X_7) - 2.37$
InP	$(\Gamma_6) - 11.4$	$(\Gamma_8)0$	$(\Gamma_7) - 0.21$	$(L_{4,5}) - 0.94$	$(X_7) - 2.06$
InAs	$(\Gamma_6) - 12.7$	$(\Gamma_8)0$	$(\Gamma_7) - 0.43$	$(L_{4,5}) - 0.9$	$(X_7) - 2.37$
InSb	$(\Gamma_6) - 11.6$	$(\Gamma_8)0$	$(\Gamma_7) - 0.82$	$(L_{4,5}) - 0.95$	$(X_7) - 2.24$
ZnS	$(\Gamma_6) - 0.8$	$\Gamma_{15} = (\Gamma_8)0$	$(\Gamma_7) - 0.067$	$(L_3) - 1.4$	$(X_7) - 2.5$
ZnSe	$(\Gamma_6) - 12.5$	$\Gamma_{15} = (\Gamma_8)0$	$(\Gamma_7) - 0.45$	$(L_{4,5}) - 0.76$	$(X_7) - 1.96$
ZnTe	$(\Gamma_3) - 4.5$	$\Gamma_{15} = (\Gamma_8)0$	$(\Gamma_7) - 0.97$	$(L_3) - 1.1$	$(X_6) - 1.3$
CdS	$(A_{5,6}) - 0.5$	$(\Gamma_5)0$	$(\Gamma_6) - 0.8$	$(L_{2,4}) - 1.4$	$(M_4) - 0.7$
CdSe		$(\Gamma_9)0$	$(\Gamma_7) - 0.416$		
CeTe	$(\Gamma_6) - 11.1$	$(\Gamma_8)0$	$(\Gamma_7) - 0.89$	$(L_{4,5}) - 0.65$	$(X_7) - 1.60$

bands can be written as (D'yakonov and Perel' 1971a, 1971b)

$$\mathbf{H} = -(A + 2B)k^2 + 3B(\mathbf{k} \cdot \hat{\mathbf{L}})^2 - \frac{1}{3}\Delta_0(\underline{\sigma} \cdot \hat{\mathbf{L}}) + \frac{1}{3}\Delta_0 \quad (7.8)$$

with

$$A = -\frac{\hbar^2}{4}\left(\frac{1}{m_l} + \frac{1}{m_h}\right), \quad B = \frac{\hbar^2}{4}\left(\frac{1}{m_l} - \frac{1}{m_h}\right) \quad (7.9)$$

where L is the angular momentum matrix, σ : is the Pauli operator spin matrix, and Δ_0 is the spin-orbit splitting.

Only the light and heavy hole bands need to be considered when Δ_0 is larger than certain energies, e.g., kT or the ionization energy of shallow acceptors.

Table 7.6 Hole effective masses, valence band splitting,^a and valence band parameters

Crystal	γ_1	γ_2	γ_3	$\Delta_0(T \text{ (K)})$	Δ_1	$m_h(100)$	$m_h(110)$	$m_h(111)$	m_l	m_{so}
Si	4.285	0.339	1.446	0.45 (10)		0.537			0.153	0.234
Ge	13.38	4.28	5.69	0.297 (10)		0.284	0.352	0.376	0.044	0.095
GaP	4.05	0.49	1.25	0.08 (100)		0.419		0.997	0.16	0.465
GaAs	6.95	2.25	2.86	0.34 (10)		0.51			0.082	0.154
GaSb	13.3	4.4	5.7	0.76		0.28			0.05	
InP	5.15	0.94	1.62			0.56		0.60	0.12	0.121
InAs	20.4	8.3	9.1	0.38 (1.5)		0.35		0.43	0.026	
InSb	3.25	-0.20	0.90	0.85 (100)		0.34	0.42	0.45	0.016	
ZnS _{cub}				0.067 (80)		1.76			0.169	
ZnS _{hex}				0.086 (77)	0.055	1.4	0.49 _⊥			
ZnSe	4.3	1.14	1.84	0.403 (80)						
ZnTe	3.9	0.83	1.30	0.97 (80)						
CdS				0.062 (77)	0.027	0.64			0.64	
CdSe				0.416 (77)	0.039	≥ 1	0.45		0.9	
CdTe	5.3	1.7	2.0	0.811 (80)		0.72	0.81	0.81	0.13	

^aThe two top valence bands are split at $k = 0$ by Δ_1 due to crystal field coupling; $\Delta_1 \neq 0$ in anisotropic crystals, such as hexagonal structures. Δ_0 is the spin-orbit splitting. Δ_0 and Δ_1 are given in eV

r These two bands, the Hamiltonian reduces considerably. Luttinger (1956) gives it in a form that does not require spherical symmetry

$$\mathbf{H} = \frac{\hbar^2}{2m_0} \left[\left(\gamma_1 + \frac{5}{2} \gamma_2 \right) \nabla^2 - 2\gamma_3 (\nabla \cdot \mathbf{J})^2 + 2(\gamma_3 - \gamma_2) (\nabla_x^2 J_x^2 + \nabla_y^2 J_y^2 + \nabla_z^2 J_z^2) \right], \quad (7.10)$$

where $\mathbf{J}$ is a pseudovector representing the spin momentum operator (Bir and Pikus 1972) and γ_i are the Luttinger parameters.

For $\gamma_3 = \gamma_2$, the eigenvalues of this Hamiltonian yield two parabolic bands

$$E_{lh} = \frac{\gamma_1 + 2\gamma_2}{2m_0} \hbar^2 k^2 \quad \text{and} \quad E_{hh} = \frac{\gamma_1 - 2\gamma_2}{2m_0} \hbar^2 k^2 \quad (7.11)$$

for light and heavy holes with effective masses

$$m_l = \frac{m_0}{\gamma_1 + 2\gamma_2} \quad \text{and} \quad m_h = \frac{m_0}{\gamma_1 - 2\gamma_2}. \quad (7.12)$$

Fig. 7.13 Typical shapes of surfaces of constant energy: (a) spherical; (b) ellipsoidal; and (c) warped

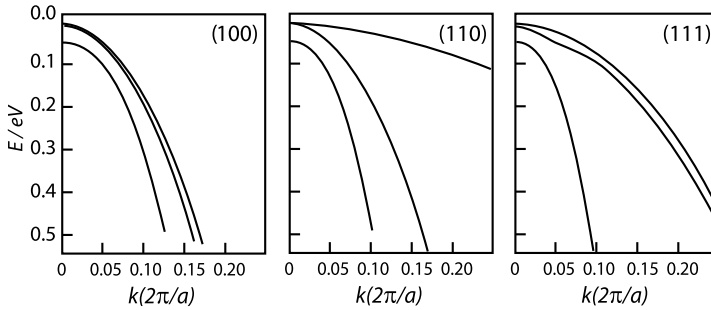
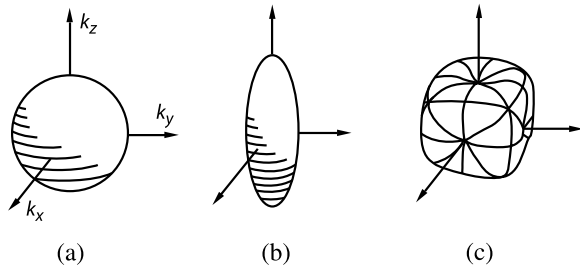


Fig. 7.14 $E(\mathbf{k})$ diagram for the valence bands of Si near the Γ -point in three symmetry directions (after Pantelides 1978)

With γ_3 substantially different from γ_2 , the two sets of valence bands become warped and are determined from the extensive dispersion equation:

$$E_{l,m} = \frac{\hbar^2}{2m_0} \left[\gamma_1 k^2 \pm \sqrt{4\gamma_2^2 k^2 + 12(\gamma_3^2 - \gamma_2^2)(k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)} \right] \quad (7.13)$$

with the $+$ and $-$ signs for light and heavy hole bands, respectively.

The degree of warping can be judged from the tabulated values of γ_i (Table 7.6). For example, it is small for Ge and GaAs ($\gamma_2 \cong \gamma_3$) and much larger for Si and InP (also see Fig. 7.14).

Often an equivalent description of these two bands is given.⁷

$$E_{\pm}(k) = Ak^2 \pm \sqrt{(Bk^2)^2 + C(k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)}, \quad (7.14)$$

with the $+$ and $-$ signs for the light and heavy hole bands, respectively. The band parameters can be interpreted as A giving the average curvature, B giving the splitting between heavy and light hole bands, and C describing the warping. These param-

⁷There are also Dresselhaus parameters L , M , and N (Dresselhaus et al. 1955) to describe the valence band. They are related to the Luttinger parameters by Eq. (7.14).

ters are related to the *Luttinger band parameters* by

$$\frac{\gamma_1}{m_0} = -\frac{2}{\hbar^2} A, \quad \frac{\gamma_2}{m_0} = -\frac{1}{\hbar^2} B, \quad \frac{\gamma_3}{m_0} = -\frac{1}{\sqrt{3}\hbar^2} \sqrt{C^2 + 3B^2}. \quad (7.15)$$

The different shapes of the surfaces of constant energy for the different conduction and valence bands are summarized in Fig. 7.13.

An impression about the degree of warping for Si can be obtained from Fig. 7.14, which shows cuts through the $E(\mathbf{k})$ surface in different crystallographic directions (Pantelides 1978).

7.1.10 Probing Bands with Cyclotron Resonance

When applying a strong enough magnetic field, the band shape can be probed by forcing the electrons into circles perpendicular to the direction of the magnetic induction (for vanishing electric field), following the Lorentz force:

$$\vec{\mathcal{F}} = \hbar \frac{d\mathbf{k}}{dt} = e(\mathbf{F} + \mathbf{v} \times \mathbf{B}). \quad (7.16)$$

These circling electrons are accelerated by the magnetic induction with a centripetal acceleration

$$\mathbf{a} = \frac{\hbar}{m^*} \frac{\partial \mathbf{k}}{\partial t} = \frac{e}{m^*} (\mathbf{v} \times \mathbf{B}) = \frac{e}{\hbar m^*} (\nabla_{\mathbf{k}} E(\mathbf{k}) \times \mathbf{B}) \quad (7.17)$$

this acceleration is a measure of the effective mass, m^* , hence of the band shape at the specific electron energy (see below). The accelerated electrons can interact with a high frequency, small amplitude probing electromagnetic field, and show a resonance absorption—the *cyclotron resonance* (in the classical limit)⁸ when the ac-frequency of the probing field coincides with the *cyclotron frequency* of the circling electrons:

$$\boxed{\omega_e = \frac{eB_0}{m^*} = 17.84 \frac{m_0}{m^*} B_0 \text{ (GHz/kG)}} \quad (7.18)$$

⁸Here cyclotron resonance is discussed within the same band, and quantum effects are neglected. This can be justified when, neglecting scattering, each electron describes full circles which have to be integers of its De Broglie wavelength [Eq. (7.6)]. This integer represents the quantum number n_q of the circle; and for the magnetic induction discussed here it is a large number. Resonance means absorption (or emission) of one quantum $\hbar\omega_c$, hence changing n_q by $\Delta n_q = \pm 1$, which is the selection rule for cyclotron transitions. Since $\Delta n_q \ll n_q$, a change in circle diameter is negligible; hence the classical approach is justified. At higher fields the circles become smaller; and when approaching atomic size, the quantum levels (Landau levels) become wider-spaced and a quantum mechanical approach is required. For reviews, see Lax (1963), Mavroides (1972), McCombe and Wagner (1975).

where B_0 is the stationary magnetic induction. This resonance absorption is quite distinct when the electrons are permitted to complete many circles⁹ before being interrupted by scattering (see Chap. 32). Since the path of an electron to complete a cycle is smaller with the decreasing radius of the circle and scattering is reduced with the decreasing density of defects and phonons, cyclotron resonance measurements are usually performed at high magnetic fields in materials of high purity and at low temperature. Excessively high magnetic fields, however, cause inconveniently large high resonance frequencies (for B_0 of 10 kG, one obtains $\nu = \omega/2\pi \cong 100$ GHz).

Although electrons along all cross sections of the Fermi surface perpendicular to the direction of the magnetic field cause resonance absorption, absorption maxima are observed at the extrema of the cross section (belly or neck) because of the higher electron density here. In addition, one observes so-called dog-bone cross sections, in which electrons circle between four adjacent Fermi surfaces near the neck of each surface, as well as many other cross-section shapes depending on the direction of the magnetic field and the shape of the Fermi-surfaces.

In semiconductors, the cyclotron resonance can be used to probe the shape of the bands near the edge of the conduction or valence band. Since the cyclotron resonance frequency depends only on the effective mass, its measurement yields the most direct information about its behavior (see Sect. 7.1.5—and reviews by Smith 1967; Pidgeon 1980).

7.1.11 Measurement of Effective Masses with Cyclotron Resonance

The effective mass is obtained directly from the cyclotron frequency [Eq. (7.18)]. By changing the relative alignment of the magnetic induction and the crystal axis, one can probe the anisotropy of the effective mass, such as that caused by the elliptical satellite bands—see Fig. 7.13b.

The resonance frequency in such elliptical bands is

$$\omega_e = e \sqrt{\frac{B_x^2}{m_y m_z} + \frac{B_y^2}{m_z m_x} + \frac{B_z^2}{m_x m_y}}, \quad (7.19)$$

tensor (m_x, m_y, m_z) in diagonal form. With $m = m_x$ and $m_x = m_y = m_z$, the longitudinal and transverse effective masses, one obtains from Eq. (7.19) for the reso-

⁹The circle diameter is typically of the order of 10^{-3} cm for a magnetic induction of 10 kG; here v_n is the thermal velocity of an electron. In metals, however, one also has to consider the skin penetration of the probing electromagnetic field. The skin depth of a metal is usually a very small fraction of the circle diameter, so that the probing ac-field can interact only at the very top part of each electron cycle close to the surface. This enhances information about near-surface behavior in metals, while in semiconductors, probing extends throughout the bulk.

Fig. 7.15 Magnetic orbit in k -space near the bottom of the conduction band in a satellite valley of Si, with arbitrary orientation of the magnetic induction

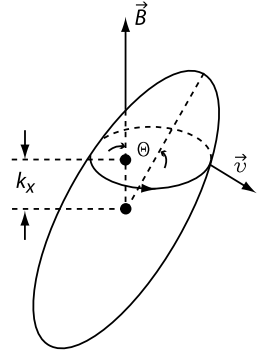
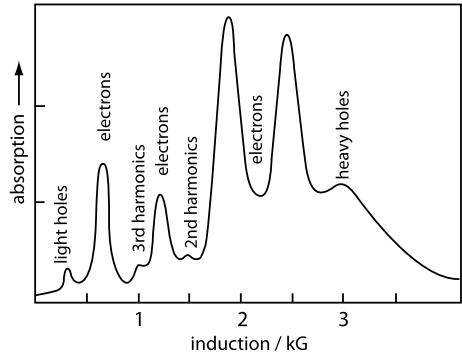


Fig. 7.16 Cyclotron resonance absorption in Si near 4 K at 23 GHz with magnetic induction parallel to the [111] axis (after Dexter et al. 1956a). The higher harmonics identified belong to the heavy hole resonance



nance frequency

$$\omega_c = eB \sqrt{\frac{\cos^2 \theta}{m_{\perp}^2} + \frac{\sin^2 \theta}{m_{\parallel} m_{\perp}}}, \quad (7.20)$$

where θ is the angle between B_0 and the principal axis of the $E(\mathbf{k})$ ellipsoid (Fig. 7.15).

Figure 7.16 shows the measured resonance spectrum in Si at a constant probing frequency of 23 GHz (cm-wave), with varying magnetic induction applied in [111] direction.

Other resonances shown in Fig. 7.16 are caused by holes in the different valence bands (see Fig. 7.10c). These resonances can be expressed (Dresselhaus et al. 1955) with $\omega_0 = eB_0/m_p$ by introducing an anisotropic hole effective mass:

$$\frac{m_p}{m_0} = \frac{1}{A \pm \sqrt{B^2 + C^2/4}} \left\{ 1 \pm \frac{C^2(1 - 3\cos^2 \theta)^2}{64\sqrt{B^2 + C^2/4}[A \pm \sqrt{B^2 + C^2/4}]} \right\}. \quad (7.21)$$

The parameters A , B , and C are the empirical valence band parameters explained in Sect. 7.1.5.

Because of the warping of the valence band, higher harmonics of the heavy hole resonance are also found in cyclotron resonance (Fig. 7.16).

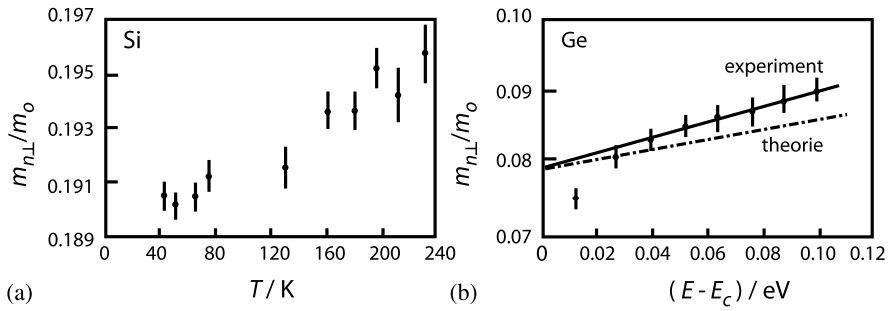


Fig. 7.17 (a) Effective transverse electron mass as a function of the temperature for Si (after Oussel et al. 1976) and (b) as a function of the energy for Ge (after Aggarwal et al. 1969)

7.1.12 The Conduction Band at Higher Energies

The parabolic approximation is no longer sufficient when a significant fraction of the electrons is at higher energies in the band—for example, at elevated temperatures, high electric fields, after optical excitation, or when pushed up by high doping. With increasing E , the band curvature decreases; hence, usually m^* increases, introducing an *energy-dependent effective mass*. When expressed by $m_n(T)$, the changes are relatively small between 0 K and 300 K (1–5 %).

This dependency is shown in Fig. 7.17 as a function of the temperature for Si and as a function of the energy above the band edge for Ge.

When a more accurate description of the band shape is needed beyond $E_c(k=0)$, we can use an expression obtained from the **k-p** theory.

For the shape of the conduction band of GaAs, for example, we have:

$$E(k \text{ near } \Gamma_6) = \frac{\hbar^2 k^2}{2m_n} + (\alpha + \beta s)k^4 \pm \gamma \sqrt{s - 9t}k^3 \quad (7.22)$$

with

$$s = \frac{k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2}{k^4} \quad \text{and} \quad t = \frac{k_x^2 k_y^2 k_z^2}{k^6}. \quad (7.23)$$

The second term in Eq. (7.22) describes the deviation from parabolicity, and the third term describes a slight band warping of the conduction band. In GaAs there is also a slight spin splitting of the conduction band (Rössler 1984). See Fig. 7.18.

7.1.13 The Momentum Effective Mass

The effective mass of a carrier is conventionally described in relation to Newton's second law, yielding the well-known relation involving the curvature of $E(\mathbf{k})$. Another way to introduce this mass in a semiconductor with a spherical band of arbi-

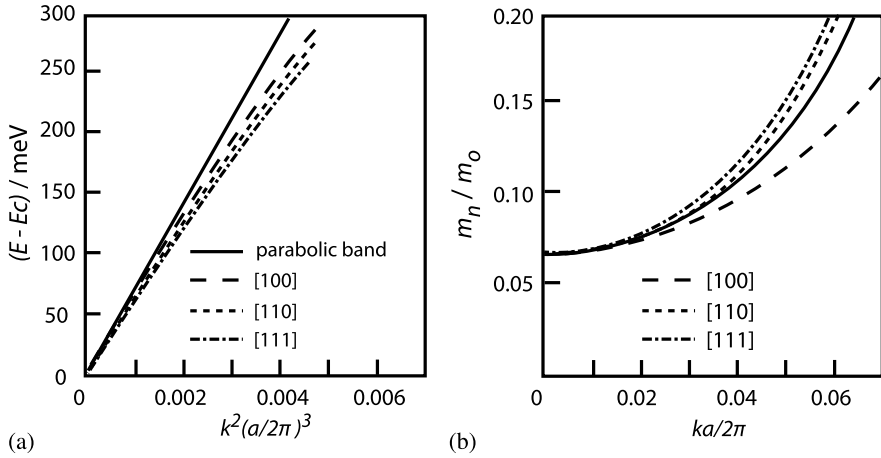


Fig. 7.18 (a) $E(\mathbf{k})$ in the lowest conduction band of GaAs as a function of the square of the wave vector. (b) Effective electron mass as a function of the wave vector with same identification. The two curves for the [110] direction show the spin splitting of the conduction band (after Rössler 1984)

trary shape is through the relationship between the carrier velocity and the pseudo-momentum

$$v_i = \sum_j \frac{\hbar}{m_{ij}} k_j \quad \text{with} \quad v_i = \frac{1}{\hbar} \frac{\partial E}{\partial k_i}. \quad (7.24)$$

In a spherical band, therefore, the *momentum effective mass* is a scalar:

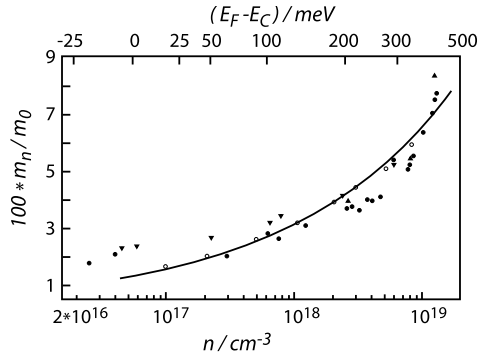
$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{1}{k} \frac{\partial E}{\partial k}. \quad (7.25)$$

In a parabolic $E(\mathbf{k})$, this definition is identical to the conventional one, relating the effective mass to the second derivative of $E(\mathbf{k})$. The common description is satisfactory as long as the discussion is restricted to the energy range near the band edge, where parabolicity is a reasonable approximation. At higher energies the momentum effective mass is more appropriate (Zawadzki 1980/1982), and it will therefore be used in the following section.

7.1.14 The Effective Mass at Higher Energies

A large fraction of the electrons can reach substantially higher energies within a band when the Fermi level is shifted into the conduction band by higher doping. Since the curvature decreases with increasing distance from the lower band edge,

Fig. 7.19 Effective masses of electrons in InSb at 300 K as calculated from the three-band Kane model (*solid curve*) and measured by various authors as a function of the position of the Fermi level below and inside the conduction band 1 (after Zawadzki 1974)



the effective mass increases. In semiconductors with a very low effective mass (here one has a low density of states near the band edge) one can reach this condition at moderate doping levels, for example, with a donor density in excess of 10^{17} cm^{-3} for InSb as can be seen by comparing upper and lower abscissae of Fig. 7.19. Kane (1957) estimates the shape of the conduction band as a function of the wave vector for a three-band model ($\Gamma_6\Gamma_7$ and Γ_8) near $k = 0$ for InSb. In GaAs the corrections are somewhat smaller (Vrehen 1968) because of a larger band gap.

Thus, one obtains for the non-parabolic conduction band

$$E(k) = \frac{\hbar^2 k^2}{2m_n^0} - \left(1 - \frac{m_n^0}{m_0}\right) \left(\frac{\hbar^2 k^2}{2m_n^0}\right)^2 \left\{ \frac{3E_g^2 + 4\Delta_0 E_g + 2\Delta_0^2}{E_g(E_g + \Delta_0)(3E_g + 2\Delta_0)} \right\} \quad (7.26)$$

where the energy is normalized to $E = 0$ at E_c ; Δ_0 is the spin-orbit splitting; and m_n^0 the effective mass at the bottom of the conduction band, which can be expressed (Kane 1957) as

$$\frac{1}{m_n^0} = \frac{1}{m_0} + \frac{4P^2}{3\hbar^2 E_g} \frac{\Delta_0 + \frac{3}{2}E_g}{\Delta_0 + E_g}. \quad (7.27)$$

Here P is the matrix element connecting the conduction band with the three valence bands.

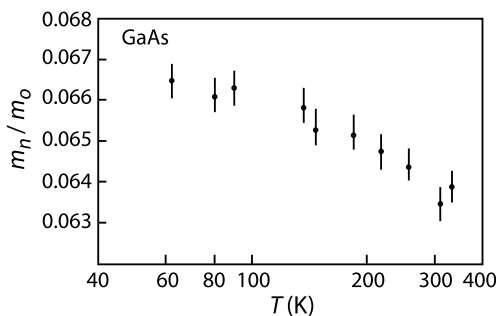
The effective mass slightly above the bottom of the conduction band can be approximated as

$$m_n(E) = m_n^0 \left(1 + \frac{2E}{E_g}\right) \simeq m_n^0 \sqrt{1 - \left(\frac{v_g}{v}\right)^2}, \quad (7.28)$$

with $v = \sqrt{E_g/(2m_n^0)}$ and v_g as the group velocity [Eq. (7.16)] (Landsberg 1987). Equation (7.28) is in fair agreement with the experiment for InSb (Fig. 7.19).

With increasing temperature, one must also consider the lattice expansion and consequent relative shift of the different bands if they are near enough to E_c . This influences the effective mass as a function of temperature and, in the given example (GaAs), causes a reduction in m_n with increasing temperature rather than an increase with increasing band filling—see Fig. 7.20.

Fig. 7.20 Electron effective mass as a function of temperature for GaAs (after Blakemore 1982a, 1982b)



7.2 The Band Gap

In *semiconductors*, the valence band is separated from the conduction band by a relatively narrow band gap; in *insulators*, the gap is much wider (Fig. 7.3). The distinction between semiconductors and insulators is arbitrary at a band gap of $\cong 2$ eV. A wide variety of materials provides a continuous transition of behavior from that of *insulators* and *wide, narrow, and zero band gap semiconductors* to *metals*.

The band gap shows a distinctive trend that is seen for various AB-compounds in Fig. 7.21 (also see Sect. 7.1, Tables 7.2, 7.3, and 7.7): it decreases with decreasing ionicity of the lattice binding forces and decreases steeply in the same class of compounds for homologous components with increasing atomic number, e.g., increasing ionic radius (interatomic spacing) or decreasing binding energy—see Phillips (1970). We must be careful, however, when using this trend for predicting the band gap of unknown compounds, since substantial deviations occur between materials with the gap at the Γ , L -, or X -point in $E(\mathbf{k})$.

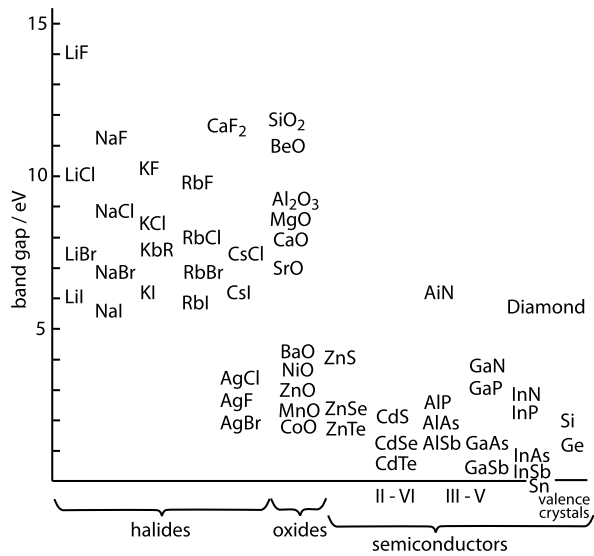
7.2.1 Band Gap Variation

A continuous variation of the width of the band gap can be achieved by *alloy* formation, or by application of hydrostatic pressure, which thereby changes the lattice composition or the lattice constant and thus the band gap (see Sect. 7.2.1). Alloys¹⁰ can be formed between similar metals or by mixing similar, homologous elements within a compound.

An example is $\text{Ga}_z\text{Al}_{1-z}\text{As}$, in which the metal atom sublattice is a homogeneous and statistical mixture (substitutional alloy) of Ga and Al, with a resulting band gap between that of GaAs and AlAs. Another example is $\text{CdS}_z\text{Se}_{1-z}$, in which

¹⁰The conventional term *alloy* of metals also encompasses crystallite mixtures of non-intersoluble metals, such as lead and tin (solder). Here, however, only materials within their solubility ranges are discussed. The *Hume-Rothery rule* identifies these metals as having similar binding character, similar valency, and similar atomic radii (Hume-Rothery 1936). Corresponding guidelines apply to the intersolubility of cations or anions in compounds.

Fig. 7.21 Band gaps for various AB-compounds and element semiconductors (after Hayes and Stoneham 1984)



the nonmetal sublattice is alloyed. There is an infinite number of such pseudo-compounds, which provides the possibility of creating any desired band gap. For quaternary alloys such as $\text{Ga}_\zeta \text{Al}_{1-\zeta} \text{P}_\eta \text{As}_{1-\eta}$ (see Pearsall 1982).

7.2.2 Band Gap Bowing

Alloy formation between components AC and BC produces a linear interpolation of the band gap

$$\overline{E}_g(\zeta) = E_g(\text{AC}) + \zeta[E_g(\text{BC}) - E_g(\text{AC})] \quad (7.29)$$

only if the alloying atoms (A and B) have nearly identical binding forces to atom C, and have nearly the same atomic radii. The bar over E_g indicates the averaging over various local configurations with different numbers of nearest neighbors of a certain atom. An example is $\text{ZnS}_\zeta \text{Se}_{1-\zeta}$ (Fig. 7.22a). If the radii are substantially different, a strong *bowing* of the band gap is observed, as shown for $\text{ZnS}_\zeta \text{Te}_{1-\zeta}$ and $\text{ZnSe}_\zeta \text{Te}_{1-\zeta}$ in Figs. 7.22b and c (Bernard and Zunger 1987). For a review, see Jaros (1985).

$$\overline{E}_g(\zeta) = E_g(\zeta) + b\zeta(1 - \zeta); \quad (7.30)$$

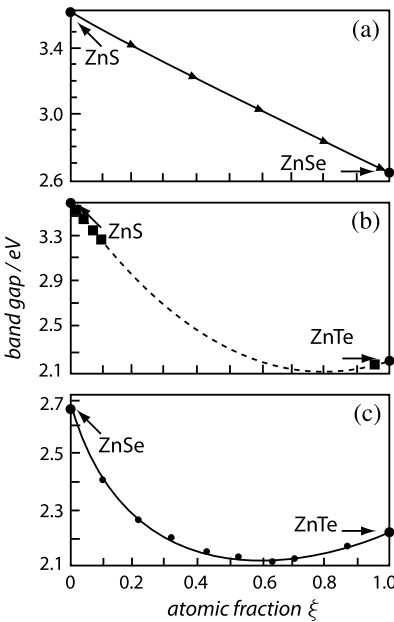
this bowing parameter is listed in Table 7.7 for a selection of II–VI and III–V compounds. Bowing is caused by a change of the lattice energy of the alloy, which is due to chemical and structural differences when a lattice atom is replaced by an alloying atom. The change in band gap is given by

$$\Delta E_g = \Delta E_g^{\text{chem}} + \Delta E_g^{\text{struct}}. \quad (7.31)$$

Table 7.7 Bowing parameter δ in eV (computed from Richardson 1973)

	GaAs	AlSb	InP	GaSb	InAs	InSb	ZnS	ZnSe	ZnTe	CdTe
GaP	0.38	2.31	1.36	3.51	2.67	5.68	0.87	1.41	3.51	2.96
GaAs		0.44	0.22	1.44	0.84	2.86	1.20	0.76	1.55	0.76
AlSb			0.01	0.005	0.05	0.92	3.64	1.88	1.17	1.55
InP				0.49	0.22	1.55	2.12	0.92	0.84	0.46
GaSb					0.008	0.24	4.08	1.85	0.44	−0.24
InAs						0.52	3.13	1.25	0.35	0.05
InSb							6.20	3.21	0.90	0.44
ZnS								0.60	3.02	2.07
ZnSe									0.90	0.02
ZnTe										−0.57

Fig. 7.22 Band gap as a function of the composition of mixed crystals between ZnTe (after Larach et al. 1957)



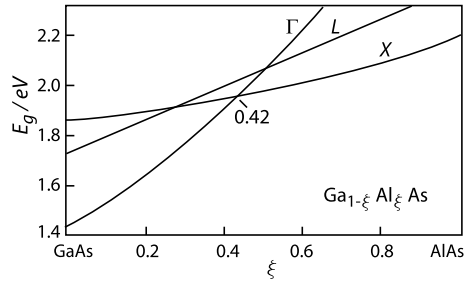
The varying chemical nature of the alloying atom may be expressed by its different *electronegativity* “*en*” and *hybridization* “*pd*” when forming the lattice bond:

$$\Delta E_g^{\text{chem}} = \Delta E_g^{\text{en}} + \Delta E_g^{\text{pd}}. \tag{7.32}$$

The changes in structure are induced by different *bond lengths* (*u*) and *tetragonal* (*bond angle*) *distortion* (η) (see below):

$$\Delta E_g^{\text{struct}} = \Delta E_g^u + \Delta E_g^\eta. \tag{7.33}$$

Fig. 7.23 Observed changes of ... Γ , X , and L conduction band minima of $\text{Ga}_{1-\zeta}\text{Al}_\zeta\text{As}$ as a function of composition at room temperature (from data of Saxena 1981)



The shifting of different conduction band minima by alloying can be substantially dissimilar from each other and consequently may change their relative position. An example is shown in Fig. 7.23 for the Γ -, X -, and L -points of $\text{Ga}_{1-\zeta}\text{Al}_\zeta\text{As}$.

The structural changes are more easily discussed when starting from a 50 % alloy. When ordered, this alloy can be described as a chalcopyrite. For example, an ordered $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ can be described as ZnCdS_2 , which in structure is similar to CuGaS_2 . The bond alternation is given by an anion displacement parameter $u = (\text{AC}^2 - \text{BC}^2)/a^2 + 1/4$ with (A, B, C) standing for the components (Zn, Cd, S in the given example), and AC as the average distance between atoms A and C, etc. The tetragonal distortion is described by the ratio $\eta = c/2a$. The more the measured u in the actual alloy deviates from the ideal ratio $1/4$ and η from 1 for an ideal chalcopyrite, the larger is the contribution from $\Delta E_g^{\text{struct}}$ to the bowing.

In ternary compounds, e.g., chalcopyrites, little bowing is observed when the anion sublattice is alloyed (e.g., $\text{CuInS}_\zeta\text{Se}_{1-\zeta}$, $\text{CuInSe}_\zeta\text{Te}_{1-\zeta}$, and $\text{CuInS}_\zeta\text{Te}_{1-\zeta}$), while there is substantial bowing when the cation sublattice is alloyed (e.g., $\text{CuGa}_\zeta\text{In}_{1-\zeta}\text{S}_2$ or $\text{Cu}_\zeta\text{Ag}_{1-\zeta}\text{GaSe}_2$). For reviews, see Martins and Zunger (1986) and also Jaffe and Zunger (1984b).

Strong bowing indicates a large change in lattice energy, which acts as a driving force for ordering, that is, for compound formation when a stoichiometric atomic ratio is reached rather than the formation of a statistical alloy. Examples are SiGe , GaInP_2 , or Ga_2AsP (Jen et al. 1986; Sritrakool et al. 1986; Ourmazd and Bean 1985).

7.2.3 Band Gap Dependence on Temperature and Pressure

The band gap (and other band features) change with temperature and pressure:

$$\Delta E_g = \left(\frac{\partial E_g}{\partial T} \right)_p \Delta T + \left(\frac{\partial E_g}{\partial p} \right)_T \Delta p. \quad (7.34)$$

Temperature-induced changes are due to:

- changes in lattice constants and
- changes in electron-phonon interaction.

The first term of Eq. (7.34), however, is closely related to the second term, which gives the changes of the band gap under pressure. The latter can be divided into several contributions, solely related to a change in the lattice constant. These changes influence the optical behavior due to changes in:

- matrix element, which depends on $1/a$ (lattice constant in a cubic crystal);
- density of states inducing changes in the effective mass;
- energy of electronic levels;
- plasma frequency containing a changed density of dipoles and a changed effective charge; and
- phonon frequency as the lattice stiffens with increasing pressure (anharmonicity of oscillations).

The changes in electron-phonon interaction dominating the first term of Eq. (7.34) are more involved. They have attracted substantial interest and can be divided into three different approaches:

- (1) the approach suggested by Fan (1951): involving an electron self-energy term that arises from spontaneous emission and reabsorption of a phonon; this approach was expanded by Cohen (1962) to include intervalley scattering;
- (2) the approach suggested by Antoncik (1955): introducing a temperature-dependent structure factor (*Debye-Waller factor*),¹¹ that is experimentally accessible from the temperature dependence of the Bragg reflections;
- (3) the approach suggested by Brooks (1955) and refined by Heine and van Vechten (1976): relating to a change in lattice vibrations from ω to ω' when an electron is excited from the valence into the conduction band:

$$E_g(T) \simeq E_g(0) - kT \sum_i \ln \left(\frac{\omega'_i}{\omega_i} \right). \quad (7.36)$$

See Lautenschlager et al. (1985).

Finally, the influence of uniaxial stress lowers the crystal symmetry, and thus removes the degeneracy. Uniaxial stress experiments can be designed to yield information on level and effective mass symmetries, and on deformation potentials.

Since the influences of temperature and pressure are many-fold and involve all bands, it is not possible to describe features which apply universally to all semiconductors. A few examples will be presented here. More comprehensive literature includes a large number of odd cases that behave substantially differently from the given examples, e.g., referenced by Marfaing (1980).

¹¹This Debye-Waller factor (W) is related to the probability of phonon emission during electron or x-ray diffraction and is given in the Debye approximation by

$$p = \exp(-2W) = \exp \left[-\frac{6E_R}{k\Theta} \left\{ \frac{1}{4} + \frac{T}{\Theta} \int_0^{\Theta/T} \frac{x dx}{\exp(x) - 1} \right\} \right], \quad (7.35)$$

where E_R is the recoil energy $= M_v^2/2$.

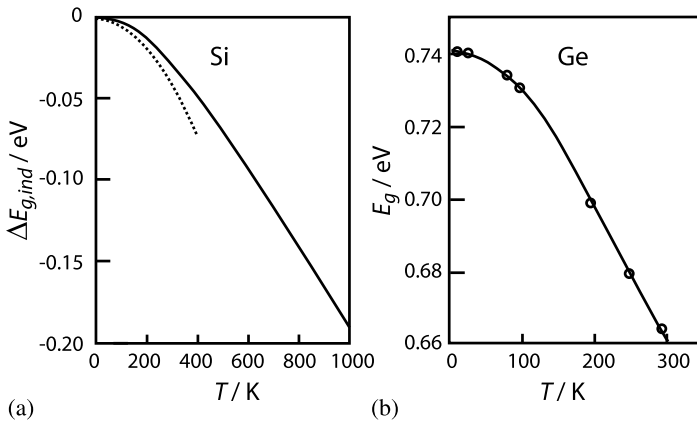


Fig. 7.24 Decrease of the band gap with increasing temperature: (a) in Si (after Lautenschlager et al. 1985), solid line = theory, circles = experimental; and (b) in Ge (after MacDonald et al. 1957)

The band gap usually decreases with increasing temperature—see Fig. 7.24. Exceptions are the lead chalcogenides, which show an increase of the gap with temperature; this band gap is determined at the L -point—see Fig. 7.5.

In a wide temperature range, the band gap changes linearly with temperature:

$$E_g = E_{g0} + \beta_E T, \quad (7.37)$$

where β_E is typically in the -10^{-4} eV/deg range—see Table 7.8. For lower temperature, however, $\beta_E T$ decreases and vanishes for $T \rightarrow 0$ according to the third law of thermodynamics.

The temperature dependence of the gap over a larger temperature range can be approximated by Varshni (1967)

$$E_g = E_{g0} - \frac{\alpha T^2}{\beta + T} \quad (7.38)$$

with α and β as empirical parameters listed by Varshni (1967).

The change of the band gap due to pressure is expressed as

$$\Delta E_g = \left(\frac{\partial E_g}{\partial p} \right)_T \Delta p; \quad (7.39)$$

however, it cannot be linearized in a wider pressure range. It often involves several bands which are influenced by different pressure coefficients that may even have different signs. As an example, the pressure dependence of the gap in GaAs is given in Fig. 7.25a. The gap first increases, shows a maximum at $6 \cdot 10^4$ atm, then decreases again with increasing pressure. The lower valley in the conduction band in GaAs (Γ -point) increases while the (100) valley decreases with pressure. At pressures above $8 \cdot 10^4$ atm, GaAs becomes an indirect band gap material.

Table 7.8 Direct (*d*) and indirect (*i*) band gaps for various semiconductors and their temperature and pressure coefficients

Crystal	E_g (0 K)	E_g (300 K)	$\frac{dE_g}{dT}$ ($\frac{\text{meV}}{\text{K}}$)	$\frac{dE_g}{dp}$ ($\frac{\text{meV}}{\text{kbar}}$)
Si	1.1695(<i>i</i>)	1.110(<i>i</i>)	0.28	−1.41
Ge	0.744(<i>i</i>)	0.664(<i>i</i>)	−0.37	5.1
α -Sn	0		−0.5 (2nd)	
GaP	2.350(<i>i</i>)	2.272(<i>i</i>)	−0.37	10.5
GaAs	1.519(<i>d</i>)	1.411(<i>d</i>)	−0.39	11.3
GaSb	0.812(<i>d</i>)	0.70(<i>d</i>)	−0.37	14.5
InP	1.4236(<i>d</i>)	1.34(<i>d</i>)	−0.29	9.1
InAs	0.418(<i>d</i>)	0.356(<i>d</i>)	−0.34	10.0
InSb	0.2352(<i>d</i>)	0.180(<i>d</i>)	−0.28	15.7
ZnS _{cub}	3.78(<i>d</i>)	3.68(<i>d</i>)	−0.47	−5.8
ZnS _{hex}	3.91(<i>d</i>)	3.8(<i>d</i>)	−0.30	
ZnSe	2.820(<i>d</i>)	2.713(<i>d</i>)	−0.45	0.7
ZnTe	2.391(<i>d</i>)	2.26(<i>d</i>)	−0.52	8.3
CdS	2.585(<i>d</i>)	2.485(<i>d</i>)	−0.41	4.5
CdSe	1.841(<i>d</i>)	1.751(<i>d</i>)	0.36	5
CdTe	1.606(<i>d</i>)	1.43(<i>d</i>)	−0.54	8

Note: For an explanation of the difference between direct and indirect band gaps, see Sect. 13.2

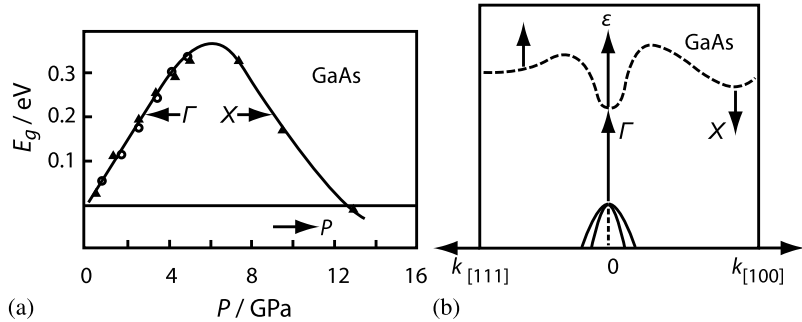


Fig. 7.25 (a) Pressure dependence of the band gap of GaAs, and (b) indicating the trend (*arrows*) of $E(\mathbf{k})$ with increasing pressure (after Edwards et al. 1959)

Pressure coefficients near 1 atm are typically on the order of 10 meV/kbar. They are listed in Table 7.8 for some semiconductors. They are usually positive for $\Gamma(000)$ and $L(111)$ valleys, and are negative for valleys along (100)—see Fig. 7.25b. A more extensive list of the temperature and pressure dependence is given in Table 7.9.

Table 7.9 Temperature and pressure dependence of the band gap

	$dE_g^{(\text{ind})}/dT$ (10^{-4} eV/K)	$dE_g^{(\text{dir})}/dT$ (10^{-4} eV/K)	$dE_g^{(\text{ind})}/dp$ (10^{-6} eV/bar)	$dE_g^{(\text{dir})}/dp$ (10^{-6} eV/bar)
Si	$E_g^{(\text{ind})} = 1.17 + 1.059 \cdot 10^{-5} T$ $- 6.05 \cdot 10^{-1} T^2$ (eV)			-1.41
Ge			-5.1	+15.3
AlAs	-3.6	-5.1	2.8	10.2
AlSb	-5.3	-3.5		
GaP	$E_g^{(\text{ind})} = 2.338 - 6.2 \cdot 10^{-4} \frac{T^2}{T-460}$ $E_g^{(\text{dir})} = 2.895$ $- 0.1081[\coth(\frac{164}{T}) - 1]$		$E_g^{(\text{ind})} = 2.14 - 0.24 p$ $- 0.048 p^2$ (p in kbar) $E_g^{(\text{dir})} = 2.76 + 0.97 p$ $- 0.35 p^2$ (p in kbar)	
GaAs	$E_g^{(\text{dir})} = 1.519 - 5.408 \cdot 10^{-4} \frac{T^2}{T+204}$		$E_g^{(\text{dir})} = 1.45 + 0.0126 p$ $- 3.77 \cdot 10^{-5} p^2$ (p in kbar)	
GaSb	-3.5 $E_g^{(\text{ind})}{}_{(L)} = 2.035 - 0.019 \frac{T^2}{94+T}$		-8.8	14
InP	-3			8.0
InAs				-11.4
InSb	$E_g^{(\text{dir})} = 0.236 - 0.06 \frac{T^2}{500+T}$			15

7.2.4 Band Gap Narrowing with Heavy Doping

The band gap in heavily doped semiconductors is substantially reduced. There are many reasons for the reduction of the band gap, summarized in an extensive review by Abram et al. (1978); see also Mahan (1980) and van Overstraeten (1982). The more important phenomena which influence the band gap at high doping densities ($N_d > 10^{17} \text{ cm}^{-3}$) are given below:

(a) The exchange energy of electrons due to their fermion nature. It tends to keep the electrons with parallel spin away from each other, but is attractive to electrons with opposite spin, resulting in a net attractive term. As a consequence, one obtains a lowering of the conduction band edge δE_{cex} relative to the Fermi level in equilibrium and at $T = 0$:

$$\delta E_{\text{cex}} = -\frac{e^2}{\pi \epsilon \epsilon_0} \Lambda_{\delta} k_F \simeq B_{\delta e} \left(\frac{N_d (\text{cm}^{-3})}{10^{18}} \right)^{\frac{1}{3}} \text{ (meV);} \quad (7.40)$$

the wave number at the Fermi-surface is given by

$$k_F = \left(\frac{3\pi^2 N_d}{v_D} \right)^{\frac{1}{3}} \quad (7.41)$$

assuming total ionization of uncompensated donors of density N_d and v_D the degeneracy factor of the band; A_δ and $B_{\delta x}$ are numerical factors listed in Table 7.11 (Mahan 1980).

(b) The attractive interaction between free electrons and charged donors, causing another reduction in the conduction band edge:

$$\delta E_{\text{ced}} = -\frac{e^2}{8\epsilon\epsilon_0\lambda_{\text{TF}}} \simeq C_{\delta e} \left(\frac{N_d \text{ (cm}^{-3}\text{)}}{10^{18}} \right)^{\frac{1}{6}} \text{ (meV)}, \quad (7.42)$$

with the Thomas Fermi screening length

$$\lambda_{\text{TF}} = \pi^{\frac{2}{3}} \sqrt{\frac{\epsilon_{\text{st}}\epsilon_0\hbar^2}{m_n e^2 (3N_d)^{\frac{1}{3}}}} \quad (7.43)$$

which is responsible for screening at sufficient doping density—see Landsberg et al. (1985).

(c) The exchange energy for holes, causing a relative increase of the valence band edge by

$$\delta E_{\text{vhx}} = \frac{m_p e^4 \sqrt{\omega_p}}{\pi (\epsilon\epsilon_0)^2 \hbar} J \simeq D_{\delta p} \left(\frac{N_d \text{ (cm}^{-3}\text{)}}{10^{18}} \right)^{\frac{1}{4}} \text{ (meV)}, \quad (7.44)$$

with ω_p as the *plasma frequency* and J as an integral (Mahan 1980) of nearly constant value ($J \cong 0.8$).

(d) The interaction between holes and donors is repulsive, and thus causes a relative lowering of the valence band edge by:

$$\delta E_{\text{vhd}} = -0.48 \frac{e^2}{\epsilon\epsilon_0} N_d^{\frac{1}{3}} \simeq E_{\delta p} \left(\frac{N_d \text{ (cm}^{-3}\text{)}}{10^{18}} \right)^{\frac{1}{3}} \text{ (meV)}. \quad (7.45)$$

The total change of the band gap is obtained as the sum of all of these contributions:

$$\Delta E_g = \delta E_{\text{cex}} + \delta E_{\text{ced}} + \delta E_{\text{vhx}} + \delta E_{\text{vhd}} = \Delta E_c + \Delta E_v. \quad (7.46)$$

The influence of the first two contributions on the conduction band is shown in Fig. 7.26a for Si. The total reduction of the band gap as a function of the doping density is shown for Si in Fig. 7.26b.

Pantelides et al. (1985) estimated that multi-valley interaction and density. Fluctuation cause a further reduction in the electrically obtained band gap, which is on the order of 50 meV at $N_d \cong 10^{20} \text{ cm}^{-3}$ in GaAs. This agrees with the optically determined band gap reduction via absorption, luminescence, or photoluminescence spectroscopy (Wagner 1984). See also Berggren and Sernelius (1984).

Simple empirical relations to approximate the change in band gaps with doping are given for three semiconductors in Table 7.10.

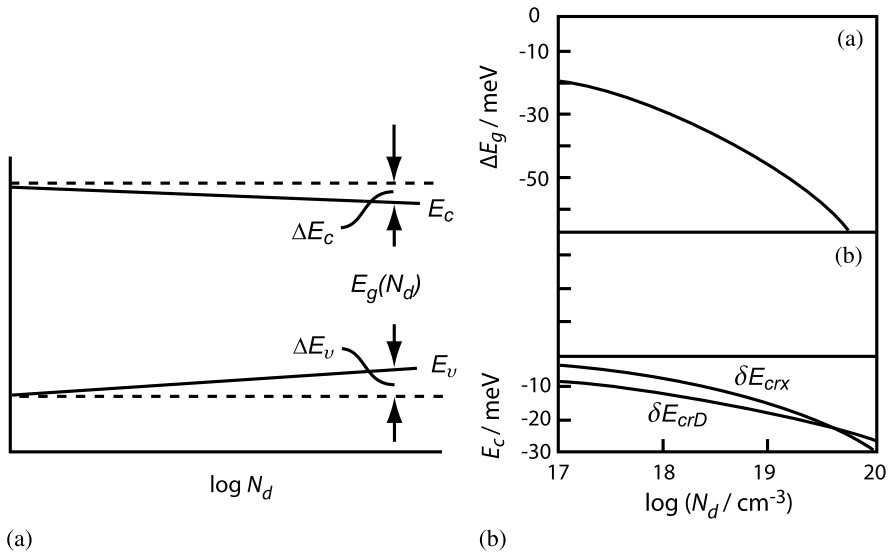


Fig. 7.26 (a) Change of the band gap with increasing donor density (schematically). (b) above) Relative lowering of the conduction band edge. (b) bottom) Band gap narrowing as a function of the density of shallow donors in Si (after Mahan 1980)

Table 7.10 Doping-dependent band gap

Material	
Si	$E_g = 1.206 - 0.0404 \ln(N_d \text{ (cm}^{-3}\text{)}) / 7.5 \cdot 10^{16}$
GaAs	$E_g = 1.45 - 1.6 \cdot 10^{-8} \sqrt[3]{n \text{ (cm}^{-3}\text{)}}$
InP	$E_g = 1.344 - 2.25 \cdot 10^{-8} \sqrt[3]{n \text{ (cm}^{-3}\text{)}}$

7.2.5 Shift of the Fermi Level into the Band at High Doping Densities

When the doping density N_d exceeds the effective level density N_c at the lower edge of the conduction band, the Fermi level moves from the band gap into the conduction band. This results in an “effective widening” of an optical gap, since, for example, optical excitation from the valence band can only proceed to empty states above the Fermi level. The shift is given for parabolic bands, using for the density of states in these bands and $n \cong N_d$:

$$\delta E_{eF} = \frac{\hbar^2}{2m_{\text{dsn}}} \left(\frac{3\pi^2 N_d}{v_D} \right)^{\frac{2}{3}} \simeq A_{\delta F} \left(\frac{N_d \text{ (cm}^{-3}\text{)}}{10^{18}} \right)^{\frac{2}{3}} \text{ (meV)}, \quad (7.47)$$

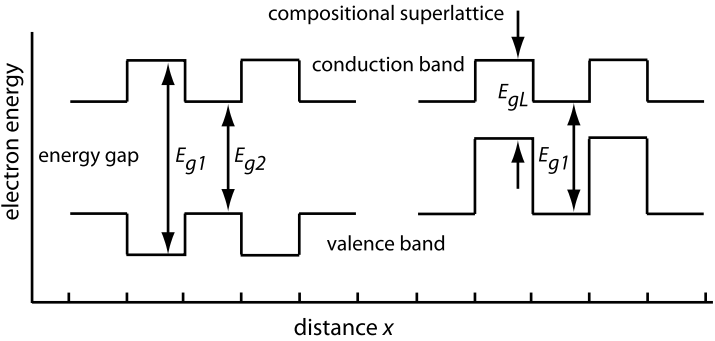


Fig. 7.27 Periodic potential for (a) a superlattice of type I and (b) a superlattice of type II

Table 7.11 Parameters for band gap narrowing (Mahan 1980)

Crystal	v_D	A_δ	Electrons			Holes	
			$A_{\delta F}$	$B_{\delta e}$	$C_{\delta e}$	$D_{\delta p}$	$E_{\delta p}$
Si	6	0.95	3.3	−6.5	−12.1	−13.1	6.1
Ge	4	0.84	6.6	−4.9	−6.0	−8.2	4.5

where v_D is the degeneracy factor of the conduction band and m_{dsn} is the density of state mass for electrons. This equation is valid when all donors are ionized and uncompensated. A similar expression can be obtained for high doping with acceptors, replacing m_{dsn} with the density of state mass for holes m_{dsp} and v_D with the degeneracy factor for the valence bands. However, the larger effective mass of holes in the heavy hole band makes this effect less favorable. Table 7.11 lists $A_{\delta F}$ and v_D for Si and Ge. Such a shift is substantial even at moderate electron densities for semiconductors with low effective mass (e.g., InP). See the Burstein-Moss effect.

7.3 Bands in Superlattices

Permitted bands separated by band gaps occur as a consequence of the quantum-mechanical properties of electrons in a periodic potential. This remains true in superstructures. The additional periodicity in the lattice potential can be provided by alternating layers of materials with different band gaps, i.e., in *superlattices*—see Esaki and Tsu (1970). Some of the effects observed in a superlattice are already present in a single layer that provides a two-dimensional quantum *well confinement* of the electronic eigenfunctions—see for a comprehensive review on single- and multilayer structures, Ando et al. (1982).

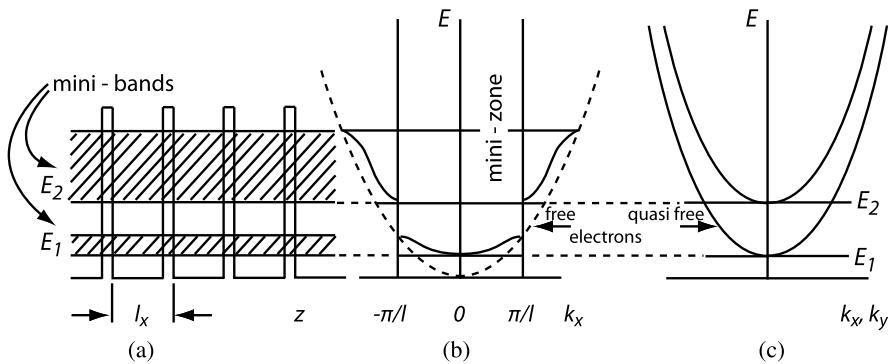


Fig. 7.28 (a) Mini-bands and (b) mini-zones in the k -direction for a superlattice. Carriers are confined in the z -direction in the lower mini-bands. There is no confinement in the x - and y -directions. In the k_x - and k_y -directions, the ordinary band picture applies, but with the band minimum lifted to the respective mini-band minimum, shown in subfigure (c)

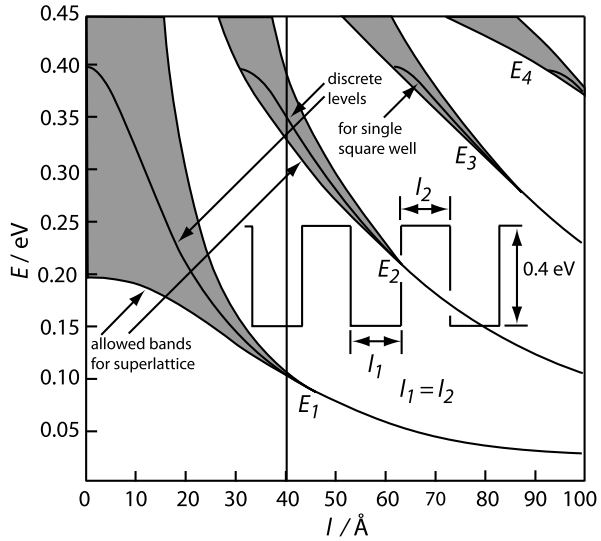
7.3.1 Mini-bands

When a semiconductor with a larger band gap is interspaced with another one of a smaller gap, the former acts as a barrier for electrons in the conduction band of the latter. To obtain the actual barrier height, it is important to know the valence band edge offset (Kroemer 1983), which is influenced by the substrate material and the deposition sequence. The periodic alternation of such layers produces a potential (Fig. 7.27) of the same form as the previously discussed Kronig-Penney potential¹² (Sect. 6.2). The resulting eigenvalue spectrum is similar to the spectrum of free electrons exposed to the periodic potential of a crystal, except that now the periodic potential is imposed on *Bloch electrons* with an effective mass m_n , and the potential has a lower amplitude and a larger period length than the periodic potential in a bulk lattice.

Consequently, within the conduction band, one observes a subband structure of *mini-bands* located within the valleys of this band; the higher mini-bands extend beyond the height of the potential barriers. The lower mini-bands are separated by *mini-band gaps* (Fig. 7.28) in the direction of the superlattice periodicity l_x . Within the plane of the superlattice layers (x, y), however, the electron eigenfunction experiences only the regular lattice periodicity. Therefore, the dispersion relations $E(k_z)$ and $E(k_y)$ are much like those for the unperturbed lattice except for the mixing with the states in the z -direction; this results in lifting the lowest energy (at $k = 0$) of the

¹²The alternating potential shown in Fig. 7.2a is of type I, i.e., a minimum of $E_c(x)$ coincides with a maximum of $E_v(X)$. Both minima and maxima coincide in a type-I superlattice (Fig. 7.27b). An example for type II is the $\text{Ga}_\zeta\text{In}_{1-\zeta}\text{As}$ and $\text{GaAs}_\zeta\text{Sb}_{1-\zeta}$ superlattice. For values of ζ and η below 0.25, the valence band of the former extends above the conduction band of the latter, resulting in quasimetallic behavior. For a review of type-II superlattices, see Voos and Esaki (1981).

Fig. 7.29 Computed mini-bands for a symmetrical superlattice (after Esaki 1985)



$E(k)$ parabola above E_c of the bulk well material (Fig. 7.28b and c). The second mini-band results in a second, shifted parabola, etc.

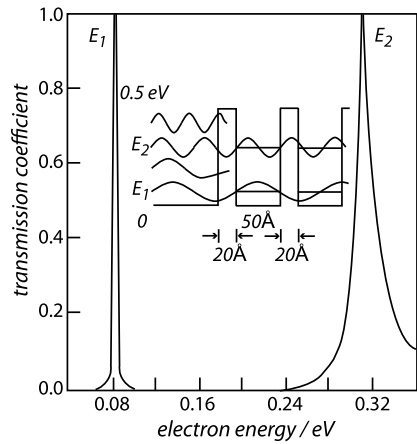
The mini-band structure is a direct band gap structure, independent of whether the host (well) material has a direct or indirect band gap. It permits optical transitions from the valence band, which has a similar mini-band structure, to the lowest conduction mini-band state at $k = 0$ (Fig. 7.31b).

Variations of the period length, barrier width, and barrier height change the width of the allowed mini-bands and the interfacing mini-gaps. Using the Kronig-Penney model, these are determined by Eq. (6.12); however, m_0 , contained in a and β [see Eq. (6.11)], is replaced by m_n and the lattice parameters a_1 and a_2 are replaced by the superlattice well and barrier widths t_1 and t_2 . This yields an implicit equation for the band edges (i.e., for $\cos(ka) = 1$ in Eq. (6.12)):

$$\frac{\alpha^2 - \beta^2}{2\alpha\beta} = ctg(\alpha l_1)ctgh(\beta l_2). \quad (7.48)$$

The resulting mini-band structure and $E(\mathbf{k})$ dispersion relation shown in Fig. 7.28b is very similar to the band structure shown in Figs. 6.3 and 6.11 for the periodic crystal potential, except that the edge of the Brillouin zone in the k_z -direction (*mini-zone*) lies at $\pm\pi/l$ with $l = l_1 + l_2$. Typically, l is on the order of $5 \dots 50$ lattice constants; thus the mini-zone is only a small fraction ($1/5 \dots 1/50$) of the Brillouin zone of the host lattice. In contrast, the Brillouin zone in the k_x - and k_y -directions extends to the full width $\pm\pi/a$ and $\pm\pi/b$. There are no mini-gaps in the x - and y -directions. Figure 7.29 shows the computed widths of mini-bands and intermittent gaps as a function of the period length ($2l$) for a symmetrical well/barrier structure with a barrier height of 0.4 eV. For $l_1 = l_2 = 40$ Å, the lowest band is rather narrow and lies at 100 mV above the well bottom. The second band extends from 320 to 80 mV. Higher bands ($E_3, E_4 \dots$) overlap above the top of the barrier.

Fig. 7.30 Electron eigenstates in a quantum well and relative transmission coefficients for a double barrier of 0.5 eV height and 20 Å width. Well width $l_1 = 50$ Å (after Esaki 1986)



Increasing the thickness or the height of the barrier layer reduces the tunneling through the barriers. The electronic eigenfunctions within each separated well can be estimated easily [see Sect. 6.1.1, Eq. (6.5)], yielding a level rather than mini-band spectrum with

$$E_n = \frac{\hbar^2 \pi^2}{2m_n l_1^2} n_q \quad \text{with } n_q = 1, 2, \dots \quad (7.49)$$

The quantum number gives the number of electron half-wavelengths in the confined state (Fig. 7.30). The dependence of the energy of these states on the quantum well thickness ($E_n \propto 1/l_1^2$) can easily be verified from optical absorption and gives a beautiful confirmation of the quantum-mechanical model. The width of these levels is lifetime broadened and can be estimated from the uncertainty relation

$$\Delta E_n \Delta t \simeq \frac{\Delta E_n l_1}{v_{\text{rms}}} \mathcal{T}_e \simeq \hbar, \quad (7.50)$$

with the tunneling probability $\mathcal{T}_e$ through such barriers given by

$$\mathcal{T}_e \simeq 16 \exp \left\{ -\sqrt{\frac{8m_n}{\hbar}} (\Delta E_c - E_n) l_2 \right\}, \quad (7.51)$$

where ΔE_c is the barrier height and E_n is the energy of the level from which tunneling takes place.

A more sophisticated approach in dealing with superlattices of various dimensions resorts to a quantum-mechanical description of the periodic superlattice as given, for example, by Schulman and McGill (1981); also see review by Bastard and Brum (1986).

The $E(\mathbf{k})$ behavior in the mini-bands of the *valence band* is a bit more complicated, since we must distinguish between light and heavy holes which result in two sets of mini-bands. Considering excited states in the valence band, we observe a

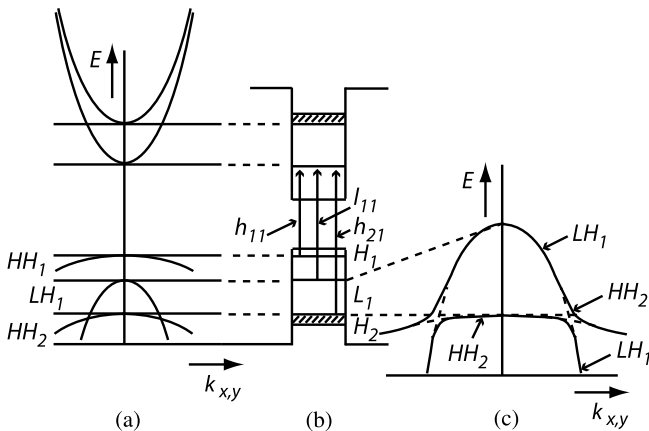


Fig. 7.31 (a) Dispersion relation for electron and hole mini-bands; (b) optical excitation transition into the ground state of the conduction band; (c) light and heavy hole dispersion relation at enlarged scale

crossing of states between heavy and light hole bands, as shown in Fig. 7.31. This results in a mixing between these states (Collins et al. 1987). As shown on an enlarged scale in Fig. 7.31c, this indicates that the dispersion curves cannot cross, and that the interaction (mixing) that takes place near the points of *intended* crossing results in a splitting, making the top of the upper band light-hole-like, and its bottom part heavy-hole-like, and vice versa for the lower band. Such mixing can be observed directly by applying an electric field or uniaxial stress that changes the energy of such states.

Superlattices that show such a beautiful illustration of quantum mechanical behavior have been fabricated from a number of semiconductor pairs that have little lattice mismatch. The best researched is the GaAs/Ga_xAl_{1-x}As couple. The height of the barrier can be changed by varying the concentration of Al in Ga_xAl_{1-x}As; typically, it is a few tenths of an eV (Cho 1971; Woodall 1972; Chang et al. 1973). Minibands are observed at the predicted energy ranges.

7.3.2 Bands in Ultrathin Superlattices

As the width of the layers in superlattices become thinner and thinner, the superlattice structure finally disappears and is replaced by the electronic structure of a single

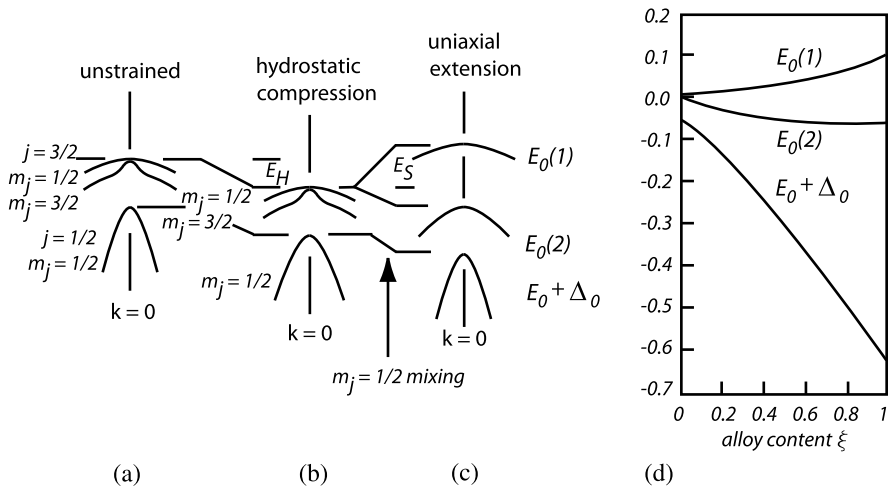


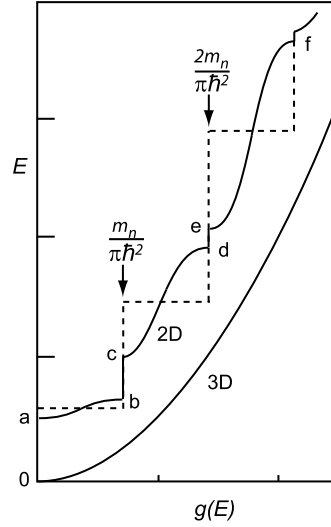
Fig. 7.32 Valence bands of a $\text{Ge}_x\text{Si}_{1-x}$ alloy. (a) Unstrained; (b) with hydrostatic compression; and (c) with uniaxial extension as in a strained superlattice which removes the degeneracy of the $J = 3/2m_1 = 1/2$ and $m_j = 3/2$ bands at $k = 0$. (d) Magnitude of the splitting and shift of the three valence bands (alloy deposited on Si) as function of the alloy composition at $T = 300$ K (after Pearsall et al. 1986)

compound. A distinction between a true superlattice and a bulk semiconductor can be made when all band gaps between mini-bands disappear and the density of states increases monotonically from the band edge into the band.

For instance, stacking single layers of GaAs and AlAs in the [100] direction results in a $(\text{GaAs})_1-(\text{AlAs})_2$ structure identical to bulk GaAlAs_2 . Consequently, the band structure must be the same. Extending this discussion to the symmetrical $(\text{GaAs})_n-(\text{AlAs})_n$ superlattices, Batra et al. (1987) have shown that for $n \geq 3$ the band alignment of the valence band becomes staggered with hole confinement in GaAs. However, electrons are confined in AlAs for $3 < n < 10$; only for $n > 10$ are electrons also confined in GaAs, as is expected for thicker superlattices with near-bulk gap properties for each layer—see also Kamimura and Nakayama (1987). For Si_nGe_m ultrathin superlattices—see Pearsall et al. (1987) and Froyen et al. (1987a).

An interesting strained-layer superlattice is composed of Si and $\text{Si}_\zeta\text{Ge}_{1-\zeta}$ layers (Abstreiter et al. 1985; People 1986). A thin strained layer of a $\text{Si}_\zeta\text{Ge}_{1-\zeta}$ alloy on top of Si shows a substantial splitting of the valence bands, as indicated schematically in Fig. 7.32 and a reduction of the band gap, which could not be obtained otherwise. For estimates of the Ge_nSi_m superlattices, see Froyen et al. (1987a). It is shown that in such a strained layer superlattice the direct band gap (at Γ) is lowered and can approach the indirect gap, making it in essence a new direct band gap material.

Fig. 7.33 Density of states for electrons in a band (3D), electrons in a quantum well (*dashed stair-case*), and electrons in mini-bands of a superlattice, with mini-bands extending between a and b , c and d , and e and f (after Esaki 1985)



7.3.3 Density of States in Mini-bands

When proceeding from a level structure of an isolated well to mini-bands in a superlattice with sufficiently permeable barriers, we can follow the broadening in the density of states. It has a staircase character for the isolated well. Each level can be occupied by the number of electrons given by its degeneracy multiplied by the number of atoms in the wells. When significant tunneling becomes possible, each level splits into bands, and the staircase behavior (dashed steps) becomes somewhat softened (Fig. 7.33).

The effective density of states near the bottom of the first mini-band (for thin enough barriers, so that the mini-band width is less than several kT) is given by

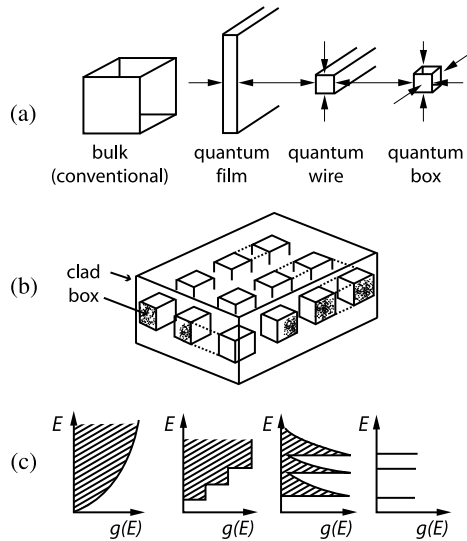
$$N_{2c} = \frac{m^* kT}{\pi \hbar^2}, \quad (7.52)$$

measured in cm^{-2} . The subscript $2c$ refers to the two-dimensionality of the structure and to a mini-conduction band. Eq. (7.52) can be derived in a similar fashion as N_c in three dimensions.

7.3.4 Two-, One-, Zero-Dimensional Quantum Well Structures

The previously described superlattices can be regarded as quantum-well layers, i.e., as an array of two-dimensional quantum wells. Alternating the deposited material in a second dimension yields *quantum wires*; alternating deposition in all three dimensions yields *quantum boxes* (Fig. 7.34a). The density of state distribution of free

Fig. 7.34 (a) Bulk and quantum well structures; (b) example of a quantum box array; (c) distribution of the density of states of quasi-free electrons as a function of the energy for bulk and quantum well structures corresponding to (a) (after Asada et al. 1986)



electrons in the mini-conduction bands becomes more confined with decreasing dimension of the quantum-well structures, as shown in Fig. 7.34c, when the barriers are high and wide enough.

7.3.5 Electronic States in Microcrystallites

The electronic structure of very small isolated crystallites, e.g., as a suspension in a liquid dielectric, may in some respects¹³ be compared with a zero-dimensional quantum-well with infinite barriers. The band gap increases from that of the bulk when the crystallite size decreases below a few hundred Å.

Electrons and holes are confined to the crystallites; therefore, the binding energy of this electron-hole pair (exciton) is increased compared to the band gap of the bulk material.

For a crystallite of radius R , the *confinement energy* becomes comparable to the gap energy for $R < 100$ Å. The energy for the lowest 1s state can be approximated as

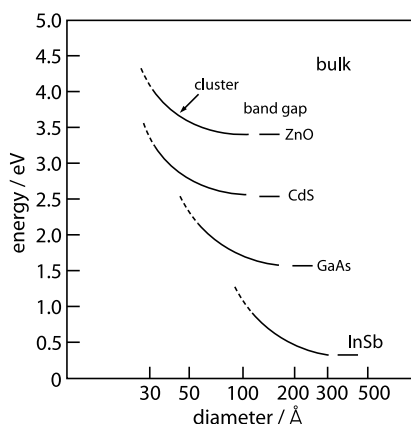
$$E_{1s} = E_g + \frac{\hbar^2}{8R^2} \left(\frac{1}{m_0} + \frac{1}{m_i} \right) - \frac{1.8e^2}{4\pi\epsilon\epsilon_0 R}, \quad (7.53)$$

where m_i is the isotropic hole mass.

The first term is the band gap (Sect. 7.2); the second term represents the ground state of a quantum well (the crystallite); the third term represents a minor Coulomb

¹³However, with an important condition missing—the periodic barrier of similar thickness and height.

Fig. 7.35 Computed dependence of the lowest electronic excited state ($1s$ ($E_8 - E_9$)) of spherical microcrystallites as a function of their radii, compared to their bulk material band gap (after Brus 1986)



correction due to the fact that screening in such a small crystallite is rather small. Figure 7.35 shows the computed energy of the lowest excited state as a function of the radius of the microcrystallite (after Brus 1986). Experimental data showing such trends in PbS are given by Wang et al. (1987).

7.4 Bands in Amorphous Semiconductors

The band structure in amorphous semiconductors cannot be determined in the same fashion as for the crystalline state since long-range periodicity is missing and k is no longer a good quantum number. Therefore, an $E(\mathbf{k})$ diagram cannot be drawn for amorphous materials. Consequently, the effective mass picture, which depends on an analysis of $E(\mathbf{k})$, cannot be used in its classical form.

Nevertheless, there is strong experimental evidence from optical absorption and reflection spectroscopy and from photoemission, that similarities exist between the band structure in amorphous and crystalline states of the same material.

This can be understood by recognizing that the major features of the electronic properties of a solid are determined by short-range order, as proposed by Joffe and Regel (1960) and shown more convincingly by Weaire and Thorpe (1971) for amorphous Si and Ge, using a tight-binding model.¹⁴

Densities of state distributions for amorphous and crystalline Ge are shown in Fig. 7.36—as obtained experimentally (a), as compared with the theoretical distribution (b). The distribution of the amorphous state is much smoother. The sharp van Hove singularities due to long-range order are absent, while several of the major features remain in both states.

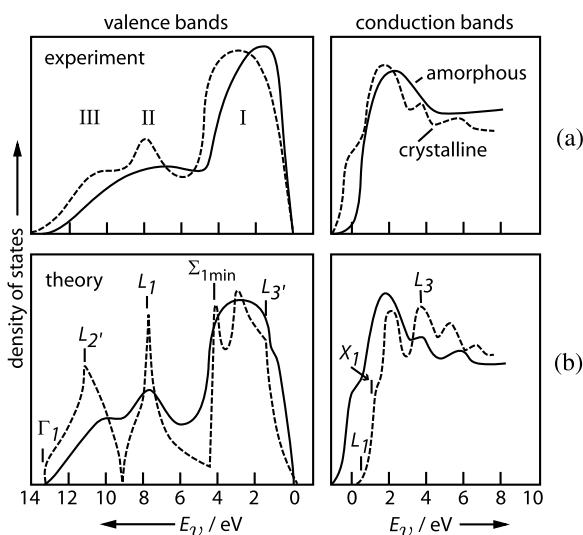
The more refined tight-binding calculation of Bullett and Kelly (1975) shows a substantially improved agreement with the experiment.

¹⁴A tight-binding model, however, provides information only about the gross properties of a semiconductor (crystalline or amorphous).

Fig. 7.36 Electron density of state distributions of amorphous and crystalline Ge.

(a) Experimental data derived from photoemission;

(b) theory (after Eastman et al. 1974)



7.5 Supercomputer

With the availability of supercomputers now a comparative analysis of a large number of compounds or possible combination of compounds now becomes practical for computing bonding and band structure elements, using similar computer approximation as for single compound analysis, the result of which was discussed in the previous chapters. This opens the potential to select advantageous material combinations for heterojunction solar cells, or even suggest such combination of compounds or alloys that have not yet be synthesized.

A review of the subject is given by Connell and Street (1980), in the book by Mott and Davis (1979), and by Robertson (1983) (see also Sect. 13.5 and Chap. 25).

The properties near the band edges are more sensitive to the actual amorphous structure. Therefore, it is no longer possible to describe the dispersion relation and the level distribution here in general terms. There seems to be a rather smooth transition between extended (band) states and localized states due to the lack of long-range order. This does not permit a cohesive discussion of the band-edge behavior similar to the discussion for crystalline semiconductors. On the other hand, the measurement of transport properties suggests the existence of an edge.

Chapter 8

Equilibrium Statistics of Semiconductors

Abstract Intrinsic semiconductors are discussed and electron distribution functions are given. Electron and hole concentration in equilibrium is elaborated. Born-Karman boundary condition is discussed; constant energy surfaces are shown. Density of states are discussed. Statistical distribution functions; Boltzmann and Fermi-Dirac distribution functions are elaborated.

Most electrons and holes in a semiconductor relate to defects in the host material: they are generated from, scattered by, or recombine through them. Almost all technically important semiconductor properties are defect-controlled. Their influence on carrier densities in equilibrium can be obtained from statistics.

Electrons and holes are the most important particles in semiconductors. Only in rare cases are they generated from the semiconductor itself, i.e., from the *host material*. By far, most of these carriers originate from *lattice defects*. In addition, the transport properties of these carriers, discussed in the following chapter, are determined almost exclusively by lattice defects, including phonons. In comparison to other fields of physics where the major effects are related to basic material properties, this is a rather unusual fact.

Nevertheless, the influences of the host material on the electronic properties are important and will be discussed first. The dominating influence of lattice defects on the density of electrons and holes will then be evaluated. In this chapter an equilibrium statistical approach is taken for a quantitative analysis of the carrier distribution as a function of temperature and doping.

8.1 The Intrinsic Semiconductor

An *intrinsic semiconductor* is a pure semiconductor with no dopants. There is negligible influence from lattice defects on its carrier density. The electronic properties of such a semiconductor are determined by the *mutual* generation or recombination of electrons and holes.

8.1.1 Electron and Hole Densities in Equilibrium

Normally, semiconductors are exposed only to thermal excitation. If they are kept long enough at a constant temperature, *thermodynamic* (short “thermal”) *equilibrium* is established. For the following discussion, it is assumed that such equilibrium is always established, no matter how long it takes to reach equilibrium. In this section we will not deal with kinetic effects.

When equilibrium is reached, the same temperature T , determining the distribution function, characterizes all subsystems, e.g., electrons, holes, and phonons (i.e., oscillating lattice atoms). The density distribution of electrons or holes in the conduction or valence band can be obtained from simple statistical arguments as the product of the level density $g(E)$ and the statistical distribution function $f(E)$:

$$n(E)dE = g(E)f(E)dE. \quad (8.1)$$

The density distribution for holes, i.e., of missing electrons, is:

$$p(E)dE = g(E)[1 - f(E)]dE. \quad (8.2)$$

Since the probability of finding an electron at energy E is proportional to $f(E) \leq 1$, with $f(E) = 1$ as the certainty, the probability of finding an electron *missing* is simply $1 - f(E)$.

8.1.2 Level Distribution Near the Band Edge

The level distribution (density of states) within a band was derived in general terms. For the purpose of carrier transport, one is interested in an explicit expression of this distribution. Such an expression can be given easily near the edge of the conduction or valence band.

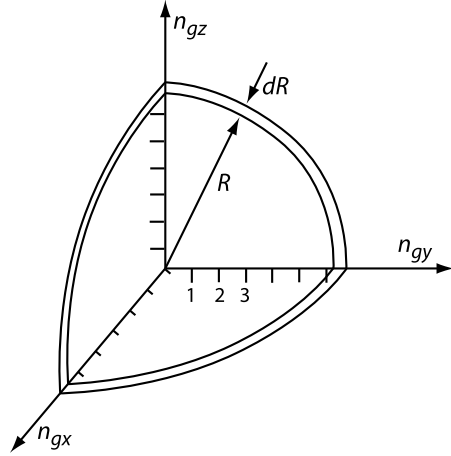
In an isotropic parabolic band, the dispersion equation of Bloch electrons is given by

$$E(k) = E_c + \frac{\hbar^2}{2m_n}k^2 + \dots \quad (8.3)$$

These electrons are confined within the semiconductor. This can be described as confinement within a “box,” for definiteness a cube of dimensions l , and requires standing wave boundary conditions with nodes at the box surface.¹ This prevents the escape of electrons from the box since no energy can be transmitted beyond a node.

¹Or cyclic boundary conditions; here energy and particle number are conserved by demanding, that with the passage of a particle out of a surface, an identical one enters from the opposite surface (Born-von Karman boundary condition). The two conditions are mathematically equivalent.

Fig. 8.1 Spheres of constant energy in quantum number space



For the three components of the wave vector, one therefore has

$$k_i = \frac{\pi}{l_i} \hat{n}_i \quad \text{with } \hat{n}_i = 0, 1, 2, \dots \quad (8.4)$$

With $i = (x, y, z)$. The wave vector and therefore the energy are represented by a set of discrete values given by the triplet of integers n_x, n_y, n_z . The requirement of finding a triple of integers is sometimes referred to as second quantization. In addition, m_s is used to identify the spin quantum state. The energy increases monotonically with these integers.

At low temperatures, the energy states are filled sequentially; each state can be occupied by a maximum of two electrons with opposite spin (*Pauli principle*).

In an n space, as shown in Fig. 8.1, one accounts for the sequential filling of these states up to a radius $R = R(n_x, n_y, n_z)$, which is determined by the number of available electrons. The number of states G within an energy range of E to $E + dE$ is obtained from the volume of the spherical shell of the octant, permitting only positive values of n_i

$$G_n^{dR} = \frac{1}{8} \frac{4\pi}{3} (R_2^3 - R_1^3) = \frac{\pi}{6} d^3 R = \frac{\pi}{2} R^2 dR. \quad (8.5)$$

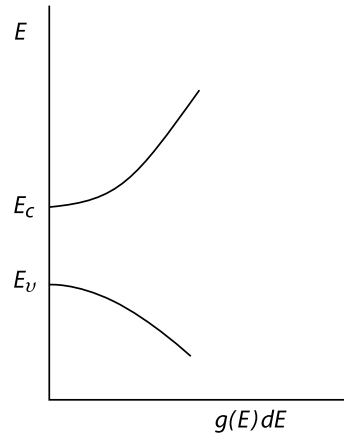
Since $R^2 = n^2$ and using Eq. (8.4), we can replace R with k and obtain the number of states in the momentum interval dk :

$$G_k^{dk} = \frac{\pi}{2} \cdot \frac{l^3}{\pi^3} k^2 dk \quad (8.6)$$

within $l^3 = V$, the volume of the semiconductor. Finally, replacing k with the energy from Eq. (8.3), we obtain

$$G_E^{dE} = \frac{\mathcal{V}}{2\tau^2} k^2 dk = \frac{\mathcal{V}}{2\pi^2} \left(\frac{2m_n}{\hbar^2} \right)^{3/2} \frac{1}{2} \sqrt{E - E_c} dE \quad (8.7)$$

Fig. 8.2 Square-root dependence of the density of states near the band edge, where the quasi-free electron or hole model can be applied



as the number of states between E and $E + dE$. Dividing by the crystal volume and permitting double occupancy, i.e., permitting for spin up and down for each state, we obtain the density of states for electrons:

$$g_n(E)dE = \frac{1}{2\pi^2} \left(\frac{2m_n}{\hbar^2} \right)^{3/2} \sqrt{E - E_c} dE. \quad (8.8)$$

This density is zero at the lower edge of the conduction band and increases proportionally to the square root of the energy near the band edge (Fig. 8.2).² A similar square-root dependence results for the density of states near the upper edge of the valence band, where a quasi-free hole picture can be applied. Replacing m_n with m_p in Eq. (8.8), and shifting the energy axis by $E_g = E_c - E_v$, yields for holes:

$$g_p(E)dE = \frac{1}{2\pi^2} \left(\frac{2m_p}{\hbar^2} \right)^{3/2} \sqrt{E_v - E} dE. \quad (8.9)$$

The result of this simple model is carried through most of the common discussions of carrier transport in solids. It is valid near both edges of the band, and is an acceptable approximation as long as the bands are parabolic in $E(\mathbf{k})$.

²Here and in several of the following figures, the energy axis is plotted vertically in order to facilitate comparison with the band model even though $g(E)dE$ is the dependent and E the independent variable.

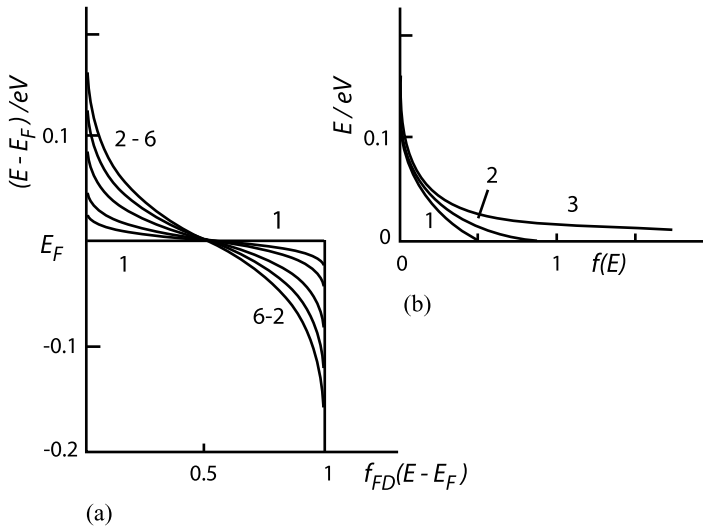


Fig. 8.3 (a) Fermi-Dirac distribution function with the temperature as family parameter 0, 50, 100, 200, 300, and 400 K for curves 1–6 respectively. (b) Comparison of Fermi-Dirac, Boltzmann, and Bose-Einstein distribution for curves 1–3 respectively, at $T = 300$ K; f_{FD} is drawn at a scale shifted by E_F

8.2 Statistical Distribution Functions

Electrons are fermions with spin $\pm$ and follow the *Fermi-Dirac distribution* function (for derivation, see any classic text, e.g., McKelvey 1966)

$$f_{FD}(E) = \frac{1}{\exp\left(\frac{E-E_F}{kT}\right) + 1}, \quad (8.10)$$

which is shown for a family of curves in Fig. 8.3 with the temperature as family parameter. This distribution function has a box-like behavior, occasionally referred to as the “Fermi iceblock,” for $T = 0$ with complete filling ($f_{FD} = 1$) of all levels for $E < E_F$, and complete depletion ($f_{FD} = 0$) for $E > E_F$. Here E_F is the *Fermi energy*. For $T > 0$, the degree of filling decreases exponentially with increasing E , and reaches 50 % at the Fermi energy: the corners of the box are rounded off- “the ice-block melts.” E_F is defined by $f_{FD}(E_F) = 0.5$.

For the evaluation of the Fermi-Dirac distribution at energy (several kT) above the Fermi energy, the distribution can be approximated by a *shifted Boltzmann distribution*

$$f_B(E) = \exp\left(-\frac{E - E_F}{kT}\right). \quad (8.11)$$

The degree of deviation from the Fermi-Dirac distribution is indicated in Fig. 8.3b.

Chapter 9

Shallow Level Centers

Abstract The shallow level trap is calculated using the hydrogen Hamiltonian with a charge, screened by the dielectric constant and dealing with a quasi-free electron, the Bloch electron. A quantum mechanical description renders this electron as a wave packet with an envelope function defining the radius of it. For a large enough dielectric function also higher energy states can lie in the band gap. Charge density functions, ESR and ENDOR are described. The chemical identity of the defect is lost and changes in the trap depth are given by ε and m_{eff} . The anisotropy of the effective mass renders higher atomic orbitals of the defect also anisotropic. Hydrogen-like defects of indirect band gap semiconductors are described and the Rydberg energy is given. A list of the binding energy of donors in Si is tabulated. Hydrogen-like acceptors are tabulated for numerous semiconductors. Bound and resonant states are described and tabulated for different acceptors in a variety of semiconductors are tabulated. Shallow defects in Compound semiconductors as well as higher charged and overcharged defects are discussed. Metal ion interstitials are covered.

Shallow level defects are closely connected to the adjacent band and determine whether the semiconductor is *n*- or *p*-type. These centers therefore, are the main centers for determining the operation of any solar cell. They have a hydrogen-like defect level spectrum.

In the previous chapters an overview was presented of the different crystal defects. In this chapter the *defect level spectrum* of shallow center is discussed. These centers have eigenfunctions that extend beyond their neighbor atoms and mix only with the nearest band states. The ground state is influenced by the chemistry, how it is to be considered, to what degree the quasi-hydrogen approximation can be used, and what refinements are necessary to obtain a better agreement with the experiment.

In addition, because of the charging of these centers, the band edges adjacent to the centers will be influenced. This influences the mobility of the freed electrons.

In the following chapter a more detailed description of the deep level centers is presented. In contrast, these have highly localized eigenfunctions of their ground states, mix with conduction *and* valence bands, and require a more thorough knowledge of the core potential for the calculation of their eigenvalues. These centers act

as traps or recombination centers and determine the quasi Fermi level distribution in solar cells.

9.1 Hydrogen-Like Defects

Shallow level defects can be described as hydrogen-like defects. As an example, the electronic states of a substitutional donor is discussed, such as a phosphorus atom on a lattice site in a silicon host crystal. The P atom becomes positively charged after it has given its electron to the host. This electron, now near the bottom of the conduction band, is a quasi-free *Bloch electron* with an energy

$$E(\mathbf{k}) = E_c + \frac{\hbar^2 k^2}{2m_n}. \quad (9.1)$$

Near the P_{Si} center, the electron can become localized. Its new eigenstate can be calculated by solving the Schrödinger equation

$$H\psi = E\psi \quad \text{with the Hamiltonian} \quad H = H_0 \quad (9.2)$$

where H_0 is the unperturbed Hamiltonian of the host lattice, to which the attractive Coulomb potential of the defect is added. This potential is modified by the screening action of the host, which is expressed by the static dielectric constant.

This is in contrast to a Bloch electron in an ideal lattice, which interacts only with the electronic part of the lattice and therefore involves the optical dielectric constant ϵ_{opt} . When trapped, the electron becomes localized near the defect and causes a shift of the surrounding ions according to its averaged Coulomb potential. Therefore, the static dielectric constant is used here.

The eigenfunctions to H_0 are Bloch functions. They form a complete orthonormalized set. The solutions to H can be constructed near the defect from a wave packet of Bloch functions

$$\psi = \sum_{\mathbf{n}, \mathbf{k}} c_n(\mathbf{k}) \psi_n(\mathbf{k}, \mathbf{r}) \simeq \sum_{\mathbf{k}} c_c(\mathbf{k}) \psi_c(\mathbf{k}, \mathbf{r}). \quad (9.3)$$

The summation over several bands with index n is dropped, since as shallow levels—here for a donor—their eigenfunctions are constructed primarily from eigenfunctions of the nearest band only: $\psi(\mathbf{k}, \mathbf{r})$ are the Bloch functions of *conduction band electrons*, appropriate for the description of the donor

$$\psi_c(\mathbf{k}, \mathbf{r}) = u_c(\mathbf{k}, \mathbf{r}) \exp(i\mathbf{k}\mathbf{r}). \quad (9.4)$$

As will be verified below, the eigenfunctions of such shallow level defects extend over several lattice constants, thus restricting $\mathbf{k}$ to values close to the center of the *Brillouin zone*. Since $u(\mathbf{k})$ changes only slowly with $\mathbf{k}$, we can pull $u_c(\mathbf{k} = k_0, \mathbf{r})$

a constant from the sum for $k \sim 0$, or near any of the minima of $E(k \sim \mathbf{k}_0)$, and introduce with¹

$$\psi(\mathbf{k}, \mathbf{r}) = \left\{ \sum_{\mathbf{k}} c_c(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}) \right\} u_c(\mathbf{k}_0, \mathbf{r}) = F(\mathbf{r}) \psi_i(\mathbf{k}_0, \mathbf{r}) \quad (9.5)$$

an *envelope function*

$$F(\mathbf{r}) = \sum_{\mathbf{k}} c_c(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}), \quad (9.6)$$

where $\psi_i(\mathbf{k}_0, \mathbf{r})$ is the Bloch function in the i th minimum of $E(\mathbf{k})$. The envelope function satisfies an appropriately modified Schrödinger equation for the quasi-hydrogen model

$$\left(-\frac{\hbar^2}{2m_n} \nabla^2 - \frac{e^2}{4\pi \varepsilon_{\text{st}} \varepsilon_0 r} \right) F(\mathbf{r}) = (E - E_c) F(\mathbf{r}) \quad (9.7)$$

with the energy normalized to the edge of the conduction band and with an effective mass m_n for Bloch electrons near this band edge. This Schrödinger equation is identical to that for a hydrogen atom, but for an electron of effective mass m_n in a medium of dielectric constant ε_{st} . Therefore, the solution can be transcribed directly from that of a hydrogen atom, and yield for the envelope eigenfunction of the $1s$ ground state:

$$F(\mathbf{r}) = \frac{1}{\sqrt{\pi a_{\text{qH}}^3}} \exp\left(-\frac{r}{a_{\text{qH}}}\right) \quad (9.8)$$

$$a_{\text{qH}} = \frac{4\pi \varepsilon_{\text{st}} \varepsilon_0 \hbar^2}{m_n e^2} = \frac{\varepsilon_{\text{st}} m_0}{m_n} a_0, \quad (9.9)$$

with an effective Bohr radius a_{qH} , the *quasi-hydrogen radius*, and $a_0 = 0.529 \text{ \AA}$, the Bohr radius of the hydrogen atom. This envelope function is shown as the dashed curve in Fig. 9.1. The total wave function (solid curve) shows the modulation with the rapidly oscillating Bloch function with a period length of the lattice constant a . The resulting eigenstates of the envelope function are bound states below the lowest free states in the conduction band E_c , and are given by a quasi-hydrogen energy spectrum²

¹This can easily be seen at the Γ -point for $k_0 = 0$: Here we have $\Psi(\mathbf{k} = 0, \mathbf{r}) = u(0, \mathbf{r}) \exp(i0 \cdot \mathbf{r}) = u(0, \mathbf{r})$.

²In semiconductors with several equivalent minima (Si, Ge), the wavefunction becomes a sum of contributions from each of the minima

$$\sum \alpha_j F_{jc}(\mathbf{r}) u_{jc}(\mathbf{k}_{j0}, \mathbf{r}).$$

Fig. 9.1 Relationship between the envelope function $F(\mathbf{r})$ and the wave function $\psi_n(\mathbf{r})$ of a Bloch wave packet for an electron localized near a hydrogen-like impurity. Here, a denotes the lattice constant

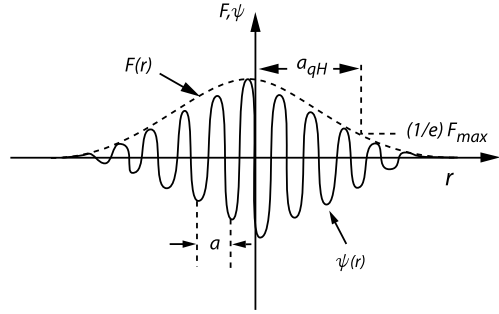
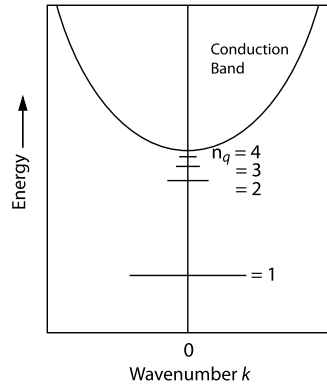


Fig. 9.2 Ground and excited states of the donor level in the $E(\mathbf{k})$ diagram, indicating the extent of these levels in k -space. The ground state has the smallest radius; hence, its extension in k -space is the largest, which yields for the ground state [compare with Eq. (9.8)]



$$E_{qH}^{(n)} = E_c - \frac{m_n e^4}{32\pi^2 (\epsilon_{st}\epsilon_0)^2 \hbar^2} \left(\frac{1}{n_q} \right)^2. \quad (9.10)$$

The dispersion behavior in k -space can be obtained from the Fourier transform of the envelope function:

$$F(\mathbf{r}) = \int F(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r} \quad (9.11)$$

$$F(k) = \frac{8\sqrt{\pi}}{a_{qH}^{5/2}} \frac{1}{[k^2 + (\frac{1}{a_{qH}})^2]^2} \quad (9.12)$$

and indicates that the wave packet extends in k -space approximately to $k \cong 1/a_{qH}$. That is, $c(k)$ [see Eq. (9.6)] is nearly constant for k up to $1/a_{qH}$ and decreases rapidly ($\propto 1/k^4$) for $k > 1/a_{qH}$. For higher excited states, the extent in k shrinks proportionally to $1/n_q^2$ as a_{qH} increases n_q^2 see Fig 9.2.

9.2 Charge Density Distribution, ESR, and ENDOR

The envelope function yields the charge distribution of such a shallow defect

$$\rho(\mathbf{r}) = \frac{1}{V} \int F^*(\mathbf{r}) F(\mathbf{r}) d^3\mathbf{r}. \quad (9.13)$$

A direct means to check such charge distribution is by analyzing the electron nuclear double resonance (ENDOR) signal with the assistance of an electron spin resonance (ESR) line width analysis (see Fehrer 1959).

The ENDOR technique is based on changes of the ESR signal caused by the spin-flip of appropriate nuclei (e.g., Si^{29}) within the reach of the electron cloud of the defect and induced by an external electromagnetic field. This *hyperfine interaction* and related super hyperfine interactions are well-known tools for analyzing the actual lattice environment of a localized deep center when the lines are resolved. The latter can also be used for analyzing the charge distribution of shallow centers where such lines can no longer be separated. Here, they are inhomogeneously broadened by various distances and densities of the active nuclei within the extended electron cloud of the shallow defect center. The analysis of the line shape of the observed resonances, and of certain bleaching dips while saturating specific spin-flip resonances, although involved, permits us to obtain the envelope function within the actual lattice.

For instance, for a hydrogen-like donor in Si, it confirms an anisotropic³ envelope function, which for the donor electron within the satellite valley (Kohn 1957), is given by:

$$F^{(x)}(\mathbf{r}_l) = F(\mathbf{r}_l)_{\text{isotr}} \sqrt{\frac{a^*3}{a^2b}} \frac{\exp[-(\frac{x_l^2}{(nb)^2} + \frac{y_l^2+z_l^2}{(na)^2})]}{\exp(-\frac{r_l}{na^*})} \quad (9.14)$$

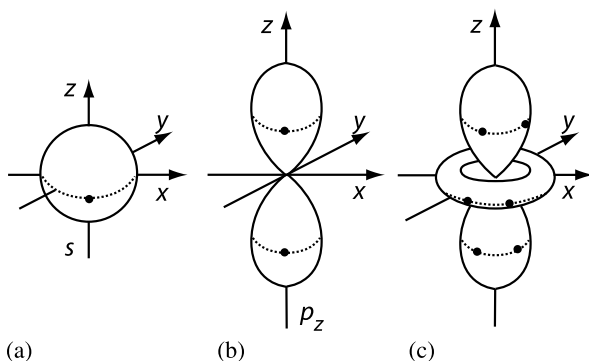
with $a = 25 \text{ \AA}$, $b = 14.2 \text{ \AA}$, $a^* = 21 \text{ \AA}$, $n = \sqrt{0.029/E_i}$, and $E_i = E_c - E_d$ as the ground state ionization energy. The r -axis is aligned with the direction of $\mathbf{k}$. Similar expressions are given for $F^{(y)}$ and $F^{(z)}$.

9.3 The Chemical Identity

In the simple hydrogen-like approximation, the chemical identity of the donor is totally lost. The identity of the host is provided by ε_{st} and m_n .

³ n_q is the *principal quantum number*, describing the entire energy spectrum for a simple hydrogen atom. All other states are degenerate. Therefore, in a pure Coulomb potential, this quantum number is the only one that determines the energy of a hydrogen level. When deviations from this spherical potential appear in a crystal, the $D = \sum l(l+1) = n_q^2$ degeneracy of each of these levels is removed, and the energy of the s -, p -, d -states are shifted according to $R_H/(n_q+l)^2$. To further lift the remaining degeneracies of the magnetic quantum number, a magnetic field must act.

Fig. 9.3 Shape of the eigenfunction of atomic orbitals s -, p -, and d -type for subfigures (a), (b), and (c), respectively



In contrast to this theory, the ground state is observed to depend significantly on the chemical identity of the donor, such as the different elements of group V impurities (P, As, Sb, or Bi) or monovalent metal interstitials such as Li. The approximation used before is too coarse to show such dependency. In the following section a number of refinements will be discussed, which will address the complexity of the ground state.

It is remarkable, however, that *excited states* (p -states) of these shallow donors lose their chemical identity and are rather well explained by the simple theory given above, provided the correct effective mass and dielectric constant are used, as will be explained in Sect. 9.1.

There are several reasons why an improved agreement is obtained for higher states:

- (a) higher s -states extend to much larger diameters⁴ ($\propto n_q^2$); and
- (b) p -states show a node of the wavefunction near the core (see Fig. 9.3), making the wavefunction less sensitive to the actual potential near the core region.

One needs extremely pure crystals, however, to avoid significant overlap of higher-state eigenfunctions with wave functions of other impurities which would cause a perturbation of these excited states. The eigenfunctions of excited states of such shallow impurities often extend beyond 1000 Å or more, interacting with each other when the distance between them is less than 1000 Å, equivalent to a density of $(1/1000 \text{ Å})^3 \cong 10^{15} \text{ cm}^{-3}$. This requires ultrapure crystals and controlled doping in the <100 ppb range. In addition, native defects, which are usually frozen-in at densities much in excess of 1 ppm interfere by influencing the surrounding lattice.

Finally, line and surface defects, which produce internal stresses and electric fields, interfere by perturbing the electronic eigenvalues of defect states. Careful preparation of near perfect crystals is therefore essential to yield unambiguous results.

Very sharp lines of many higher excited states are indeed measured in ultrapure silicon and germanium.

⁴The anisotropy is observed because of the satellite band ellipsoid resulting in an anisotropy of the effective masses with m_t and m_l in the main axis.

9.4 Hydrogen-Like Donors in Indirect Band-Gap Semiconductors

Most free electrons in indirect semiconductors are in one of the side valleys rather than at $k = 0$. The energy of such electrons is given

$$E(\mathbf{k}) = E_c^{(i)} + \frac{\hbar^2}{2} \left\{ \frac{k_x^2 + k_y^2}{m_l} + \frac{k_z^2}{m_t} \right\} \quad (9.15)$$

where m_l and m_t are the longitudinal and transverse effective masses due to the ellipsoidal shape of these valleys. The effective mass Schrödinger equation for the envelope function in one of these valleys, here in the z -direction, is

$$\begin{aligned} & -\frac{\hbar^2}{2} \left\{ \frac{1}{m_t} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{1}{m_l} \frac{\partial^2}{\partial z^2} \right\} F^z(\mathbf{r}) - \frac{\varepsilon^2}{\varepsilon_{st}\varepsilon_0 r} F^z(\mathbf{r}) \\ & = (E - E_c) F^z(\mathbf{r}). \end{aligned} \quad (9.16)$$

In addition, in non-cubic semiconductors the dielectric constant is anisotropic (*anisotropic shielding*). The corresponding Schrödinger equation for the envelope function is given by

$$\begin{aligned} & -\frac{\hbar^2}{2} \left\{ \frac{1}{m_t} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{1}{m_l} \frac{\partial^2}{\partial z^2} \right\} F_j(\mathbf{r}) \\ & - \frac{e^2}{\sqrt{\varepsilon_{\perp}\varepsilon_{\parallel}} \sqrt{x^2 + y^2 + \frac{\varepsilon_{\perp}}{\varepsilon_{\parallel}} z^2}} F_j(\mathbf{r}) = (E - E_c) F_j(\mathbf{r}), \end{aligned} \quad (9.17)$$

with $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ denoting directions parallel or perpendicular to the z direction, and aligned with the crystallographic c -direction. It shows substantial anisotropy of the envelope function in its $1s$ state as an ellipsoid rather than a sphere—see Eq. (9.14). The nomenclature $1s$, $2s$, etc., is usually retained for these states, to which the eigenfunctions would converge in the limit of vanishing anisotropy.

Quasi Bohr radius and effective Rydberg energy are defined by using m_t and rather than m_n and ε_{st} .

The degree of changes of various excited states as a function of the degree of side-valley anisotropy⁵ can be seen from Fig. 9.4. The values of for Ge and Si are marked by dots in the figure. Higher anisotropy compresses the eigenfunctions in one direction and thereby increases the binding energy as the electron is forced closer to the nucleus ($m_t > m_n$; $\varepsilon_0 > \varepsilon_{st}$).

⁵For instance, when $a_{qH} \sim 50 \text{ \AA}$ for the $1s$ state, it is $200 \text{ \AA}$ for the $2s$ and $450 \text{ \AA}$ for the $3s$ states, making the hydrogenic effective mass approximation a much improved approximation. In addition, in semiconductors where e/m is already very large, e.g., in GaAs with $\varepsilon_{st}m_0/m_n = 192.5$, resulting in $a_{qH} = 101.9 \text{ \AA}$. *18a*, this approximation is quite good for the $1s$ state. In GaAs, it results in $E_{qH} = 5.83 \text{ meV}$, while the experimental values vary from 5.81 to 6.1 mV for GaAs:Si and GaAs:Ge. For more comparisons between theory and experiment, see Bassani et al. (1974).

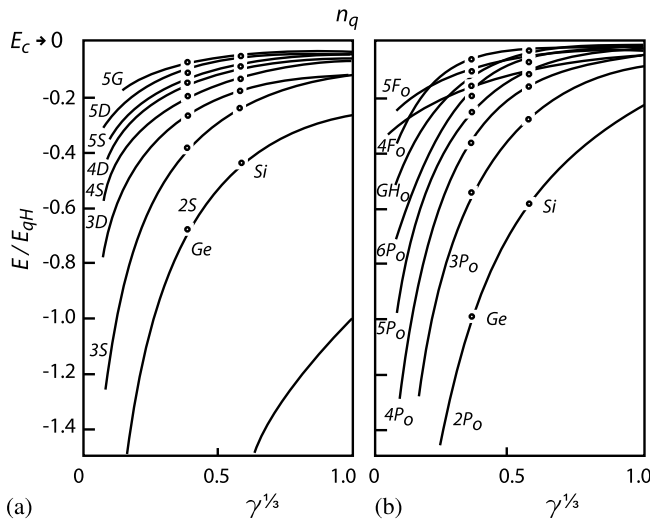
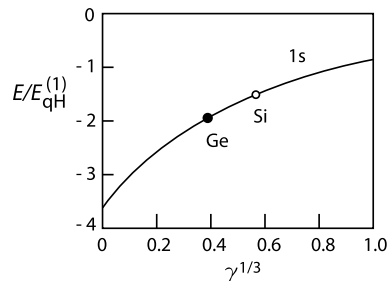


Fig. 9.4 Energy levels of donor states calculated with hydrogenic effective mass approximation as a function of the anisotropy parameter [Eq. (9.18)] for (a) *s*-like and (b) *p*-like states. The limits $\gamma = 1.0$ and $\gamma = 0$, indicate isotropic and two-dimensional semiconductors, respectively. The dots show the levels for Ge and Si (after Faulkner 1969)

Fig. 9.5 Ground-state energy (normalized to the 1s state energy of the quasi-hydrogen donor in an isotropic crystal) as a function of the anisotropy factor (after Luttinger and Kohn 1955)



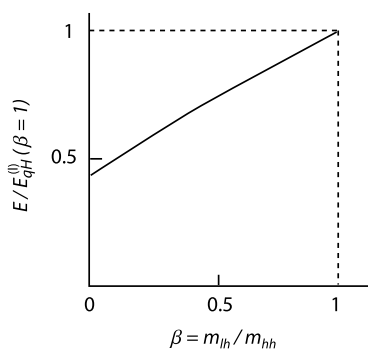
Changes of the eigenstates can be significant as a function of the anisotropy parameter (up to a factor of 4 for the ground-state energy—see Shinada and Sugano, 1966, as shown for the ground state in Fig. 9.5, Pollmann 1976).

The ground-state energies, although improved, do not yet agree with the experiment. Excited states, however, show rather impressive agreement, all experimental values are shifted so, that the $2p_0$ level agrees with the theory. This figure also includes an alkali interstitial and a group VI element. The S^* -defect yields an energy four times higher because of the double charge of the center. This example shows that the agreement goes beyond the original quasi-hydrogen list of shallow donors in group IV semiconductors. Measurements summarized by Grimmeiss (1986) extend this list even further when crystals are carefully prepared to avoid built-in (electric and stress) fields.

For donors, the *chemical shift* of the ground state is largest in Si, namely 111 meV between B and In. The shift is much less severe in semiconductors with smaller

Table 9.1 Binding energy of donors in Si (meV) (after Pantelides 1975)

Semiconductor	State						
	1s	2p ⁰	2s	2p [±]	3p ⁰	3s	3p [±]
Si (theor.)	31.27	11.51	8.82	6.40	5.48	4.75	3.12
Si (P)	45.5; 33.9; 32.6	11.45		6.39	5.46		3.12
Si (As)	53.7; 32.6; 31.2	11.49		6.37	5.51		3.12

Fig. 9.6 Energy of the acceptor ground state as a function of the effective mass ratio between light and heavy holes (after Gel'mont and D'yakonov 1971)

effective mass and larger dielectric constant. In Ge this shift is smaller by a factor of ~ 100 (Luttinger and Kohn 1955; Faulkner 1969; also, see review by Baldereschi and Lipari 1973; Bassani et al. 1974).

9.5 Hydrogen-Like Acceptors

In principle, the hydrogenic effective mass theory for a shallow acceptor is much like that for a donor, except that three bands must be considered: the light and heavy hole valence bands and the split-off spin-orbit band. With larger split-off energies compared to kT , the contribution from the split-off band to the ground-state energy can be neglected. In addition, band warping causes an anisotropy of the effective masses, which needs to be considered. For example, the characteristic decay length of the eigenfunction in the (111) direction in Ge:Ga is 92 Å, and in the (100) direction is 87 Å.

The ground-state *energy* for acceptors depends on the ratio between light and heavy hole masses ($\beta = m_{pl}/m_{ph}$), as computed by Gel'mont and D'yakonov (1971) and shown in Fig. 9.6. It decreases nearly linearly with decreasing β . Holes in each of these bands contribute to the *excited state level spectrum* of the acceptors, and thereby produce a greater wealth of levels. This is shown in Fig. 9.7, with levels identified as *Hydrogen-Like Defects* corresponding to the light and heavy hole bands of symmetry Γ_8 and spin-orbit split band of symmetry Γ_7 .

The quantum number preceding the band notation in Fig. 9.7 is the sum of quantum numbers, indicating successively higher excited states. In addition, the valence

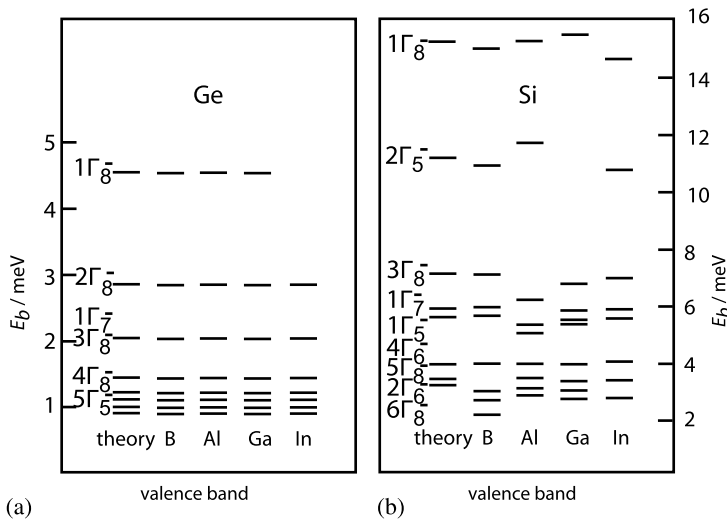


Fig. 9.7 (a) Ground and (b) excited states of acceptors in Ge and Si (after Lipari and Baldereschi 1978; experimental data from Haller and Hansen 1974)

Table 9.2 Acceptor levels (in meV) computed from point charge screened potentials (after Baldereschi and Lipari 1973)

Material	$1S_{3/2} (\Gamma_8)$	$2S_{3/2} (\Gamma_8)$	$P_{1/2} (\Gamma_6)$	$P_{3/2} (\Gamma_8)$	$P_{5/2} (\Gamma_8)$	$P_{5/2} (\Gamma_7)$
Si	31.56	8.65	4.13	12.13	8.51	5.86
Ge	9.73	2.89	0.61	4.30	2.71	2.04
AlSb	42.45	12.40	3.35	18.46	12.00	8.22
GaP	47.40	13.69	4.21	19.17	13.04	9.42
GaAs	25.67	7.63	1.60	11.38	7.20	5.33
GaSb	12.55	3.77	0.650	5.74	3.59	2.61
InP	35.20	10.53	1.97	15.89	9.98	7.32
InAs	10.31	5.00	0.420	7.91	4.76	3.63
ZnS	175.6	51.98	11.65	77.02	49.55	35.37
ZnSe	110.2	32.98	6.07	50.04	31.47	22.68
ZnTe	77.84	23.07	5.09	34.72	22.32	15.36
CdTe	87.26	26.42	3.70	41.43	25.85	17.68

bands are anisotropic, requiring the use of the appropriate Luttinger parameters, also called the inverse effective mass constants—see Luttinger and Kohn (1955) and Luttinger (1956). For a review, see Bassani et al. (1974) and Panitz (1978).

Baldereschi and Lipari (1973) have computed a number of acceptor levels (Table 9.2) in various semiconductors with point charge screened potential. These com-

Table 9.3 Observed shallow acceptor levels in meV (after Bassani et al. 1974)

Semi-conductors	Acceptors	Transitions								Ionization energy
		1st	2nd	3rd	4th	5th	6th	7th	8th	
Ge	B	6.24	7.57	7.94	8.69	9.06	9.32	9.65	9.81	10.47
	Al	6.59		8.27	9.02		9.67	10.02	10.15	10.80
	Ga	6.74	8.02	8.44	9.19		9.84	10.17	10.31	10.97
	In	7.39	8.42	9.08	9.86	10.20	10.48	10.81	10.96	11.61
	Tl	8.87	9.83	10.57	11.32	11.65	11.92	12.26	12.43	13.10
Si	B	30.38	34.53	38.35	39.64	41.52	42.50	42.79	43.27	44.5
					39.01					
	Al	54.88	58.49		64.08	66.28	66.75	(67.1)	67.39	68.5
					64.96					
					65.16					
	Ga	58.23		67.12	67.95	69.85	70.49	(70.8)	71.11	72
					68.25					
					68.43					
	In	141.99	145.79	149.74	150.80	(152.8)	153.27		153.97	155
					151.08					
AlSb		24.66	26.21	27.17	29.41	30.9	32.2			33
				27.53						
				27.87						
InSb	Zn	5.7	6.94	7.31	7.93					
	Cd	25.5	26.5	27.3	27.9					
	Ag									

putations provide the correct trend, but the so-obtained levels still show some differences to the experimental values given in Table 9.3.

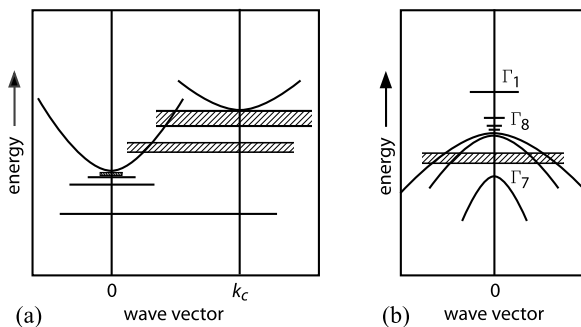
9.6 Bound and Resonant States

The bound electron can be described as a wave packet of Bloch states with vanishing group velocity, which is *localized* at the lattice defect. These Bloch functions must be centered around critical points where $\Delta_k E(k)$ vanishes—see Callaway (1976).

At higher energies and multiple bands, one obtains a permitted excited state of the defect center within the gap with similar features as previously described.

Alternately, one finds states which are related to higher bands (e.g., the *X*-band in GaP or the spin orbit split-off valence band in Si) and observes an overlap of these states with lower bands (Fig. 9.8). Here, the eigenfunctions form a *resonant state* within such a band composed of running Bloch waves (Bassani et al. 1969, 1974).

Fig. 9.8 Schematic of (a) a donor or (b) an acceptor with excited localized states within the gap and resonant states within the band (after Bassani and Pastori Parravicini 1975)



The resonant states have a width that depends on the exchange integral between localized and nonlocalized states. The broadening of the resonant state occurs because the electron has a much reduced lifetime in the quasi-hydrogen state relating to the upper band before it tunnels to the lower band and relaxes to its $E(k)$ minimum. This is easier for higher energies; here the lifetime is smaller, and therefore the broadening is larger—see Fig. 9.8a. Similar features are obtained for localized and resonant states of an acceptor relating to the spin-orbit split-off band, and tunneling into the light and heavy hole bands (Fig. 9.8b). Resonant states with substantial broadening have been observed experimentally—see Onton et al. (1967), Bassani et al. (1969), Onton (1971), and Onton et al. (1972).

9.6.1 Shallow Defects in Compound Semiconductors

The shallow donor or acceptor in a compound semiconductor is more complex than in an elemental semiconductor for two reasons:

- (1) the interaction of the electron or hole with the alternatingly charged ions of the lattice, and
- (2) the differentiation between incorporating the defect on an anion or cation site.

Although the degree of ionicity of good compound semiconductors is small, the above-stated effects are not negligible. For example, isochoric acceptors in GaP should be well described by point-charge quasi-hydrogenic models. However, the two isochoric acceptors, GaP:Zn_{Ga} and GaP:Si_P, have substantially different ground-state energies—64 and 204 meV, respectively. This difference cannot be explained by site-dependent screening, even though neighboring anions are expected to screen more effectively since they are surrounded by more electrons. It needs a more sophisticated analysis, beyond that of the effective mass approximation (Bernholm and Pantelides 1977).

The degree of ionicity in compound semiconductors also determines the coupling of electrons with the lattice, i.e., with phonons; it is described by Fröhlich's coupling constant a_c . Such interaction can be included by considering, instead of a Bloch electron, a *polaron* to interact with the defect center, with an effective

mass $m_{\text{pol}} = m_n/(1 - \alpha_c/6)$ —the eigenstates of a hydrogen-like defect in compound semiconductors can be estimated as

$$E_{\text{qH}}^{(c)} = \left(1 + \frac{\alpha_c}{6} + \frac{\alpha_c}{24} \frac{E_{\text{qH}}}{\hbar\omega_{\text{LO}}} \right) E_{\text{qH}} \quad (9.18)$$

(see Sak 1971) where E_{qH} is the quasi-hydrogen energy. However, this approximation is not sufficient to explain the observed variations of the ground-state energies indicated above.

The modified hydrogenic effective mass approximation describes reasonably well the level spectrum of *excited states* of shallow donors and acceptors in compound semiconductors with a sufficiently large ε/m_p ratio, i.e., for many III–V and II–VI compounds—see Grimmeiss (1986).

9.6.2 Higher Charged Coulomb-Attractive Centers

With higher charges, a Coulomb-attractive center has its eigenfunctions closer to the core and requires more attention to core correction. Therefore, its ground state is more akin to deep level centers—see Chap. 10.

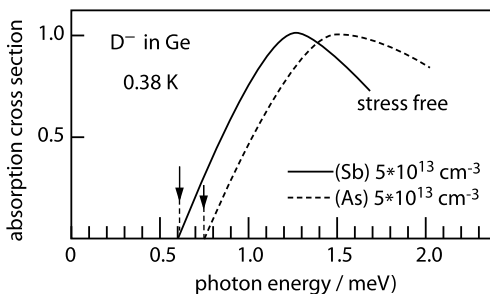
Higher charged centers can be created by substitutional impurities. These are further away from the group of the replaced element, and act similarly to a hydrogen-like donor or acceptor, except that more electrons or holes are donated. For instance, if in a Si lattice one of its atoms is replaced by a sulfur, selenium, or tellurium atom, two electrons can be donated. Since the first electron is bound to a doubly charged center, it is bound at a level four times as deep (charge $Z = 2$):

$$E_i = \frac{Z^2 e^4}{2(4\pi\varepsilon_0\hbar)^2} \frac{m_n}{\varepsilon_{\text{st}}^2} = R_H \frac{Z^2}{\varepsilon_{\text{st}}^2} \frac{m_n}{m_0}. \quad (9.19)$$

The second electron behaves like an electron attached to an ordinary hydrogen-like donor. Hence the substitutional sulfur can be represented by a double donor with two levels. Occupancy, however, determines which of the two levels is active: when filled with two electrons, only the shallow level is active; ionized once, the other electron becomes more strongly bound and the deeper level is active. From the quasi-hydrogen model, we estimate ionization energies of ~ 50 meV and ~ 120 meV for the second donor level in Ge and Si, respectively, compared to 10 or 32 meV for the first level. The actual energies for S in Si are 302 and 587 meV for the first and second ionization levels (Grimmeiss et al. 1980). The larger energies indicate tight binding, which makes the hydrogen-like approximation less accurate and requires central cell potential consideration. We will therefore return to these centers in Chap. 10.

A similar behavior is expected and observed for *two-level acceptors* from substitutional group II elements, e.g., Zn or Cd in Ge or Si with a second acceptor level at

Fig. 9.9 Photo-ionization cross section for D^- states in ultrapure Ge with As or Sb doping at 0.38 K. The low energy threshold indicates the binding energy for the D^- center (after Narita 1985)



~ 25 or ~ 210 meV, respectively, compared to 10 or 53 meV for the first level. Elements from further-removed groups are more difficult to implant as substitutionals. Anions are often too large for the host lattice; cations tend to become more easily incorporated as interstitials (see below).

In an *AB-compound* the situation is more complex, as illustrated by incorporating a group IV element such as Sn (which is two groups removed from Cd) as a substitutional into CdS. Replacing the Cd ion, it acts as a two-level donor; replacing an S ion, it acts as a two level acceptor. This ambiguity makes it difficult to predict the behavior of such type of dopants without additional information.

9.6.3 Over-Charged Donors or Acceptors

One observes doubly charged normal donors (or acceptors) when the neutral donor (or acceptor) can trap an additional electron (or hole). These are known as $D'1$ or A^+ centers, and can be compared to an H^- ion (Faulkner 1969).

The binding energy of the additional carrier is very small (0.54 and 1.7 meV for hydrogen-like impurities in Ge and Si, respectively see Lampert 1958), and results in a very large radius of the quasi hydrogen eigenfunction, requiring high purity to avoid complications due to overlap. The ionization energy can be measured from the photo conduction threshold (see Fig. 9.9), and shows a chemical shift for As_{Ge} and Sb_{Ge} . Anisotropy and multivalley effects are responsible for the deviations from the simple H^- ion model estimates.

Another type of center develops when a doubly charged donor (or acceptor), as described in the previous section, traps another electron (or hole); it becomes over-charged and binds three carriers. Because of the Pauli principle, this center does not have an isolated atom (such as He^-) as an analogue, which exists only in the metastable $(1s)(2s)(2p)$ state. On the other hand, the over-charged $Z = 2$ center can exist in a $(1s)^3$ binding state (McMurray 1985). The ground-state energy of such a center requires central cell consideration as well as radial and angular correlation between the trapped carriers.

9.6.4 Metal-Ion Interstitials

Cation interstitials, either extrinsic or intrinsic, usually behave as donors. An example was given in Sect. 9.1 (Fig. 9.6) with Li as an interstitial in Si—see Reiss et al. (1956) and Hall et al. (1981). The metal atom on an interstitial position prefers to donate its valence electron (s). When it has no counterpart to form a charge-compensating bond, it can be described as a hydrogen-like donor. Since ionized cations are usually much smaller than anions, they are more easily incorporated on interstitial sites. Therefore, interstitial donors are more readily observed than interstitial acceptors.

The ground-state level of the interstitial depends on its site of incorporation—see Jansen and Sankey (1986); for interstitials in II–VI compounds, see Watkins (1977). Depending on the valency of the incorporated metal ion, they can act as single- or multilevel donors.

In a simple hydrogen-like model, higher excited states of these impurities cannot be distinguished from the classical substitutional donor. The chemical shift of the ground state, however, is substantial. In a pseudopotential approximation (Pantelides 1975), a complication arises since there is no cancellation, such as for the potential of a replaced host atom in a substitutional impurity.

Self-interstitials in elemental semiconductors are rather deep centers, and will be discussed in Sect. 10.4.3.

Chapter 10

Deep Level Centers

Abstract The deep level centers are determined by a short range potential in a tight binding approximation. Several models are discussed from a simple square well model with added Coulomb well (hydrogen model) for higher energy states. Typical donors and acceptors in different materials are depicted. Other theoretical models include perturbation methods, cluster calculation, super cell and Green's function techniques. Semi-empirical tight binding approximations indicate supercomputer use. Jahn Teller effect. Crystal field theory, splitting of levels. Examples of deep centers in alkali halides, *F*-centers with typical energies listed, and others. Vacancies in covalent crystals. Self-interstitials. Anti site defects, hydrogen in Si. Substitutional defects replacing a vacancy. Symmetry aspects. Isoelectronic defects. Chalcogens in Si and tabulation of their energy. Oxygen in GaAs. *EL2* and *DX* centers. Negative *U*-centers. Shallow/deep center instability. Metastable Lattice relaxation. Transition metal impurities, energy tabulation. Isoelectronic defects, charge character. Tabulation of deep center energies and effective crystal field splitting. Measured ionization energies in Ge, Si, GaAs, and CdS.

Deep level centers are responsible for fixing the space charges by trapping carriers, and some of them to provide a preferred path for carrier recombination. As such they are essential for determining the quasi-Fermi level distribution in a solar cell, that is necessary for explaining its performance.

In general, deep level centers require a tight-binding analysis in which the wavefunction of the ground state remains localized close to the core of the defect. They cannot be described by a hydrogenic effective mass approximation. Deep levels, however, do not necessarily have a large binding energy.¹ They are connected to the conduction *and* valence bands, i.e., these deep trap levels do not follow one specific band when perturbed by alloying *or* by the application of hydrostatic pressure. Their central core potential dominates their behavior at the ground state (higher excited states, however may also follow effective mass-like distribution) or they have unsaturated inner shells in transition metal impurities, permitting electronic transitions

¹Deep levels also appear in narrow band gap materials (see Lischka 1986).

here. Specifically, such defects may or may not be charged relative to the lattice; they may be isoelectronic *or* isovalent.

The levels of these centers are described by a short-range potential. The pseudopotential method is an advantageous tool for determining $V(r)$. In addition, the deformed lattice environment must be considered, and also for Jahn-Teller distortion that is discussed later in this chapter. The deep states extend throughout the entire Brillouin zone. States from both bands and all near-band gap valleys are necessary to construct the electron ground state eigenfunction of this center. The resulting deep defect levels act as deep traps for electrons or holes or as recombination centers. A review of such deep centers can be found by Queisser (1971), Stoneham (1975), Lannoo and Bourgoin (1981), and by Pantelides (1978, 1986).

In contrast to shallow level centers, which are easily identified chemically in their specific lattice environment and are rather well understood in their electronic level structure, it is much more difficult to identify a specific deep level lattice defect and to describe theoretically its electronic behavior. Except for a large variety of centers in ionic crystals, which were identified earlier (the well-known class of F -centers in alkali halides is an example), most deep centers in semiconductors are still described by a combination of letters and numbers (Hayes and Stoneham 1984), given to them by the authors who started their analysis; these centers are identified by their spectral signature.

Only by a concerted effort of various experimental methods, was it possible to identify some of them unambiguously. These methods include optical absorption, luminescence emission and excitation spectroscopy, electron-spin resonances, optical detection of magnetic resonances (ODMR), ENDOR, EXAFS, and deep level transient spectroscopy (DLTS). An important contribution was the improved growth techniques of ultrapure and stress-free crystals, which eliminate disturbing influences of the defect environment. In spite of new results, other deep level centers seem to escape an identification that is agreeable to all. The main problem with deep centers is their tendency to form associates or to incorporate into their structure major lattice deformation with decisive consequences.

These various influences are difficult to evaluate in a comprehensive theory, however, some of the principal features of deep levels can be seen in rather simple models. Starting with such a model, more complex elements will be introduced stepwise.

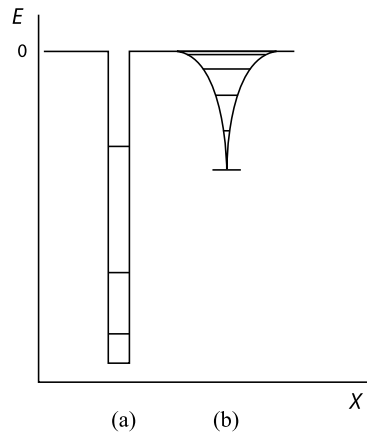
10.1 Mathematical Models of Deep Level Centers

First, a very simple model is presented with a one-dimensional potential of a deep potential well that is connected to *one band only*.

10.1.1 Square Well Potential

A means of introducing the chemical individuality of a center is provided by assuming a rectangular one-dimensional well of depth V_0 and width $2a$.

Fig. 10.1 Electron eigenstates **(a)** in rectangular well and **(b)** in a Coulomb-attractive well of a quasi-hydrogen defect



Solving the Schrödinger equation for such a well yields the eigenstates of such a well

$$E_n \simeq \frac{\hbar^2 \pi^2}{2m_0 a^2} n_q^2 + V_0 \quad \text{with } n_q = 1, 2, \dots \quad (10.1)$$

The electron restmass is used here since the electron remains close to the center, and *increase quadratically* with n_q . The individuality of each center is given by a different a and V_0 .

In contrast, the eigenstates of a simple *hydrogen-like defect* are given by

$$E_n = \frac{m_n e^4}{2\hbar^2 (4\pi \epsilon_{st} \epsilon_0)^2} \frac{1}{n_q^2} \quad \text{with } n_q = 1, 2, \dots, \quad (10.2)$$

and with eigenstates *converging* toward *the continuum* of free decreases $\propto 1/n_q^2$ at the edge of the conduction band—see Fig. 10.1b.

The use of a better central cell potential $V(r)$ of the defect in the Schrödinger equation would yield more realistic results for the deeper defect level spectrum. However, the connection of *both* valence and conduction bands into the model of deep centers permits the distinction between deep and shallow levels, as will be discussed in the following section. This will replace the linear relation between well depth (V_0) and the depth of the ground state with a much compressed relationship, as indicated in the example shown for the square well in Figs. 10.2 and 10.14; see Sects. 10.2, and 10.4.6.

10.2 Coulomb Tail and Deep Center Potential

In addition to the central cell potential, we have to consider the long-range Coulomb potential of *charged* deep centers. The *Coulomb tail determines higher excited states*

Fig. 10.2 Influence of an increasingly attractive square well potential, added to a screened Coulomb potential $\varepsilon = 10$, $m_n = 0.1$, well diameter $5 \text{ \AA}$ (after Vogl 1981a)

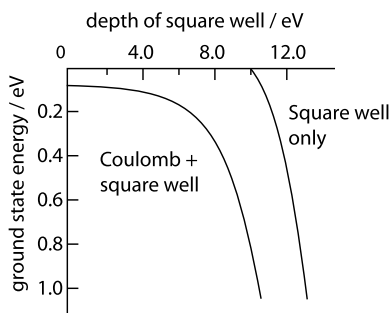
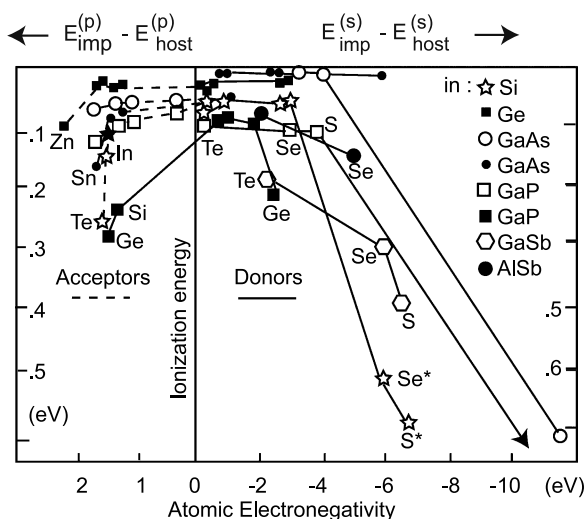


Fig. 10.3 Ionization energy of donors and acceptors in a selection of host lattices, plotted versus the difference of s - or p -energies, respectively of impurity and host atoms. Deeper levels are identified. For identification of shallow levels, see Vogl (1981a)



of these centers and renders them hydrogen-like, similar to shallow centers. Consequently, *one or several deep levels are observed, followed by a series of hydrogen-like shallow levels close to the respective bands* (see Grimmeiss 1986). The model potential combination of a square well and Coulomb potential describes the ground state of centers with the Coulomb potential predominating until, with increasing well depth, the short-range part of the potential becomes very large ($>10 \text{ eV}$) as shown in Fig. 10.3. The ground state of the center then shows typical deep level behavior, here calculated properly with interaction of valence *and* conduction bands.

The *atomic electronegativity*² can be used as an indicator for the depth of the square well representing the core potential. Figure 10.4 shows the experimentally observed chemical trend: namely, a fiat branch for Coulomb-dominated centers, and a steeply decreasing branch for core-dominated centers, which have a deeper well

²The atomic electronegativity is defined as the difference between the s -energy of host and impurity atoms for donors, and the respective p -energy for acceptors.

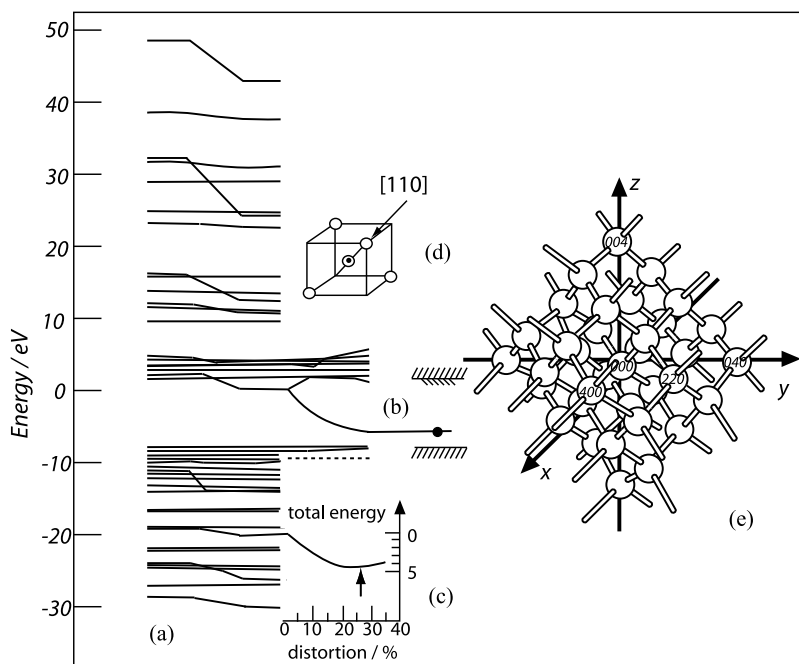


Fig. 10.4 (a) Electron energy level distribution for the cluster of 35 carbon atoms (left half of **a**) depicted in (e) and including a nitrogen atom in its center (right half of **a**); (b) the deformed spectrum when the carbon atoms surrounding the center nitrogen atom relax; (c) Jahn-Teller shift as a function of the lattice relaxation (minimum total energy at 26 % distortion); (d) unit cell; and (e) 35 atom cluster (after Watkins and Messmer 1970)

potential. The reason for this empirical relationship will become clear in the discussion of Sect. 10.4.6.

The most important results obtained for deep level defects can be summarized as follows:

- deep centers are connected to both valence and conduction bands;
- the energy of the deep level varies at least an order of magnitude less than the impurity potential; and
- although the short-range potential is dominating, the eigenfunctions of some of the deep level impurity centers, such as substitutional chalcogens in Si or in III–V compounds, extend well beyond nearest neighbors and do not change much with the chemistry of the impurity if incorporated at the same site (Ren et al. 1982).

10.3 Theoretical Methods to Analyze Defect Centers

The theoretical methods deal with approximations for solving the Schrödinger equation of the defect within the lattice environment.

10.3.1 Perturbative Methods

Perturbative methods use a defect potential that can be written as

$$V = V^0 + U \quad \text{with the Hamiltonian } H = H^0 + U \quad (10.3)$$

where H^0 is the one-electron Hamiltonian of the unperturbed lattice and U is the defect perturbation. The eigenfunctions of the corresponding Schrödinger equation $H\psi_v = E\psi_v$ are determined by expanding ψ_v in terms of a complete set of functions Φ_i

$$\psi_v = \sum_{\lambda} F_{\lambda} \phi_{\lambda}. \quad (10.4)$$

As such a set of functions, one may choose Bloch functions, Wannier functions, or other orthonormalized functions—for instance, simple exponentials or Gaussian orbitals. The eigenvalues are then obtained from the secular matrix.

When the range of the perturbation potential is shorter, one advantageously uses Wannier or other *localized* functions for the expansion of ψ_v . Thus, one obtains the eigenvalues from the corresponding determinant (Koster and Slater 1954, see also Bassani et al. 1969; Jaros and Brand 1976).

10.3.2 Cluster Calculation

The eigenstates of a deep center can be estimated by considering only the atoms in its neighborhood, i.e., in an atomic cluster (Messmer and Watkins 1973).

Cluster calculations are carried out by calculating the eigenfunctions of such a group of atoms, treating it as a large molecule. When initially calculating it with atoms from the ideal crystal, and then inserting the impurity into its center, one obtains information on its energy level structure. Although these cluster calculations are easily implemented, they converge slowly with cluster size and the results are very sensitive to conditions at the cluster boundary. Moreover, the defect-level energy is not very accurate, and corresponding changes of band states are difficult to obtain. An example for a diamond crystal is given in Fig. 10.4. A level splits into the band gap when a nitrogen atom is incorporated into this cluster.

In addition, a large shift to lower energies is seen in Fig. 10.4, when lattice relaxation in the neighborhood of the N atom is permitted (Jahn-Teller distortion—see Sturge 1967). The replacement of a carbon atom by a nitrogen atom causes a substantial trigonal distortion of the four neighbor atoms.

10.3.3 Supercell Technique

Related to a cluster calculation is the supercell technique, in which the defect center is placed periodically in an otherwise perfect crystal. This technique replaces the

questionable boundary condition for a cluster with less problematic *periodic* boundary conditions. The method, however, produces artificially broadened defect levels caused by defect interaction (Louie et al. 1976; Kauffer et al. 1977). With large computers, this effect can be minimized by using larger clusters for each cell. Then the supercell technique is a valuable tool.

10.3.4 Green's Function Technique

Self-consistent Green's function calculations powerfully determine the differences between an ideal crystal and the changes introduced by the defect center, recognizing their *localization in space*. Although more complicated than cluster calculations, they supply more accurate solutions (Bernholc and Pantelides 1978; Baraff and Schlüter 1980).

This method has been used extensively, providing very valuable information on deep level defect centers (Hjalmarson et al. 1980). For a brief review, see also Pantelides (1986).

10.3.5 Semiempirical Tight-Binding Approximation

The chemical trend of deep impurities can be obtained rather well from a semiempirical pseudo-Hamiltonian based on a small number of pseudo-orbitals (one *s*-, three *p*-, and one excited *s**-orbital) for A_1 -symmetric substitutionals in tetrahedrally bonded semiconductors. The approximation is based on the band orbital model of Harrison (1973), and adopted by Vogl et al. (1983), to reproduce valence and conduction band structures of semiconductors. Hjalmarson et al. (1980) employed the same model to obtain information of the chemical trend on deep levels of substitutional impurities—see Sect. 10.4.6.

10.3.6 Supercomputer Use

The above described approximation are easily used in computer evaluation and yield reasonable results in close agreement with the experiment provided one knows the proper values of the parameters. Here are most of the difficulties since not all of them can be derived from basic principles. With supercomputers available the computation of a specific problems can be reduced to a few second cpu time, and a large variety of variational method can be employed for defects in different positional arrangements or in connection with various other impurities.

10.3.7 The Jahn-Teller Effect

When defects with a high degree of symmetry are incorporated in a lattice which distorts this symmetry, degenerate states of the defect are split. In addition, the symmetry of the perfect lattice is reduced in the neighborhood of the defect, causing further splitting; and at least one of the states will be lower than the degenerate state of the undisturbed defect (*Jahn-Teller theorem*, Jahn and Teller 1937). For further information, see Bersuker (1984), and in paramagnetic crystals, see Bates (1978).

One distinguishes *static* and *dynamic Jahn-Teller effects*, the former is described above, the latter is caused by anisotropies induced from the different modes of the oscillating lattice.

In addition, a linear and quadratic contributions can be differentiated, depending on the degree of distortion from the surrounding lattice (Sturge 1967).

10.3.8 Crystal Field Theory

Some qualitative information about the electronic behavior of deep centers can be obtained by starting from the electron eigenvalue spectrum of the isolated impurity atom in vacuo. Then one can determine to what extent this spectrum is influenced after the atom is exposed within the crystal to the field of the surrounding atoms, the *crystal field*. This crystal field is used then as a perturbation.

Such description is relatively simple when the symmetry of the surrounding lattice environment is known. When introduced as a substitutional impurity without lattice relaxation, the symmetry of the lattice environment is that of the undisturbed crystal.³ This causes splitting of degenerated energy levels of the free atom: the eigenfunctions of any free atom *in vacuo* must be invariant against rotation and reflection, resulting in a large degeneracy of the eigenvalues. However, this is no longer true within a crystal, where the point group of the lattice determines the remaining degeneracies with lesser symmetry.

The *crystal field theory* deals only with a symmetry-related influence of the surrounding atoms but neglects the effects of the neighboring valence electrons. Therefore, it specifically addresses electrons in deeper shells that are partially filled and are shielded from the influence of other valence electrons. Such impurities are transition rare metal atoms.

For an illustrating example, the level splitting is discussed for an atom with two *d*-electrons (for instance, Ti, Zr, or Th) substituting for an atom of a host with O_h (cubic) symmetry, such as Si or Ge. Each of these electrons has 10 states available with $l = 2$, $m = -2, -1, 0, 1, \text{ and } 2$, and $s = \pm 1/2$, resulting in 45 different states

³However, in actuality, deformations of the surrounding lattice result, with consequent lowering of the symmetry.

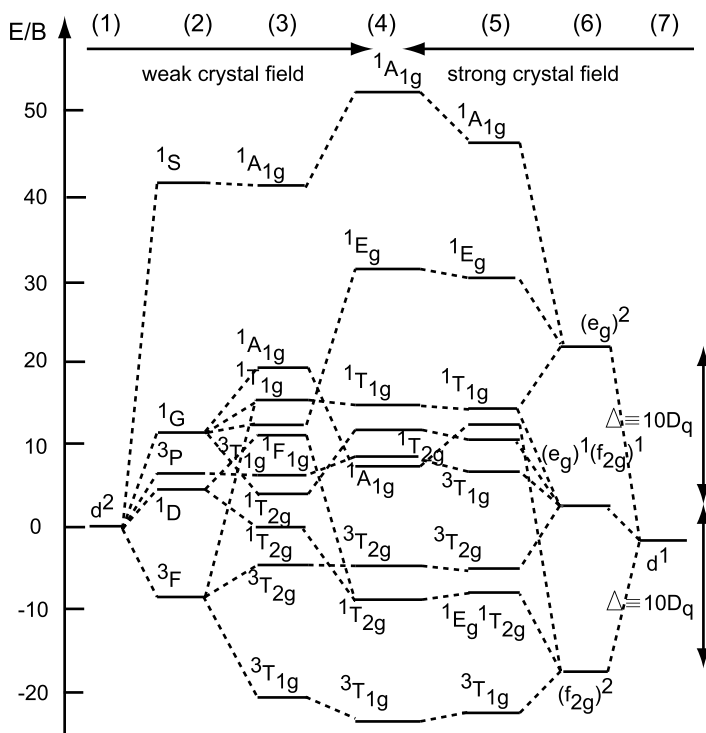


Fig. 10.5 Splitting of d^2 -levels in cubic lattices: (1) and (7) unperturbed atoms; (2) electron-electron interaction only; (3) crystal field interaction added; (5) electron-electron interaction and crystal field; and (6) crystal field only (after Schäfer and Gliemann 1967)

one	^1S -state	with	$L = 0$	$S = 0$
nine	^3P -states	with	$L = 1$	$S = 1$
five	^1D -states	with	$L = 2$	$S = 0$
twenty-one	^3F -states	with	$L = 3$	$S = 1$
nine	^1G -states	with	$L = 4$	$S = 0$

The splitting of these levels becomes transparent after sequentially introducing electron-electron interaction and crystal field. This is shown in Fig. 10.5. Electron-electron interaction results in a splitting of the d^2 -level into five levels, distinguished by L is shown in the second column of Fig. 10.5. The addition of the crystal field results in a further splitting of the ^1D (into 2), ^3F (into 3), and the ^1G (into 4 levels),

⁴The use of lower- and upper-case letters to describe the states gives a good example to distinguish between one- and multi-electron states. The latter includes electron-electron interaction.

as shown in the third column of Fig. 10.5. When the interaction between different levels is finally taken into consideration, many levels are shifted substantially (without further splitting), presenting a reordered level arrangement as given in the fourth column of Fig. 10.5.

Additional splitting is caused by spin-orbit coupling. The corresponding optical spectra of some of these transition metal impurities in wide band gap material are therefore quite complicated—see Hellwege (1970), McClure (1961), and Schläfer and Gliemann (1967). In semiconductors of smaller band gap, only a few of these levels fall within the gap and are easily identifiable—see Ludwig and Woodbury (1962), Milnes (1983), and Bates and Stevens (1986).

By including the short-range defect potential and the host crystal symmetry in the neighborhood of the defect, and using Green's function techniques, Pantelides (1978) arrives at improved estimates for the deep defect energy levels.

10.4 Examples of Deep Centers

Very early deep defect centers in alkali halides were identified. These will be given first as examples.

10.4.1 *Vacancies in Alkali Halides*

Anion vacancies act like donors, and *cation vacancies* act like acceptors, however, both are deep centers. They are easy to identify by their optical absorption spectrum of broad isolated lines within wide band gaps, and their unambiguous response to specific treatments, which stimulate unique defect reactions. These centers show a large amount of lattice relaxation (large Huang-Rhys factor—see Sect. 22.5.1) when recharged, providing excellent examples for electron-lattice interaction.

10.4.2 *F-Centers*

The classical example of an anion vacancy is an *F*-center in an alkali-halide crystal⁵ (Fig. 10.6). The missing negative charge of the anion is replaced by an electron in order to restore local neutrality. That electron is not as tightly bound to the vacancy as it was to the Cl^- anion in Fig. 10.6, which is now missing. The level associated

⁵F-centers (“Farb” centers: German for color centers) were the first lattice defects correctly identified and described by their electronic structure by Pohl and coworkers (see the review by Pohl 1938). Later associates of two, three, or four F-centers were observed and referred to as *M*-, *R*- and *N*-centers (N_1 in planar and N_2 in tetrahedral arrangement)—see Schulman and Compton (1962).

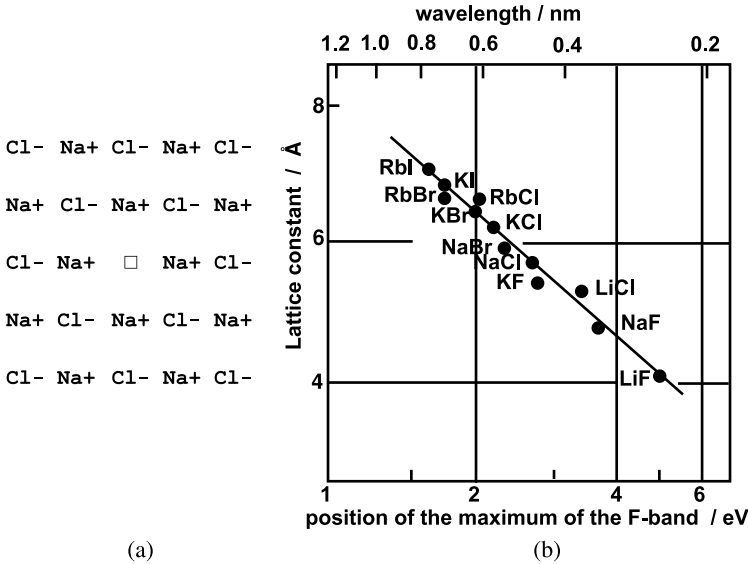


Fig. 10.6 (a) *F*-center in a sodium chloride crystal. (b) Position of the maximum of the *F*-center absorption as a function of the lattice constant (after Mollwo 1931)

with this defect therefore lies in the band gap; in NaCl with a gap of 7.5 eV, the *F*-center lies 2.7 eV below the conduction band. It becomes deeper with increasing lattice binding strength. This is indicated in Fig. 10.6b as a function of the lattice constant that decreases monotonically with increasing binding strength.

The vacancy changes its charge character with ionization from neutral to positive,



relative to the lattice (10.5) and thus acts as a donor. *Excited states of the F-center* have been observed by Lüty (1960) and are referred to by the symbols K , L_1 , L_2 , and L_3 . These levels are probably resonant states with X minima of the conduction band (Chiarotti and Grassano 1966). They are located with large energy spacings of ~ 0.6 eV for each consecutive L ; level in KCl, which are typical for deep centers.

Replacing the missing ion with an electron does not completely restore the ideal lattice periodicity. The resulting lattice perturbation produces another level which lies closer to the respective band (Fig. 10.7).

A second carrier can be trapped in this level. The center, derived from an *F*-center, is called, *F'*-center, and returns to an *F*-center when ionized:



In the example of KBr, the ionization energy of the *F'*-center is 1.4 eV, which is substantially less than the ionization energy of the *F*-center-2.05 eV.

In addition, the surrounding lattice near the vacancy is also perturbed; its eigenstates split off into levels in the band gap. When the vacancy is empty, the resulting

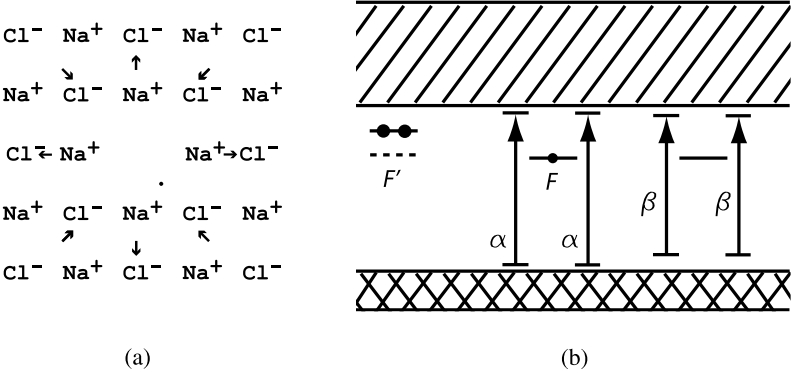
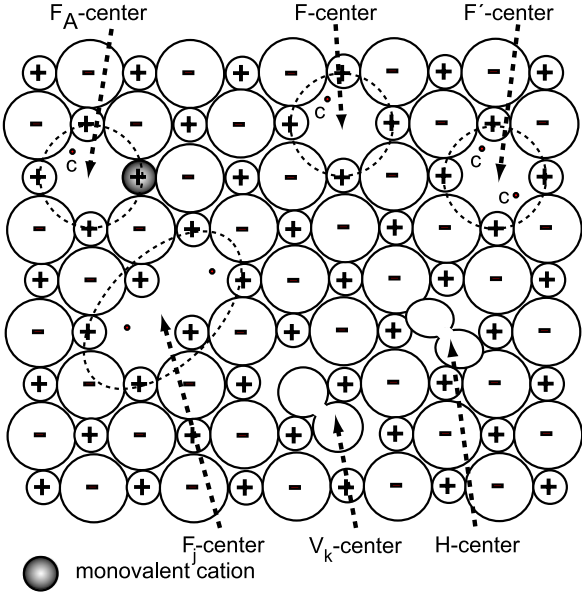


Fig. 10.7 Disturbance of the anion and cation lattice around an anion vacancy. The displacement is indicated by arrows in subfigure (a). The resulting split-off levels near valence and conduction band are shown as β in subfigure (b). A smaller perturbation is observed if an electron is trapped, i.e., near an F -center, resulting in a split-off α in subfigure (b). These perturbations represent the corresponding energies of the trapped excitons (Sect. 10.2)

Fig. 10.8 Some of the color centers in alkali halides (after Hayes and Stoneham 1984)



perturbation is larger than when this vacancy has an electron trapped in it. These levels are shown schematically in Fig. 10.8, and are called α - or β -bands. Such levels are observed in alkali halide crystals. They result in a decrease of the band gap in the immediate neighborhood of the defect for KBr from 6.55 to 6.44 and 6.15 eV,

respectively, at 90 K. These can be interpreted as excitons trapped at the empty vacancy or at the F -center.

10.4.3 Other Centers in Alkali Halides

A cation vacancy in an alkali halide is called a V -center, and acts as an acceptor. It is deeper than the F -center in the same crystal and less sharp, probably because of stronger lattice relaxation or of distant pair formation. Nearest-neighbor associates of such centers are termed V_2 - and V_3 -centers (Seitz 1954).

There are more intrinsic centers which can be formed. These include the V_k -center, the I -center, and the H -center, all of which are related to halogen defects (see e.g., Castner et al. 1958) and are, respectively, a self-trapped hole, a halogen ion interstitial, and a halogen molecule on a single halogen lattice site (Itoh 1982). A few of these *color centers* are shown in Fig. 10.8. Each of these defects has a characteristic signature in optical absorption, luminescence, or in spin resonance. The wide band gap and tight-binding of defects in alkali halides permit separate identification, and give convincing evidence of a wealth of intrinsic defects, which are much more difficult to identify in common semiconductors. For a review, see Schulman and Compton (1962), Fowler (1968), Farge (1973), Williams (1978b), Itoh (1982), and Stoneham (1986).

10.4.4 Vacancies in Covalent Crystals

One of the most important centers in covalent crystals is the vacancy; it permits an estimate of the resulting changes when a substitutional impurity replaces the vacancy. An understanding of its configuration and electronic structure is a prerequisite for the analysis of substitutionals.

Vacancies in covalent crystals result in deep levels which can have several occupation states. Typically, one distinguishes five charge states of the vacancy $V^\cdot$, $V^{\cdot\cdot}$, V^x , V' , and V'' ; two of them, V^x and V' , are observed in Si in spin resonance, and two by diffusion experiments (Watkins 1968, 1976). The breaking of covalent bonds results in *dangling bonds*, which group with the vacancy to form molecular orbitals—a singlet state with a_1 and a triplet state with t_2 symmetry.

These yield the ground states of the differently charged vacancies by population of the states with electrons of appropriate spin (Fig. 10.9). For Si, the corresponding states are $V^{\cdot\cdot}(a_1^2)V^\cdot(a_1^2t_2)V^x(a_1^2t_2^2)V'(a_1^2t_2^3)$ and $V''(a_1^2t_2^4)$ see Hayes and Stoneham (1984).

A strong tetragonal Jahn-Teller distortion lowers the symmetry to D_{2d} , and significantly shifts and splits these levels as shown in Fig. 10.9a. The unpaired electron in the $V_{Si}^\cdot$ and V_{Si}' states is spread equally over four or two of the surrounding atoms, respectively. The entire electronic behavior of the vacancy can be explained in a one-electron model (Pantelides and Harrison 1976).

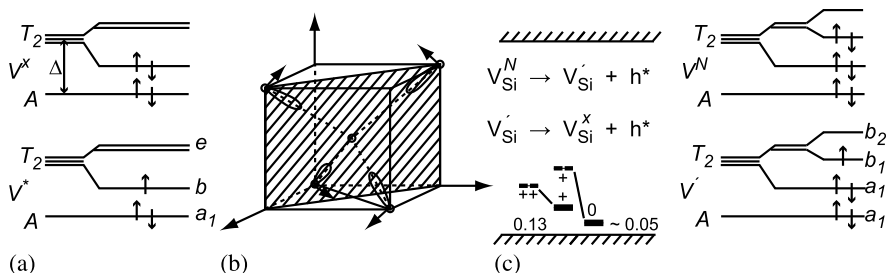


Fig. 10.9 (a) Electronic structure of Si vacancies with symmetry of one-electron orbitals indicated; (b) Jahn-Teller distortion in the neutral vacancy; and (c) shift of levels before (left) and after lattice relaxation (right) with charge character indicated (after Watkins 1968)

The states V^* and V' are observed by ESR resonance V^x , V' , and V'' are indirectly observed after photo-excitation, and the V'' level is seen to shift below the V^* level, which is typical for a negative- U behavior—see Sect. 10.5. This behavior was predicted by Baraff et al. (1980) and later experimentally confirmed by Watkins (1984). See also Stoneham (1975), Lipari et al. (1979), and Jaros et al. (1979).

The V_{Si}^* state is metastable and disproportionates to V_{Si}^x and the stable V_{Si}'' (Fig. 10.9), which lies ≈ 0.13 eV above E_v . This center releases *two* holes when excited, since the V_{Si}^* center is shallower (0.05 eV) and dissociates immediately after creation.

In diamond, a number of very sharp lines appear which are related to the vacancy and identified as *GR1*...*GR8* (Collins 1981). At present, their origin is not completely understood.

A convenient method⁶ for producing such vacancies is by bombardment with relatively fast electrons (Loferski and Rappoport 1958) at cryogenic temperatures, and trapping the cogenerated, highly mobile interstitial (Sect. 19.1.1) at other lattice defects, e.g., group III atoms (Watkins 1968). The threshold energy for producing vacancies with electrons in Ge and Si is 14.5 eV and 12.9 eV, respectively.

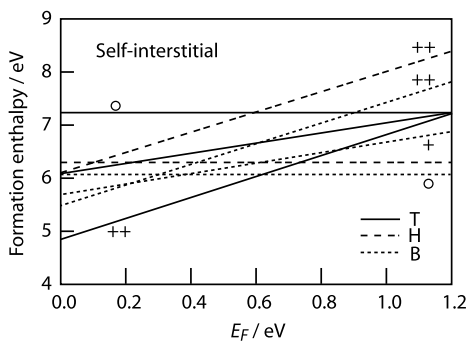
Vacancies in *binary* semiconductors require multi-electron approximations. While the states of the silicon vacancy are sp^3 hybrids, the state of a Ga vacancy in GaP are p -like.

10.4.5 Self-interstitials

Elemental semiconductors such as Si and Ge have a rather loosely packed lattice with coordination number 4 and sufficient space to accommodate interstitials of the host lattice, i.e., *self-interstitials*.

⁶Quenching from high temperature is not fast enough to freeze-in measurable densities of vacancies (Watkins 1986).

Fig. 10.10 Si self-interstitial formation enthalpy as a function of the position of the Fermi level for the different interstitial position and charging states (after Car et al. 1984). More recently, a slightly lower (~ 1 eV) formation enthalpy was calculated by the same authors



There are several possibilities for incorporating an additional Si atom in an Si lattice. Three of them are indicated as T, H, and B and have tetragonal, hexagonal, and bond-centered geometry. Two, indicated as S and S' , have a split configuration: the lattice atom has moved to one of the split positions while the interstitial atom moves to the other. The two equally displaced atoms are sometimes also referred to as an *interstitialcy*. After incorporation, the surrounding atoms relax to shifted positions.

The formation energy of the interstitials depends on their specific site as well on their charge state. This is shown in Fig. 10.10, with the formation energy plotted as a function of the position of the Fermi level (Car et al. 1984). Such dependency indicates that the recharging of an interstitial makes it more stable at a different position. Alternating recharging, e.g., by recombination with excess carriers followed by thermal ionization at the changed position, can therefore stimulate diffusion.

The Si_i^+ center is metastable; when recharging and relaxing into the Si_i^- center, it shows a negative U -character. Si interstitials are deep level centers with levels 0.6 and 0.8 eV below the conduction band.

10.4.6 Antisite Defects

Antisite defects are identified in some of the III–V compounds, e.g. As_{Ga} . This center is believed to be responsible for compensation of electrically active defects, consequently causing a reduction in semiconductivity. The defect by itself, or as an associate with As_i is probably the so-called EL2 center in GaAs.

In compound (AB) semiconductors, one distinguishes A_B and B_A as possible antisite defects. In higher compounds, such antisite formation is often more probable and presents a larger variety of defects: six in ABC-compounds, although only a few of them are energetically preferred.

10.4.7 Hydrogen in Silicon

Hydrogen in Si requires special attention. It is known to passivate many deep centers, and is therefore often used with great benefit for device fabrication (Pearton

et al. 1987). It can be introduced into the Si lattice in a variety of ways (Seager et al. 1987). It diffuses easily and is known to attach itself to dangling bonds (Pearson et al. 1987). It strongly reduces the conductivity of *p*-type and weakly reduces it in *n*-type Si (Sah et al. 1983; Bergman et al. 1988). However, *H* also induces defect levels of its own in the band gap.

Substantially improved insight into the structure of defects has been gained after more reliable energy profiles, including lattice relaxation, were computed (Denteneer et al. 1989a, 1989b).

It has been shown that hydrogen atoms are preferably introduced in *p*-type Si as *H'* at a B-site after lattice relaxation by 0.4 Å in the bond direction (Van de Walle et al. 1989). For a review see Patterson (1988).

In *n*-type Si, hydrogen is preferably incorporated as *H^x* or *H'*. The *H^x* seems to find several shallow minima near *C*- or *T*-sites with little barriers in between, easing interstitial diffusion. The *H'* is more stable at a *T*-site, which is a high electron density location. The *H^x*, *H'* center is a deep donor and seems to act as a negative-*U* center—see Sect. 10.5.

The incorporation, diffusion, and recharging of hydrogen interstitials resemble to some extent the corresponding properties of self-interstitials. They also depend sensitively on the position of the Fermi level.

10.4.8 Substitutional Defects Replacing a Vacancy

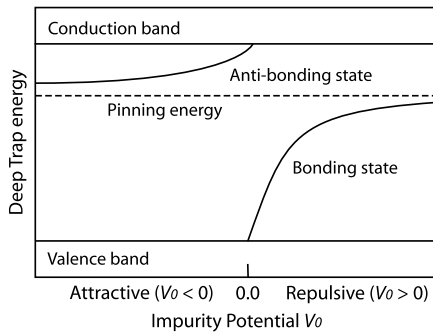
Substitutionals can be considered as impurities replacing a vacancy. Inserting an Si atom into a vacant site of an Si host can be considered as having its *s* and *p* orbitals interacting with the *A*₁ and *T*₂ states of the vacancy, producing bonding and antibonding states which merge with valence and conduction bands, respectively. Inserting an impurity with substantially lower energy orbitals will produce only a small shift in the levels, causing an impurity-like hyper-deep bonding level in or below the valence band, and a vacancy-like anti-bonding level slightly lower than the vacancy states usually within the band gap.⁷ For impurities with energy levels higher than Si, the corresponding levels lie within the conduction band, and slightly above the vacancy states for the bonding-antibonding pair. The vacancy states are limiting cases for donor- or acceptor-like states.

This indicates how the influence of two bands compresses the spectrum of ground states of deep level from $\partial E/\partial V \cong V_0$ in the simple one-band model (Sect. 10.1.1) to the actual $|\partial E/\partial V|$ that is rapidly decreasing with increasing $|V_0|$, where V_0 is the depth of the potential well. This is shown schematically in Fig. 10.11.

This behavior is deduced from Green's function calculation using semi-empirical tight-binding Hamiltonians (Hjalmarson et al. 1980). It has been used to calculate

⁷The *A*₁ state of the acceptor is always strongly bound and lies within or below the valence band, while the *T*₂ states may emerge from the conduction band into the gap, to which both approach asymptotically with increasing depth of the binding potential of the electron or hole in the impurity.

Fig. 10.11 Depth of deep donor and acceptor states as function of their impurity binding potential V_0 . The asymptotic “pinning energy” is that of the electron state of the vacancy (after Vogl 1981a)



the chemical trend of numerous deep level centers as a function of the impurity potential. These levels are shown in Fig. 10.12. For the impurities to the right of the intersect of the curves in Fig. 10.12 with the conduction band, the impurity potential is not large enough to offer a bond state. Here, the effective mass approximation for hydrogen-like states yields shallow levels connected to one band only (the conduction band in this example). For a short review, see Dow (1985).

When using an impurity potential comprised of a deep well and a Coulomb tail (e.g., like the Abarenkov-Heine potential) with

$$V(r) = \lambda V_0(r) + \frac{e^2}{4\pi\epsilon\epsilon_0 r} \quad \text{with} \quad V_0(r) = \begin{cases} V_0 & \text{for } r \leq r_0 \\ 0 & \text{for } r \geq r_0 \end{cases} \quad (10.7)$$

and a deep enough well to create a bound ground state in the gap, one can follow the transition from a deep level center with essentially a vacancy-like charge density distribution to a hydrogen-like spread out distribution with decreasing impurity potential (Pantelides 1986), as shown in Fig. 10.15.

10.4.9 Impurity and Site Symmetry

The chemical identity of an impurity (i.e., its size, bonding type, and valency) is responsible for changes of the local symmetry after the incorporation of an impurity. Some of these changes are related to the symmetry-breaking lattice relaxation, known as the Jahn-Teller effect. Others deal with the strength and angle relation of the bonding forces of the impurity in relation to the tetrahedrally arranged available dangling bonds of the impurity.

The arrangement of atoms nearest to an impurity has an important influence on the density of state (DOS) distribution of the resulting levels. This influence is strong enough to make the DOS of substitutional *S*-donor look rather similar to an interstitial Si atom, both in a tetrahedral environment (Vigneron et al. 1982).

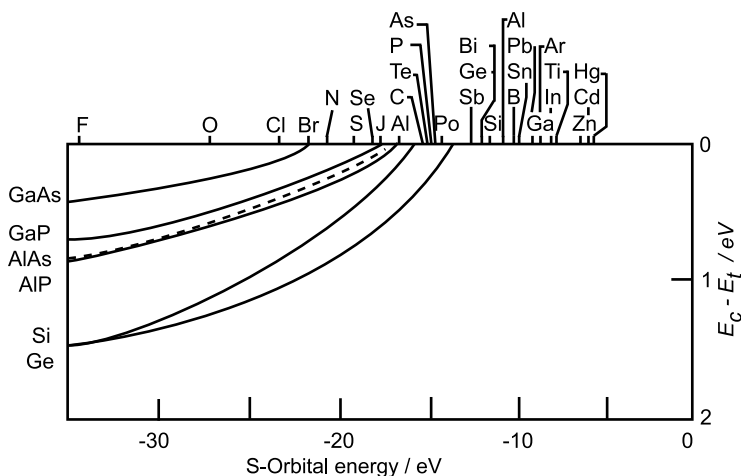


Fig. 10.12 Calculated ionization energies $E_c - E_t$ for deep level substitutional impurities on anion sites in semiconductors listed at left margin (after Hjalmarson et al. 1980). Impurities with a lower value of the binding potential than shown by the intersection of the curves with E_c lie as resonant “deep” states *within* the conduction band

10.4.10 Isoelectronic Defects

Isoelectronic defects are formed by substitutionals from the same column of elements as the host atom. Different homologous elements have a different energy spectrum, since the long-range potential—the Coulomb term—cancels: the replacing atom has the same valency. The remaining central cell potential reflects the chemical identity of the center. Replacing a middle-row host atom (e.g., P in GaP) with highest row atom (here N) one obtains a defect state that acts as an electron trap with a binding energy of 20 meV.

Replacing it with a lower-row atom (here Bi), the defect acts as a hole trap with a binding energy of 38 meV (Dean et al. 1969). Replacement with mid-range atoms usually does not produce electronic defect centers, but instead produces *alloys* with the respective sublattice: As forms a $\text{GaAs}_{1-\zeta}\text{P}_\zeta$ mixed crystal, as does Sb, which forms $\text{GaSb}_{1-\zeta}\text{P}_\zeta$. There are no corresponding levels in the band gap.

When traps are created, some of them can be rather deep; for instance, $\text{ZnTe}:\text{O}$, with $E_c - E_t = 0.4$ eV, and $\text{CdS}:\text{Te}$, with $E_t - E_v = 0.19$ eV (Cuthbert and Thomas 1967). An extensive review of the experimental observations of isoelectronic traps is given by Dean (1973a, 1973b, 1973c). Theoretical models are quite sensitive to central cell approximations (Faulkner 1968; Baldereschi and Hopfield 1972; Jaros and Brand 1979).

In contrast to the hydrogenic effective mass treatment of shallow donors or acceptors, where the central cell corrections are often minor compared to the far-reaching Coulomb contributions, such short-range potentials are dominant. Furthermore, minor deviations (by 1 %) in the estimated potential can result in major changes (by a factor of 2) of the electronic eigenstates of the defect (see Fig. 10.13).

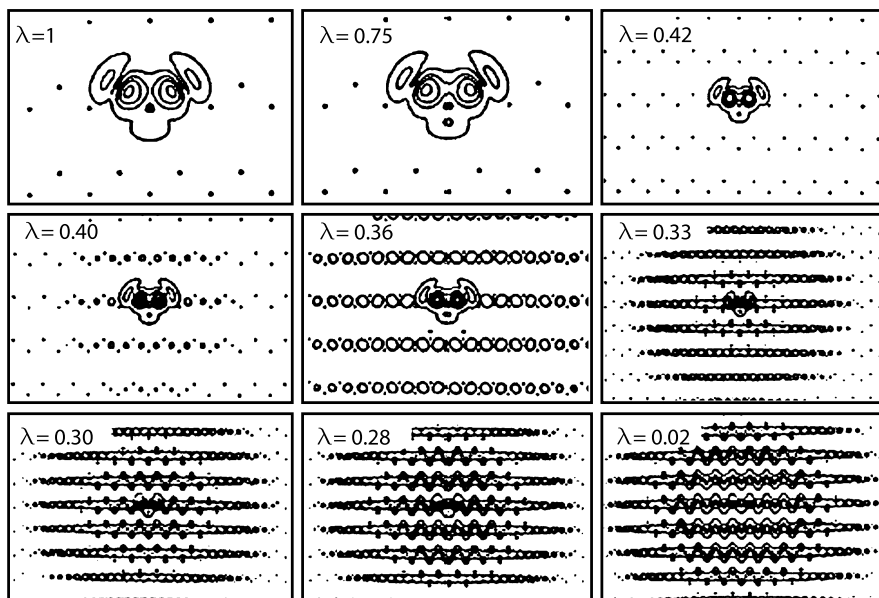


Fig. 10.13 Charge-density distribution of a substitutional impurity in Si, computed from a potential similar to Eq. (10.7) for decreasing strength of short rang potential from $\lambda = 1$ to $\lambda = 0.02$ in the nine subfigures. $\lambda = 1$ corresponds to the T_2 state of the Si vacancy (after Vigneron et al. 1982)

Extensive theoretical and experimental work has been done with GaP. GaP: O_p is discussed as one example. For reviews, see Stoneham (1975) and Pantelides (1978).

10.4.11 Chalcogens in Si

Chalcogens (O, S, Se, and Te), incorporated in Si, act as deeper donors. They easily form associates, especially oxygen. Single substitutional donors are observed for neutral and singly charged S, Se, or Te: they act as double donors. The charge density distribution of these donors has been calculated by Ren et al. (1982).

The ground state of neutral and single ionized donors is rather deep (Table 10.1), and shows a substantial chemical shift. In addition, the ground $1s$ -state is split into A , E , and T_2 states, which are non-degenerate, doubly, and threefold degenerate, respectively. The p -states are shallow and follow rather well the effective mass (hydrogen-like) approximation, as can be seen by comparison with the last column of Table 10.1.

The small difference of the ionization energy of $1s$ (A_1) states between S and Se is similar to the minor variance of the ionization energy of the free atoms, compared to a more substantial difference to Te.

The larger hydrostatic pressure coefficient of the ground state compared to the hydrogen-like centers, indicates the connection to conduction bands (in addition to

Table 10.1 Binding energy (in meV) and pressure coefficient (in meV/Pa) of ground and excited states of neutral and singly ionized chalcogens (after Wagner et al. 1984)

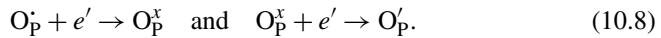
	S ^x	Se ^x	Te ^x	S [·] /4	Se [·] /4	Te [·] /4	E _{qH}
1s (<i>A</i> ₁)	318.2	306.5	198.7	153.3	148.3	102.8	31.27
1s (<i>T</i> ₂)	34.6	34.5	39.2	46.5	41.5	44.3	
1s (<i>E</i>)	31.6	31.2	31.6				
2 <i>p</i> _o	11.4	11.5	11.5	11.4	11.5	11.8	11.75
2 <i>s</i>	9.37	9.3	9.7				8.83
2 <i>p</i> _±	6.4	6.4	6.3	6.43	6.4	6.4	6.40
3 <i>p</i> _o	5.46	5.47	5.5				5.48
3 <i>p</i> _±	3.12	3.12	3.12				3.12
3 <i>d</i> _o		3.8	4.0				3.75
4 <i>p</i> _±	2.2	2.2	2.1				2.19
5 <i>p</i> _±		1.5					1.44
							−0.05
$\partial E(1s)/\partial p$ ($\times 10^{-8}$)	−1.7	−1.8	−0.9	−2.05	−2.1	−1.2	(typical)

valence bands). This shift is a result of a substantial shift in respect to the X-valley. For a review, see Grimmeiss and Janzen (1986).

Oxygen-related centers are part of the family of so-called *thermal donors*,⁸ some of which may be isolated oxygen centers, incorporated as interstitials, or combined with Si as an interstitialcy, or a substitutional. For original literature on the different types of incorporation, see Wagner et al. (1984).

10.4.12 Oxygen in GaP

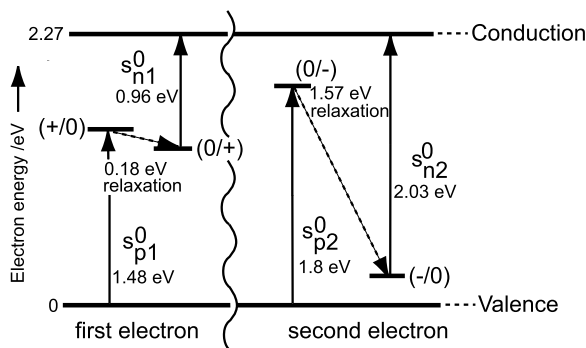
The oxygen in GaP is one of the more extensively studied defect centers, since it is of practical interest for light-emitting diodes. Incorporated as a substitutional of phosphorus, it yields two deep centers stemming from the same defect:



The first center with $(E_c - E_d) \sim 0.8$ eV has a rather small lattice coupling with a Huang-Rhys factor of $S \sim 3$: it relaxes to $(E_c - E_d)^{\text{x}} = 0.96$ eV. The second center with $(E_c - E_d)^{\text{x}} \sim 0.6$ eV relaxes to $(E_c - E_d)^{\cdot} = 2.03$ eV; that is, it has a very large Huang-Rhys factor of $S \cong 28$. The corresponding band diagram is shown in Fig. 10.14. For a review, see Dean et al. (1983).

⁸Due to the thermal nature of incorporation, i.e., during a heat treatment between 350 and 555 °C in Czochralski-grown Si.

Fig. 10.14 Band diagram of GaP with one- and two-electron Op-states at 300 K, obtained from photocapacity measurements (after Dean et al. 1983)



The strong lattice relaxation that occurs when a second electron is captured produces a lower level than that for the captured first electron. This is indicative of a *negative U-center*, which will be discussed in Sect. 10.4.10. More recent observations indicate a much more complex behavior of the different oxygen-related centers, a discussion of which is beyond the scope of this book. For a review, see Dean (1986).

With the incorporation of an acceptor in addition to Op (e.g., Zn_{aa}), the spectrum becomes very complicated. It shows a large series of additional lines which are due to donor-acceptor pairs—for a review, see Jaros and Dean (1983).

10.4.13 Other Deep Defect Centers (EL2, DX)

There is a large variety of other impurity centers which cause deep levels in the band gap. Many of these are yet unidentified with respect to their chemical origin, despite substantial technical interest in some of these centers to produce lowly conductive semiconductors for field-effect transistors.

An example of such centers is the so-called *EL2 defect*, which plays a key role in creating semi-insulating GaAs, and presents a level near the center of the band gap. Its origin is probably related to an anion antisite defect—see Sect. 10.4.4.

Another defect in III–V compounds is often referred to as the *DX center*: *D*, since it acts like a donor and, *X*, because it does not behave effective-mass-like and is probably associated with an unknown defect *X*. These centers show major lattice relaxation and have deep center characteristics. They are involved in carrier trapping and recombination traffic, and are responsible for persistent photoconductivity and large Stokes shifts (Lang and Logan 1977).

The *DX* centers are most pronounced in heavily doped *n*-type III–V compounds and alloys (e.g., AlGaAs or GaAsP—Lang 1986), and are related to the chemical nature and concentration of dopants, specifically involving S, Se, Te, Si, and Sn. The *DX* centers probably relate to interstitial configuration (for a review, see Bhat-tacharya 1988).

A very large group of deep centers are those involving transition metals. Many of them act as recombination centers. Others, such as Cu in II–VI compounds, are efficient activators for luminescence or for sensitizing the semiconductor for high-gain photoconductivity. For a review of Fe-, Cr-, and Cu-related centers, see the corresponding chapters in Pantelides (1986).

Many of these deep level centers are probably related to more complex defect structures involving an impurity, as well as adjacent lattice defects such as vacancies, interstitials, and antisites.

10.5 Negative- U Centers

In Sects. 10.4.4, 10.4.6, and 10.4.8, examples are given for a negative- U center. U is the *Hubbard correlation energy* that was introduced by Hubbard (1963) as an energy penalty when two electrons with opposite spin occupy the same site. For a free atom, U is the difference between the ionization energy and the electron affinity; typically, it is on the order of 10 eV. Embedded in a crystal lattice, U is greatly reduced by lattice shielding and interaction to generally 0.1–0.5 eV. For most crystal defects, U is positive; this means that a defect, which has several charge states, has the higher charged state closer to the related band. This ordering of levels is easily understood once it is recognized that a second electron is less bound to a defect than the first because the two electrons repulse each other.

Consequently, a negative- U center indicates that with one electron already trapped, the second one is even more attracted. This can only happen when the first electron has polarized the defect configuration sufficiently so that the second one is trapped into a substantially different defect environment: for this, a substantial lattice interaction (relaxation) is required. The electron-lattice interaction can be expressed as

$$V(u) = -\lambda u(n_{\uparrow} + n_{\downarrow}) + \frac{\beta u^2}{2}, \quad (10.9)$$

with u as the atomic displacement. For equilibrium ($\partial^2 V / \partial u^2 = 0$), we obtain for the energy of single and double occupancies $\lambda^2 / 2\beta$ and $-\lambda^2 / 2\beta$, respectively, with $n_{\uparrow}$ and $n_{\downarrow} = 0$ or 1 as spin occupancy numbers, λ as the electronic lattice coupling, similar to α_c , however not dimensionless, and β the elastic restoring term. After adding the always-positive normal Hubbard correlation energy, we have

$$U = U_n - \lambda^2 / \beta \quad (10.10)$$

which is a defect property and can become negative for large electron-lattice coupling and small lattice restoring forces. In effect, the lattice near the defect site now harbors a bipolaron, as suggested by Anderson (1975b). This can be described as forming an *extrinsic Cooper pair*, similar to the Cooper pair formation in a metal. Here, however, the *defect* center assists such pair-formation, consequently yielding a substantially increased binding energy (U). For calculation of λ , c , and U , see Baraff et al. (1980).

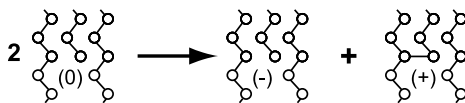


Fig. 10.15 Negative- U model by disproportionation at a dangling bond with charge character indicated (after Street and Mott 1975)

As a result, the negative- U center is not stable in its singly occupied state, since the energy (U) can be gained by trapping another carrier. Consequently, the singly occupied shallow state is not observed after the filling process (e.g., via optical excitation) is switched off and sufficient time has passed for relaxation. With continued excitation, however, both the shallow and deep states can be observed (Watkins 1984). In addition to the $\text{GaP}:\text{O}_p^x$ center, the $V_{\text{Si}}^{\bullet}$ and the $\text{Si}_i^{\bullet}$ are known to have negative U character and many more deep centers are probably of a similar type (Watkins and Troxell 1980).

10.5.1 Negative- U in Chalcogenide Glasses

Some optical and electron-spin resonance behavior of chalcogenide amorphous semiconductors can be explained by assuming negative- U centers (Street and Mott 1975). Such centers were identified by Kastner et al. (1976) as valence alternation pairs. For instance, dangling bonds in broken chains can be bound to an adjacent unbroken chain by a valence alternation, shown here as a charge disproportionation



the two dangling Se atoms in such a chain disproportionate to form a negatively charged dangling bond in one-fold coordination, shown as subscript, and one positively charged Se atom attached to the neighboring chain with threefold coordination (see Fig. 10.15), in an exothermic reaction: the charged pair has a *lower* energy than the neutral defects. The Coulomb energy between the two electrons in the negatively charged defect is more than compensated by the lattice energy. Therefore, this center is a negative- U center.

The existence of negative- U centers in amorphous semiconductors can explain the pinning of the Fermi level by such defects without showing a high density of uncompensated spins, which would otherwise be expected when compensation occurs between ordinary donors and acceptors (Fritzsche 1976).

10.6 Shallow/Deep Center Instabilities

There are centers which show metastability as a shallow or as a deep center. Examples are metal-acceptor pairs in covalent crystals or bond excitons at a donor in

AlGaAs. These centers can be explained as having a negative- U character. When occupied with one electron, they behave as a typical shallow center, but turn into a deep center when a second electron is trapped.

10.6.1 Metastable Lattice Relaxation

When a carrier is captured by a deep center, it relaxes often to a substantially lower energy. When the center has a bond, higher energy state, the degree of lattice relaxation changes and could drive the state into a metastability. The return to the ground state then requires an activation energy. The *EL2* defect in GaAs has such a state (Chantre et al. 1981). For a discussion of these metastabilities, see Hamilton (1988).

10.6.2 Transition Metal Impurities

Transition metal impurities include $3d$, $4d$, and $5d$ transition metals, $4f$ rare earth, and $5f$ actinides. All of these elements have unsaturated inner shells. Their outer-shell electrons shield part of the interaction with the host lattice. The center is described by a *tight-binding approximation*, i.e., like an individual atom, but perturbed by the surrounding lattice field—see Sect. 10.3.

The properties of the center are determined by its chemistry and its character relating to the host lattice, such as

- its *site character*, as *interstitial* or *substitutional* within a host lattice of given symmetry;
- its *charge character* in relation to the *oxidation state*, conventionally identified by its remaining valence electrons, e.g., Cr^{3+} when replacing Ga^{3+} in a GaAs lattice, and its *charge state, relative to the host lattice*, e.g., $(\text{Cr}^{3+})_{\text{aa}}$ neutral, $(\text{Cr}^{2+})_{\text{a}}$, or $(\text{Cr}^{4+})_{\text{aa}}$ as negatively or positively charged when incorporated in a GaAs lattice on a Ga site;
- its *spin character*, as *high-spin*, when the unsaturated d-shell electrons have preferably parallel spin (Hund's rule), resulting in a high electron-electron and weak crystal-field interaction, and as *low-spin*, when electrons have more antiparallel spin,⁹ resulting in weak electron-electron and stronger crystal-field interactions (see Table 10.2); and
- its *transition character* with respect to an optical excitation, for an intracenter *transition* with charge conservation at each center, or an *ionization* with charge transfer to the conduction or valence band or to another center.

⁹With parallel spins there are less alternatives to populate states of equal energy (less degeneracy). With antiparallel spin orientation, there is more degeneracy, giving the opportunity to the Jahn-Teller splitting to produce an even lower level. For transition metal impurities, Hund's rule, and for Si-vacancies, the Jahn-Teller effect produces the lower ground state (Zunger 1983).

Table 10.2 Occupancies of *d* orbitals for octahedral coordination (see Fig. 10.17)

Number of <i>d</i> electrons	High-spin		Low-spin	
	<i>t</i> ₂	<i>e</i>	<i>t</i> ₂	<i>e</i>
1	↑		↑	
2	↑↑		↑↑	
3	↑↑↑		↑↑↑	
4	↑↑↑	↑	↑↓↑↑	
5	↑↑↑	↑↑	↑↓↑↓↑	
6	↑↓↑↑	↑↑	↑↓↑↓↑↓	
7	↑↓↑↓↑	↑↑	↑↓↑↓↑↓	↑
8	↑↓↑↓↑↓	↑↑	↑↓↑↓↑↓	↑↑
9	↑↓↑↓↑↓	↑↓↑	↑↓↑↓↑↓	↑↓↑

The solubility of 3*d* impurities in Si is extremely low, typically 10¹⁴ cm^{−3}. This makes positive identification difficult since the solubility limit lies below the threshold of conventional analytic chemistry. The 3*d* elements are preferably incorporated in interstitial sites of Si, while 5*d* elements are mostly substitutionals.

The solubility of Cu and Ni in Si, however, is much larger, up to 5 · 10¹⁷ cm^{−3}. Transition metal atoms are gettered in Si by incorporated oxygen, probably by stress-enhanced diffusion toward such centers. Cu decoration of dislocations which attracted oxygen is an example.

In III–V and II–VI compounds, the solubility of the 3*d*-elements is somewhat higher, typically 10¹⁷ cm^{−3}. An exception is Mn, which forms continuous solid solutions with II–VI compounds: it produces a dilute magnetic semiconductor.

10.6.3 Site Character

Incorporated as a substitutional, the transition metal impurity entails interaction with the vacancy states. This means that certain states hybridize strongly with the corresponding states of the vacancy, e.g., the *d*(*T*₂) state of CrSi with the *T*₂ state of the vacancy (see Zunger and Lindefelt 1983). Interstitials of the Zn to Ti group have little interaction of their *d* orbital with the crystal state.

10.6.4 Charge Character

It is characteristic of these impurities that many of them have several stable charge characters (Fig. 10.16), yielding levels in the band gap with a relatively small energy difference between them, typically 0.5 eV rather than 2–3 eV. Each of these levels split due to the crystal field and the Jahn-Teller effect (dynamic and cooperative—see Bates and Stevens 1986). The strain, induced by the defect, causes a change

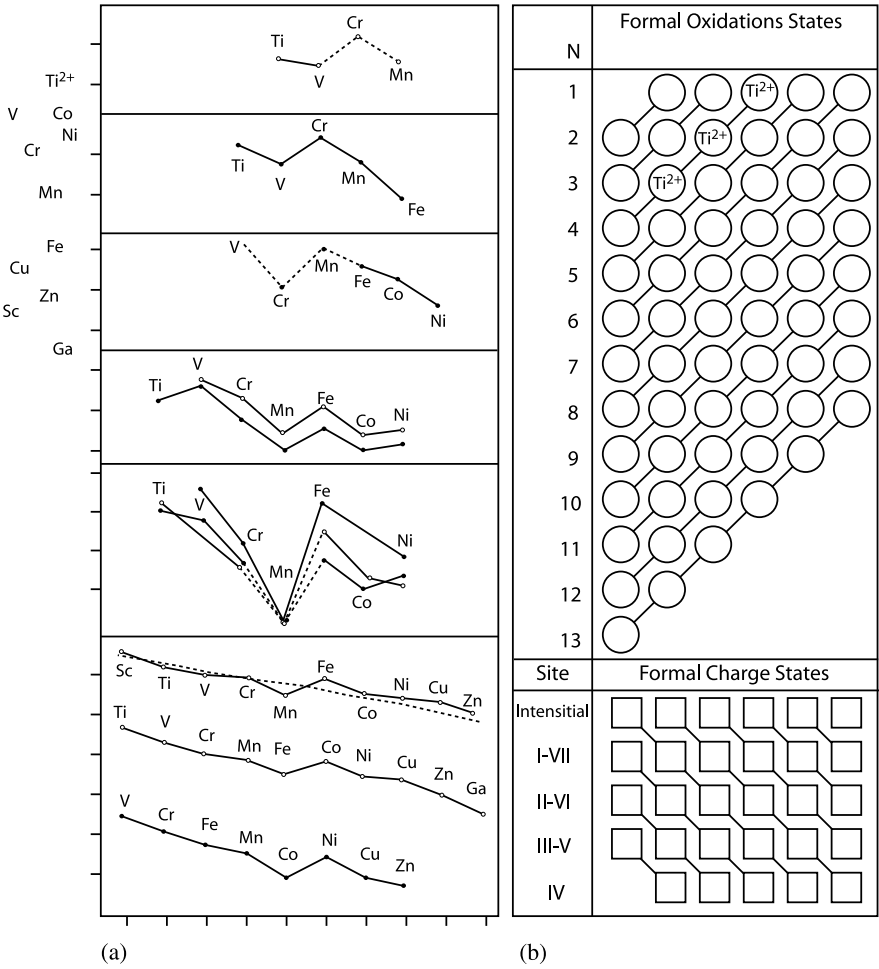
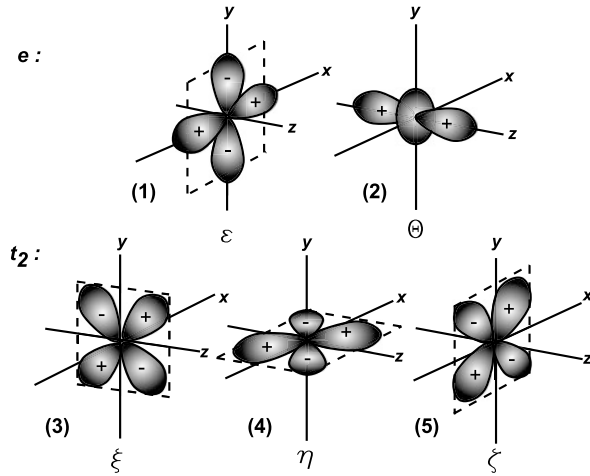


Fig. 10.16 (a) Ionization energy for 3d transition elements, free ions and as impurities in various compounds. (b) Formal oxidation states with total number N of electrons in 3d and 4s shells and free ion charges (*upper diagram*). Corresponding charges relative to the semiconductor lattice for cation substitutional incorporation (*lower diagram*) (after Zunger 1986b)

in symmetry surrounding each defect center. The tetrahedral symmetry of GaAs becomes orthorhombic with incorporation of Cr^{3+} , and tetragonal with Cr^2 (Bates and Stevens 1986). In Si, interstitial 3d impurities cause an increase in distance of the four nearest neighbors, and a decrease in distance of the six next-nearest neighbors. This makes the lattice surrounding the 3d impurity nearly tenfold coordinate (Lindelfelt and Zunger 1984).

Significant concerns include the identification of the ground state and the proper sequencing of higher excited states. A number of empirical rules are used in the classical discussions (Kaufmann and Schneider 1983). Important factors are the *Hund*

Fig. 10.17 *d*-Orbitals of wavefunctions in e symmetry (1) and (2) and in t_2 symmetry (3)–(5)



rules, which require that the ground state has maximum multiplicity ($2S + 1$) and maximum L , and that $J = L \pm S$ when the shell is less (+) or more (–) than half full (see Ashcroft and Mermin 1976).

For instance, when a Cr atom replaces a Ga atom in *n*-type GaAs and traps an additional electron, it may change from a $3d^5 4s^1$ configuration to a $3d^5 4s^2$ or $3d^3 4s^2 4p^2$ configuration; the latter is more Ga-like and more probable. The remaining three electrons in the d shell determine the defect level spectrum and distribute themselves between e orbitals, transforming to $(2z^2 - x^2 - y^2)/\sqrt{6}$, $(x^2 - y^2)\sqrt{2}$ (fourfold degenerate) and t_2 orbitals, transforming to yz , zx , xy (sixfold degenerate); lower-case letters indicate one-electron states—see Fig. 10.17.

The ground states of the differently charged Cr substitutional centers in GaAs are

$$(\text{Cr}^{4+})^\bullet \rightarrow (3d^2) \quad E - E_v = 0.45 \text{ eV}, \quad s_n = 9 \cdot 10^{-17} \text{ cm}^2$$

$$(\text{Cr}^{3+})^\times \rightarrow (3d^3) \quad E - E_v = 0.74 \text{ eV}, \quad s_n = 10^{-17} \text{ cm}^2$$

$$(\text{Cr}^{2+})' \rightarrow (3d^4) \quad E - E_c = 0.12 \text{ eV}, \quad \text{inside cond. band.}$$

Many other centers in GaAs as well as other semiconductors are identified and reviewed by Clerjaud (1985) and Zunger (1986b). A list of the different oxidation states and charges relative to the semiconductor is shown in Fig. 10.16b. The ionization energy of 3d-transition metal ions is given in Fig. 10.16a.

10.6.4.1 Transition Character

The transitions at the transition metal dopant can be described as intracenter transitions; for instance

$$(e)^2 t_2 + h\nu \rightarrow e(t_2)^2 \quad (10.12)$$

or, when carriers from one of the bands are involved, as ionization, such as, e.g.,

$$(e)^3 + h\nu \rightarrow (e)^4 + h^\cdot. \quad (10.13)$$

The corresponding energies for intracenter transitions are listed in Table 10.3 and for ionization in Table 10.4—see also Pantelides and Grimmeiss (1980).

10.6.5 The Energy of Levels

The crystal-field splitting can be estimated in tetrahedral symmetry as

$$\Delta = |E(e) - E(t_2)| = -\frac{4}{15} \frac{Ze^2}{R} \frac{\langle r^4 \rangle}{R^4}, \quad (10.14)$$

where R is the distance to the nearest neighbor (ligand) and $\langle r^4 \rangle$ is the expectation value of r^4 for the $3d$ wavefunction (Hayes and Stoneham 1984).

Here Δ increases with increasing covalency, higher charge of the transition metal, and higher transition series.

The effective crystal-field splitting is given in Table 10.5 for some of the $3d$ impurities in a few binary compounds.

The multi-electron levels in the *irreducible representation* of the tetrahedral T_d point group are a_1 , a_2 , e_2 , t_1 , and t_2 —see Bassani et al. (1974) or Madelung (1978). In Fig. 10.18, an example for the transition from the lower ${}^5T_2(t^2e^2)$ to the excited ${}^5E(t^3e^1)$ state is given for GaAs:(Cr $^{2+}$)' (Clerjaud 1985). A list of possible splitting of the free transition metal ion states after incorporation in a semiconductor of T_d symmetry is given in Table 10.6. In addition, one has to consider for splitting due to spin-orbit, lattice-phonon, and the Jahn-Teller effect interactions.

The relationship of the level spectrum to the host lattice and the chemical identity of the transition metal have been analyzed using a self-consistent quasiband crystal-field method, and employing a density-functional Green's function approach, introduced by Lindefelt and Zunger (1982).

This method was first applied to $3d$ -transition metal impurities in an Si host lattice (Zunger and Lindefelt 1983), and yields results in agreement with the experiment when spin polarization is included (Beeler et al. 1985; for comparative remarks, see Zunger 1986b). Typical examples are shown in Fig. 10.19, identifying t_2 and e states, which are contained within the bands for some of the transition metal impurities. Their energy sequence is inverted when comparing interstitial and substitutional incorporation into the host lattice.

The charge character of these levels is given in Fig. 10.21b, and identifies donors ($' \rightarrow x$) and acceptors ($\bullet \leftarrow x$). The level spectrum for substitutional defects is less structured, and no deep levels are obtained for Ti and Fe. For $4d$ impurities, see Beeler et al. (1986); for other transition metals in III–V compounds, see Clerjaud (1985).

Table 10.3 Observed excitation energies (eV) in cation substitutionals 3d-transition metal doped semiconductors (after Zunger 1986a, 1986b)

Ground state impurity	$^3A_2$ Ti ²⁺	$^4T_1$ V ²⁺	$^5T_2$ Cr ²⁺	$^6A_1$ Mn ²⁺	^5E Fe ²⁺	$^4A_2$ Co ²⁺	$^3T_1$ Ni ²⁺
Host							
ZnS	1.21 ($^3T_1$)	0.53 ($^4T_2$) 1.14 ($^4A_2$) 1.39 ($^4T_1$)	0.64 (^5E) 1.36 ($^3T_2$) 1.75 ($^3T_1$)	2.34 ($^4T_1$) 2.53 ($^4T_2$) 2.67 (^4E)	0.44 ($^5T_1$) 2.07 ($^3A_2$) 2.14 ($^3A_1$)	0.46 ($^4T_2$) 0.77 ($^4T_1$) 1.76 ($^4T_1$)	0.54 ($^3T_2$) 1.13 ($^3A_2$) 1.52 ($^3T_1$)
ZnSe	0.74 ($^3T_1$) 1.22 ($^3T_1$)	0.50 ($^4T_2$) 1.08 ($^4A_2$) 1.24 ($^4T_1$)	0.68 (^5E) 1.61 ($^3T_2$) 1.85 ($^3T_1$)	2.31 ($^4T_1$) 2.47 ($^4T_2$) 2.67 (^4E)	0.34 ($^5T_1$) 1.26 ($^3A_2$)	0.43 ($^4T_2$) 0.78 ($^4T_1$) 1.67 ($^4T_1$)	0.50 ($^3T_2$) 1.10 ($^3A_2$) 1.46 ($^3T_1$)
ZnTe	–	–	0.68 (^5E)	2.3 ($^4T_1$) 2.4 ($^4T_2$) 2.6 (^4E)	0.31 ($^5T_2$)	0.72 ($^4T_1$) 1.44 ($^4T_1$)	–
CdS	0.40 ($^3T_2$) 0.71 ($^3T_1$) 1.22 ($^3T_1$)	0.61 1.08 1.80 ($^4T_1$)	0.66 (^5E)	–	0.32 ($^5T_2$)	0.68 ($^4T_1$) 1.73 ($^4T_1$)	0.51 ($^3T_2$) 1.01 ($^3A_2$) 1.58 ($^3T_1$)
CdSe	0.38 ($^3T_2$) 0.62 ($^3T_1$) 1.18 ($^3T_1$)	0.43 ($^4T_2$) 0.86 ($^4A_2$) 1.31 ($^4T_1$)	0.62 (^5E)	–	0.37 ($^5T_2$) 0.29 (ZPL*)	0.37 ($^4T_2$) 0.35 (ZPL) 0.68 ($^4T_1$) 1.61 ($^4T_1$)	0.52 ($^3T_2$) (0.45, ZPL) 0.99 ($^3A_2$) 1.42 ($^3T_1$) (1.35, ZPL)

Table 10.3 (Continued)

Ground state impurity	$^3A_2$ T_1^{2+}	$^4T_1$ V^{2+}	$^5T_2$ Cr^{2+}	$^6A_1$ Mn^{2+}	^5E Fe^{2+}	$^4A_2$ Co^{2+}	$^3T_1$ Ni^{2+}
CdTe	0.35 ($^3T_2$)	0.82 ($^4A_2$)	0.63 (^5E)	2.2 ($^4T_1$)	0.28 ($^5T_2$)	0.37 ($^4T_2$)	—
	0.32 ($^3T_1$)	1.11 ($^4T_1$)		2.5 ($^4T_2$)		0.72 ($^4T_1$)	
	1.14 ($^3T_1$)					1.44 ($^4T_1$)	
GaP	0.60 ($^3T_2$)		0.87 (^5E)	1.34 ($^4T_1$)	0.41 ($^5T_2$)	0.56 ($^4T_2$)	0.82 ($^3T_2$)
	—	1.07		1.53 (ZPL)		0.87–1.24 ($^4T_1$)	1.24 ($^3T_1$)
						1.50 ($^4T_1$)	1.43 ($^3A_2$)
GaAs	0.565 ($^3T_1$)		0.9	—	0.37 ($^5T_2$)	0.56 (ZPL) ($^4T_2$)	1.15 ($^3T_2$)
	0.66 ($^3T_1$, $^3T_2$)	1.03	0.84 (ZPL, ^5E)			0.87–1.05 ($^4T_1$)	
	1.04 ($^3T_1$)	0.69				1.40 (ZPL) ($^4T_1$)	
InP	—	—	0.76 (ZPL, ^5E)	—	0.35 ($^5T_2$)	0.47 (ZPL) ($^4T_2$)	—
						0.92 ($^4T_1$)	—
						0.79 (ZPL)	
						0.78–0.92	

*ZPL = Zero photon line

Table 10.4 Ionization energies (eV) of substitutional 3d-transition metal dopants in compound semiconductors and interstitial 3d dopants in Si. Where levels are not yet observed, but predicted in valence or conduction bands, or in the gap, this is indicated (VB, CB, or gap) (after Zunger 1986a, 1986b)

Crystals	$h\nu$	Si	Ge	GaP	GaAs	GaSb	InP	InAs	InSb	$h\nu$
R	= 1.5 eV	0.327	0.419	0.272	0.327	0.398	0.305	0.337	0.406	= 1.5 eV
	2.0 eV	0.351	0.495	0.290	0.349	0.487	0.317	0.370	0.443	2.0 eV
	2.5 eV	0.390	0.492	0.320	0.395	0.484	0.349	0.454	0.447	2.5 eV
	3.0 eV	0.461	0.463	0.369	0.472	0.444	0.427	0.412	0.416	3.0 eV
	3.5 eV	0.575	0.502	0.458	0.425	0.485	0.403	0.371	0.474	3.5 eV
	4.0 eV	0.591	0.556	0.452	0.421	0.583	0.376	0.393	0.608	4.0 eV
	4.5 eV	0.740	0.713	0.461	0.521	0.651	0.449	0.566	0.598	4.5 eV
	5.0 eV	0.675	0.650	0.580	0.668	0.585	0.613	0.583	0.537	5.0 eV
α_o (in 10^3 cm^{-1})	5.5 eV	0.673	0.598	0.677	0.613	0.592	0.542	0.521	0.563	5.5 eV
	6.0 eV	0.677	0.653	0.583	0.550	0.610	0.461	0.448	0.572	6.0 eV
	1.5 eV	0.78	45.30	0.00	12.21	52.37	30.79	65.69	97.79	= 1.5 eV
	2.0 eV	4.47	189.12	0.00	42.79	279.43	64.32	128.43	359.46	2.0 eV
	2.5 eV	18.48	604.15	1.63	111.74	579.07	129.56	452.64	562.77	2.5 eV
	3.0 eV	81.73	652.25	68.26	592.48	641.20	379.23	618.46	606.27	3.0 eV
	3.5 eV	1069.19	946.01	290.40	714.20	902.86	691.21	622.13	892.82	3.5 eV
	4.0 eV	1454.11	1352.55	880.10	778.65	1477.21	701.54	729.23	1497.79	4.0 eV
	4.5 eV	2317.99	1960.14	994.27	1331.28	1547.17	996.95	1571.19	1320.24	4.5 eV
	5.0 eV	1806.67	1620.15	1839.99	2069.81	1394.02	1771.52	1455.26	1237.01	5.0 eV
	5.5 eV	1840.59	1584.57	1982.53	1636.68	1474.51	1428.14	1306.62	1300.55	5.5 eV
	6.0 eV	1769.27	1686.84	1635.71	1503.20	1469.28	1285.10	1284.15	1300.85	6.0 eV

Table 10.5 Effective crystal-field splitting of $3d$ impurities in binary semiconductors (after Zunger 1986b)

Impurity	Host	Δ_{eff} (eV)	Impurity	Host	Δ_{eff} (eV)
Ni	ZnS	0.520	Fe	ZnS	0.430
	ZnSe	0.510		ZnSe	0.41
	GaAs	0.91		InP	0.43
	GaP	0.97		GaAs	0.44
Co	ZnS	0.453	Mn	GaP	0.45
	ZnSe	0.459		ZnS	0.402
	InP	0.575		ZnSe	0.400
	GaAs	0.590		GaP	0.52
	GaP	0.608	Cr	ZnS	0.540
				ZnSe	0.540
				InP	0.64
				GaAs	0.65
				GaP	0.67

Fig. 10.18 Level scheme for $\text{GaAs}:(\text{Cr}^{2+})'$ with weight factors for competing transitions (not to scale); (after Clerjaud 1985)

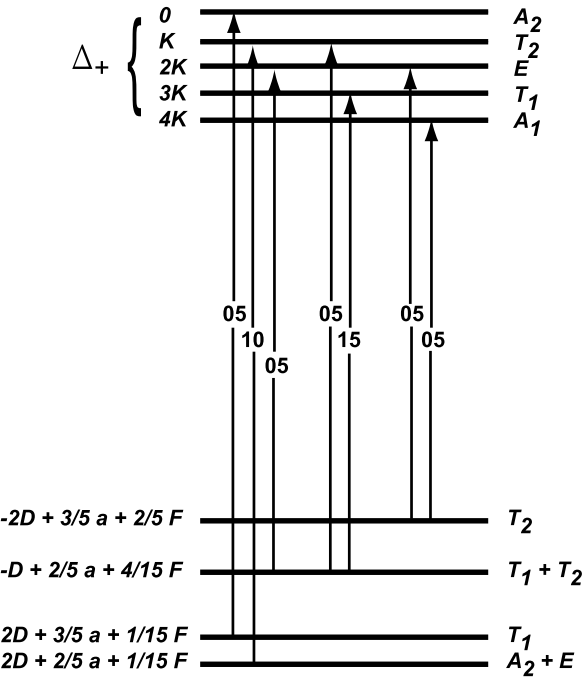


Table 10.6 Splitting of free transition metal ion terms into many electron terms after incorporation into semiconductors of T_d symmetry at lattice (*solid underlining*) or interstitial (*dashed underlining*) sites

Free-ion many-electron terms	T_d crystalline many-electron terms	Ground state	
		S	J
<i>S Terms</i>			
$\text{Fe}^{3+}, \text{Mn}^{2+}, \text{Cr}^{+}; d^5, {}^6S$	$\underline{\underline{{}^6A_1(t^3e^2)}}$	$\frac{5}{2}$	$\frac{5}{2}$
<i>D Terms</i>			
$\text{Sc}^{2+}; d^1, {}^2D$	$\frac{{}^2T_2(t^1e^0) + {}^2E(e^1t^0)}{2}$	$\frac{1}{2}$	
$\text{Mn}^{3+}, \text{Cr}^{2+}; d^4, {}^5D$	$\frac{{}^5T_2(t^2e^2) + {}^5E(t^3e^1)}{2}$	2	1, 2, <u>3</u>
$\text{Co}^{3+}, \text{Fe}^{2+}; d^6, {}^5D$	$\frac{{}^5T_2(t^4e^2) + {}^5E(t^3e^3)}{2}$	2	0, $\frac{1}{2}$, 1
$\text{Cu}^{2+}, \text{Ni}^{+}; d^9, {}^2D$	$\frac{{}^2T_2(t^5e^4) + {}^2E(t^6e^3)}{2}$	$\frac{1}{2}$	$\underline{\underline{\frac{1}{2}}}$, $\frac{3}{2}$
<i>F Terms</i>			
$\text{V}^{3+}, \text{Ti}^{2+}; d^2, {}^3F$	$\frac{{}^3T_1(t^2e^0) + {}^3T_2(t^1e^1) + {}^3A_2(e^2t^0)}{3}$	1	
$\text{Cr}^{3+}, \text{V}^{2+}; d^3, {}^4F$	$\frac{{}^4T_1(t^1e^2) + {}^4T_2(t^2e^1) + {}^4A_2(t^3e^0)}{4}$	$\frac{3}{2}$	$\frac{1}{2}$, $\frac{3}{2}$, $\underline{\underline{\frac{5}{2}}}$
$\text{Ni}^{3+}, \text{Co}^{2+}, \text{Fe}^{+}; d^7, {}^4F$	$\frac{{}^4T_1(t^5e^2) + {}^4T_2(t^4e^3) + {}^4A_2(t^3e^4)}{4}$	$\frac{3}{2}$	
$\text{Cu}^{3+}, \text{Ni}^{2+}; d^8; {}^3F$	$\frac{{}^3T_1(t^4e^4) + {}^3T_2(t^5e^3) + {}^3A_2(t^6e^2)}{3}$	1	<u>0</u> , 1, 2

The investigations of Zunger (1985) have shown some universality of binding energies within the gap. When normalized to the vacuum level using the intrinsic workfunction of the host, all binding energies of the same $3d$ impurity in different host crystals are approximately the same—see Fig. 10.20.

Transition metal atoms in covalent crystals show only minor net charges, i.e., a minor fraction of ionic bonding, and tend to approach a noble metal configuration. In Ni this is best achieved. Its extremely high diffusivity in Si ($D = 10^{-4} \text{ cm}^2 \text{ s}^{-1}$) may be an indicator of this fact as it renders the Ni atom small and inert.

The ability of transition metal impurities to trap carriers is used for compensation, i.e., to produce less conductive semiconductors.

Much of the earlier work to identify the level spectrum was done by electron-paramagnetic resonance (EPR)-Ludwig and Woodbury (1962). For a recent review, see Weber (1983).

10.6.6 The Level Spectrum of Various Point Defects

A summary of the different energies of some point defects is shown in Fig. 10.21 for the four semiconductors: Ge, Si, GaAs, and CdS (Sze 1981; Landolt and Börnstein 1982a, 1982b). This figure has to be used with some caution. The reference to certain elements often refers to the *involvement* of the element, but possibly in conjunction with other defects as an associate. A review of defect levels in Si is given by Chen and Milnes (1980).

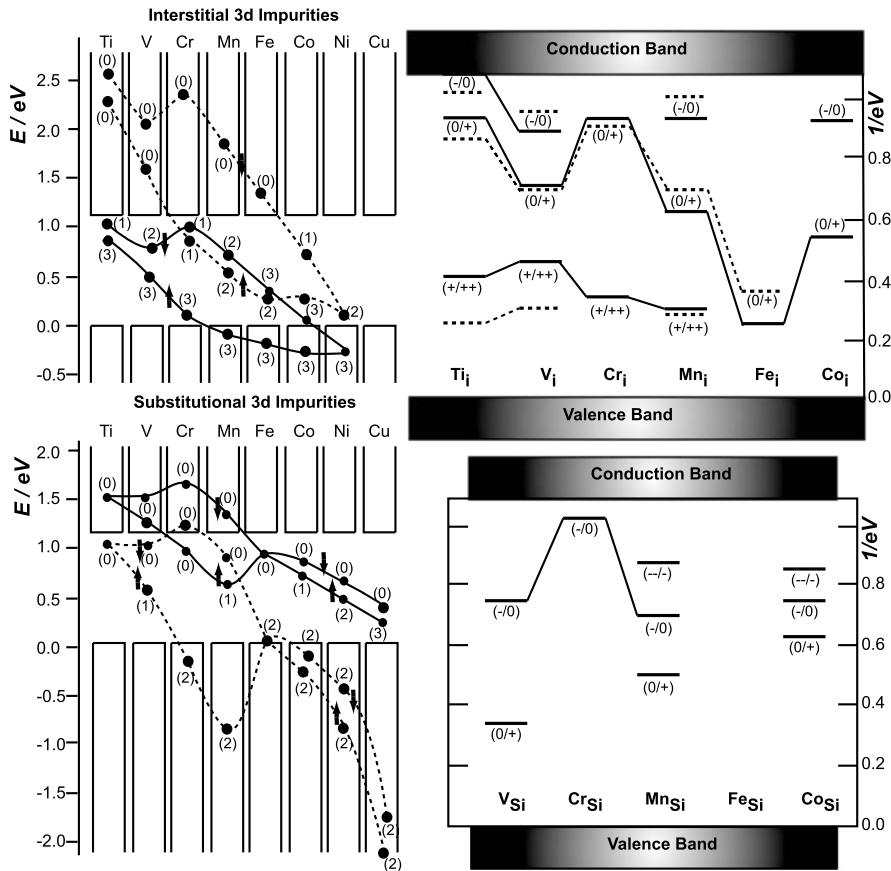


Fig. 10.19 (a) Ground-state energies of neutral 3d impurities in a Si host with level occupancy in parentheses. (b) Calculated (*solid curves*) and observed (*dashed*) 3d-impurity levels in Si at interstitial and lattice (substitutional) sites (after Beeler et al. 1985)

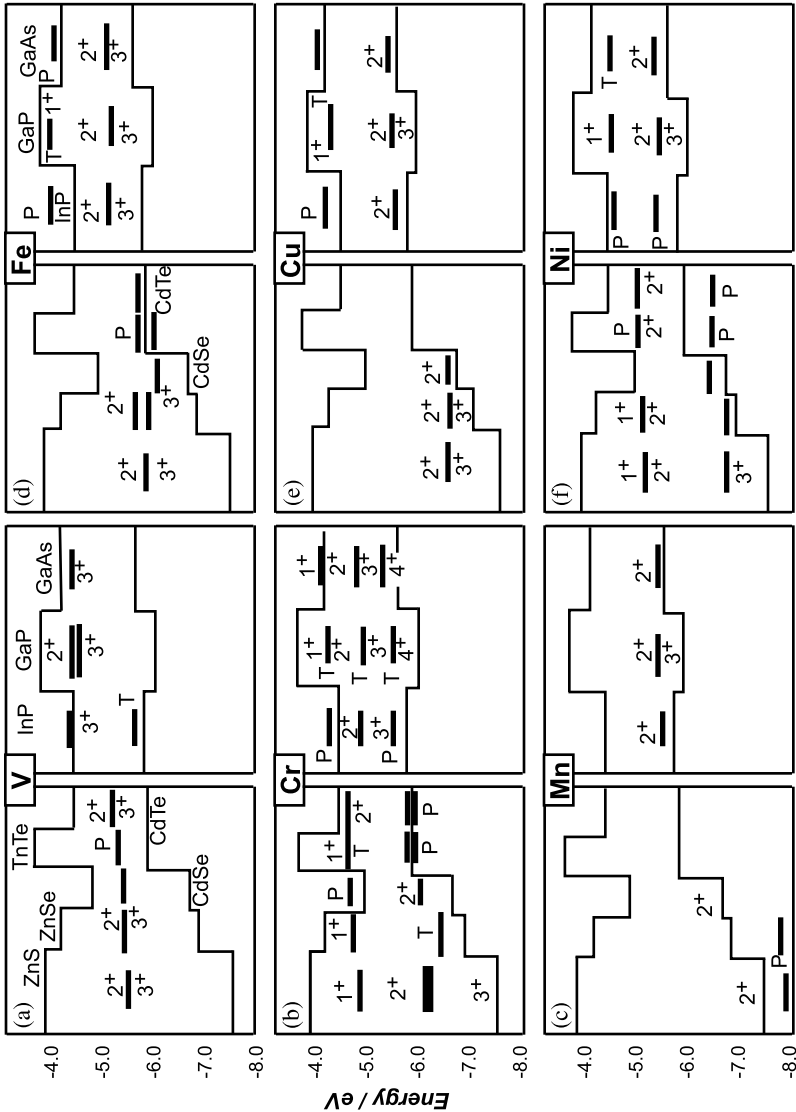


Fig. 10.20 Binding energies of 3d impurities (V and Cr) in different host semiconductors [only identified in the upper diagrams (a) and (d)]. Energies are related to the vacuum level. The numbers 1⁺, 2⁺, ... indicate stable oxidation states. P: predicted; T: tentative (after Caldas et al. 1985)

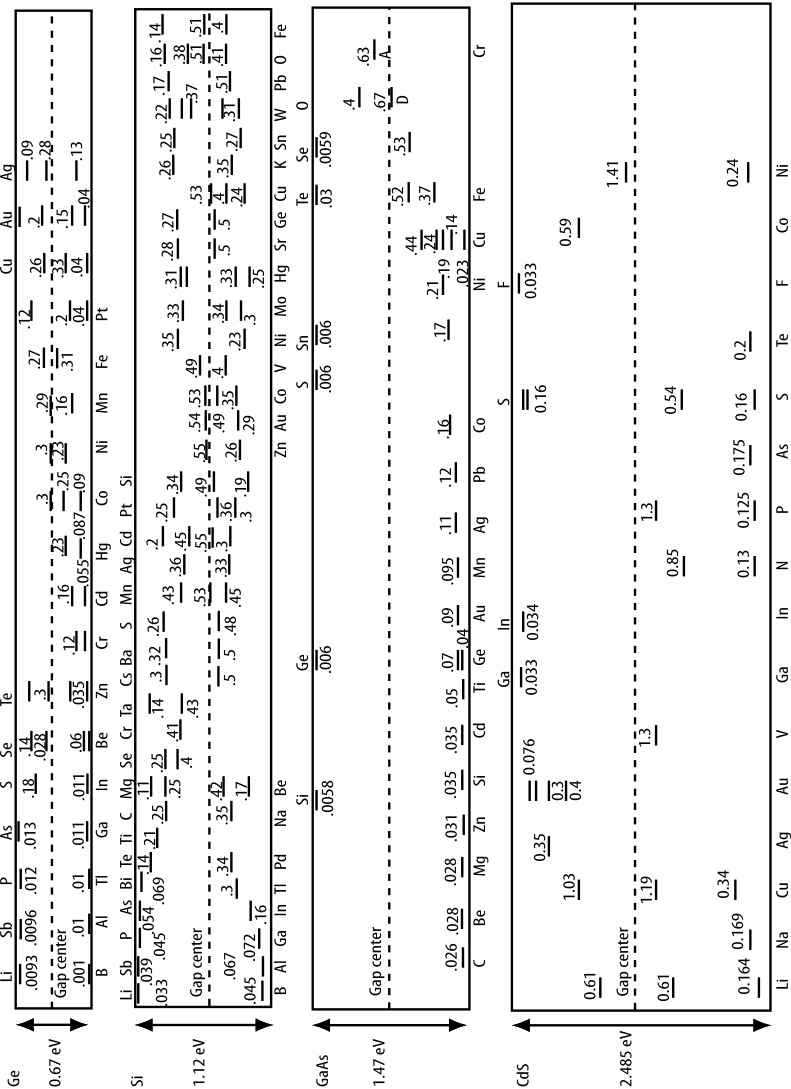


Fig. 10.21 Measured ionization energies of various impurities in Ge, Si, GaAs, and CdS from top to bottom at 300 K. Centers above and below the center of the band gap are donors or acceptors respectively, except when otherwise indicated by a D or an A (Sze 1981)

Chapter 11

Defect Associates

Abstract Defects in associates interact with each other and present a spectrum of new levels in the band gap, such as pairs, specifically donor/acceptor pairs. Examples are given Chalcogen and hydrogen pairs in Si are discussed, their energy is tabulated. Triple and higher defects are discussed. Defect clusters due to radiation damage are given. Measured atomic displacement energies are tabulated. Electron damage in II–VI compounds is given as example.

Many atomic crystal defects interact with each other, and thereby form defect associates with their own set of defect properties. There is a very large group of point defects, which easily form associates, with their nearest neighbor position energetically preferred. There can be associates of *two* or more defects, as well as larger clusters causing phase segregation.

In addition, there are defects in a heavily disturbed crystal environment which may be classified as associates of impurities with intrinsic defects, or as clusters of intrinsic defects.

In this section, a short overview is given with a few typical examples of how these centers are created, and what their main properties are.

11.1 Defect Center Pairs

Defects may arrange themselves as nearest neighbors or, statistically, in different distant pair positions. These defect pairs can act as one center if the distance between them provides sufficient overlap of their electronic eigenfunctions. Different intra-pair distances, however, produce different level spectra. Consequently, this causes a great abundance of defect levels which can be observed in the optical spectra of such defects.

11.1.1 Donor-Acceptor Pairs

The formation of *donor-acceptor pairs* is intensively studied. Since ionized donors and acceptors are Coulomb-attractive to each other, they occupy preferably nearest

lattice sites at low temperatures. In addition to electrostatic attraction discussed below, space-filling aspects also create attractive forces. For instance, incorporation of an As donor in Si causes a slight shrinkage of the lattice

$$\frac{\Delta a}{aN_{\text{As}}} \simeq -0.4 \cdot 10^{-24} \text{ cm}^3 \quad (11.1)$$

while inclusion of a Ga acceptor dilates the lattice

$$\frac{\Delta a}{aN_{\text{Ga}}} \simeq 0.8 \cdot 10^{-24} \text{ cm}^3 \quad (11.2)$$

resulting in a strain-induced attraction of Ga and As within the Si lattice. Normally, a distribution of these pairs is found with various distances between them.

Such donor-acceptor pairs may be composed of cation vacancies or impurities that act as acceptors, as well as substitutionals, cation interstitials, anion vacancies, or other impurities that act as donors. See Williams (1968), Dean (1973a, 1973b, 1973c), and Taguchi and Ray (1983) for II–VI compounds.

Donor-acceptor pairs in GaP are well-investigated. One distinguishes substitutionals of the same sublattice, such as a C_P-O_P (carbon or oxygen on a phosphorus site) pair acting as acceptor and donor, respectively, and are referred to as type-I pairs. An example of a type-II pair is Zn_{Ga}-O_P in GaP, in which the two sublattices are involved.

The energy of donor-acceptor pairs is influenced by their relative distance r_{da} and can be expressed as

$$E_{\text{da}} = E_g - (\bar{E}_d + \bar{E}_a) - \frac{e^2}{4\pi\epsilon^*\epsilon_0 r_{\text{da}}} - E^*(r_{\text{da}}), \quad (11.3)$$

where E_d and E_a are the distance of donor or acceptor levels from the respective band edges. The pair energy is substantially influenced by the Coulomb attraction between donor and acceptor, and by a correction energy term $E^*(r_{\text{da}})$, caused by overlap of donor and acceptor eigenfunctions. The latter term is much reduced at larger distances.

At low temperatures ($T < 10$ K), the absorption lines are sharp enough to distinguish a large number of pairs with different pair distance. This distance can be identified in crystallographic notation by the position of both atoms—the first assumed at 000, the second at $n_1n_2n_3$, with m the *shell number*:

$$2\hat{m} = n_1^2 + n_2^2 + n_3^2. \quad (11.4)$$

The separation distance in a cubic lattice with lattice constant a is then given for type-I pairs or for type-II pairs

$$(r_{\text{da}})_I = \sqrt{\frac{3\hat{m}}{2}}a, \quad \text{or} \quad (r_{\text{da}})_{II} = \sqrt{\left(\frac{3\hat{m}}{2}\right) - \left(\frac{5}{16}\right)}a. \quad (11.5)$$

Table 11.1 Binding energies (in meV) of chalcogen pairs in Si (after Wagner et al. 1984)

	S_2^x	Se_2^x	Te_2^x	$S_2^-/4$	$Se_2^-/4$
1s (A_{1g})	187.5	206.4	158.0	92.5	97.3
(E_u)	26.4	31.14	33.0	37.3	30.9
(A_{1u})	31.2	25.8	25.6	23.9	23.2
(E_g)	34.4	33.2			
2p _o	11.4	11.6	11.5	11.7	12.3
2p $\pm$	6.3	6.5	6.3	6.4	6.68
3p _o	5.54	5.54	5.44	5.45	5.83
3p $\pm$	3.12	3.12	3.12		3.12
3d _o	3.92	3.89			
4p $\pm$	2.2	2.2	2.1		
5p $\pm$		1.51	2.1		

11.1.2 Chalcogen Pairs in Si

Molecular pairs of S, Se, or Te act as single, deep centers with slightly lower depth than the ground states of single chalcogen substitutionals (compare the relevant binding energies in Table 11.1). Again, the higher excited states lie very close to the correspond ending hydrogen-like states.

These pairs are incorporated in (111) axial symmetry and show four 1s ground states: A_{1g} , E_g , E_u and A_{1u} —see Janzen et al. (1985). There are also mixed pairs observed, e.g., Si:S; Se or Si:Se; Te.

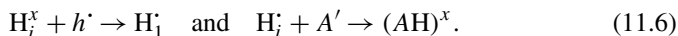
Oxygen centers are more difficult to identify because of the large variety of oxygen associates in *thermal* donors. There are interstitial pairs of oxygen and an oxygen interstitialcy replacing one Si atom proposed as possible diatomic oxygen centers. For more information on chalcogen pairs and higher associates—see Wagner et al. (1984).

Still other pairs involve vacancies. For instance, a divacancy of Cd in CdS with two holes attached is equivalent to an S2 molecule, which is covalently bound and probably rather stable. Any pair is *anisotropic*, even when embedded in an isotropic crystal. For instance, in a cubic crystal a nearest-neighbor pair can be oriented in the [100], [010], or [001] directions. Consequently, optical excitation is polarization-dependent. This can be observed by bleaching properly oriented pairs of such defects.

11.1.3 Hydrogen Pairing in Silicon

Hydrogens known to diffuse at moderate temperatures ($\leq 400^\circ\text{C}$) as an interstitial into Si. It dramatically reduces *p-type* conductivity, while it has almost no effect on *n-type* conductivity (Pankove et al. 1985). The spatial distribution of H tracks

that of acceptors (Johnson 1985); an electrically neutral hydrogen-acceptor pair is probably formed via compensation and consequent Coulomb attraction (Pantelides 1986):



Only recent computation of the total energy profiles surrounding some impurities (e.g., B or Be) has helped to identify the character and site arrangement of such defect associates with hydrogen. The total energy depends critically on the specific interstitial position of H and the relaxation of the surrounding lattice.

The disassociation energy of the B–H associate with H at the BM site, according to $(\text{BH})^x \rightarrow \text{B}' + \text{H}^x$ with H^x at a BC site, was estimated at 0.59 eV. This value is probably too low to explain the observed reactivation of B-acceptors in hydrogenated Si at $\sim 150^\circ\text{C}$ (Johnson 1985; Denteneer et al. 1989a, 1989b). The BM site lies at about 43 % off B, between B and Si in the (110) plane. The BC site lies halfway between Si atoms in an undisturbed lattice.

Other pairs in Si involve a variety of elements. Those contained in the atmosphere or supplied during crystal growth are of special interest (Taguchi and Ray 1983). Examples are pairs containing hydrogen or oxygen as a partner (Haller 1986). Because of their abundance, and the great variety of such pairs, little is yet known about them, despite highly sensitive methods of detection, e.g., photo-thermal ionization spectroscopy.

11.2 Triple and Higher Defect Centers

The variety of defects involving more than two atoms is even greater, and only the first steps of identification have been made, e.g., C, H, H, C, H, D, or C, H, T isotope combinations discussed by Haller (1986) and shown in Fig. 11.3.

Other impurities tend to order themselves and surround intrinsic lattice defects, such as four Li atoms surrounding a lattice vacancy in Si and creating a more complex defect center. Such a center is observed after irradiation of Li-doped Si with 2 MeV electrons (De Leo et al. 1984). The resulting defect level spectrum of such centers can be rather complicated, and can be measured in emission (luminescence) as well as in absorption at sufficient density of these centers (Lightowers and Davis 1985). More information about the center can be drawn from bound excitons and their behavior in a magnetic field (Fig. 11.4).

Large defect associates, e.g., $(\text{Cu}_{\text{Cd}} \text{V}_s)_n$ in CdS can finally lead to phase segregation of a small precipitate, such as, in this example, copper in CdS. A similarly well-known phase segregation is that of silver in silver halides. It can be described as a large association of F-centers, and is the basis for the photographic process.

Clustering often occurs when we want to obtain high doping densities. This develops near the solubility limit. Occasionally, the segregation occurs in the melt, and the associates remain separate because of the charging. This *colloidal* distribution can remain during solidification, and in glasses is known to be responsible

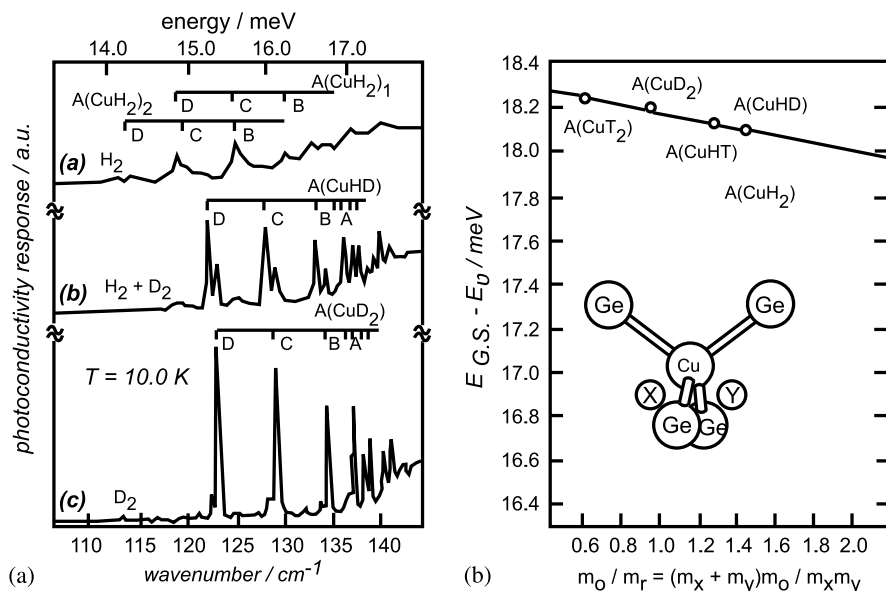


Fig. 11.3 (a) Photothermal ionization spectra of copper-dihydrogen (or isotopes) acceptors in ultrapure Ge 0 at 10 K. (b) Copper-dihydrogen complex (x and y stands for H, D, or T) and binding energies ($E_{G,s}$ is the ground-state energy of the acceptor) as a function of the reciprocal reduced mass (after Haller et al. 1986)

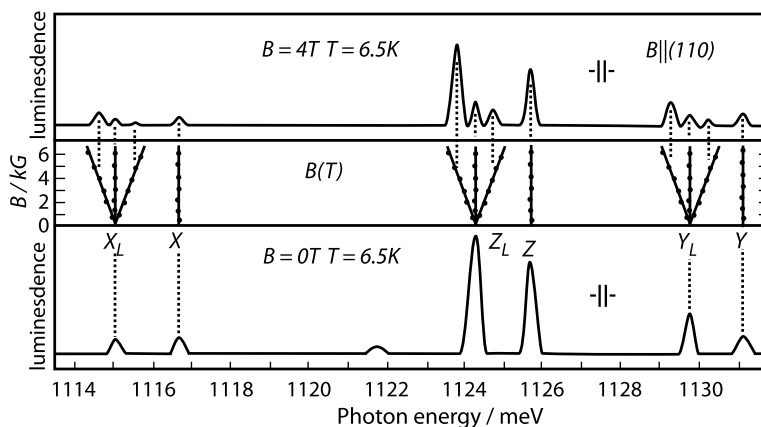
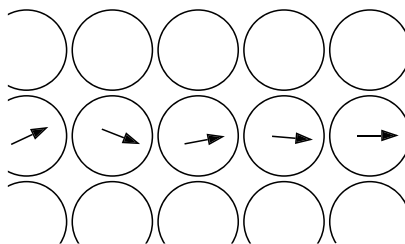


Fig. 11.4 Bound-exciton spectrum related to the (4Li-V_s) complex, which shows three triplet-singlet line pairs, revealed after application of a magnetic field (after Lightowlers and Davis 1985)

for specific spectral absorption (coloration), which is different from bulk absorption, and sensitively depends on particle size. Very high densities of defects can be created by radiation damage.

Fig. 11.5 Energy transfer in a focused collision along a row of atoms with successively more aligned secondary impacts



11.3 Defect Clusters Due to Radiation Damage

The defect associates created by radiation damage are different from the previously discussed associates. They are more of a cluster of highly disordered atoms, and can best be described by following their specific generation mode, as discussed below.

Radiation with energetic particles, such as electrons, nuclei, or ions results in the creation of lattice defects if the energy and momentum of the impacting particle are sufficiently large. The maximum transferred energy $E_{\max}$ is given by

$$E_{\max} = E_i \frac{4M_i M}{(M_i + M)^2} \quad (11.7)$$

where E_i and M_i are the energy and mass of the impacting particle, and M is the mass of the lattice atom. The energy transfer depends on the incident angle

$$E(\theta) = E_{\max} \sin^2\left(\frac{\theta}{2}\right). \quad (11.8)$$

Here θ is the scattering angle in the center-of-mass reference frame.

One distinguishes three cases:

- For a head-on collision, $\theta = \pi$, and the impacting particle is reflected back.
- When the impacting angle is almost aligned with a low index crystallographic direction, i.e., of closely packed atoms, the target atom moves in a direction even closer to the low index direction. The process continues with more and more alignment of forward motion. This is referred to as a *focusing collision* (Fig. 11.5). It proceeds until a crystal defect or the opposite surface is reached, where reflection, radiation damage, or ejection occurs (Wedell 1980; Überall and Saenz 1985).
- When the angle with a low index direction is larger, the target ion moves nearly perpendicular to the path of the incident particle.

The actual collision (scattering) event is more angle-dependent when far-reaching Coulomb forces provide the interaction, e.g., for protons or α -particles. This event does not depend on θ for so-called *hard-sphere collisions*, i.e., for neutrons or fast ions.

The value(s) before the slash refers to the first atom, and the value(s) after the slash to the second atom of a compound. A range is indicated for diamond, Ge, and II–VI compounds.

Table 11.2 Measured atomic displacement energies (in eV) in semiconductors (after Hayes and Stoneham 1984)

IV		III–V		II–VI (Fourfold Coordination)	
C	25 Graphite 35–80 Diamond	GaAs	9/9.4 6.7/8.7	ZnO ZnS	30–60/60–120 7–9/15–20
Si	13	InAs	6.7/8.3	ZnSe	7–10/6–8
Ge	13–16	InSb	5.7/6.6	CdS	2–7/8–25
Sn	12			CdSe	6–8/8–12
				CdTe	5.6–9/5–8

Table 11.3 Displacement energy thresholds for *A* or *B* Frenkel pair formation by radiation damage calculated (experimental) (after van Vechten 1980)

Crystal <i>AB</i>	$E_d(A)$ (eV)	$E_d(B)$ (eV)	Crystal <i>AB</i>	$E_d(A)$ (eV)	$E_d(B)$ (eV)
SiC	27.6	26.1	BeO	28	64 (76)
AlAs	13.7	19.5	MgO		53 (60)
AlSb	11.1	16.2	ZnO	18.5	41.4 (57)
GaN	24.3	32.5	ZnS	12.1	27.5
GaP	13.7	19.2	ZnSe	10.8 (10)	24.8
GaAs	12.4 (15–17)	17.6	ZnTe	9.5 (7.4)	21.5
GaSb	10.1	14.7	CdS	11.0 (8)	24.3
InP	12.2	16.5	CdSe	10.1	22.4
InAs	10.8	14.9	CdTe	8.7	19.5
InSb	9.1	12.9			

Here, θ is the angle between impacting and scattered particle trajectories. The first type of collision is described as *Rutherford scattering*, with a collision cross section of

$$\sigma(\theta) = \frac{R^2}{[2 \sin(\frac{\theta}{2})]^4} \tag{11.9}$$

where R is the distance of closest approach of both particles.

The result of a particle impact can be divided into metastable atomic displacements (i.e., radiation damage) and electronic ionization.

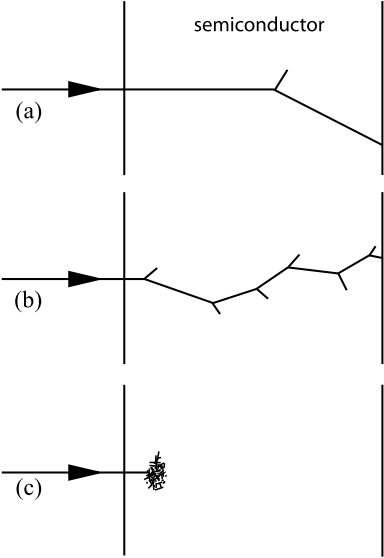
The minimum energy necessary for displacing a lattice atom after an impact is typically on the order of $5 \cdots 50$ eV, and is shown in Tables 11.2 and 11.3 for some of the semiconductors.

From energy and momentum conservation, we estimate that the minimum energy for *impacting electrons* is on the order of 100 keV to cause radiation damage. Atoms displaced in such a manner have insufficient energy to cause secondary damage; however, displacement occurs preferably in the neighborhood of lattice defects. For

Table 11.4 Electron damage in II–VI compounds with bonding energy (E_{bond}), electron threshold energy (T_d), atomic displacement energy (E_d), recoil energy for 100 keV electrons (E_{recon}), and activation energy for vacancy diffusion (E_{diff}) (after Taguchi and Ray 1983)

Compound	E_{bond} (eV)	T_d (keV)	E_d (eV)	E_{recoil} (keV)	Vacancy	E_{diff} (eV)
ZnS	5.4	240	9.9	7.9	V'_{Zn} (300 K)	1.04
		185	15.0		V_{S} (673 K)	
ZnSe	4.9	195	7.6	5.4	V'_{Zn} (373 K)	1.26
		240	8.2		V_{Se} (150 K)	
ZnTe	4.7	110	4.2	3.1	V'_{Zn} (340 K)	0.78
		300	6.7		V'_{Te} (200 K)	
CdS	5	290	7.3	5.4	V'_{Cd} (300 K)	
		115	8.7		V_{S}	
CdSe	4.9	320	8.1	4.1	V'_{Cd}	
		250	8.6		V'_{Se}	
CdTe	4.3	235	5.64	3.3	V'_{Cd} (353 K)	0.8
		340	7.79		V'_{Te}	

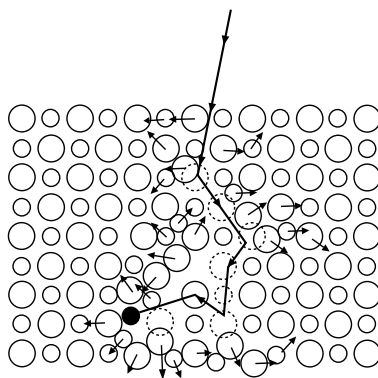
Fig. 11.6 Typical damage tracks after bombarding a semi-conductor with: (a) electrons; (b) protons or light ions; and (c) fast neutrons or heavy ions



electron-induced radiation damage, the relevant characteristic energies are listed in Table 11.4

Bombardment with *protons or neutrons* transfers substantially more energy, and results into numerous secondary damage events, which are wider-spaced for protons, and in a more compact region for neutrons. A similar, compact region of high disorder is observed after bombardment with *high energy ions*—see Fig. 11.6.

Fig. 11.7 Schematics of a variety of different disorder processes, initiated by the impact of a fast ion (after Weissmantel and Hamann 1979)



Ion bombardment from a gas discharge creates disorder in a region close to the surface. Ion implantation leaves even larger defect clusters. Figure 11.7 provides a graphic illustration of possible lattice defects after an impact with a fast ion. Careful post-treatment annealing is required to restore sufficient order to re-obtain attractive semiconductive properties (i.e., high mobility and low recombination rates), since these defect clusters usually act as major scattering or recombination centers. For a short summary, see Hayes and Stoneham (1984).

Atomic displacement at lower energy can be achieved with photons after ionization, which, in conjunction with multiphonon events, cause photochemical reactions.

Chapter 12

Defect States and Band States

Abstract Defect states and band states, band tailing is discussed. Disorder effects in semiconductor alloys are elaborated. Impurity influence on fundamental absorption with heavy doping, and shrinking of the band gap is shown. The Burstein-Moss effect is discussed.

Disordered lattices show a high density of states, extending from the band edge of ideal crystals and decreasing exponentially into the band gap.

Most point defects in an otherwise ideal lattice can be regarded as missing lattice atoms, which are replaced by lattice defects. For every defect that creates one or more levels in the band gap, the same number of levels that would have been created by the missing lattice atom within the bands are missing. Moreover, the lattice atoms surrounding the lattice defect relax into shifted positions, and also create levels which could be shifted into the band gap. Finally, thermal vibration of the lattice atoms gives rise to a perturbation of the band edge. All of these states contribute to perturbations near the band edge, and will be discussed in this chapter.

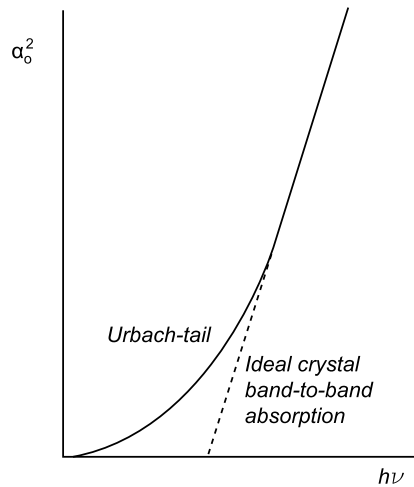
12.1 Band Tailing

For a crystal with a large concentration of point defects, the density of states inside each band is reduced. An equal number of levels extend from the band edge into the band gap as a consequence of the theorem of the conservation of eigenstates—the *golden rule*—see Bassani and Pastori Parravicini (1975).

Such a *tail of band states* into the band gap is often referred to as a *Lifshitz tail* (Lifshitz 1964). It is well pronounced in heavily doped and amorphous semiconductors, and can be experimentally observed from the spectral distribution of the optical absorption (Shklovskii and Efros 1984). For disorder due to dopants, having a correlation length on the order of interatomic spacing, the absorption coefficient shows an exponential decline and can be expressed as

$$\alpha_o = \alpha_{o0} \exp\left(\frac{h\nu - E_g}{E_0}\right). \quad (12.1)$$

Fig. 12.1 Optical absorption spectrum of a typical direct band-gap semiconductor with the absorption constant α_o proportional to the extended density of states in the Urbach tail



Here, α_{o0} and E_o are empirical parameters depending on the semiconductor and its defect structure as it relates to preparation, doping, and treatment of the semiconductor. This dependence of the optical absorption is widely observed, and is referred to as the *Urbach tail*—see Fig. 12.1 (Urbach 1953). A detailed analysis of the optical behavior is involved (Casey and Stern 1976). Some aspects of it were already discussed in Sect. 13.3. For a review, see Sa-yakanit and Glyde (1987).

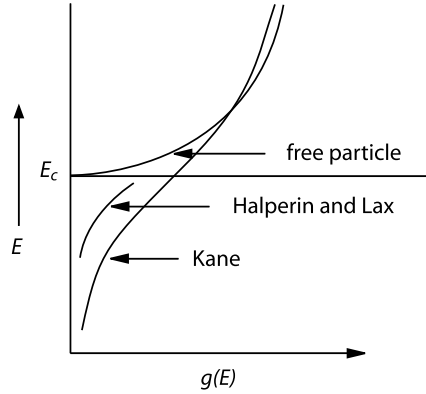
There are several approaches for estimating the level distribution caused by a statistical distribution of point defects in an otherwise ideal lattice. The general behavior can be obtained from a semiclassical model evaluated by Kane (1963)—see also Bonch-Bruevich (1962) and Keldysh and Proshko (1964). Using an independent electron model, considering the lattice by replacing m_o with m_n , and ignoring any change in the electron kinetic energy due to the impurities, the density of states is locally perturbed by the potential of lattice defects $V(\mathbf{r})$. When this potential lowers the conduction band, as a *Coulomb-attractive* center does, there are additional levels accessible to quasi-free electrons at energies below the unperturbed band edge. Near a *repulsive* center, however, there are fewer levels. That is, we assume that the density of states is given by the usual expression for a Fermi gas [Eq. (9.8)], however, with an energy scale shifted by the potential energy $eV(\mathbf{r})$ at any point $\mathbf{r}$, yielding

$$g(E, \mathbf{r}) = \frac{1}{2\pi^2} \left(\frac{2m_n}{\hbar^2} \right)^{3/2} \sqrt{E - eV(\mathbf{r})}. \quad (12.2)$$

Integrating over the entire volume, we obtain the density of states $g(E)$. This integration can be replaced by an integration over an actual potential distribution

$$g(E)dE = \frac{1}{2\pi^2} \left(\frac{2m_n}{\hbar^2} \right)^{3/2} \int_{-\infty}^E \sqrt{E - eV} f(V) dV, \quad (12.3)$$

Fig. 12.2 Density of states for quasi-free electron near the edge of the conduction band (E_c) in an ideal lattice, and Kane tail of states extending into the band gap in a lattice with random point defects (after Kane 1963). The figure also contains the results of the Halperin and Lax approximation Halperin and Lax 1966, 1967)



with $f(V)$ as the distribution function of the potential. $V(\mathbf{r})$ is assumed to be variable with a Gaussian distribution around a mean potential V_0 , i.e.,

$$f(V) = \frac{1}{\sqrt{\pi \bar{V}^2}} \exp \left\{ -\frac{(V - \bar{V})^2}{\bar{V}^2} \right\}, \quad (12.4)$$

where $e^2 \bar{V}^2$ is the mean square potential energy:

$$e^2 \bar{V}^2 = \frac{e^4}{(4\pi \epsilon \epsilon_0 r_0)^2} \frac{4\pi}{3} r_0^3 N, \quad (12.5)$$

N is the density of charged centers, and r_0 is the Debye screening length. Consequently, we obtain from Eqs. (12.3) and (12.4)

$$g(E)dE = \frac{1}{2\pi^2} \left(\frac{2m_n}{\hbar^2} \right)^{3/2} \int_{-\infty}^E \frac{\sqrt{E - eV}}{\sqrt{\pi \bar{V}^2}} \exp \left\{ -\frac{(V - \bar{V})^2}{\bar{V}^2} \right\} dV. \quad (12.6)$$

At high energy within a band ($E \gg eV$), Eq. (12.6) yields the unperturbed density of states, e.g., for the conduction band:

$$g(E)dE = \frac{1}{2\pi^2} \left(\frac{2m_n}{\hbar^2} \right)^{3/2} \sqrt{E - E_c} dE. \quad (12.7)$$

That is, high within a band, there are no changes in the density of states compared with the ideal lattice. For $E < E_c$, however, the density of states is modified to

$$g(E)dE = \frac{1}{4\pi^2} \left(\frac{m_n}{\hbar^2} \right)^{3/2} \sqrt{E^2} (E_c - E)^{-3/2} \exp \left(-\frac{(E - E_c)^2}{E^2} \right) dE, \quad (12.8)$$

with $E^2 = e^2 V^2$. Equation (12.8) indicates that $g(E)$ decreases exponentially ($\propto \exp(-E^2)$) below the edge of the conduction band—see Fig. 12.2. For a review of more rigorous approaches, see Shklovskii and Efros (1984).

Halperin and Lax (1966, 1967) developed a quantum-mechanical theory for deeper tail states, based on statistical fluctuation of the potential of lattice defects. They apply a variational method that maximizes the density of states with respect to the wavefunction containing statistically fluctuating potentials of Coulomb centers, which are assumed to be of the Yukawa screened Coulomb type. The Halperin and Lax theory gives the level distribution in the tail as

$$g(E)dE = c(v) \exp \left\{ -\frac{a_{\text{qH}}^2}{16\pi N \lambda_{\text{scr}}^5} b(v) \right\} dE, \quad (12.9)$$

with $v = 2m_n|E|\lambda_{\text{scr}}^2/h^2$, a_{qH} as the quasi-Bohr radius, and λ_{scr} as the screening length.¹ The value of $b(v)$ is approximately 10 for $v = 1$, increases $\propto v^2$ for $v \gg 1$, and decreases $\propto v^{1/2}$ for $v \ll 1$; $c(v)$ is a proportionality factor that varies only slowly with v compared to the exponential. The Halperin and Lax distribution is also shown in Fig. 12.2, and decreases more rapidly than the Kane approximation.

Other more rigorous estimates of the density of state distribution (Sa-yakanit and Glyde 1980, 1982) near the band edge also use randomly distributed Coulomb-attractive centers and employ a Feynman's path-integral method (Feynman and Hibbs 1965).

They obtain analytic results for $g(E)$, which can be written as

$$g(E) \propto \exp \left(-\frac{E_L^2}{2\bar{E}^2} c(v) v^{n(v)} \right). \quad (12.10)$$

Here, $v = (E_c - E)/E_L$; $E_L = h^2/(2m_n L^2)$ is the energy to localize an electron within the correlation distance L ; and $c(v)$ is a slowly varying function of the order of 1/10. The exponent n depends on this correlation distance (Sa-yakanit 1979) as

$$n(v) = \frac{32v}{(\sqrt{1+16v}-1)(\sqrt{1+16v}+7)} = \begin{cases} 2 & \text{for } v \rightarrow \infty \text{ or } L \rightarrow \infty, \\ 0.5 & \text{for } v \rightarrow 0 \text{ or } L \rightarrow 0. \end{cases} \quad (12.11)$$

With a correlation distance of the defects typically between 1 and 10 Å, n is usually bracketed between 1 and 1.2, yielding with $c(1) \approx 1/(18\sqrt{3})$

$$g(E) \propto \exp \left[-\frac{E_L^2 c(1)}{2\bar{E}^2} \left(\frac{E_c - E}{E_L} \right)^n \right] \simeq \exp \left(-\frac{E - E_1}{E_0} \right) \quad (12.12)$$

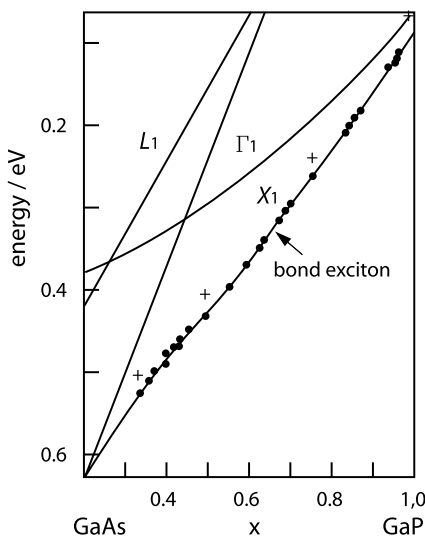
and

$$E_0 \simeq \frac{2\bar{E}^2}{E_L c(1)} \simeq 0.06 \frac{\bar{E}^2}{E_L}. \quad (12.13)$$

For semiconductors with $m_n \cong m_0$, we have $\bar{E}^2/E_L \cong 1$ eV; hence, $E_0 \cong 0.06$ eV. E_0 is identical with the characteristic energy for the Urbach tail.

¹For a self-consistent determination of the screening, which depends on the carrier density, which in turn depends on the level density, which again is influenced by the screening length—see Hwang and Brews (1971).

Fig. 12.3 Band minima positions and ground state energies for N -donor (+) (after Jaros and Brand 1979) and bound exciton (zero-phonon) line (after Wolford et al. 1976)



These results confirm the tailing nature for deeper tail states, calculated numerically by Halperin and Lax. They approach the Kane approximation in the classical limit, and result in an improved agreement with the experiment (Sritrakool et al. 1985, 1986).

For heavily doped semiconductors with lower effective mass ($m_n < 0.1m_0$), the correlation length is on the order of the screening length, i.e., typically 20–100 Å. The characteristic energy of such semiconductors is typically one to two orders of magnitude smaller than given above. Here the extent of the Urbach tail is much reduced in agreement with the experiment Sritrakool et al. 1986.

12.2 Disorder Effects in Semiconductor Alloys

Semiconductor alloys contain homologous elements at a nonstoichiometric ratio. Alloys can be formed in element semiconductors such as $\text{Si}_\zeta\text{Ge}_{1-\zeta}$ in binary compounds such as $\text{Al}_\zeta\text{Ga}_{1-\zeta}\text{As}$, or in higher compounds such as $\text{CuInSe}_{2(1-\zeta)}\text{S}_{2\zeta}$ etc.

Except for stoichiometric ratios [e.g., $\text{Al}_\zeta\text{Ga}_{1-\zeta}\text{As}$ for $\zeta = 1/4, 1/2$, and $3/4$ (Kuan et al. 1985), or GaInP_2], the atoms in the alloyed sublattice are statistically arranged. This causes random fluctuation of the composition in the microscopic volume elements of the crystal, and results in a broadening of resonances that depend on composition. Such resonances can be due to oscillating lattice atoms (phonon spectrum) or to specific electronic eigenfunctions (band edge, exciton spectrum, and defect excitation spectra). They are caused by the different masses, radii, and binding forces of the substituting atoms, which influence the lattice force constants, microscopic symmetry, band gap, dielectric constant, and other derived material pa-

rameters. Although the relative variation of some of these parameters is small, the result of such a fluctuation can result in sizable effects.

The shift of shallow levels from one band, e.g., the Γ point in GaAs, to a different one, the X point in the indirect gap of GaP, is shown in Fig. 12.3 for various degrees of alloying in $\text{GaP}_{\zeta}\text{As}_{1-\zeta}$.

The shift of the optical absorption edge caused by the changing composition was discussed in a previous section. A fluctuation in ζ results in band-gap fluctuations, which result in extended or localized states close to the band edge $E_g(\zeta)$.

The exciton state also varies from position to position, depending on the actual (local) values of ζ :

$$E_{\text{exc}}(\mathbf{r}) = E_g(\mathbf{r}) - E_b(\mathbf{r}), \quad (12.14)$$

where E_b is the binding energy. Thereby, it results in a line shift, shown in Fig. 12.3, and a line broadening. This shift is distinctively different from the shift of a donor with pressure, where the energy difference to the lowest band does not change. For a review, see Jaros (1985).

12.3 Impurity Influence, Fundamental Absorption

In *heavily doped* semiconductors, the absorption edge is shifted and deformed due to several reasons:

- tailing of band states into the band gap;
- shrinking of the band gap because of many-body effects and partial filling of the conduction band states with electrons (Burstein-Moss effect).

Such changes can be detected via excitation spectroscopy (Wagner 1985), with an optical transition probability from filled states in or near the valence band to empty states in the conduction band. For reasons relating to highly disordered lattices, we will deviate here from this treatment as explained below.

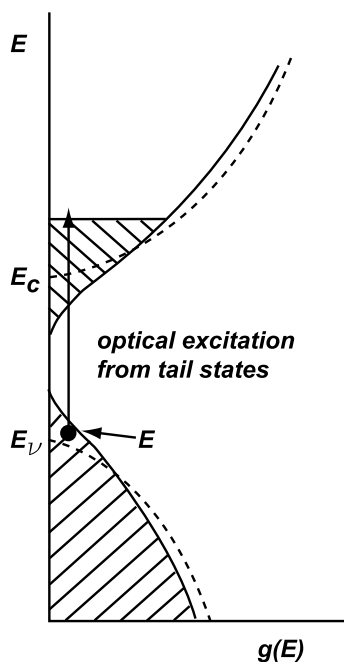
Since the translational symmetry is broken by the random potential of the impurities, k is no longer a good quantum number. Consequently, it is more appropriate to use the energy as a label, yielding for the absorption coefficient (Abram et al. 1978)

$$\alpha_o(v) = \frac{\pi e^2 \hbar^2}{m_0^2 v c n_r} \int f_n(E) f_p(E + hv) P_i(E, E + hv) N_v(E) N_c(E + hv) dE, \quad (12.15)$$

where the probability P_i can be expressed by the sum of the matrix elements in a small energy interval around E and around $E + hv$:

$$P_i(E, E + hv) = \frac{1}{3} \sum \left| \int \psi_E \nabla_j \psi_{E+hv} dp \right|^2. \quad (12.16)$$

Fig. 12.4 Optical transition from tailing states of the valence band to free states above the Fermi level within the conduction band



Examples of some quantitative estimates of such probabilities are given by Lasher and Stern (1964), Casey and Stern (1976), and Berggren and Sernelius (1981).

$N_v(E)$ and $N_c(E + h\nu)$ are the density of state functions near the respective band edges. These band edges are deformed from the ideal band distribution by the tailing of states, due to band perturbation from the random impurity potential as described in Sect. 12.1.

The occupancy factor, given by the Fermi distributions $f_n(E)$ and $f_p(E + h\nu)$, accounts for the probability of finding occupied states near the valence band edge (E) and empty states near the conduction band edge ($E + h\nu$). The tailing of valence band states and partial filling of conduction band states with heavy doping result in an asymmetric excitation, e.g., for n -type material from the tail of the valence band states to states above the Fermi level. These upper states may be shifted to lie well within the conduction band—Fig. 12.4.

12.4 The Burstein-Moss Effect

In semiconductors with a low effective mass, the density of states near the lower edge of the conduction band can be so low that even with moderate donor doping, the lower states in the conduction band become filled. Hence, the Fermi level can be

Fig. 12.5 Band edge shift of HgTe due to the Burstein-Moss effect, caused by Al doping at densities of 0.75 , 1.45 , 3.12 , and $3.8 \cdot 10^{18} \text{ cm}^{-3}$ for curves 1–4, respectively (after Verie 1967)

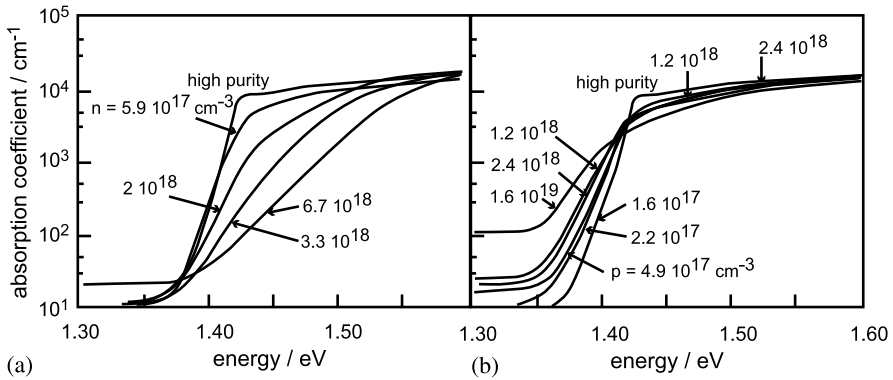
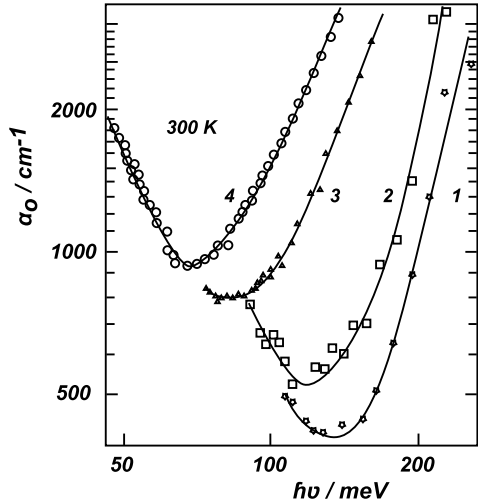


Fig. 12.6 Absorption coefficient for (a) *n*-type and (b) *p*-type GaAs measured at room temperature with doping densities as family parameter (after Casey et al. 1975)

significantly shifted above this band edge.² Since an optical excitation can proceed only into free states, this filling results in a shift of the absorption edge toward higher energies, causing a *band-gap widening* (see Moss 1961a). The shift, referred to as *Burstein-Moss shift*, can be estimated from the position of the Fermi level:

$$E_{g\text{B-M}} \simeq E_{g0} + (E_F - B_c). \quad (12.17)$$

²For instance, in InSb with $m_n = 0.0116$, the effective density of states is $N_c \cong 3 \cdot 10^{16} \text{ cm}^{-3}$; hence doping with a shallow donor density in excess of 10^{17} cm^{-3} will cause a significant filling of conduction band states.

With this effect, a fine-tuning of the absorption edge can be achieved, which is used to produce optical filters of a rather precisely determined long wavelength cut-off. An example is given in Fig. 12.5 for HgTe.

The *band edge narrowing*, and the tailing of band states, complicate this picture, as they have the opposite effect of the Burstein-Moss shift. In GaAs, both effects can be seen. The change of the optical absorption with higher doping densities, measured by Casey et al. (1975), shows the tailing (Fig. 12.6). In *n-type* GaAs, the Burstein-Moss shift predominates because of the lower effective mass for electrons, causing a significant shift of the Fermi level into the conduction band. For similar doping densities in *p-type* GaAs, however, the heavier hole mass permits only a negligible Burstein-Moss shift. Therefore, the shrinking of the gap and tailing state transitions provide the major cause for the changes in the absorption spectrum: the absorption edge shifts in the opposite direction, and the effective band gap narrows—see Fig. 12.6.

Chapter 13

Defects in Amorphous Semiconductors

Abstract Defects in amorphous semiconductors manifest themselves as band tailing. Classes of amorphous semiconductors, examples are given. Defect types in amorphous semiconductors are enumerated. Strain-related defects are discussed. Under and over coordinated defects are defined. Dangling and floating bonds are explained. Deviation from optimal bonding is shown. Doping in semiconducting glasses is explained. Microcrystalline boundaries and void are discussed. Recrystallization of amorphous Si is shown. Defect spectrum in amorphous semiconductors are given. Anderson model and localization, and Anderson-Mott localization are differentiated. Band tails and localization are summarized.

Defects in amorphous semiconductors can be defined with respect to specific classes of such semiconductors. Most of these defects are rather gradual displacements from an ideal surrounding.

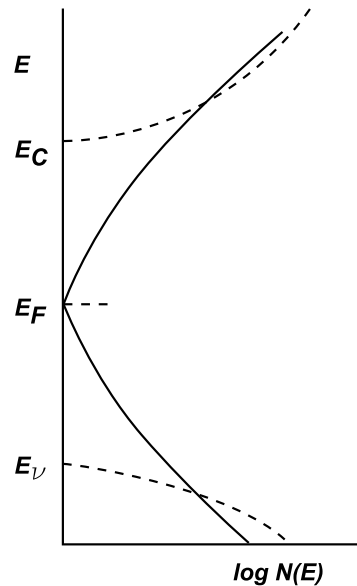
In the preceding chapter, we have shown that heavily disordered crystalline semiconductors have band tails extending into the band gaps. In some respects, *amorphous* semiconductors may be described as heavily disordered crystals. Therefore, it is reasonable to explain some of their properties also with the concept of tailing states into the band gap (Mott 1987).

13.1 Band Tails

Band tails, induced by disorder, are often referred to as *Lifshitz tails* (Lifshitz, 1964). When the degree of disorder is very large, the tailing states from valence and conduction bands may overlap (Fig. 13.1). It was originally believed that the transfer of electrons from donor- into acceptor-like states would pin the Fermi level near the center of the band gap properties do not support this explanation. A negative correlation energy of defects, caused by negative U-centers, is probably the reason for such pinning (Kastner et al. 1976). We will explain this behavior in Sect. 13.2.

Such behavior is suggested for the *chalcogenide glasses*, which are alloys containing elements of group VI and others, such as of groups IV and V, as the main glass-forming components; for instance, α -Te₄₀As₃₅Si₁₅Ge₇P₃, a well-known ma-

Fig. 13.1 Strong tailing of states into the band gap and pinning of the Fermi level in the gap center in a semiconducting glass



material because of its switching¹ capability (Cohen et al. 1969). In these materials, it is nearly impossible to move the Fermi level from its near-midgap position by doping. Some chemical modification, i.e., changing its conductivity to become extrinsic while maintaining the band gap, however, was achieved in a few chalcogenide glasses by adding modifying elements.

These should not be confused with dopants, since the necessary concentration of the modifier is relatively large to become effective. As such modifiers, the transition metals Ni, Fe, and Co can be used, and also in some instances, W, B, or C (Ovshinsky 1977, 1980). For a review, see Adler (1985).

However, *tetrahedrally bound amorphous semiconductors*, such as α -Si:H, behave substantially different: these materials, when properly prepared, react easily to doping with a shift in their Fermi level much like a crystalline semiconductor. These semiconductors can be made *n-type* or *p-type* by doping with donors or acceptors, respectively. Nevertheless, α -Si:H also has a strong tailing of defect states into the band gap, although these tails do not overlap significantly near the center of the band gap.

Before exploring the specific nature of defects in amorphous semiconductors, it is prudent to emphasize the distinction of these two classes of semiconductors.

¹Bipolar devices made from such materials are capable of switching at high speed from a low to a high conducting state at a critical bias (Ovshinsky 1968).

13.2 Classes of Amorphous Semiconductors

There are at least two different classes of covalent amorphous semiconductors, distinguished by their electronic reaction to changes in the defect structure. The first class of *amorphous chalcogenides* includes multicomponent alloys, mentioned in the previous section, as well as the less complex compounds, such as α -As₂Se₃ and monatomic α -Se. Typically, these chalcogenides have a low average coordination number, below 2.4. For comparison, the average coordination numbers of some crystals with relatively low values are given here, e.g., 4 for Si, Ge, GaAs, etc., 3 for As or GeTe, 2.7 for GeTe₂, 2.4 for As₂Se₃, and 2 for Se (Adler 1985).

The other class is composed of *tetrahedrally bound amorphous semiconductors*, such as α -Si:H, α -GaAs, and α -CdGeAs₂, with an average coordination number >2.4 . A third class, somewhat in between these two, contains α -P and α -As.

Aside from a pinning of the Fermi level due to overlapping tail states for the first class, and sensitivity to doping for the second class, there are other experimental distinctions for these two major groups. These relate to the strength of *electron-spin resonance* (ESR) signal, which indicates the existence of unpaired spin electrons (charged defects); the steepness of the *optical absorption edge*, which indicates the degree of band tailing; and other properties relating to carrier transport.

13.3 Defect Types in Amorphous Semiconductors

Defects are easily identified in *crystal lattices*, where vacancies, interstitials, and even small deviations from the periodic structure can be identified. This is much more difficult in *amorphous semi-conductors*, where deviations from the average *bond length* a , *bond angle* Θ , and *coordination number* m are the principal defect features. In general, many defects in glasses are of a gradual rather than distinct nature, and may be classified into

- local strain-related defects, i.e., variations of a , Θ , and m ,
- deviation from an optimal bonding configuration,
- incorporation of small concentrations of impurities,
- dangling or floating bonds,
- microcrystallite boundaries, observed in some glasses, and
- variably sized small voids.

Most of these defects cause changes in the electron energy spectrum by deforming the band edge and extending states into the band gap. Depending on the type of amorphous semiconductor, the ensuing defect spectrum may extend nearly exponentially from the band edge into the band gap, the Urbach tail, or may produce well-defined-although broad-peaks of the distribution function within the gap (Fig. 13.2).

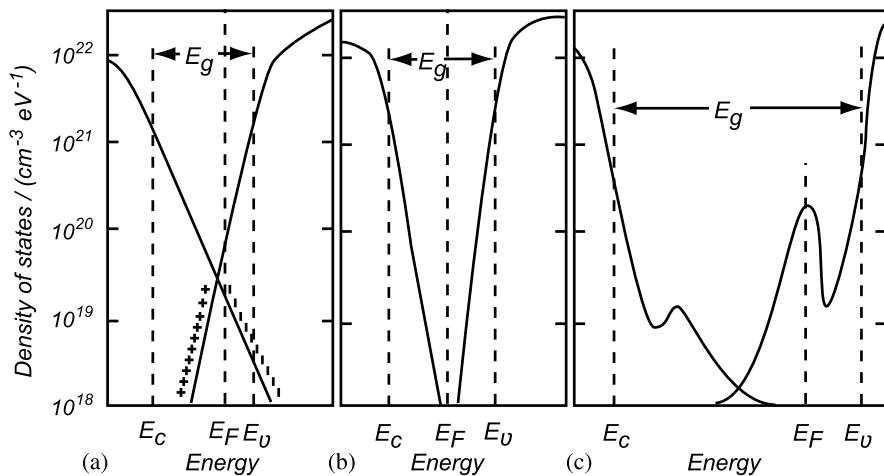


Fig. 13.2 Exponential distribution of states into the band gap: (a) in chalcogenide glasses; (b) in tetraivalent glasses; and (c) in tetraivalent glasses with distinct peaks

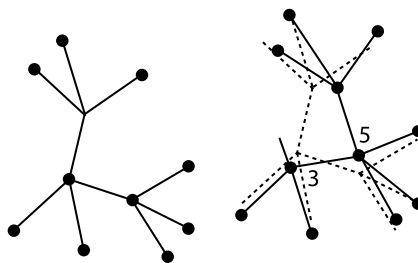
13.3.1 Strain-Related Defects

The *local strain-related defects* may be seen as similar to acoustic phonon-induced deformations of the band edge. Here, however, they are caused by a stationary, frozen-in strain, often also with a larger amplitude than for thermal phonons. Each of these stretched bonds or deformed bond angles can produce a level in the band tail when the deformation from the ideal values is sufficiently large. In tetrahedrally bound semiconductors, deviations of the bonding angle and coordination number can also result in different types of bonding between neighboring atoms. For instance, in amorphous Si, an sp^3 -, an sp^2 -hybrid, or a p^3 -configuration produces a neutral, positively, or negatively charged dangling bond, while s^2p^2 -hybrid produces a twofold coordinated Si atom. These bonds may be formed to relieve some of the stress. The corresponding bond angles are 109.5° (sp^3), 120° (sp^2), and 95° (sp^3 and s^2p^2) (Adler 1985).

Often, these defect centers are identified as A_m^e , with A identifying the chemical specie: **T** for tathogen, **P** for pnictogen, and **C** for chalcogen, i.e., elements of the IV, V, or VI groups, respectively; m is the coordination number and e is the charge character relative to the lattice (‘, ‘, ‘, ‘ or ‘).

For instance, T_4^x represents a neutral, fourfold coordinated Si atom, while T_3^x describes a neutral dangling bond, both for the sp^3 ground state. As possible defects in α -Si, all of Ti_2^x , Ti_2^x , $Ti_2^x Ti_2^x$, Ti_2^x , as well as T_3^x , T_3^x and T_3^x , are being considered as centers with lower-than-normal coordination, and as possible alternatives for local stress-relief.

Fig. 13.3 Pair creation (and recombination) of dangling (3) and floating (5) bonds (after Pantelides 1988)



13.3.2 Under- and Over-Coordinated Defects

There is evidence that two types of “intrinsic defects” are prevalent in α -Si:H the threefold coordinated Si-atom, which is equivalent to a vacancy in crystalline Si, and the fivefold *over-coordinated*

Si-atom, equivalent to a self-interstitial. These two types can be created in pairs, as indicated in Fig. 13.3, somewhat similar to a Frenkel pair creation. This reaction may be initiated by light and provides a possible mechanism for the Staebler-Wronski effect (Pantelides 1987).

13.3.3 Dangling and Floating Bonds

Dangling bonds do not seem to play a major role in most semi-conducting glasses of technical interest. The elimination of these dangling bonds can be obtained, for example, by H or F in α -Si:H or α -Si:F. Such removal results in the major differences between the amorphous Si and the amorphous Si:H or Si:F alloys. The description as an alloy is used here since a large atomic fraction ($>10\%$) of H or F is incorporated. As a consequence of the dangling bond removal, α -Si:H or α -Si:F can be doped and turn *n*- or *p*-type, similar to crystalline Si, as shown in Fig. 13.4a.

The dominant intrinsic defect in α -Si:H, the *D-center*, characterized by paramagnetic resonance ($g = 2.0055$), was initially assigned to the dangling bond, i.e., a threefold coordinated Si-atom.

Recently, however, evidence is growing that the center may be related to a floating bond, i.e., the fivefold coordinated Si-atom (Pantelides 1988). The close relation of these two centers is shown in Fig. 13.5. In contrast to the dangling bond, the floating bond is highly mobile and is of interest to interstitial-mediated diffusion.

13.3.4 Deviation from Optimal Bonding Configuration

The *deviations from an optimal bonding configuration* occur predominately in chalcogenide glasses, and may be understood by comparing the relative bonding

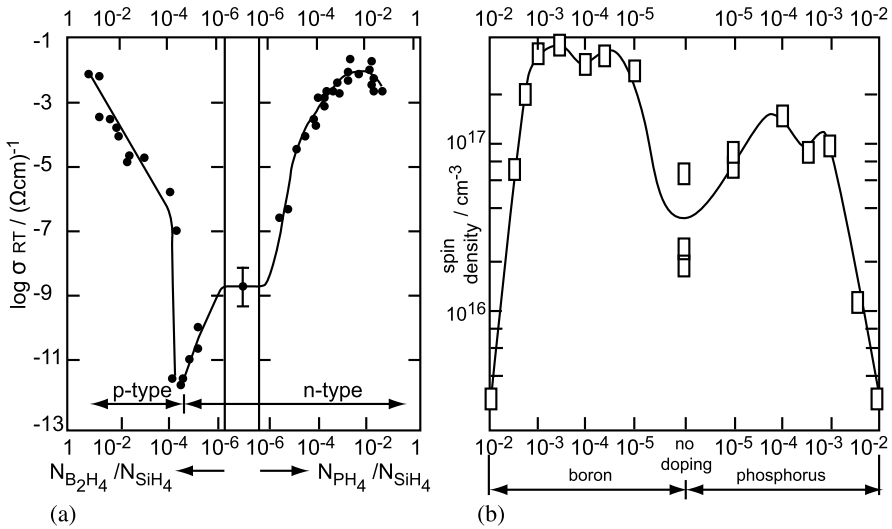
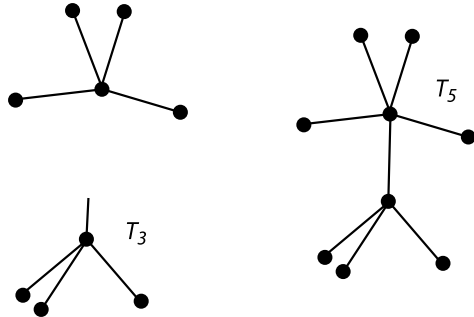


Fig. 13.4 (a) Room temperature electrical conductivity of α -Si:H as a function of the phosphine or diborane concentration during deposition (after LeComber and Spear 1976). (b) Spin density optically induced in α -Si:H as a function of doping gas pressure (after Knights et al. 1977)

Fig. 13.5 Relationship of threefold (T_3) and fivefold (T_5) coordinated Si-atoms with possible inter-conversion of these dangling and floating bonds (after Pantelides 1988)



strengths of various bonds. For example, in amorphous $\text{Ge}_5\text{Te}_{1-\zeta}$, a configuration wherein the stronger Ge–Ge bond appears most frequently while the number of the weaker Te–Te bond is minimized in the entire material, may be termed an *ideal amorphous* $\text{Ge}_5\text{Te}_{1-\zeta}$ *structure*. Any deviation from it may be identified as a defect of the structure, and has a lower overall binding energy.

Another deviation from optimal bonding relates to a *valence alternation*, in which the valency of nearby atoms is changed. Charged dangling bonds may also be formed. As charged, but compensated defects, they effectively pin the Fermi level.

In chalcogenide glasses, *defect states with negative correlation energy*, i.e., negative U -centers, can occur (Anderson 1975a; Ovshinsky 1976b). These states can bind two electrons, the second with a larger binding energy than the first. This can be explained when a strong electron-lattice interaction exists, and the energy released

by the lattice deformation near the polarized defect is larger than the Coulomb repulsion of the second from the first electron. As a result, we expect in a system with N defect states and n electrons that $n/2$ states are doubly occupied in the lowest energy state, causing a pinning of the Fermi level. This also explains why these materials are diamagnetic.

13.3.5 Doping in Semiconducting Glasses

When the density of *foreign atoms* is small enough, and the atoms are not incorporated as part of the glass-forming matrix in tetragonal glasses, the ensuing defect may result in a distinct level similar to that in a crystalline semiconductor. Depending on the actual surrounding, however, the resulting energy level of a deep level defect is different. The same defect may have even a donor- or an acceptor-like character, or, with external excitation, act as a recombination center in a different microscopic environment of the host.

In these tetrahedrally bound amorphous semiconductors, e.g., in α -Si:H, the chemical nature of shallow defects determines their electronic defect behavior with less ambiguity. These act as *dopants*, with a similar effect as in crystals, though with a more complicated configuration. Incorporation of a P atom is likely to occur in an sp^3 configuration rather than a p^3 bonding. It is observed to shift the Fermi level to within 0.1 eV of the conduction band edge (or better, the electron mobility edge-) and thereby act as an effective donor. The incorporation of a B-atom can be accomplished in an sp^3 - or sp^2 -configuration, with bond angles of 109.5° or 120° and a coordination number of 4 or 3, respectively, or as a complex with bridging H atoms (Adler 1985). It acts as an acceptor. Other local bonding configurations can occur with the incorporation of N (pnictogen), O, or S (chalcogen), which result in different sets of donor levels within the gap.

13.4 Microcrystalline Boundaries and Voids

Microcrystallite boundaries seem to be out of order for true glasses. However, there is some evidence that in a few semiconducting glasses precrystallization takes place. This is possibly the result of imperfect growth techniques, and caused by the formation of small crystallite nuclei. In this case, the internal strain of the nuclei is relaxed by the creation of a boundary (micro-surfaces) that resembles crystal boundaries with localized strain.

Small voids of variable size can be identified in the center of large-number rings in certain glasses. These defects show some similarities to vacancies in a crystal lattice, although they vary in size and bond reconfiguration.

13.4.1 Recrystallization of Amorphous Si

Amorphous Si layers on crystalline Si recrystallize with an activation energy of ~ 2.5 eV (Lietoile et al. 1982). Such recrystallization may occur through diffusion of dangling bonds (Mosley and Paessler 1984), mediated by floating bonds (Pantelides 1989), converting all rings into six-member rings.

13.5 Spin Density of Defects

Electron-spin resonance yields additional information about a defect. When this defect possesses an electron unpaired with another one of opposite spin (short *unpaired spin*), the resulting magnetic momentum can be picked up by a spin-flip electromagnetic resonance experiment. The frequency and line shape of the resonance is influenced by the surrounding of the defect and yields more detailed information in crystalline solids. This hyperfine structure is washed out in amorphous semiconductors. However, from the density of unpaired spins, we still obtain valuable information. This density is small ($\cong 10^{16} \text{ cm}^{-3}$) in α -Si:H, and verifies a low density of dangling bonds, T_3^x (sp^3), which represent unpaired spins (see Adler 1985).

Coexistent with T_3^x centers are pairs of T_3 and T_3' centers, which have compensated spins. Their total energy depends on the relative distance (Kastner et al. 1976), and has its minimum value when they are nearest neighbors (*intimate charge transfer defect*—Adler and Joffa 1977).

The spin density can be used as a measure of uncompensated donors or acceptors, and is shown in Fig. 13.4b. However, the observed decrease of unpaired spin density for high doping densities causes some problems in explanation.

In contrast, nonhydrogenated α -Si shows spin densities which are substantially larger and increase with damaging ion bombardment up to 10^{19} cm^{-3} . With subsequent annealing, the spin density is reduced as expected (Stuke 1976).

13.6 Defect Spectrum in Amorphous Semiconductors

There is a continuous transition from band states that are *not localized* to *localized states* of major defects within the band gap. Depending on the degree of disturbance of the lattice potential, the eigenstate of an arbitrary host atom may lie in the band, near the band edges, or further separated within the gap.

An important question relates to the distribution of these levels in a typical amorphous semiconductor. More specifically, we are interested when such levels can be considered part of the band, and when they become defect levels in the band gap. This distinction is relatively easy in a crystalline semiconductor, in which band states can be occupied by electrons that are described by nonlocalized Bloch wavefunctions, as opposed to gap states described by localized electron eigenfunctions.

In amorphous semiconductors, this is not possible since k is no longer a good quantum number.

One way to approach this question (Anderson 1958) is to change from a strictly periodic potential, representing a crystal and yielding bands separated by gaps in the classical sense, to a perturbed potential, which can be made less and less periodic, and analyze the resulting eigenfunctions. This approach is illuminating, and will be discussed in the following section.

13.6.1 The Anderson Model

Anderson starts from a *three-dimensional* Kronig-Penney potential, which yields simple bands interspaced with band gaps, much like the one-dimensional case discussed in Sect. 7.1. The band width ΔE_B can be expressed as

$$\Delta E_B = 2\hat{m}I, \quad (13.1)$$

where m is the coordination number and I is the transfer integral

$$I = \int \psi^*(\mathbf{r} - \mathbf{R}_n) H \psi(\mathbf{r} - \mathbf{R}_{n+1}) d\mathbf{r}, \quad (13.2)$$

which can be approximated in the form

$$g(E)dE = \frac{1}{2\pi^2} \left(\frac{2m_n}{\hbar^2} \right)^{3/2} \int_{-\infty}^E \sqrt{E - eV} f(V) dV, \quad (13.3)$$

it decreases with increasing well depth $V = (1/e)I$. Here r is the distance from the well center and r_0 is the fall-off radius of the transfer integral. For a hydrogen-like potential well, I_0 is given by

$$I_0 = \left[\frac{3}{2} \left(1 + \frac{r}{r_0} \right) + \frac{1}{6} \left(\frac{f}{r_0} \right)^2 \right] \frac{\sqrt{2me^2E_0}}{\hbar} \quad (13.4)$$

with E_0 as the ground state in a single well and

$$r_0^2 = \frac{\hbar^2}{2mE_0}. \quad (13.5)$$

With periodic wells, the ground state E_0 broadens to a band with band width ΔE_B —see Eq. (13.1). It results in a rather narrow band when the wells are sufficiently deep and spaced widely enough.

This model has a wide range of application. For instance, one can use the results to explain that donors, when spaced close enough to each other, produce a narrow band rather than a sharp ground state level.

When the model is applied to a periodic lattice potential, however, with changes from the strict periodicity, introduced by changing the interatomic distance or the potential. Anderson superimposes a random potential V with a spread of $\pm\Delta V/2$ onto the average well depth V_0 (Fig. 13.6b), and consequently obtains a broader

level distribution with tails beyond the original band edges. When ΔV is very small compared to the well depth, only small deviations from the periodic Bloch-type solutions occur. These result in some scattering of essentially free Bloch electrons within this band, with a mean free path given by (Mott and Massey 1965):

$$\lambda = \frac{\hbar}{\pi} \left(\frac{2}{\Delta V} \right)^2 \frac{v_e}{a^3 g(E)} \quad \text{with } v_e = \frac{\hbar}{m} k. \quad (13.6)$$

When $\lambda \gg a$, all levels are extended band levels.² The fluctuating potential results only in a slight perturbation of the band edges.

13.6.1.1 Anderson Localization

From Eq. (13.6) we see that the mean free path decreases with increasing spread of the fluctuating potential. When the mean free path is reduced to the distance between the wells, all states within the band become localized. An estimate for the relative mean free path can be obtained from Eq. (13.6), using the classical formula for $g(E)$:

$$g(E)dE = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E} dE, \quad (13.7)$$

yielding

$$\frac{\lambda}{a} = 32\pi \left(\frac{I}{\Delta V} \right)^2 = \frac{8\pi}{\hat{m}^2} \left(\frac{\Delta E_B}{\Delta V} \right)^2 \quad (13.8)$$

Localization occurs when $N_a = 1$, i.e., when V increases to $0.7\Delta E_B$ for $m = 6$. The electron is no longer free to move within the band but is localized within the radius of one atom.

Anderson determines, as a criterion for localization, a more stringent decrease of the wavefunction, with increasing distance from a center, so that the remaining overlap is insufficient for diffusion from neighbor to neighbor of an electron in such a center.

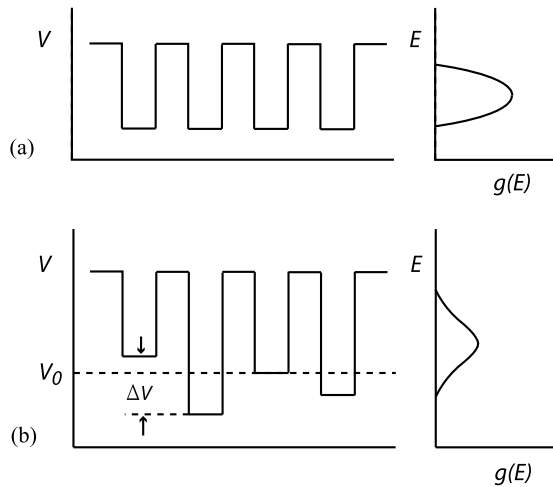
This yields for an *Anderson localization*

$$\Delta V_A \gtrsim \frac{\sqrt{8\pi}}{\kappa_A \hat{m}} \Delta E_B, \quad (13.9)$$

with a numerical factor $K_A \approx 6$. Others have obtained values of K_A between 1.3 and 5. A review of these estimations is given by Thornton (1974).

²It should be noted that the definition of a band state is related to the coherence length of an electron wave, which is essentially the same as the mean free path λ (see Sect. 13.3.1 for more details).

Fig. 13.6 Anderson model:
(a) periodic potential and
resulting level distribution;
and (b) Anderson potential
with random potential V
added to potential well depth
and resulting level
distribution



13.6.1.2 Anderson-Mott Localization

Mott has applied the Anderson idea to randomly distributed defects as they may exist in heavily doped crystals, or for defect states in amorphous semiconductors, which results in an *impurity band* of width ΔE_i . Instead of a random distribution of the potential well depth, a random distribution of centers *in space* is now assumed. If the density of the randomly placed centers is sufficiently large, we can think of these as forming an amorphous semiconductor with lateral disorder.

With a density of N_i of such centers, the average distance of any two of these is given by

$$r_i = \sqrt[3]{\frac{2}{N_i}}. \quad (13.10)$$

When close enough, they interact with each other and influence their eigenstates as given by the transfer integral

$$I_i \propto V_i = V_0 \exp\left(-\frac{r_i}{r_0}\right). \quad (13.11)$$

Equating this V_i , which fluctuates with r_i , with the fluctuating potential in the Anderson model, and assuming [Eq. (13.9)] that localization occurs when

$$V_i' \simeq \Delta V_A \simeq 2\Delta E_i, \quad (13.12)$$

we have with Eq. (13.1):

$$V_0 \exp\left(-\frac{r_i}{r_0}\right) \simeq 4\hat{m} V_0 \exp\left(-\frac{r_A}{r_0}\right). \quad (13.13)$$

For an average coordination number $m \approx 5$, we obtain from Eq. (13.13)

$$\frac{r_A - r_i}{r_0} \simeq \ln(4\hat{m}) \simeq 3. \quad (13.14)$$

A somewhat lower coordination number for covalent crystals or amorphous semiconductors has only minor influence on the numerical value of condition (13.16). With an Anderson-Mott density, below which localization occurs,

$$(N_i)_{\text{loc}} = \left(\frac{4\pi}{3} r_A^3 \right)^{-1}, \quad (13.15)$$

we now obtain from Eq. (13.14) with Eqs. (13.10) and (13.15), (13.16).

Assuming hydrogen-like centers, this yields with $r_0 = a_{\text{qH}}$ the condition for Anderson-Mott localization—see Mott and Davis (1979):

$$\boxed{N_{\text{AM}}^{1/3} a_{\text{qH}} \simeq 0.2.} \quad (13.16)$$

This is essentially the same condition that was used for an insulator-metal transition when the density N described donors in a crystalline semiconductor.

13.7 Band Tails and Localization

We will now apply this concept to an amorphous semiconductor. Most of the states well within the conduction or valence band are similar to the states within a crystal. This can be justified by the measured $g(E)$ distribution. We may consider the tailing states extending into the band gap as disorder, resulting in a continuous distribution of states. Deeper states occur less frequently because the centers which produce such states are less frequent. When deep enough, each type of defect center will produce a localized level. Only if these centers are close enough will the corresponding levels broaden to bands, and electron transport can take place within such levels. Overlapping levels and narrow bands will all melt into the tailing states. These states are no longer localized.

In summary, when the disordered atoms are close to each other, the resulting states are band-like and not localized. When the spacing between disordered centers exceeds 5 times the quasi-hydrogen radius, localization occurs, and the resulting levels can be described as isolated levels in the band gap.

In an amorphous semiconductor, there seems to be a smooth transition between ideal and disordered states; hence, it is difficult to define a band edge in the classical sense. However, with the help of the localization criterion, a pseudo-band-edge can be defined as the energy of the defect level at which localization occurs. This will be explained in more detail, when carrier transport is discussed—see Gotze (1981).

Chapter 14

Defects in Superlattices

Abstract Doping and compositional superlattices are explained with examples given. Isolated lattice defects are identified. Delta function doping is shown. Strained Layer superlattices are discussed. Superlattice induced phase changes are indicated. Doping superlattice detail is given.

Doping of superlattices has a significant effect on their electrical properties, which are substantially different from that of homogeneous semiconductors. It provides attractive alternatives for device application.

There are significant differences between defects in superlattices and similar defects in bulk semiconductors. They relate to two different classes of defects: those which comprise an intimate part of superlattices; and those, such as point defects, which influence electronic and optical properties, similar to dopants.

The first class of defects relates to the superlattice interfaces in compositional superlattices or to periodic changes of doping, resulting in so-called *doping superlattices*: when the doping is done in alternating layers of an otherwise homogeneous material, one also obtains superlattice properties. These doping superlattices are discussed in Sect. 14.3, although the doping is no longer considered a defect within these superlattices.

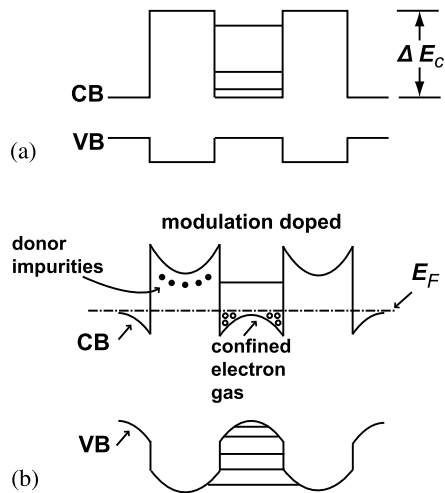
Compositional superlattices have been discussed previously in this book. Lattice mismatch between layers of different composition significantly influences the properties of such superlattices, and is discussed in Sect. 14.2.

Finally, individual layers of the superlattice can be doped. Because of confinement, such dopants play a special role. The influence of such doping will be discussed first.

14.1 Defects in Compositional Superlattices

Donors or acceptors are preferably introduced in the large band-gap material. The free carriers produced here consequently move into the potential wells created by the smaller gap material. This results in a unique separation of doped material with few carriers and undoped material with a substantial density of carriers. This structure

Fig. 14.1 (a) Undoped compositional superlattices and (b) the same superlattice with donor doping in the large band-gap material



has obvious advantages for the carrier transport within the wells, i.e., in a high-purity undoped material, and permits very high carrier mobilities (Dingle et al. 1978).

As a consequence of the redistribution of carriers, a space charge is created in each layer: the depleted wide gap layer, if *n-type*, is charged positively; the lower gap layer, enriched with electrons, is charged negatively. Consequently, a bending of the bands occurs as shown in Fig. 14.1, and results in a somewhat more complicated periodic potential $V(x)$ —see Dahler (1986).

14.1.1 Isolated Lattice Defects in Superlattices

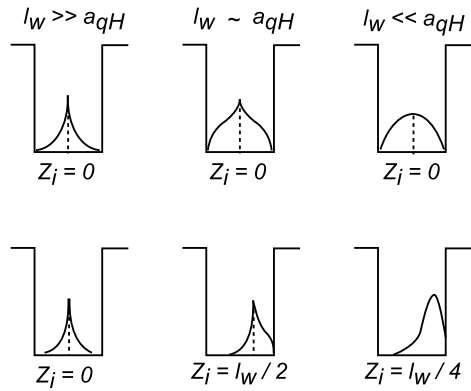
When the extension of the wavefunction of a hydrogen-like impurity becomes comparable to the well thickness of the superlattice, an influence due to the difference in effective mass, dielectric constant and, most importantly, when the defect is introduced into the well material, a wavefunction confinement, due to the potential barriers, occurs. This is reviewed by Bastard and Brum (1986), and Abstreiter et al. (1986a, 1986b).

The anisotropic confinement between the barriers reduces the quasi-Bohr radius of the impurity normal to the superlattice plane, and thereby increases the electronic binding energy of the defect. This change is relatively large when the impurity sits close to the barrier or when the well thickness is less than the Bohr radius and the barriers are sufficiently high. There are indications that a shallow-to-deep level transition occurs when the distance of the defect to the well barriers becomes small enough (Ren et al. 1988).

However, when $l_w \ll a_{qH}$ the defect eigenfunction extends beyond the well, the barriers become permeable, if thin enough, and the binding energy decreases again.

In Fig. 14.2, changes of the ground state of the wavefunction in such a superlattice are shown when the well becomes thinner (upper row) or the defect is lo-

Fig. 14.2 Schematics of the eigenfunctions of a hydrogen-like ground state in a quantum well of different width l_w relative to a_{qH} (*upper row*) and of different proximity to the well wall in a wider well (*lower row*). Z_i is the position offset of the defect from the center plane ($Z_i = 0$) (after Bastard and Brum 1986)



cated closer to the right barrier wall (*lower row*). Substantial deformation from the hydrogen-like behavior, shown undisturbed in the left column, becomes visible.

In addition, resonance effects occur with impurity states derived from higher subbands and overlapping with the continuum of the barrier material (Priester et al. 1984).

Acceptors in wells of superlattices. The properties are a bit more complex because of the split of heavy and light hole subbands, which causes a splitting of the corresponding hydrogen-like levels of the acceptor.

14.1.2 δ -Function Doping

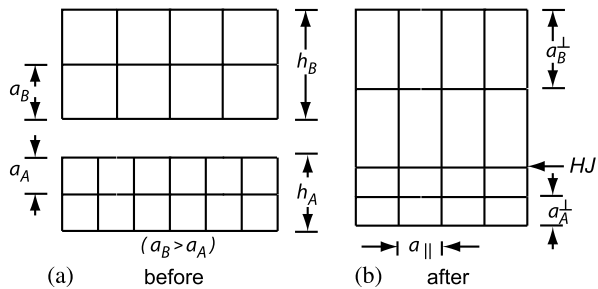
When doping is confined to a single atomic layer within a superlattice, doping subbands are formed within a V-shaped potential well surrounding this monolayer (Zrenner et al. 1984) and carrier saturation effects occur (Zrenner and Koch 1986; Ploog 1987).

14.2 Strained-Layer Superlattices

Another type of lattice imperfection plays an important role: the large built-in strains due to some lattice mismatch in compositional superlattices. Such strains result in the formation of dislocations for an extended lattice. Consequently, such types of superlattices have similarities with a sequence of heterojunctions, containing arrays of mismatch dislocations.

In sufficiently thin alternating layers, however, this strain cannot be relieved. The strain can no longer be considered a lattice defect but becomes an intimate part of the superlattice. There is a critical distance necessary for the creation of mismatch dislocation. This critical thickness d_c is a function of the lattice mismatch $\epsilon = a - a_0$, and

Fig. 14.3 (a) Two thin layers of unstrained materials with substantial lattice mismatch (*upper part*) and (b) after connection with each other (HJ), showing a substantial tetragonal lattice deformation without stress relief into a dislocation network



is evaluated for a number of semiconductor pairs (van der Merve 1978; Fiori et al. 1984; Fritz et al. 1985; Osbourn 1986).

A first estimation of the critical thickness is given by

$$d_c \simeq \frac{a}{\Delta a} \frac{b}{4\pi(1+\nu)} \left\{ \ln \left(\frac{d_c}{b} \right) + 1 \right\} \quad (14.1)$$

where b is the length of the Burgers vector and ν is the Poisson ratio (≈ 0.3). Typically, with $b \approx 4 \text{ \AA}$ and $\Delta a/a \approx 2\text{--}5\%$, one estimates a critical thickness on the order of $100 \text{ \AA}$, below which mismatch dislocations are not formed.

Large strains from lattice pairs with substantial mismatch cause major tetragonal deformations (see Fig. 14.3), which cause changes in lattice constant and band structure. This provides additional flexibility in designing a wide variety of superlattices with different band interconnections. Of special interest is the strain-induced splitting of the valence band; it causes a change in hole masses (Osbourn 1986), which is otherwise difficult to achieve. Various devices made from strained-layer superlattices are reviewed by Osbourn et al. (1986).

Figure 14.4 gives an example of the $\text{Ge}_{\zeta}\text{Si}_{1-\zeta}$ -superlattice, with a dividing curve between the strained superlattice regime (lower left) and the relaxed regime (upper right) in which mismatch dislocations can be formed. Such strained-layer superlattices grow at an appropriate temperature: at too low temperatures, amorphous layers are grown; at too high temperatures, interdiffusion takes place.

14.2.1 Superlattice-Induced Phase Changes

Under large hydrostatic pressure of 100–300 kbar, the open tetrahedral structure with a coordination number 4 of many semiconductors can be changed in a first-order phase transition to a body-centered tetragonal structure with coordination number 6 and a 15–20 % volume reduction (Hanneman et al. 1964).

As a result, the band gap is dramatically reduced, and some transitions result in a metallic phase as shown in Fig. 14.5 (see also Froyen and Cohen 1983). A few of these high-pressure modifications can be retained metastable at atmospheric pressure (Kasper and Richards 1964).

Fig. 14.4 Critical thickness of a layer of $\text{Ge}_\xi\text{Si}_{1-\xi}$ on Si (lower scale) or on Ge (upper scale) for creation of dislocations (after Pearsall et al. 1986)

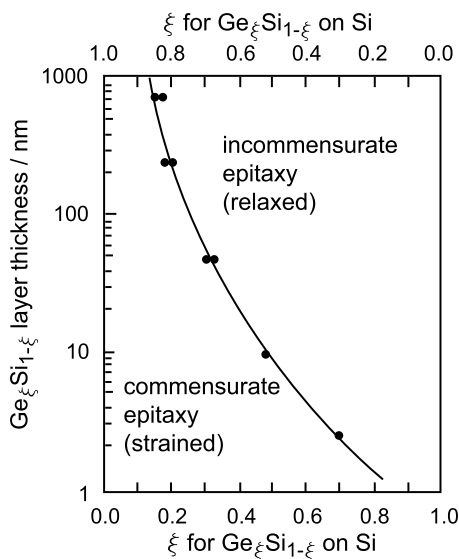
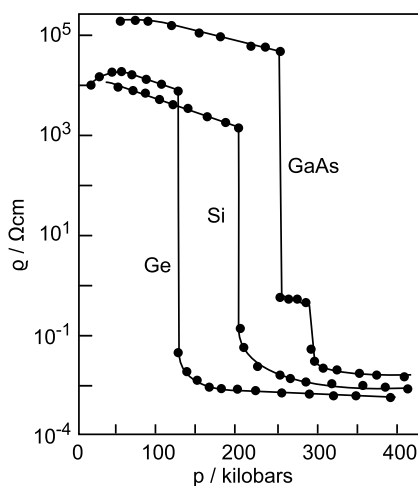
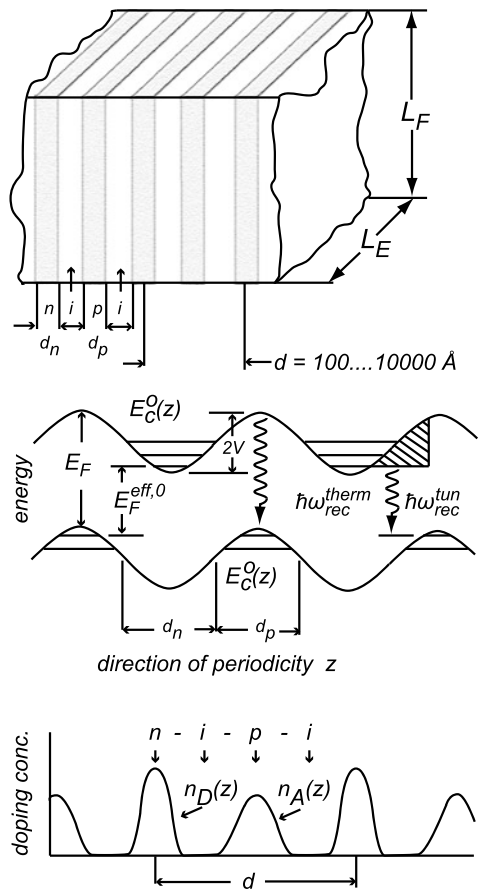


Fig. 14.5 Resistivity of some semiconductors as a function of the hydrostatic pressure with phase transitions; recent results put transitions at 30–50 % lower pressures (after Minomura and Drickamer 1962)



Embedding such a semiconductor between layers of a material with a different lattice constant creates a strained-layer superlattice, which enhances such stabilization. After a transformation is induced by high pressure, the reverse transformation is suppressed, resulting in a hysteresis. In some cases, for example, the GaAs/AlAs superlattice remains stable down to room pressure in the tetragonal structure, after inducing it at 155 kbar (Weinstein 1987), provided the individual layer is thin enough: 19 Å in the given example.

Fig. 14.6 Doping superlattice with alternating n - and p -type layers of the same host material, interfaced with thin undoped (i) layers (after Dahler 1986)



14.3 Doping Superlattices

A periodic modulation of the bands, which is characteristic for superlattices, can also be achieved by a periodic alternation of n - and p -type doping (first proposed by Dahler 1972). Such a *doping superlattice* is shown in Fig. 14.6. For better separation, i layers (undoped, or compensated *intrinsic layers*) can be inserted between each of the n - and p -type layers.

This periodic structure shows a similar type of minibands as the compositional superlattice, however, with minibands that are wider for shorter superlattice constants d and lower barriers. Because doping superlattices depend on the Debye length for their change in space charge, their lattice constant is usually larger than that of compositional superlattices, and typically is on the order of 300 to 3,000 $\text{\AA}$.

A lowering of the barriers can be achieved by increasing the carrier densities in the n - and p -conducting layers. Such an increase, in turn, can be produced by light, resulting in optical carrier generation, or by an electric field resulting in car-

rier injection. The positive and negative space charges in the n - and p -type layers, respectively, are thereby reduced.

As a consequence, the electrical and optical properties of the doping superlattice become *tunable* by a changing carrier density. Such tunability includes a change in the effective band gap, the carrier lifetime, the luminescence spectrum, and other optical parameters (Dahler 1986). Doping superlattices have been produced in GaAs, Si, InP, PbTe, and other semiconductors (Ruden 1987).

Chapter 15

Carriers and Their Motion

Abstract Carrier motion within their respective band is discussed. Velocity distributions and random walk are shown. Sign convention is given. Electronic conductivity and Joule's heating is given. Gas kinetic model of electronic scattering is introduced. Electron and hole drift currents. Momentum and energy relaxation and their average time constants are distinguished. Mean free path is identified. Phonon and electron drag are discussed. Electric fields and fields in graded band gap semiconductors are defined. Diffusion and maximum diffusion currents are identified. The Einstein relation is given. Electrochemical fields and quasi-Fermi levels are defined. External and built-in fields are distinguished. Penalties for simple transport models are explained. Carrier distributions in built-in or external fields are differentiated. Mobilities in built-in or external fields are distinguished. A summary table of potential gradients and currents is given.

Carrier transport proceeds under external forces,¹ resulting in drift, and under internal quasiforces, resulting in diffusion. This may involve different charged particles which contribute additively to the current, or have an indirect effect when it involves neutral particles, e.g., excitons.

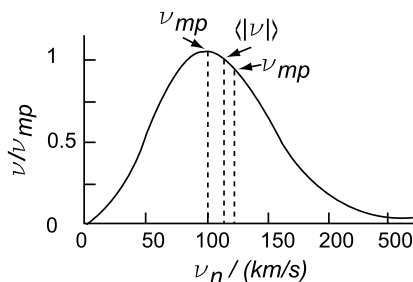
Carrier transport occurs in bands near the band edges, i.e., near E_c for electrons and near E_v for holes. For materials with a large enough defect density, carrier transport may proceed also via tunneling between trapping states. It may also involve carriers hopping from traps into the band. These carriers then travel a short distance in the band and later are recaptured, then reemitted, and so on.

15.1 Carriers Within Their Bands

All of these processes add up to produce the total current, and usually have vastly different magnitudes. Ordinarily, only one transport process predominates in homo-

¹Strictly speaking, steady-state carrier transport is due to external forces *only*. The diffusion current originates from a deformed density profile due to external forces, and is a portion of the conventionally considered diffusion component. The major part of the diffusion is used to compensate the built-in field, and has no part in the actual carrier transport: both drift and diffusion cancel each other and are caused by an artificial model consideration.

Fig. 15.1 Classical velocity distribution, with root mean square, average, and most probable speed identified



geneous semiconductors. In nonhomogeneous materials, however, at least two, and frequently four contributions are important in different regions of the devices. These are drift *and* diffusion currents of electrons and holes.

First, a rather simple picture of the carrier transport is presented, which serves as guidance for a more sophisticated approach in later chapters.

At finite temperatures, carriers are found above the edge of the respective band according to their statistical distribution function. In semiconductors, they usually follow the Boltzmann distribution function within the bands when they are not degenerate, i.e., when the carrier densities are below $0.1N_c$ or $0.1N_v$ [Eq. (15.18)].

Their thermal velocity, the root mean square velocity,² is obtained from the equipartition principle, i.e., kinetic energy = $kT/2$ per degree of freedom [Eqs. (13.1)–(13.3)]:

$$\frac{m_n}{2}\langle v^2 \rangle = \frac{3}{2}kT; \quad (15.1)$$

hence

$$\sqrt{\langle v^2 \rangle} = v_{\text{rms}} = \sqrt{\frac{3kT}{m_n}} \quad (15.2)$$

or

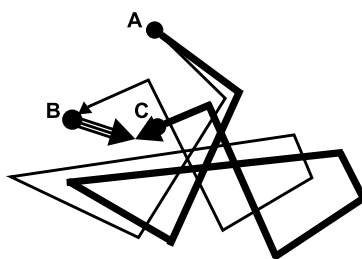
$$v_{\text{rms}} = 1.18 \cdot 10^7 \sqrt{\frac{m_0}{m_n} \frac{T(\text{K})}{300}} \text{ (cm/s)}. \quad (15.3)$$

In thermal equilibrium and in an isotropic lattice, the motion of the carriers is random.

The quantum-mechanical model of a periodic potential teaches that, in contrast to a classical model, an ideal lattice is transparent for electrons or holes within their respective bands. That is, the carriers belong to the entire semiconductor, and as waves are not localized: their position cannot be identified, except stating that n

²The rms (*root mean square*) velocity, which is more commonly used, should be distinguished from the slightly different *average velocity* and from the *most probable speed*. Their ratios are $v_{\text{rm}} : \langle |v| \rangle : v_{\text{mp}} = \sqrt{3} : \frac{\sqrt{8}}{\pi} : \sqrt{2} = 1.2247 : 1.1284 : 1$, as long as the carriers follow Boltzmann statistics. For a distinction between these different velocities, see Fig. 15.1.

Fig. 15.2 Random walk of a carrier with (heavy lines) and without (thin lines) an external electric field. The triple-lined arrow from B to C indicates the relative displacement in field direction after the indicated nine scattering events



carriers (per cm^3) are within the given crystal. *There is no scattering of carriers within such an ideal crystal.*

This behavior of carriers is unexpected in a classical model, which visualizes the filling of space with atomic spheres and expects only very limited possibilities for an electron traversing between these spheres without being scattered.

The introduction of crystal defects, including phonons, provides centers for scattering. In this way, a carrier motion results, which can be described as a *Brownian motion*³ with a *mean free path* commensurate with the average distance between scattering centers. This distance is several hundred Angstroms in typical crystalline semiconductors, i.e., the mean free path extends to distances much longer than the interatomic spacing.

When a carrier responds to an external field, it is accelerated in the direction of the electric field. Many important features of the carrier motion can be explained by assuming only inelastic scattering. Since it takes place at defects, which themselves are in thermal equilibrium with the lattice, the carrier tends to lose the excess energy gained between the scattering events. Figure 15.2 illustrates the typical motion of a carrier with and without an external electric field. The changes due to the field are exaggerated; under normal external fields, the changes from the random walk without field are very small perturbations.

15.2 Sign Conventions

In previous chapters, the elementary charge is used as $e = |e|$. When the *transport* of electrons and holes is discussed, it is instructive to discuss the proper signs: $-e$ for electrons and $+e$ for holes. This has an influence on derived parameters, e.g., the mobility, as will be discussed in Sect. 15.5.

The electric field⁴ F is defined as the negative gradient of the vacuum level. The bias V is conventionally labeled $+$ for the anode and $-$ for the cathode, while the electrostatic potential Ψ has the opposite signs: electrons have a larger potential

³This motion resembles a random walk (Chandrasekha 1943).

⁴In chapters dealing with carrier transport, F is chosen for the field, since E is used for the energy.

energy at the cathode than at the anode. The relation to the field is therefore

$$F = \frac{dV}{dx} = -\frac{d\psi}{dx}. \quad (15.4)$$

With $E_c = |e|\Psi = \text{const}$, it yields a positive field when the band slopes downward from the cathode toward the anode, giving the visual impression that electrons “roll downhill” and holes “bubble up.” We will use the proper signs in the following sections, however, reverting back to the commonly used $e = |e|$ later in order to avoid confusion in comparison to familiar descriptions.

When expressing forces, we need to distinguish the sign of the carrier; therefore, for an accelerating force we have

$$\mathcal{F} = (-eF)_n = (+eF)_p, \quad (15.5)$$

with subscripts n and p for electrons and holes.

15.3 Electronic Conductivity

In following the arguments introduced by Drude (1900); later refined by Lorentz (1909), and Sommerfeld (1928), electrons are accelerated in an electric field by the force $F = -e\mathbf{F}$:

$$m_n \frac{d\mathbf{v}}{dt} = -e\mathbf{F}. \quad (15.6)$$

During a free path, the electron gains an incremental velocity, for an arbitrarily chosen field in z direction $\mathbf{F} = (F_x, 0, 0)$:

$$\Delta v_x = -\frac{e}{m_n} F_x \tau_{\text{sc}}. \quad (15.7)$$

After averaging the *incremental velocity* between collisions, and replacing T_{sc} with the average time τ -between scattering events, we obtain the *drift velocity* v_D :

$$v_D = -\frac{e}{m_n} \bar{\tau} F_x. \quad (15.8)$$

With an electron density n and a charge $-e$, we obtain for the *current density* for electrons

$$\boxed{j_n = en v_D}, \quad (15.9)$$

or, introducing the *electron conductivity* σ_n

$$j_n = \sigma_n F \quad \text{with} \quad \sigma_n = \frac{e^2}{m_n} \bar{\tau} n. \quad (15.10)$$

In a homogeneous semiconductor, the external field is given by the bias V , divided by the electrode distance d , yielding *Ohm's law*

$$\boxed{j_n = \sigma_n \frac{V}{d} = \frac{V}{AR}}, \quad (15.11)$$

with A as the area of the semiconductor normal to the current and the resistance with the *specific resistivity* $j_n = 1/\sigma_n$.

$$R = \frac{d}{A\sigma_n} = \frac{\rho_n d}{A}. \quad (15.12)$$

15.4 Joule's Heating

The additional energy from the external electric field is delivered during inelastic collisions, generating phonons. This *Joule's heating* can be calculated by accounting for the additional energy obtained from the field between scattering events $(m_n/2)(\Delta v_x)^2$, and the number of scattering events per second $n/\Delta t$, yielding the thermal energy gain Q of the lattice:

$$Q = \frac{n}{\Delta t} \cdot \frac{m_n}{2} (\Delta v_x)^2 = \frac{n}{\bar{\tau}_n} m_n \left(\frac{e}{m_n} \bar{\tau}_n F \right)^2, \quad (15.13)$$

with $\tau = \Delta t$. This yields Joule's law after some reordering:

$$Q = \frac{(en \frac{e}{m_n} \bar{\tau}_n F)^2}{en \frac{e}{m_n} \bar{\tau}_n} = \frac{j_n^2}{\sigma_n}. \quad (15.14)$$

15.5 Electron Mobility

The quantity

$$\boxed{\frac{e}{m_n} \bar{\tau}_n = \mu_n} \quad (15.15)$$

is the *electron mobility* (Fig. 15.3), since carriers are more *mobile* when they experience less scattering, i.e., the time between collisions is larger, and when their effective mass is smaller, i.e., they can be accelerated more easily. With $-e$ for electrons and $+e$ for holes, the mobility is negative for electrons and positive for holes, while the conductivity is always positive. Conventionally, however $\mu = \mu_n$ is used and we will follow this convention here.

The *electron conductivity* and *hole conductivity* are given by

$$\boxed{\sigma_n = e\mu_n n} \quad \text{and} \quad \boxed{\sigma_p = e\mu_p p}. \quad (15.16)$$

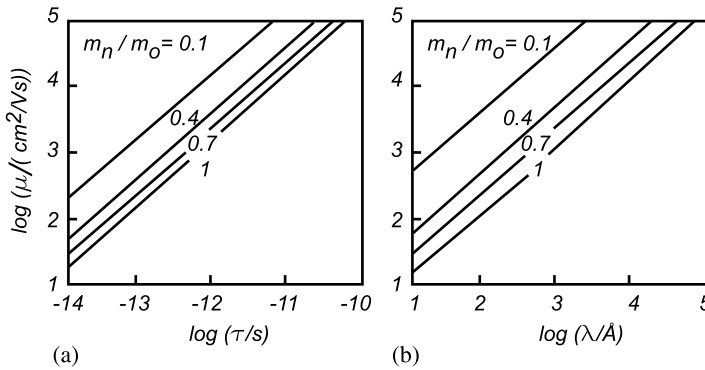


Fig. 15.3 Carrier mobility as a function of (a) T_{sc} and of (b) λ with m_n as family parameter

15.6 Gas-Kinetic Model for Electron Scattering

Different types of lattice defects are effective to a differing degree in carrier scattering. In a simple gas-kinetic model, *scattering centers* have a well-defined *scattering cross section* s_n ; a *scattering event*, i.e., a marked deflection⁵ from an otherwise straight carrier path with exchange of momentum and/or energy takes place when the carrier approaches the scattering center within its cross section. A *mean free path* can then be derived by constructing a cylinder of cross section S_n around an arbitrary straight carrier path, and computing the average distance from the last scattering center to which this cylinder will extend until it incorporates the centerpoint of the next scattering center. At this length the cylinder volume $\lambda_n s_n$ equals the average volume that one of these centers occupies: $1/N_{sc}$ (cm^3); hence,

$$\lambda_n = \frac{1}{s_n N_{sc}}. \quad (15.17)$$

Here, N_{sc} is the density of scattering centers. Consequently, the time between scattering events is given by

$$\tau_{sc} = \frac{1}{v_{rms} s_n N_{sc}}. \quad (15.18)$$

This time is used to obtain an estimate for the carrier mobility in the Drude approximation:

$$\mu_n = \frac{e}{m_n} \tau_{sc} = \frac{e}{m_n} \frac{\lambda}{v_{rms}}, \quad (15.19)$$

$$\mu_n = 1.8 \cdot 10^{15} \frac{m_0}{m_n} \tau_{sc}(s) (\text{cm}^2/\text{Vs}), \quad (15.20)$$

⁵Often a minimum scattering angle of 90° is used to distinguish scattering events with loss of memory from forward scattering events.

or, using the expression [Eq. (26.16)] for V_{rms} :

$$\mu_n = 1.5 \cdot \lambda \text{ (\AA)} \left(\frac{m_0}{m_n} \right)^{3/2} \left(\frac{300}{T(\text{K})} \right)^{1/2} (\text{cm}^2/\text{V s}). \quad (15.21)$$

The application of this simple gas-kinetic model, however, has to be taken with caution because of its simplified assumptions. Generally, it yields too large densities of tolerable scattering centers.

15.6.1 Electron and Hole Drift Current

The drift current is the product of the elementary charge, the carrier mobility, the single carrier density, and the electric field. For electrons or holes, it is

$$\boxed{j_{n,\text{drift}} = en\mu_n F} \quad \text{or} \quad \boxed{j_{p,\text{drift}} = ep\mu_p F}. \quad (15.22)$$

15.7 Momentum and Energy Relaxation

With each scattering event, momentum is exchanged; the carrier changes the direction of its path. In addition, more or less energy is exchanged, with the carrier losing or gaining energy from the scattering center.

15.7.1 The Average Momentum Relaxation Time

The average momentum relaxation time is defined as

$$\langle \tau_m \rangle = - \frac{\int \tau_m(v) v_x \frac{\partial f}{\partial v_x} d^3v}{\int f_0 d^3v} = \frac{m_n}{kT} \frac{\int \tau_m v_x^2 f_0 d^3v}{\int f_0 d^3v}. \quad (15.23)$$

It can be obtained from the net increment of the electron momentum, which is proportional to the average drift velocity,

$$\bar{v}_x = \frac{\int v_x f(v) g(v) d^3v}{\int f(v) g(v) d^3v}, \quad (15.24)$$

where $g(v)$ is the density of states. Assuming only small changes from the thermal distribution, $g(v)$ can be expressed as the effective density of states at the edge of the band and cancels out in Eq. (16.24).

In spherical coordinates, with $d^3v = v^2 \sin \Theta dv d\Theta d\Phi$, one obtains from Eq. (15.24)

$$\bar{v}_x = \frac{\int_0^{2\pi} d\phi \int_0^\infty \int_0^\pi f_0(v) \left(1 - \frac{e}{kT} \tau_m(v) F_x v \cos \theta\right) v^3 \cos \theta \sin \theta dv d\theta}{\int_0^{2\pi} d\phi \int_0^\infty \int_0^\pi f_0(v) \left(1 - \frac{e}{kT} \tau_m(v) F_x v \cos \theta\right) v^2 \sin \theta dv d\theta}, \quad (15.25)$$

which can be integrated over Φ and Θ , and, after some reordering, yields

$$\bar{v}_x = -\frac{eF_x}{3kT} \frac{\int_0^\infty v^4 \tau_m f_0(v) dv}{\int_0^\infty v^2 f_0(v) dv} \quad (15.26)$$

$$\bar{v}_x = -\frac{eF_x}{3kT} \langle v^2 \tau_m(v) \rangle. \quad (15.27)$$

Using the equipartition law for a Boltzmann gas of electrons, $m/2 \langle v^2 \rangle = 3/2$ one obtains for the average drift velocity

$$\bar{v}_x = -\frac{eF_x}{m_n} \frac{\langle v^2 \tau_m(v) \rangle}{\langle v^2 \rangle} = -\frac{e}{m_n} \langle \tau_m \rangle F_x. \quad (15.28)$$

This result is closely related to the Drude equation, however, having replaced r Eq. (15.19) with the *average momentum relaxation time*

$$\boxed{\langle \tau_m \rangle = \frac{\langle v^2 \tau_m(v) \rangle}{\langle v^2 \rangle}}. \quad (15.29)$$

For an evaluation of Eq. (15.29), one needs the distribution function f_0 and the actual scattering mechanism to determine $\tau_m(v)$ —see Seeger (1973).

After a collision, the electron path changes by an angle Θ , and the fractional change of angle per collision is on the average $(1 - \cos \Theta)$. The momentum relaxation time is the time after which the electron path is totally randomized, i.e., its “memory” is lost; hence,

$$\boxed{\tau_m = \frac{\tau_{sc}}{\langle 1 - \cos \theta \rangle}}, \quad (15.30)$$

where τ_{sc} is the average time between two collisions. Scattering with $\Theta > 90^\circ$ is memory-erasing. Only the collisions in which all angles Θ are equally probable result in $\langle \cos \Theta \rangle = 0$ and, therefore, yield $\tau_m = \tau_{sc}$. For small-angle scattering events, one needs several scatterings before the momentum is relaxed: $\tau_m > \tau_{sc}$.

15.7.2 The Average Energy Relaxation Time

The energy loss or gain due to scattering of electrons with phonons is given by

$$\langle \tau_m \rangle = \frac{\langle v^2 \tau_m(v) \rangle}{\langle v^2 \rangle}$$

$$\frac{dE}{dt} = \frac{\mathcal{V}}{8\pi^3} \int \{ [\hbar\omega_q S(\mathbf{k}, \mathbf{k}')]_{\text{eq}} - [\hbar\omega_q S(\mathbf{k}', \mathbf{k})]_{\text{aq}} \} d\mathbf{k}'. \quad (15.31)$$

The subscript “eq” stands for emission, “aq” for absorption of a phonon.

When multiplying the Boltzmann equation with E and integrating over k , one obtains (Seeger 1973)

$$\frac{d\langle E \rangle}{dt} = e\mathbf{F}\langle \mathbf{v} \rangle - \frac{\langle E \rangle - E_L}{\tau_e} \quad (15.32)$$

with E_L the equilibrium energy at lattice temperature,

$$\langle E \rangle = \frac{\int E f d\mathbf{k}}{\int f d\mathbf{k}}, \quad \text{and} \quad \langle \mathbf{v} \rangle = \frac{\int \mathbf{v} f d\mathbf{k}}{\int f d\mathbf{k}}. \quad (15.33)$$

The *energy relaxation time* is then obtained from Eq. (15.30) after switching off the field, yielding:

$$\tau_e = \frac{\langle E \rangle - E_L}{\frac{d\langle E \rangle}{dt}} \quad (15.34)$$

that is, T_e is given by the ratio of the average surplus energy to the rate of *energy loss* due to scattering and is a function of E ; the energy loss rate is not a simple exponential function. It shows a maximum when the electron energy equals the optical phonon energy.

The rate of momentum or energy loss depends on the actual scattering mechanism. From gas-kinetic arguments, one obtains for collisions between an electron and a *lattice defect* of mass M an energy exchange rate of

$$\left(\frac{\tau_e}{\tau_{\text{sc}}} \right)_{\text{ion}} = \frac{m_n}{M}. \quad (15.35)$$

The energy loss is negligible in one scattering event if the scattering center is a defect atom, since $M \gg m_n$.

The fraction of energy lost by an electron in a collision with *acoustic* phonons can also be obtained from an effective mass ratio. Using the *equivalent phonon mass*

$$m_{\text{ph}} = \frac{kT}{v_s^2}, \quad (15.36)$$

where v , is the sound velocity; one obtains

$$\left(\frac{\tau_e}{\tau_{sc}}\right)_{ac\ ph} = \frac{m_n}{m_{ph}} = \frac{m_n v_s^2}{kT} = \frac{3v_s^2}{v_{rms}^2}, \quad (15.37)$$

which is on the order of 10^{-3} . In other words, only 0.1 % of the electron energy can be lost to an acoustic phonon during any one scattering event.

In contrast, the ratio of energy relaxation time to scattering time for *optical phonons* is

$$\left(\frac{\tau_e}{\tau_{sc}}\right)_{op\ ph} = \frac{\hbar\omega_0}{kT}, \quad (15.38)$$

which is on the order of 1 at room temperature.

This means that many scattering events usually pass before the accumulated energy obtained from the field can be dissipated to the lattice by emitting one optical phonon, while the momentum is relaxed after one, or only a few collisions. This modifies the rather crude model given in the previous sections by introducing the momentum relaxation time for evaluating the mobility and the energy relaxation time for Joule's heating.

For a more detailed discussion, however, one must await an analysis of the different scattering mechanisms, and a better estimate of the magnitude of energy obtained from the field.

15.8 The Mean Free Path of Carriers

Between collisions, the carrier traverses one free path. The mean free path is obtained by averaging:

$$\bar{\lambda} = \frac{\langle v^2 \lambda(v) \rangle}{\langle v^2 \rangle}. \quad (15.39)$$

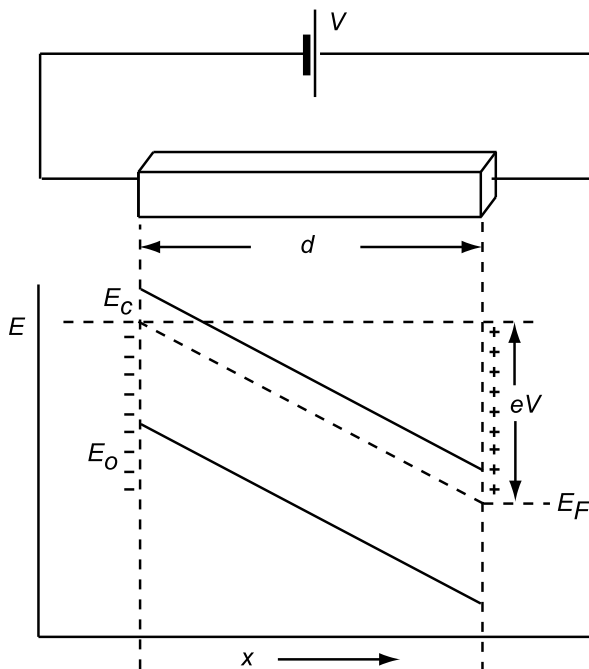
λ is related to the momentum relaxation time

$$\bar{\lambda} = \langle \tau_m \rangle \frac{\langle v^2 \rangle}{\langle v \rangle} = \sqrt{\frac{3\pi}{8}} \langle \tau_m \rangle v_{rms} = 1.085 \langle \tau_m \rangle v_{rms}. \quad (15.40)$$

15.9 Phonon and Electron Drag

Interacting electrons and phonons exchange energy and momentum. A drift motion superimposed on the random motion of one ensemble transfers part of the net momentum to the other ensemble during scattering. This means that electrons drifting in an external field tend to push phonons in the same direction, which causes

Fig. 15.4 Preferred quasi-one-dimensional geometry with band diagram subject to an external bias V , resulting in band-tilting



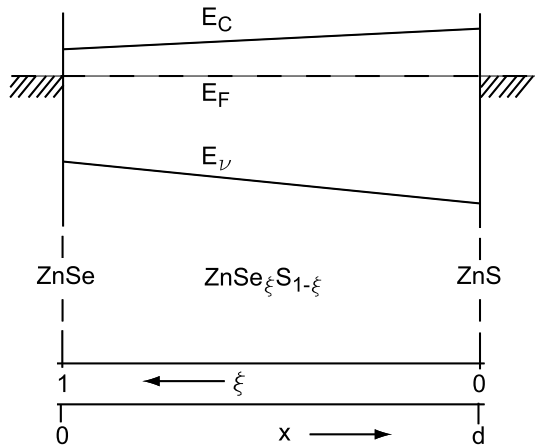
a slight temperature gradient in the field direction, superimposed on the homogeneous Joule's heating. This process is called *electron drag* (Hubner and Shockley 1960). Similarly, a temperature gradient tends to push electrons from the warm to the cold end of a semiconductor. This is known as *phonon drag*. The drag effect can be quite large, e.g., up to a factor of 6 compared to simple thermopower in *p*-Ge at 20 K, as shown by Herring (1954). When phonons propagate as acoustic waves, ac-electric fields can be induced; or, vice versa, when sufficiently high electric fields are applied, coherent phonon waves can be generated when the drift velocity of electrons surpasses the (sound) velocity of the phonon waves (McFee 1966). These *acousto-electric effects* have technical application for creating current oscillators (Bray 1969).

15.10 The Electric Field

In *homogeneous semiconductors*, disregarding space charge effects near the contacts, and for steady-state conditions—assumed with few exceptions throughout this book—the electric field is given by the applied voltage (*bias*) divided by the distance between the electrodes in a one-dimensional geometry—see Fig. 15.4:

$$F = \frac{V}{d}. \quad (15.41)$$

Fig. 15.5 Band diagram for a mixed crystal with varying composition ξ along the x -axis. At $x = 0$, the material is ZnSe; at $x = d$, the material is ZnS with varying ξ linearly in between



For the field concept to apply, the distance between electrodes d must also be large compared to the interatomic spacing. The field can then be expressed by the macroscopic sloping of the bands:⁶

$$F = \frac{1}{e} \frac{dE_c}{dx} = \frac{1}{e} \frac{dE_v}{dx}. \quad (15.42)$$

It is also given, and more importantly so, by the slope of the Fermi potential (see Sect. 26.5.1) which, within the homogeneous material, is the same as the slope of the bands:

$$F = \frac{1}{e} \frac{dE_F}{dx}. \quad (15.43)$$

The bias is expressed as the difference of the Fermi levels between both electrodes.

When using the electrostatic potential ψ_n with

$$-\frac{d\psi_n}{dx} = F, \quad (15.44)$$

the drift current can be expressed as a product of the electrical conductivity and the negative gradient of this potential

$$\boxed{j_{n,\text{drift}} = -\sigma_n \frac{d\psi_n}{dx}} \quad \text{and} \quad \boxed{j_{p,\text{drift}} = -\sigma_p \frac{d\psi_p}{dx}}. \quad (15.45)$$

For reasons it is apparent that, two electrostatic potentials are introduced ψ_n and ψ_p for conduction and valence bands, respectively, with $e(\psi_n - \psi_p) = E_g$.

In a homogeneous semiconductor in steady-state, and with vanishing space charge, these drift currents are the total currents, and the slopes of both potentials are the same.

⁶ As a reminder: here and in all following sections lei is used when not explicitly stated differently.

There are special cases, however, in which the band edges of the valence and conduction bands are no longer parallel to each other. One of these will be mentioned briefly in the following section.

15.11 Fields in Graded Band-Gap Semiconductors

A semiconductor with a graded composition produces a position-dependent, varying band gap. If this composition varies smoothly without steps, e.g., without phase segregation, one or both bands are sloped without an applied bias, representing built-in fields. As an example, in $\text{ZnSe}_\xi\text{S}_{1-\xi}$, there is complete miscibility in the entire range ($0 \leq \xi \leq 1$), with the S-Se sublattice being a statistical alloy. The band gap changes linearly⁷ from 2.45 eV for ZnSe at the left side of the crystal shown in Fig. 15.6 to 3.6 eV for ZnS at its right side. ZnSe and ZnS are both *n-type* materials. Depending on doping, the Fermi level in ZnSe can be shifted easily between 0.8 and 0.2 eV below E_c and in ZnS between 1.0 and 0.4 eV. Depending on the doping profile in the mixed-composition region, a wide variety of relative slopes, including nonmonotonic slopes, of valence and conduction bands can be designed for a vanishing bias, i.e., for a horizontal Fermi level. In Fig. 15.6, an example with opposite and linear sloping of $E_c(x)$ and $E_v(x)$ is shown, resulting effectively in a built-in field of opposite sign for electrons and holes. In thermodynamic equilibrium, however, there is no net current in spite of the sloping bands. This is accomplished by exact compensation of finite drift currents with opposing diffusion currents, which self-consistently determine the slopes of the bands. The change in the band gap can be expressed as

$$E_c(x) = E_v(x) + E_{g0} + \Delta E_g(x) \quad (15.47)$$

or, using a conventional asymmetry factor A_E , which measures the fraction of the band gap change $\Delta E_g(x)$ occurring in the conduction band relative to the horizontal Fermi level, we obtain

$$E_c(x) - E_c(x=0) + A_E \Delta E_g(x) = e\psi_n(x) \quad (15.48)$$

and

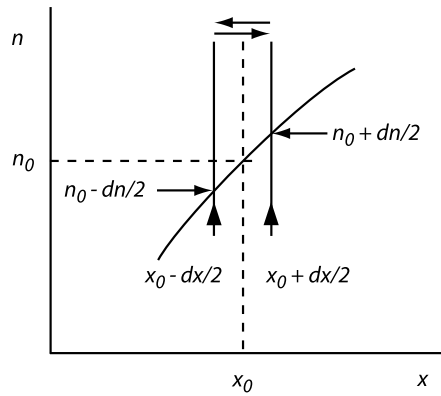
$$E_v(x) = E_v(x=0) - (1 - A_E) \Delta E_g(x) \leftarrow -e\psi_p(x). \quad (15.49)$$

⁷Major deviations from linearity of E_g with composition are observed when the conduction band minimum lies at a different point in the Brillouin zone for the two end members. One example is the alloy of Ge and Si. Other deviations such as bowing are observed when the alloying atoms are of substantially and

$$F_p = -(A_E - 1) \frac{\partial \Delta E_g(x)}{e \partial x} = -\frac{\partial \psi_p}{\partial x}, \quad (15.46)$$

justifying the introduction of separate electrostatic potentials for electrons and holes: with $\Delta E_g \neq 0$ and $A_E \neq 1/2$, we have $F_n \neq F_p$.

Fig. 15.6 Illustration of the derivation of the diffusion current



The corresponding built-in fields for electrons and holes are given by

$$F_p = -(A_E - 1) \frac{\partial \Delta E_g(x)}{e \partial x} = -\frac{\partial \psi_p}{\partial x}. \quad (15.50)$$

15.12 Diffusion Currents

Carrier diffusion by itself can be observed when the external field vanishes and a concentration gradient exists. An example in which these conditions are approximately fulfilled is the diffusion of minority carriers created by an inhomogeneous optical excitation. The *diffusion current* is proportional to the diffusion coefficient D and to the carrier density gradient; for electrons or holes it is

$$\boxed{j_{n,\text{diff}} = e D_n \frac{dn}{dx}} \quad \text{or} \quad \boxed{j_{p,\text{diff}} = -e D_p \frac{dp}{dx}}. \quad (15.51)$$

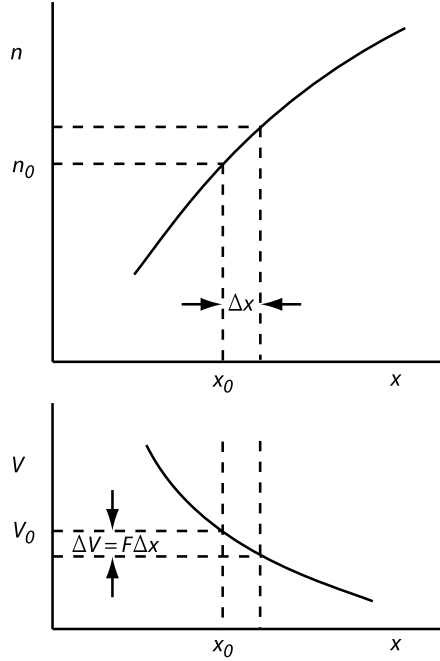
The negative sign of the hole current is due to the fact that in both equations $\pm e = |e|$ is used. The diffusion current can be derived as the difference between two currents caused by a completely random motion of carriers originating in adjacent slabs with slightly different carrier densities (Fig. 15.7). The current, originating at $x_0 + dx/2$ and crossing the interface at x_0 from right to left, is caused by the Brownian motion of electrons of a density $n_0 + dn/2$. It is given by

$$\overleftarrow{j}_{n,\text{diff}} = e \left(n_0 + \frac{dn}{2} \right) \frac{v_{\text{rms}}^2}{3} \frac{\tau_n}{dx}; \quad (15.52)$$

the current crossing the boundary from left to right is given by

$$\overrightarrow{j}_{n,\text{diff}} = e \left(n_0 - \frac{dn}{2} \right) \frac{v_{\text{rms}}^2}{3} \frac{\tau_n}{dx}. \quad (15.53)$$

Fig. 15.7 Electron density and electrostatic potential distribution in the Boltzmann region in thermal equilibrium (schematic)



The current is proportional to the carrier velocity V_{rms} and the carrier mean free path λ_n . In turn, λ_n is given by $v_{\text{rms}}T_n$. The factor $1/3$ arises from gas-kinetic arguments when the root mean square velocity is obtained from an isotropic velocity distribution: $v^2 = v_{\text{rms}}^2 = v_x^2 + v_y^2 + v_z^2$, with $v_x^2 = v_y^2 = v_z^2$; we then obtain for the x -component used in Eq. (15.34) $v_x^2 = (1/3)v_{\text{rms}}^2$.

The difference of both currents [Eqs. (15.31) and (15.32)] is the net diffusion current

$$j_{n,\text{diff}} = \vec{j}_{n,\text{diff}} - \overleftarrow{j}_{n,\text{diff}} = e \frac{v_{\text{rms}}^2 \tau_n}{3} \frac{dn}{dx}, \quad (15.54)$$

with the diffusion coefficient given by

$$D_n = \frac{v_{\text{rms}}^2 \tau_n}{3}. \quad (15.55)$$

By using $v_{\text{rms}} = 3kT/m_n$ [Eq. (26.15)], we obtain the more commonly used equation for the diffusion current

$$\boxed{j_{n,\text{diff}} = \mu_n kT \frac{dn}{dx}} \quad \text{and} \quad \boxed{j_{p,\text{diff}} = -\mu_p kT \frac{dp}{dx}}. \quad (15.56)$$

Both diffusion currents for electrons and holes have the same negative sign for a positive gradient of $n(x)$ or $p(x)$ when recognizing that μ_n is negative and μ_p is positive. However, since the conventional notation with $\mu_n = |\mu_n|$ is used, the difference in signs appears.

15.13 Maximum Diffusion Currents

As the carrier density gradient increases, the diffusion current increases proportionally to it [Eq. (15.33)]. However, this proportionality is limited, when the density gradient becomes so steep that the reverse current [Eq. (26.49)] becomes negligible compared to the forward current [Eq. (15.53)]. When increasing the distance dx to the mean free path λ_n , we obtain from Eq. (15.36) with $j_{n,\text{diff}} \ll j_{n,\text{diff}}$ for the maximum possible diffusion current through a planar surface

$$j_{n,\text{diff},\text{max}} = en_0 \frac{v_{\text{rms}}^2}{3} \frac{\tau_n}{\lambda_n} \quad (15.57)$$

or, for carriers following Boltzmann statistics and within a device with planar geometry,

$$j_{n,\text{diff},\text{max}} = \frac{en}{\sqrt{6\pi}} v_{\text{rms}}. \quad (15.58)$$

This current is known as the *Richardson-Dushman current* (Dushman 1930). It is equal to the *thermionic emission current* into the vacuum if the semiconductor is cut open at x_0 (Fig. 15.7), and if a vanishing workfunction is assumed; that is, if all electrons in the conduction band at x_0 , with a velocity component toward the surface, could exit into the vacuum.

15.14 Einstein Relation

Comparing the diffusion equations, Eq. (26.47) with Eq. (26.52), we obtain a relation between the diffusion constant and the carrier mobility:

$$D_{n,p} = \frac{\mu_{n,p} kT}{e}, \quad (15.59)$$

which is known as the *Einstein relation* and holds for systems that follow Boltzmann statistics. This can be seen from the following arguments. In thermal equilibrium, the total current, as well as each carrier current, vanish: $j = j_n = j_p = 0$. The electron current is composed of drift and diffusion currents; hence,

$$\mu_n n F + D_n \frac{dn}{dx} = 0, \quad (15.60)$$

which can be integrated to yield

$$n(x_0 + \Delta x) = n(x_0) \exp\left(-\frac{\mu_n F \Delta x}{D_n}\right). \quad (15.61)$$

On the other hand, electrons obey the Boltzmann distribution in equilibrium in the conduction band of a semiconductor. Their surplus energy, obtained in an electric field at a distance Δx is $\Delta E = e\Delta V = eF\Delta x$ (Fig. 15.8), yielding a density

$$n(x_0 + \Delta x) = n(x_0) \exp\left(-\frac{eF\Delta x}{kT}\right). \quad (15.62)$$

The assumptions used beyond the Boltzmann distribution are that of a one-carrier model near equilibrium and that the total current is small compared to drift and diffusion currents; hence, Eq. (15.2) holds. At high fields, one or more of these conditions are no longer fulfilled. Consequently, the Einstein relation needs to be modified. For nonparabolic bands, see Landsberg and Cheng (1985).

15.15 The Electrochemical Fields

For the total current, we need to consider the gradient of $\Psi(x)$ and the gradient of $n(x)$. In thermal equilibrium, n is given by the Fermi distribution. When the Fermi level is separated by several kT from the band edge, we can approximate this equation with the Boltzmann distribution:

$$E_c(x) - E_F(x) = kT \ln \frac{N_c}{n(x)}. \quad (15.63)$$

Replacing $E_c(x)$ with $e\Psi(x) + c_1$, and differentiating both sides of Eq. (13.4) with respect to x , we obtain after division by e :

$$-\frac{d\psi_n}{dx} - \frac{1}{e} \frac{dE_F}{dx} = -\frac{kT}{e} \frac{1}{n} \frac{dn}{dx}. \quad (15.64)$$

After multiplying both sides with $\sigma_n = e\mu_n n$ and rearranging, we obtain

$$\sigma_n \frac{1}{e} \frac{dE_F}{dx} = -\sigma_n \frac{d\psi_n}{dx} + \mu_n kT \frac{dn}{dx}. \quad (15.65)$$

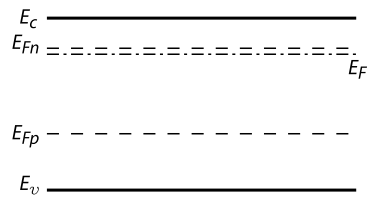
The right-hand side is the total electron current; thus, the left-hand side must also be equal to j_n :

$$j_n = -\sigma_n \frac{1}{e} \frac{dE_F}{dx}. \quad (15.66)$$

Since in thermal equilibrium, i.e., with vanishing external field, the Fermi level must be horizontal, we conclude that the electron, and hole, current must vanish separately in equilibrium:

$$\boxed{\text{for } \frac{dE_F}{dx} \equiv 0 \quad \rightarrow \quad j_n \equiv j_p \equiv 0.} \quad (15.67)$$

Fig. 15.8 Band model with external excitation resulting in a split of the Fermi level into two quasi-Fermi levels; zero-field case



15.15.1 Quasi-Fermi Level

In steady state, e.g., with an external excitation, the electron and hole densities deviate from thermodynamic equilibrium values.

Nevertheless, we may use the Fermi distribution to describe their density in the bands, using the *quasi-Fermi levels* E_{Fn} and E_{Fp} according to the definition equations

$$n \stackrel{\text{def}}{=} N_c \frac{1}{\exp \frac{E_c - E_{Fn}}{kT} + 1} \quad (15.68)$$

and

$$p \stackrel{\text{def}}{=} N_v \frac{1}{\exp \frac{E_{Fp} - E_v}{kT} + 1}, \quad (15.69)$$

with $E_{Fn} \neq E_{Fp}$. This rather useful approximation introduces errors which may or may not be acceptable depending on the cause for deviation from the thermal equilibrium. In general, the error is quite small for optical excitation and for low external fields. For high external fields, the distribution function is substantially deformed, and a more sophisticated approximation is required.

With optical or field-induced carrier generation, n and p are increased above their thermodynamic equilibrium value; hence, $E_{Fp} < E_p < E_{pn}$, resulting in a decreased distance of both quasi-Fermi levels from their corresponding bands—see Fig. 15.8. In certain cases, the recombination may be increased above the equilibrium value, as for instance in a pn -junction in reverse bias; here, E_{Fn} can drop below E_{Fp} .

In using the same algebraic procedure as described in the previous section, we have for the total electron current in steady state:

$$j_n = -\sigma_n \frac{1}{E} \frac{dE_{Fn}}{dx}; \quad (15.70)$$

that is, the *total electron current* is proportional to the negative slope of the quasi-Fermi potential, as the drift current is proportional to the negative slope of the electrostatic potential [Eq. (15.27)]. For both currents, the conductivity is the proportionality constant.

In order to emphasize this similarity, we define the electrochemical potentials for electrons and holes:

$$\varphi_n = \frac{1}{e} E_{Pn} \quad \text{and} \quad \varphi_p = \frac{1}{e} E_{Fp}. \quad (15.71)$$

The total currents can now be expressed as

$$\boxed{j_n = -\sigma_n \frac{\partial \varphi_n}{\partial x}} \quad \text{and} \quad \boxed{j_p = -\sigma_p \frac{\partial \varphi_p}{\partial x}}. \quad (15.72)$$

For homogeneous semiconductors with homogeneous generation of carriers, these currents become the drift currents, and Eq. (15.55) becomes equal to Eq. (25.36)

In steady state, the total current is divergence-free, i.e., $j_n + j_p = \text{const}$. Therefore,

$$\sigma_n \frac{\partial \varphi_n}{\partial x} + \sigma_p \frac{\partial \varphi_p}{\partial x} \equiv \text{const} \quad (15.73)$$

or

$$\mu_n n(x) \frac{\partial \varphi_n}{\partial x} + \mu_p p(x) \frac{\partial \varphi_p}{\partial x} \equiv \text{const}. \quad (15.74)$$

Since a semiconductor is predominantly *n*- or *p*-type, except for the inner part of a junction, we usually can neglect one part of the sum. For example, for the *n*-type region,

$$n(x) \frac{\partial \varphi_n}{\partial x} \equiv \text{const}; \quad (15.75)$$

i.e., if there is a gradient in the carrier density, then the highest slope in $Pn(x)$ is expected where the carrier density is lowest for an inhomogeneous $n(x)$ distribution.

From Eq. (15.69), we also conclude that for vanishing currents in steady state, the slopes of the quasi-Fermi potentials must be opposite to each other. The lower the corresponding carrier densities, the higher the slopes:

$$\mu_n n(x) \frac{\partial \varphi_n}{\partial x} = -\mu_p p(x) \frac{\partial \varphi_p}{\partial x}. \quad (15.76)$$

15.16 External and Built-in Fields

There are substantial differences between an external and a built-in field. The most significant being that an external field can heat a carrier gas, while a built-in field cannot. The *external field* is created by an external bias resulting in a surface-charge on the two electrodes with no space-charge within the semiconductor (Fig. 15.5). Within a typical semiconductor, however, space-charge regions exist because of intentional or unintentional inhomogeneities in the distribution of charged donors or

acceptors.⁸ This charge density ϱ causes the development of an *internal field* according to the Poisson equation:

$$\boxed{\frac{dF_i}{dx} = \frac{\varrho}{\varepsilon\varepsilon_0}} \quad (15.77)$$

The acting field is the sum of both internal, subscript i , and external, subscript e , fields:

$$F = F_i + F_e. \quad (15.78)$$

External and internal fields result in the same slope of the bands. Therefore, this distinction between internal and external fields is usually not made, and the subscripts at the fields are omitted. In this chapter some of the basic differences will be indicated between external and internal fields as they relate to carrier transport. For some additional discussion, see Sect. 17.9.

15.16.1 Penalties for a Simple Transport Model

There are, however, penalties one must pay for a general description of fields, which can best be seen from carrier heating in an electric field. *Carrier heating* is used to describe the field dependence of the mobility in a microscopic model. Carriers are shifted up to higher energies within a band. Consequently, their effective mass changes, it usually increases, and the scattering probability changes—most importantly, due to the fact that it becomes easier to create phonons. For all of these reasons, the mobility becomes field-dependent; it usually decreases with increasing field.

The heating *is absent in thermal equilibrium*: the carrier gas and the lattice with its phonon spectrum is in equilibrium within each volume element; thus, carrier and lattice temperatures remain the same (Stratton, 1969). No energy can be extracted from an internal field, i.e., from a sloped band, due to a space charge *in equilibrium*.⁹ This situation may be illustrated with an example replacing electrical with gravitational forces: a sloping band due to a space-charge region looks much like a mountain introduced on top of a sea-level plane, the Fermi level being equivalent to the sea level. As the introduction of the mountain does little to the distribution of molecules in air, the introduction of a sloping band does little to the distribution of

⁸ *pn*-junctions are the best studied intentional space-charge regions. Inhomogeneous doping distributions—especially near surfaces, contacts, or other crystal inhomogeneities are often unintentional and hard to eliminate.

⁹ This argument no longer holds with a bias, which will modify the space-charge; partial heating occurs, proportional to the fraction of external field. This heating can be related to the tilting of the quasi-Fermi levels (Böer 1985a).

electrons in the conduction band. Since there are fewer molecules above the mountain, the air pressure is reduced, just as there are fewer electrons in a band where it has a larger distance from the Fermi level (Fig. 16.1).

However, when one wants to conveniently integrate over all altitudes (energies) in order to arrive at a single number, the air pressure (or the electron density), one must consider additional model consequences to prevent winds from blowing from the valleys with high pressure to the mountain top with low pressure by following only the pressure gradient. Neither should one expect a current of electrons from the regions of a semiconductor with the conduction band close to the Fermi level, which results in a high electron density, to a region with low electron density in the absence of an *external field*.

To prevent such currents in the electron-density model, one uses the *internal fields*, i.e., the built-in fields, and balances the diffusion current with an exactly compensating drift current. The advantage of this approach is the use of a simple carrier density and a simple transport equation. The penalty is the need for some careful definitions of transport parameters, e.g., the mobility, when comparing external with built-in fields, and evaluating the ensuing drift and diffusion currents when the external fields are strong enough to cause carrier heating—see the following sections.

15.17 Distributions in Built-in or External Fields

The carrier distribution is determined relative to the Fermi level. For vanishing bias, the distribution is independent of the position; the Fermi level is horizontal. The distribution remains unchanged when a junction with its built-in field is introduced.¹⁰ The sloping bands cut out varying amounts from the lower part of the distribution, much like a mountain displaces its volume of air molecules at lower altitudes (Fig. 15.9).

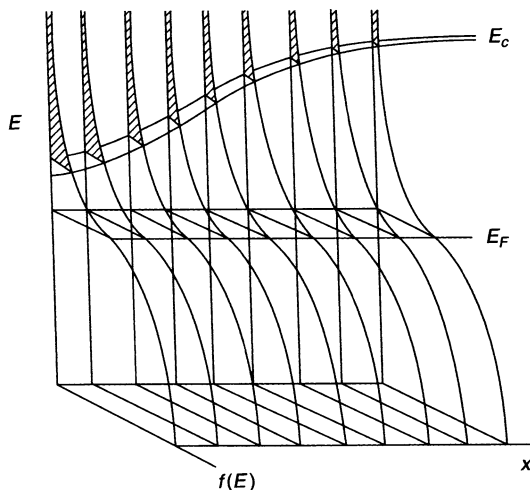
The carrier concentration n becomes space-dependent through the space dependence of the lower integration boundary, while the energy distribution of the carrier $n(E)$ remains independent in space:

$$n(x) = \int_{E_c(x)}^{\infty} n(E) dE. \quad (15.79)$$

This is similar to the velocity distribution of air molecules, which is the same at any given altitude, whether over a mountain or an adjacent plane; whereas the integrated

¹⁰With bias, the Fermi level in a junction is split into two quasi-Fermi levels which are tilted, however, with space-dependent slope. Regions of high slope within the junction region will become preferentially heated. The formation of such regions depends on the change of the carrier distribution with bias and its contribution to the electrochemical potential (the quasi-Fermi level). Integration of transport-, Poisson-, and continuity equations yields a quantitative description of this behavior (Böer 1985a).

Fig. 15.9 Fermi distribution for different positions in a semiconductor with a built-in field region (junction) and zero-applied bias



number, i.e., the air pressure near the surface of the sloping terrain, is not. This does not cause any macroscopic air motion, since at any stratum of constant altitude the molecular distribution is the same; hence, the molecular motion remains totally random.

In a similar fashion, electrons at the same distance above the Fermi level are surrounded by strata of constant electron density; within such strata their motion must remain random. During scattering in thermal equilibrium, the same amount of phonons are generated as are absorbed by electrons, except for statistical fluctuations: on the average, all events are randomized. Electron and hole currents both vanish in equilibrium *for every volume element*. Figure 15.10a gives an illustration of such a behavior.

In an *external field*, however, Fermi level and bands are tilted parallel to each other; that is, with applied bias, the carrier distribution becomes a function of the spatial coordinate (Fig. 15.10b). When electrons are accelerated in the field, they move from a region of higher density $n(E_1 - E_F)_{x1}$ to a region of lower density $n(E_1 - E_F)_{x2}$. These electrons can dissipate their net additional energy to the lattice by emitting phonons and causing lattice (Joule's) heating. In addition, while in net motion, electrons fill higher states of the energy distribution, thereby causing the carrier temperature to increase. The carrier motion in an *external field* is therefore no longer random; it has a finite component in field direction; the *drift velocity* $v_D = \mu F$ and the collisions with lattice defects are at least partially inelastic. A net current and lattice heating results.

15.18 Mobilities in Built-in or External Fields

At higher fields the carrier *mobility* becomes field-dependent. The difference between the built-in and the external fields relates to the influence of carrier heating

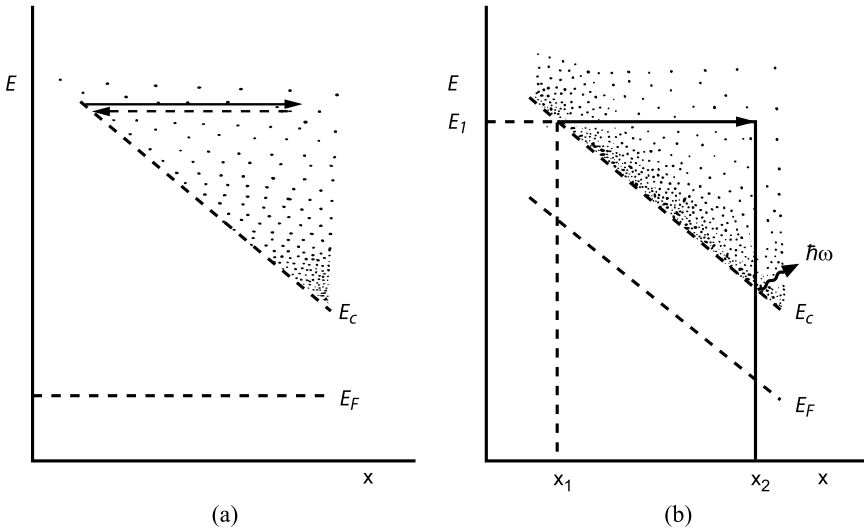


Fig. 15.10 Sloping band due to (a) an internal (built-in) field with horizontal Fermi level; and (b) due to an external field with parallel sloping bands and Fermi level. The electron distribution is indicated by a *dot* distribution, and the action of field and scattering by *arrows*

on the mobility, since the averaging *process* for determining the mobility uses the corresponding distribution functions. For instance, with an electric field in the x -direction, one obtains for the drift velocity of electrons

$$v_D = \mu_n F_x = \bar{v}_x = \frac{\iiint v_x f(v) g(v) d^3 v}{\iiint f(v) g(v) d^3 v}, \quad (15.80)$$

where $g(v)$ is the density of states in the conduction band per unit volume of velocity space, and $d^3 v$ is the appropriate volume element in velocity space. If F_x is the built-in field F_i then the distribution function is the Boltzmann function $f_B(v)$. If F_x the external field F_e , the distribution function is modified due to carrier heating according to the field strength $f F(v)$.

The averaging process involves the distribution function, which is modified by both scattering and effective mass contributions. This is addressed in numerous papers dealing with external fields (for a review, see Nag 1980; see also Jacobini et al. 1977; Seeger 1973; Conwell 1967). In contrast, when only a built-in field is present, the averaging must be done with the undeformed Boltzmann distribution, since lattice and electron temperatures remain the same at each point of the semiconductor.

15.19 Summary: Potential Gradients and Currents

The *total current* is given as the sum of drift and diffusion currents; for electrons, one has:

$$j_n = j_{n,\text{drift}} + j_{n,\text{diff}} = e\mu_n n F + eD_n \frac{dn}{dx}, \quad (15.81)$$

and for holes,

$$j_p = j_{p,\text{drift}} + j_{p,\text{diff}} = e\mu_p p F - eD_p \frac{dp}{dx}. \quad (15.82)$$

The *total carrier current* is the sum of both:

$$j = j_n + j_p. \quad (15.83)$$

In homogeneous semiconductors, only one of the four components is usually predominant, while in a *pn*-junction with sufficient bias each one becomes predominant within a different region (Böer 1985a, 1985b).

The various currents in a semiconductor can be expressed in a similar fashion. They are proportional to the negative gradient of electrostatic or electrochemical potentials with the conductivity as a proportionality factor.

$$\begin{aligned} j_n &= -\sigma_n \frac{\partial \varphi_n}{\partial x} \\ j_p &= -\sigma_p \frac{\partial \varphi_p}{\partial x} \\ j_{n,\text{Drift}} &= -\sigma_n \frac{\partial \psi_n}{\partial x} \\ j_{p,\text{Drift}} &= -\sigma_p \frac{\partial \psi_p}{\partial x} \\ j_{n,\text{Diff}} &= -\sigma_n \frac{\partial (\varphi_n - \psi_n)}{\partial x} \\ j_{p,\text{Diff}} &= -\sigma_p \frac{\partial (\varphi_p - \psi_p)}{\partial x} \end{aligned} \quad (15.84)$$

Drift and total currents are proportional to negative potential gradients: the first one being the electrostatic potential, and the second the electrochemical potential. The proportionality factor of both is the conductivity.

Chapter 16

Carrier Transport

Abstract The carrier transport in magnetic fields or temperature gradients need the discussion of the Boltzmann equation including the magnetic field and temperature gradients. The transport equation is given in general form. Thermo-electric effects are discussed with a table of various electric and thermo-electric effects. Tables of galvano-magnetic and thermo-magnetic effects are given. Inhomogeneous thermo-electric effects are discussed. Isothermal Hall effect, traverse magneto-resistance, and cyclotron resonance are discussed. The geometry factor in galvano magnetic effects is explained. Quasi free carriers are discussed in strong magnetic fields. Diamagnetic and paramagnetic resonance are discussed. Lande g -factor table. Density of states in magnetic fields. Magneto-phonon effects are identified. The quantized Hall effect and the fractional quantum Hall effect are discussed.

Important information about the carrier transport can be obtained when, in addition to the electric field, a magnetic field is applied or a temperature gradient is acting. A magnetic field or a temperature gradient will be introduced into the Boltzmann equation, and their influences on the electron transport analyzed.

16.1 Boltzmann Equation

The steady-state Boltzmann equation, which describes the transport of electrons under the influence of external fields

$$\mathbf{k} \cdot \nabla_k f + \mathbf{r} \cdot \nabla_r f = \left(\frac{\partial f}{\partial t} \right)_{\text{coll}}, \quad (16.1)$$

(see Chap. 30) can easily be expanded to include the *magnetic field*¹ when expressing the forces acting on the electrons by the sum of field and Lorentz

¹In the following sections the *magnetic induction* B is used, which is connected to the *magnetic field* H by $B = \mu\mu_0 H$, with μ_0 the *permeability of free space* and μ the *relative permeability*. Occasionally, the *magnetization* M is used, which, similar to the polarization, is introduced via $B = \mu_0 H + M$ with $M = \chi_m \cdot \mu_0 \chi H$ and $\mu\mu = 1 + \chi_m$ with χ_m the *magnetic susceptibility*.

forces:

$$\dot{\mathbf{k}} = \frac{e}{\hbar}(\mathbf{F} + \dot{\mathbf{r}} \times \mathbf{B}) \quad (16.2)$$

where $\mathbf{r}$ is the group velocity of the electron wave packet and $\mathbf{B}$ is the magnetic induction. The distribution function $f = f(\mathbf{r}, \mathbf{k}, T, t)$ contains the temperature, which also can include temperature gradients. Using a relaxation-time approximation and setting $f = f_0 + \delta f$, where δf is a small perturbation of the Fermi distribution f_0 , we have

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = -\frac{\delta f}{\tau(E)}; \quad (16.3)$$

assuming that each collision probability is independent of the collision angle, the Boltzmann equation can be integrated. This can be done in a closed form when $B = 0$:

$$f = \frac{f_0(1-f_0)\tau}{kT} \left(\mathbf{v} \cdot \left[e\mathbf{F} - \nabla_r E_F - \frac{E - E_F}{T} \nabla_r T \right] \right); \quad (16.4)$$

the derivation of Eq. (16.4) is left as an exercise problem. Here and in the following equations, the electrochemical energy E_F (Fermi energy) is used, which includes the potential energy as well as changes in the carrier density, and permits a simplified expression. When applying the equation to a deviation from thermal equilibrium, E_F must be replaced by the quasi-Fermi energies E_{Fn} or E_{Fp} for electrons or holes, respectively.

When the magnetic induction is included, its influence can no longer be treated as a small perturbation.² In contrast to the electrical and thermal conductivities, which are observed at small fields, typical magnetical effects, such as the Hall effect and magnetoresistance, require rather large fields to become observable. Mathematically, this means that the term proportional to the gradient of δf must also be taken into consideration. This yields

$$\begin{aligned} \delta f = & \frac{f_0(1-f_0)\tau}{kT} \left(\mathbf{v} \cdot \left[e\mathbf{F} - \nabla_r E_F - \frac{E - E_F}{T} \nabla_r T \right] \right) \\ & + \frac{e}{\hbar} \tau (\mathbf{v} \times \mathbf{B}) \nabla_k \delta f, \end{aligned} \quad (16.5)$$

which can be solved by iteration. Evaluating the solution near the bottom of the conduction band, where, for spherical equi-energy surfaces, the electron velocity can be expressed as $v = \hbar k / m_n$ one obtains

$$\boxed{\delta f = \frac{f_0(1-f_0)}{kT} \left[\frac{\tau}{1+b^2} \{ \mathbf{v} \cdot \mathbf{f} + \mathbf{v} \cdot (\mathbf{b} \times \mathbf{f}) + (\mathbf{v} \cdot \mathbf{b})(\mathbf{b} \cdot \mathbf{f}) \} \right]} \quad (16.6)$$

²If $\mathbf{v} \times \mathbf{B}$ is on the order of $\mathbf{F}$, its influence becomes negligible since, from Eq. (16.2), a term $\mathbf{v} \cdot (\mathbf{v} \times \mathbf{B})$ would appear in Eq. (31.4) which vanishes, since $\mathbf{v}$ is orthogonal to the vector $\mathbf{v} \times \mathbf{B}$.

with the abbreviations

$$\mathbf{b} = \frac{e}{m_n} \tau \mathbf{B} \quad \text{and} \quad \mathbf{f} = e\mathbf{F} + \nabla_r E_F + \frac{E - E_F}{T} \nabla_r T. \quad (16.7)$$

The distribution function $f = f(\mathbf{r}, \mathbf{k}, T(\mathbf{r}), \mathbf{B}, t)$ now contains the influence of electric, thermal, and magnetic fields—for more detail, see Haug (1972) and Madelung (1973).

The deformed distribution function causes changes in the transport properties, i.e., changes in the electrical or thermal currents as a result of the interacting fields. Rather than following a stringent development of the transport from the Boltzmann equation, a task first solved for carrier conduction by Bloch, the following section will take an alternative, semiempirical approach by describing the different currents with proportionality constants. These constants are later interpreted by a microscopic model.

16.2 Transport Equations

The two governing transport equations, dealing with carrier current $\mathbf{j}$ and an energy (heat) current $\mathbf{w}$, are given in their general form as

$$\mathbf{j} = -\frac{e}{\hbar} \int \nabla_k E(\mathbf{k}) g(\mathbf{k}) f(\mathbf{r}, \mathbf{k}, T(\mathbf{r}), \mathbf{B}, t) d\mathbf{k} \quad (16.8)$$

$$\mathbf{w} = \frac{1}{\hbar} \int \nabla_k E(\mathbf{k}) E(\mathbf{k}) g(\mathbf{k}) f(\mathbf{r}, \mathbf{k}, T(\mathbf{r}), \mathbf{B}, t) d\mathbf{k}, \quad (16.9)$$

and contain the density of states and the distribution functions developed in the previous section.

In addition, one needs two conservation laws to describe the transport behavior in a homogeneous semiconductor: the *conservation of the number of carriers*

$$e \frac{\partial n}{\partial t} + \nabla \cdot \mathbf{j} = 0, \quad (16.10)$$

and the *conservation of energy*³

$$\rho \frac{\partial u}{\partial t} + \nabla \cdot \mathbf{w} = -\mathbf{F} \cdot \mathbf{j}, \quad (16.11)$$

where ρ is the density and u is the specific internal energy.

³Although the electric and magnetic fields act as external forces, and one has $-(\mathbf{F} + \mathbf{v} \times \mathbf{B})$ as total force, the scalar product of $(\mathbf{v} \times \mathbf{B}) \cdot \mathbf{j}$ is zero since the vectors $\mathbf{v} \times \mathbf{B}$ and $\mathbf{j}$ are perpendicular to each other; in first approximation, there is no energy input into the carrier gas from a magnetic field.

The solution of these transport equations in steady state can be expressed as a linear combination of transport parameters and driving forces. For example, when only electric fields act

$$\begin{aligned}\mathbf{j} &= \alpha_{11} \nabla \varphi \\ \mathbf{w} &= \alpha_{21} \nabla \varphi;\end{aligned}\tag{16.12}$$

when electric and thermal fields act

$$\begin{aligned}\mathbf{j} &= \alpha_{11} \nabla \varphi + \alpha_{12} \nabla T \\ \mathbf{w} &= \alpha_{21} \nabla \varphi + \alpha_{22} \nabla T;\end{aligned}\tag{16.13}$$

and when incorporating a magnetic field

$$\begin{aligned}\mathbf{j} &= \alpha_{11} \nabla \varphi + \alpha_{12} \nabla T + \beta_{11} (\mathbf{B} \times \nabla \varphi) + \beta_{12} (\mathbf{B} \times \nabla T) \\ &\quad + \gamma_{11} \mathbf{B} \cdot (\mathbf{B} \nabla \varphi) + \gamma_{12} \mathbf{B} \cdot (\mathbf{B} \nabla T) \\ \mathbf{w} &= \alpha_{21} \nabla \varphi + \alpha_{22} \nabla T + \beta_{21} (\mathbf{B} \times \nabla \varphi) + \beta_{22} (\mathbf{B} \times \nabla T) \\ &\quad + \gamma_{21} \mathbf{B} \cdot (\mathbf{B} \nabla \varphi) + \gamma_{22} \mathbf{B} \cdot (\mathbf{B} \nabla T).\end{aligned}\tag{16.14}$$

Here, φ is the electrochemical *potential*, distinguished from $E_F = e\varphi$ the electrochemical energy. For steady state, one has to replace φ with φ_n for electrons and φ_p for holes—see Sect. 26.5.2. The coefficients α_{ik} , β'_{ik} and γ_{ik} are the well-known transport coefficients, e.g. $\alpha_{11} = \sigma_c$, the electrical conductivity, and $\alpha_{22} = K_c$, the thermal conductivity involving the respective carriers (with subscript $c = n$ or p). The other parameters will be explained below. The total thermal conductivity is related to all four coefficients $\kappa = (\alpha_{11}\alpha_{22} - \alpha_{12}\alpha_{21})/\alpha_{11}$ (Beer 1963).

Important relations connect the different transport coefficients, such as the *Onsager relations*, obtained from the reciprocity of the effects

$$\alpha_{ik}(\mathbf{B}) = \bar{\alpha}_{ki}(-\mathbf{B}),\tag{16.15}$$

where α_{ki} is the transposed tensor of α_{ik} . In anisotropic semiconductors, each of the transport parameters is a *tensor*, e.g., $\sigma_n = \sigma_{ik}^n = en\mu_{ik}$. The transport coefficients are directly accessible through experimental observation. Their magnitudes depend on the relative orientation of the different fields and, for an anisotropic semiconductor, also on the relative crystallographic orientation. In samples that permit electrical currents in the z direction only, one also distinguishes *isothermal* and *adiabatic galvanomagnetic effects*, depending on whether $\Delta_y T = 0$ or $W_y = 0$ (see Madelung 1978).

An overview of the different possibilities on an isotropic semiconductor is given in Tables 16.1 and 16.2. Some of the effects listed have gained technical interest or are used extensively for analytical purposes; the Peltier effect and the Hall effect are examples.

In the following sections, some of the more important effects will be discussed in some detail and the corresponding transport parameters will be analyzed in a microscopic model to yield information about the basic transport properties.

Table 16.1 Electric and thermoelectric effects

			Given	It results	Coefficient	Name
			Electric field	Current	$\sigma = en\mu$ $= \frac{e^2 n}{m^*} \frac{E_r}{E}$	Conductivity
Homog. effects	Thermoelectric	1. Order	Generation gradient	Photo-emf		Dember effect
			Temperature gradient	Heat flow Thermo-emf	$k = \frac{n}{m^* T} \left(\frac{E_r(E-E_F)}{E E_r} - \frac{E_r(E-E_F)^2}{E} \right)$ Heat conductivity $\alpha = -\frac{T}{e} \frac{E_r(E-E_F)}{E_r}$ Thermopower	Seebeck effect (1.Benedick's effect)
			Temperature gradient in semiconductor with neck	Temperature gradient near neck		2.Benedick's effect
		2. Order effects	Temperature gradient parallel to electric current	Change of temperature gradient (heat evolution)	$x = -\frac{1}{e} \frac{E_r(E-E_F)}{E_r}$ Peltier coefficient	Thomson effect
			Changing temperature gradient	Thermo-emf		Inverse Thomson effect
Inhomog. effects	Thermo-electric	Optical carrier generation between two materials	Photo-emf			Photovoltaic effect
		Temperature difference between two materials	Thermo-emf	$\Delta V = (\alpha_2 - \alpha_1) \Delta T$ $\alpha_2 - \alpha_1$ Seebeck coefficient		Seebeck effect
		Current through sequence of two materials	Temperature difference between contact points (heat evolution)	$x_2 - x_1$ Peltier coefficient		Peltier effect

16.3 Thermoelectric Effects

There are four experimentally accessible constants that describe the relations between the electric and thermal fields and the electric and thermal currents given in Eq. (16.13). It is convenient to invert these equations, which directly yields the four conventional parameters (electrical resistivity σ) = $1/\rho$ thermoelectric power a , Peltier coefficient π_i , and thermal conductivity κ):

$$\begin{aligned}\mathbf{F}^* &= \rho \mathbf{j} + \alpha \nabla T, \\ \mathbf{w}^* &= \pi \mathbf{j} - \kappa \nabla T,\end{aligned}\tag{16.16}$$

with $F^* = \mathbf{F} - \nabla \varphi$ and $w^* = \mathbf{w} - \mathbf{j} \varphi / e$. The coefficients can be obtained by solving the Boltzmann equation for a small perturbation. The results are listed in Table 16.1 (see Conwell 1982).

Table 16.2 Galvanomagnetic and thermomagnetic effects

Transversal effects B ⊥ (j or VT)				Longitudinal effects B (j or VT)		
Applied	Result	Name	Result	Name	Result	Name
Galvanomagnetic effects		Hall effect $R_H = \frac{F_y}{j_r B_x} = \frac{1}{ne}$	Change of conductivity 	Transversal magneto-resistance $\frac{F_x^*}{Q_{xx}} = \frac{j_x}{j_x}$	Change of conductivity 	Longitudinal magneto-resistance $\frac{F_x^*}{Q_{xx}} = \frac{j_x}{j_x}$
		Ettinghausen effect $P = \frac{\nabla_y T}{j_r B_x} = \frac{\pi_{yx}}{k_{xx} B_x}$	Longitudinal temperature difference 	Nernst effect $\nabla_x T = j_r \frac{\pi_{xx}}{k_{xx}}$	Longitudinal temperature difference 	Longitudinal Nernst effect $\nabla T_x = j_x \frac{\pi_{xx}}{k_{xx}}$
		Right-Leduc effect $S = \frac{\nabla_y T}{\nabla_x T B_x}$	Change of thermal conductivity 	Maggi-Right-Leduc effect $k_{xx} = \frac{\omega_x^*}{\nabla_x T}$	Change of thermal conductivity 	Longitudinal Maggi-Right-Leduc effect $k_{xx} = \frac{F_x^*}{\nabla_x T}$
Thermomagnetic effects		Ettinghausen-Nernst effect $Q = \frac{F_y^*}{\nabla_x T B_x}$	Longitudinal emf 	Ettinghausen-Nernst effect $\alpha_{xx} = \frac{\omega_x^*}{\nabla_x T}$	Longitudinal emf 	Longitudinal Ettinghausen-Nernst effect $\alpha_{xx} = \frac{F_x^*}{\nabla_x T}$

One relation between the Peltier coefficient and the thermopower, called the *Kelvin relation*, is often useful:

$$\alpha = \frac{\pi}{T}. \quad (16.17)$$

Another relation is the *Wiedemann-Franz law*, which holds for metals, i.e., as long as the thermal conductivity is determined by the electron gas alone and the lattice conductivity is negligible:

$$\kappa = L\sigma T \quad \text{with} \quad L = \frac{1}{3} \left(\frac{\pi k}{e} \right)^2 = 2.45 \cdot 10^{-8} \left(\frac{\text{WV}}{\text{AK}^2} \right); \quad (16.18)$$

where L is the Lorentz number. For a comprehensive review, see Beer (1963). When exposed to a temperature gradient, the electron gas at the hotter end obtains a higher kinetic energy. Therefore, some of these electrons in a “simple metal,” i.e., an alkali metal, move preferentially to the cooler end, charging it negatively. The thermoelectric power can be obtained classically by setting equal to each other the currents caused by an electric field and by a thermal gradient, yielding (Drude) $\alpha = e_v^{(e)} / (3ne)$. When replacing the specific heat of the electron gas with $e_v^{(e)} = (\pi^2/2)(kT/E_F)nk$, one obtains

$$\alpha = -\frac{\pi^2}{3} \frac{k}{e} \frac{kT}{E_F}; \quad (16.19)$$

except for a factor of 2 due to insufficient consideration of scattering. With $k/e = 86 \mu\text{V/K}$, one has α typically on the order of $1 \mu\text{V}$ per degree. The Seebeck coefficient a at $T = 300 \text{ K}$ is -8.3 , -15.6 , -4.4 , and $+1.7$, $+11.5$, and $+0.2 \mu\text{V/K}$ for Na, K, Pt; Au or Cu, Li, and W, respectively.

For semiconductors, the thermoelectric power is usually much larger, and is approximated by

$$\alpha_n = -\frac{k}{e} \left[r - \ln \left(\frac{N_c}{n} \right) \right] \quad \text{or} \quad \alpha_p = \frac{k}{e} \left[r - \ln \left(\frac{N_v}{p} \right) \right] \quad (16.20)$$

for n -type or p -type semiconductors, respectively. Here r is a parameter depending on the scattering mechanism:

- $r = 1$ for amorphous semiconductors (Fritzsche 1979)
- $r = 2$ for acoustic phonon scattering
- $r = 3$ for (polar) optical phonon scattering
- $r = 4$ for ionized impurity scattering, and
- $r = 2.5$ for neutral impurity scattering.

For an ambipolar semiconductor, one obtains

$$\alpha = \frac{\alpha_n \sigma_n + \alpha_p \sigma_p}{\sigma_n + \sigma_p}. \quad (16.21)$$

See, for example, Smith (1952) and Tauc (1954).

16.3.1 The Inhomogeneous Thermoelectric Effect

The thermo-emf is usually measured between two endpoints of a metal wire that is connected to a second metal wire. The two connecting points are kept at different temperatures. The resulting *thermo-emf* is then given by the difference of the thermoelectric power of the two metals, times the temperature difference between the two connecting points

$$\Delta\varphi = (\alpha_2 - \alpha_1)(T_2 - T_1). \quad (16.22)$$

When measured against a metal with exceptionally small α , e.g., lead, one obtains the value for an *absolute thermoelectric power* which is tabulated. For a review, see Pollock (1985).

16.3.1.1 Magneto-electric Effects

With a magnetic induction, the Lorentz force results in a curving of the electron path. When the magnetic induction is small enough, so that between scattering events only a small deviation from the straight path occurs, the superposition of electric field and magnetic induction results in a bending of the electron path independently. This means that in the relaxation-time approach of the Boltzmann equation, two components must be distinguished: from

$$e[\mathbf{F} + (\mathbf{v} \times \mathbf{B})] \nabla_p f = -\frac{\delta f}{\tau_m} \quad \text{with} \quad \delta f = \delta f_1(\mathbf{F}) + \delta f_2(\mathbf{F}, \mathbf{B}), \quad (16.23)$$

one obtains

$$\delta f_1(\mathbf{F}) \simeq -e\tau_m F \nabla_p f = \frac{e}{kT} \tau_m \mathbf{F} \cdot \mathbf{v} f_0 \quad (16.24)$$

as previously discussed [Eq. (16.18)], and

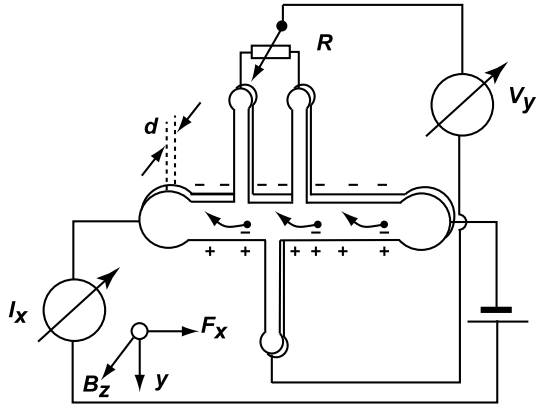
$$\delta f_2(\mathbf{F}, \mathbf{B}) \simeq -e\tau_m (\mathbf{v} \times \mathbf{B}) \cdot \nabla_p f = \frac{e^2 \tau_m^2}{m_n kT} (\mathbf{v} \times \mathbf{B}) \cdot \mathbf{F} f_0. \quad (16.25)$$

From Eq. (16.25) it follows that a magnetic induction parallel to the electric field has no effect ($\delta f_2 = 0$); whereas with a magnetic induction component perpendicular to $\mathbf{F}$, the contribution of δf_2 becomes finite. This contribution determines the Hall effect.

16.3.2 The Isothermal Hall Effect

For definiteness, one assumes $\mathbf{F} = (F_x, 0, 0)$ and $\mathbf{B} = (0, 0, B_z)$ for the relative orientations of the electric field and magnetic induction. The current density is given

Fig. 16.1 Experimental set-up for Hall effect measurement in a long two-dimensional sample. The Hall angle is determined by a setting of the rheostat R , which renders the current component $j_{11} = 0$. The Hall voltage is given by $V_{31} = R_H I_x B_z / d$, and is used to determine the Hall constant R_H



by

$$\mathbf{j} = \frac{e^2}{kT} \left[\sum_{\mathbf{v}} \tau f_0 \mathbf{F} \cdot \mathbf{v} \mathbf{v} - \frac{e}{m_n} \sum_{\mathbf{v}} \tau^2 f_0 (\mathbf{v} \times \mathbf{B} \cdot \mathbf{F}) \mathbf{v} \right], \quad (16.26)$$

which has the components

$$j_x = \frac{e^2}{kT} \left[\sum_{\mathbf{v}} \tau f_0 \overline{v_x^2} F_x + \frac{e}{m_n} \sum_{\mathbf{v}} \tau^2 f_0 \overline{v_x^2} B_z F_y \right] = \sigma_{xx} F_x + \sigma_{xy} F_y \quad (16.27)$$

$$j_y = \frac{e^2}{kT} \left[\sum_{\mathbf{v}} \tau^2 f_0 \overline{v_y^2} B_z F_x + \sum_{\mathbf{v}} \tau f_0 \overline{v_y^2} F_y \right] = \sigma_{yx} F_x + \sigma_{yy} F_y. \quad (16.28)$$

The components of the *magneto-conductivity tensor* are

$$\sigma_{xx} = \sigma_{yy} = \frac{ne^2}{m_n} \frac{\langle E\tau \rangle}{\langle E \rangle} \quad (16.29)$$

and

$$-\sigma_{yx} = \sigma_{xy} = \frac{ne^2}{m_n} \frac{eB_z}{m_n} \frac{\langle E\tau^2 \rangle}{\langle E \rangle}. \quad (16.30)$$

A more general expression of the average is used here in terms of the energy distribution function, which is equivalent to the relation $(v^2\tau)/(v^2)$ for quasi-free electrons with $\langle \mathbf{E} \rangle = (mv^2)/2$. When more complex equi-energy surfaces are involved, the anisotropy of the effective carrier mass must be considered.

For a two-dimensional semiconductor, a platelet of the shape shown in Fig. 16.1, the initial $\mathbf{B}$ -induced current in the y direction causes a charging of the corresponding surfaces until the polarization field forces j_y to vanish. From Eq. (16.28) one obtains

$$\frac{F_y}{F_x} = -\frac{\sigma_{yx}}{\sigma_{xx}} = \frac{e}{m_n} B_z \frac{\langle E\tau^2 \rangle}{\langle E\tau \rangle}. \quad (16.31)$$

The ratio of the resulting fields determines the *Hall angle*

$$\theta_H = \tan^{-1} \left(\frac{F_y}{F_x} \right) = B_x \frac{e}{m_n} \langle \tau_m \rangle = B_z \mu_H. \quad (16.32)$$

This permits a direct measurement of the *Hall mobility* μ_H . The subscript H is used to distinguish the Hall mobility from the carrier mobility, which is usually slightly smaller than μ_H , namely $\mu_H/\mu = (E\tau^2)(E)/(E\tau) = 3\pi/8$ for acoustic mode scattering $\mu_H/\mu = 1.7$ for ionized impurity scattering, and $\mu_H/\mu = 1$ for higher defect densities and temperatures (Mansfield 1956).

Often the *Hall constant* R_H is used instead, and is defined as

$$R_H = \frac{F_y}{j_x B_z} = -\frac{1}{B_z} \frac{\sigma_{yx}}{\sigma_{xx} \sigma_{yy}} = \frac{1}{en} \frac{\langle E\tau^2 \rangle \langle E \rangle}{\langle E\tau \rangle^2}. \quad (16.33)$$

The Hall constant is $\cong 1/(en)$, except for a numerical factor that depends on the scattering mechanism and is on the order of 1—see the above remarks on $\mu_H/\mu L$.

For ellipsoidal equi-energy surfaces, the Hall constant is given by (Herring 1955)

$$R_H = \frac{1}{ne} \frac{\langle E\tau^2 \rangle \langle E \rangle}{\langle E\tau \rangle} \frac{3(\frac{1}{m_x m_y} + \frac{1}{m_y m_z} + \frac{1}{m_z m_x})}{(\frac{1}{m_x} + \frac{1}{m_y} + \frac{1}{m_z})^2}. \quad (16.34)$$

When electrons and holes are present in comparable densities (compensated semiconductors) or two types of carriers (electrons or holes in different bands, or polarons) are present, both types contribute to the Hall constant:

$$R_H = \frac{n_1 e_1 \mu_1 \mu_{H1} + n_2 e_2 \mu_2 \mu_{H2}}{(n_1 e_1 \mu_1 + n_2 e_2 \mu_2)^2}. \quad (16.35)$$

With $(e_1, e_2) = (-e, +e)$ for electrons and holes, respectively, the sign of the Hall constant indicates the *type* of majority carrier: it is negative for n -type and positive for p -type conduction. Here, the signs of e and μ are carried in accordance with the sign convention—see Sect. 26.2.1.

16.3.3 Transverse Magneto-resistance

For higher magnetic induction, one can no longer ignore second-order terms ($\propto B^2$). These terms cause a reduction in the conductivity with increased magnetic induction. This results from the fact that the Hall field compensates only for the deflection of electrons with average velocity, while slower or faster electrons of the distribution are more or less deflected, resulting in a less favorable path average for the carrier conductivity. Scattering itself, however, is not influenced by magnetic induction. This *magneto-resistance* effect, discovered by W. Thomson in 1856, yields information about the anisotropy of the effective mass (Glicksman 1958).

For a quantitative evaluation, an alternative method to the evaluation of the Boltzmann equation will be used (Seeger 1973). It is based on the equation of motion for quasi-free electrons (Brooks 1955):

$$m_n \frac{d\mathbf{v}}{dt} = e(\mathbf{F} + \mathbf{v} \times \mathbf{B}). \quad (16.36)$$

With $\mathbf{B} = (0, 0, B_z)$ in Eq. (16.36), one has two components

$$\frac{dv}{dt} = \frac{eF}{m_n} - i\omega_e v \quad (16.37)$$

where ω_e is the cyclotron frequency. These two components can be discussed in a complex plane:

$$v = v_x + i v_y \quad \text{and} \quad F = F_x + i F_y, \quad (16.38)$$

yielding from Eq. (16.37)

$$\frac{dv}{dt} = \frac{eF}{m_n} - i\omega_e v. \quad (16.39)$$

This equation can be integrated after both sides are multiplied by $\exp(i\omega_e t)$, yielding for the drift velocity (McKelvey 1966)

$$v_D = v_0 \exp(-i\omega_e t) + \frac{eF}{i\omega_e m_n} \{1 - \exp(-i\omega_e t)\}, \quad (16.40)$$

which shows oscillatory behavior. Scattering, however, interferes so that only a fraction of a cycle is completed for $\omega_e \tau_m < 1$. Considering a distribution of relaxation times, one obtains for the average drift velocity

$$\langle v_D \rangle = \frac{\int_0^\infty v_D(t) \exp(-\frac{t}{\tau_m}) dt}{\int_0^\infty \exp(-\frac{t}{\tau_m}) dt} = \frac{1}{1 + i\omega_e \tau_m} \left[v_0 + \frac{eF \tau_m}{m_n} \right]. \quad (16.41)$$

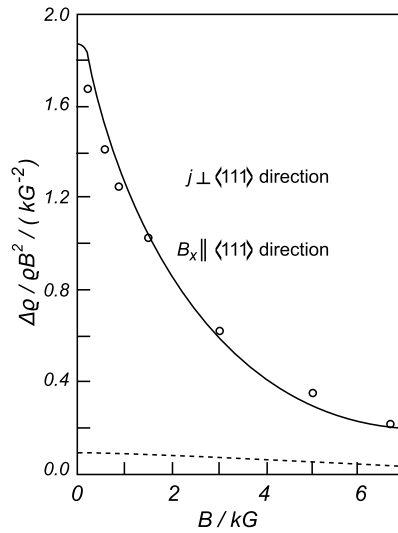
The first term (v_0) of Eq. (16.41) drops out when averaging over all angles. Separating the real and imaginary parts of v and F , one obtains

$$\begin{aligned} v_x &= \frac{e}{m_n} \left\{ \left(\tau_m - \omega_e^2 \frac{\tau_m^3}{1 + \omega_e^2 \tau_m^2} \right) F_x + \omega_e \frac{\tau_m^2}{1 + \omega_e^2 \tau_m^2} F_y \right\} \\ v_y &= \frac{e}{m_n} \left\{ -\omega_e \frac{\tau_m^2}{1 + \omega_e^2 \tau_m^2} F_x + \frac{\tau_m}{1 + \omega_e^2 \tau_m^2} F_y \right\}. \end{aligned} \quad (16.42)$$

For the current densities, $j = en v_D$ in the z and y directions, one must average these velocities, yielding

$$j_x = en \frac{e}{m_n} \left\{ \left[(\tau_m) - \omega_e^2 \left(\frac{\tau_m^3}{1 + \omega_e^2 \tau_m^2} \right) \right] F_x + \omega_e \left(\frac{\tau_m^2}{1 + \omega_e^2 \tau_m^2} \right) F_y \right\} \quad (16.43)$$

Fig. 16.2 Transverse magneto-resistance of *p*-Ge at 205 K as observed (*solid curve*) and calculated for a single carrier heavy hole model (*dashed curve*) (after Harman et al. 1954)



and

$$j_y = en \frac{e}{m_n} \left\{ -w_c \left(\frac{\tau_m^2}{1 + \omega_c^2 \tau_m^2} \right) F_x + \left(\frac{\tau_m}{1 + \omega_c^2 \tau_m^2} \right) F_y \right\}. \quad (16.44)$$

For $\omega_c \tau_m \cong 1$, which is generally fulfilled, one can neglect the frequency dependence in the denominators. With $j_n = 0$, one then obtains from Eqs. (16.43) and (16.44) by eliminating F_y

$$j_x = en \frac{e}{m_n} (\tau_m) F_x \left\{ 1 - \frac{e^2 B_z^2 (\tau_m^3)(\tau_m) - (\tau_m^2)^2}{m_n^2 (\tau_m)^2} \right\}. \quad (16.45)$$

This expression contains a second-order term that causes a decrease of the current j_z with increasing magnetic induction. With $\rho = 1/\sigma$ and $e(\tau_m)/m_n = \mu_n$ and thus $j_x = \sigma F_x \{1 - f(B_x^2)\}$, one obtains for the *magneto-resistance coefficient*

$$\frac{\Delta\rho}{\rho B_z^2} = \mu_n^2 \frac{(\tau_m^3)(\tau_m) - (\tau_m^2)^2}{(\tau_m)^4}; \quad (16.46)$$

that is, the coefficient is essentially equal to μ_n^2 except for the term containing the relaxation-time averages. This term represents a numerical factor that depends on the scattering mechanism, and lies between 0.38 and 2.15 (Seeger 1973).

The case of magneto-resistance with two carriers is straight forward (McKelvey 1966), and is additive for both carriers, even though they may be of opposite sign. The case of nonspherical equi-energy surfaces is rather involved, and is summarized by Conwell (1982); see also Beer (1963).

As an example, the magneto-resistance of a two-carrier semiconductor, *p*-type Ge, is given in Fig. 16.2. The two carrier types are light (p_l, μ_l) and heavy (p_h, μ_h)

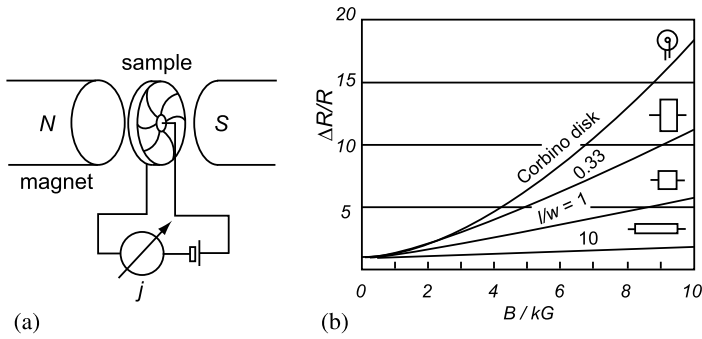


Fig. 16.3 (a) Corbino disk with indicated current flow from the central electrode to the circumference electrode. (b) Relative change in resistance of n -InSb as a function of the magnetic induction for different sample geometries; length with (l/w) ratio indicated (after Welker and Weiss 1954)

holes. Predominant carrier scattering is assumed to be due to acoustic phonons. The magneto-resistance coefficient is given by (Seeger 1973)

$$\frac{\Delta\rho}{\rho B_z^2} = \mu_h^2 \cdot \frac{9\pi}{16} \left\{ \frac{1 + \eta\beta^3}{1 + \eta\beta} - \frac{\pi}{4} \left[\frac{1 + \eta\beta^2}{1 + \eta\beta} \right]^2 \right\}, \quad (16.47)$$

with $\eta = P_l/P_h$ and $\beta = \mu_l/\mu_h$. Although in p -Ge at 205 K only 4 % of the holes are in the light hole band $\eta = 0.04$, the large ratio of the effective mass ($\beta = 8$) renders the numerical factor in Eq. (16.47) greater by a factor of 24 than for a single carrier model. As a result, the magneto-resistance is substantially enhanced by the light carriers, as shown in Fig. 16.2—compare the solid curve with the dashed curve.

16.3.4 Geometry Factors in Galvanomagnetic Effects

The Hall effect, depends on the sample geometry, since the initial charging of the sample surfaces in the y direction causes the y component of the current to vanish. The transverse magneto-resistance is usually determined in a long (z) and thin (y) sample rod or filament.

Another extreme is a sample geometry in which surfaces perpendicular to the main current direction do not exist. This can be achieved in a *Corbino disk* (Corbino 1911), shown in Fig. 16.3a. The current flows from a circular hole in the center to its circumference. The magneto-resistance is maximized since no compensation of any curved electron path is possible. The change of resistance of the Corbino disk is given by

$$\frac{\Delta R}{R} = \left(\frac{\Delta\rho}{\rho} \right)_f + \mu_H^2 \frac{B_z^2}{1 + (\Delta\rho/\rho)_f}, \quad (16.48)$$

where μ_H is the Hall mobility, and $(\Delta\rho/\rho)_f$ is the magneto-resistance change in a filament-type sample of the same material and at the same magnetic induction. Figure 16.3b presents the magneto-resistances of samples of different shapes; a thin filament sample shows the smallest effect.

16.3.5 Cyclotron Resonance

When the magnetic field is strong enough, and the mean free path is long enough for carriers to complete cyclic paths in the applied magnetic induction, strong resonances in an oscillating electromagnetic probing field are observed at the cyclotron frequency

$$\omega_c = \frac{eB}{m^*} = 17.84 \frac{m_0}{m^*} B \text{ (GHz/kG)}. \quad (16.49)$$

For the derivation of resonance conditions—see McKelvey (1966). The cyclotron-resonance line width decreases rapidly the more cycles are completed before scattering occurs. Scattering, with its limiting relaxation time, acts as the damping parameter in the resonance equation (Eq. (16.41)], and with $\tau_m = 1/\gamma$ determines the resulting line shape.

Cyclotron-resonance measurements are well suited for determining the effective mass in different crystallographic directions.

16.4 Carrier Quantum Effects in Magnetic Field

When the magnetic induction becomes large enough so that $\hbar\omega_c$ is no longer $\ll kT$, quantum-mechanical effects must be considered, i.e., splitting into Landau levels. The influence of a strong magnetic induction will be discussed in two steps: excluding scattering to obtain information on changes in the density of states, and, as in the following section, including scattering.

16.4.1 Quasi-free Carriers in a Strong Magnetic Field

Assuming that the magnetic induction acts in the z direction ($B = 0, 0, B_z$), the electron motion is described by the Schrödinger equation (Landau 1930):

$$\left\{ -\frac{\hbar^2}{2m_n} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{m_n \omega_c^2}{8} (x^2 + y^2) - i\hbar\omega_c \left[x \frac{\partial}{\partial y} + y \frac{\partial}{\partial x} \right] \right\} \psi = E\psi, \quad (16.50)$$

which has two additional terms caused by the magnetic induction, and depends on the *cyclotron frequency* ω_e . These terms impose a constraint on the electron motion

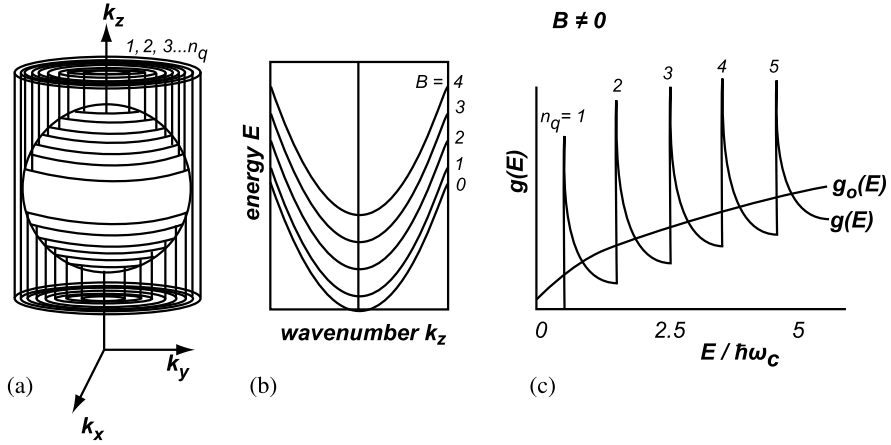


Fig. 16.4 (a) Constant energy surfaces in k space for a given magnetic induction, resulting in concentric cylinders for each of the Landau levels. (b) $E(k)$ curve and for a constant magnetic induction showing the split into a sequence of Landau bands. (c) Density of state without magnetic induction ($g_0(E)$) and with magnetic induction ($g(E)$) including the first five Landau levels and neglecting lifetime broadening. The total areas under both curves up to any given E are the same

in the y plane due to the Lorentz force. The electron motion is given semiclassically by

$$\begin{aligned}
 x &= x_0 + \sqrt{\frac{2\hbar}{m_n\omega_c} \left(n_q + \frac{1}{2} \right)} \cos(\omega_c t) = x_0 + r_{nq} \cos(\omega_c t) \\
 y &= y_0 + \sqrt{\frac{2\hbar}{m_n\omega_c} \left(n_q + \frac{1}{2} \right)} \sin(\omega_c t) = y_0 + r_{nq} \sin(\omega_c t),
 \end{aligned} \tag{16.51}$$

which are circles with a radius r_{nq} , determined by the magnetic induction and the quantum number n_q . In k space, one consequently obtains, using $k_x = (m_n/\hbar)(dx/dt)$ and $k_y = (m_n/\hbar)(dy/dt)$,

$$k_x^2 + k_y^2 = k_{nq}^2 = \frac{2m_n\omega_c^2}{\hbar} \left(n_q + \frac{1}{2} \right), \tag{16.52}$$

which is a set of cylinder surfaces determined by n_q with a radius proportional to B_z , as shown in Fig. 16.4a.

The energy of the electrons on these surfaces, obtained as eigenvalues of the Schrödinger equation (16.50), is given by

$$E = \frac{\hbar^2}{2m_n} k_z^2 + \left(n_q + \frac{1}{2} \right) \hbar\omega_c, \tag{16.53}$$

in anisotropic semiconductors, or those with anisotropic effective mass, the relative direction of the magnetic field and the crystal orientation must be considered, and are included in the cyclotron frequency.

This shows that the application of a strong magnetic induction substantially changes the behavior of Bloch electrons from being quasi-free to being confined in the zy plane. It results in a splitting into magnetic subbands⁴ or *Landau levels* at a given magnetic field according to the quantum number; whereas in the k_z direction, although the $E \propto k_x$ relation known for free electrons holds, it is offset by steps of the height of the cyclotron energy.

16.5 Diamagnetic and Paramagnetic Electron Resonance

The interactions between free electrons and a magnetic field due to the Lorentz force, leading to cyclotron resonances, are *diamagnetic interactions*. With a sufficient density of free electrons, the semiconductor becomes diamagnetic, i.e., its magnetic moment becomes negative: an oblong probe of the semiconductor suspended from a filament to permit free rotation, turns perpendicular to the magnetic flux. The induced magnetic momentum opposes its inducing force.

When including the electron spin in this discussion, one must consider an additional *paramagnetic interaction*. This interaction produces a positive contribution to the magnetic moment.

The eigenvalues of the Schrödinger equation, including spin interaction, (last term) are

$$E = \frac{\hbar^2}{2m_n} k_z^2 + \left(n_q + \frac{1}{2} \right) \hbar \omega_c \pm \frac{1}{2} g \mu_B B \quad (16.54)$$

with $-$ or $+$ dependent on parallel or antiparallel spin, respectively $\mu_H = eh/(2m^*)$ is the *Bohr magneton*, and g is the *Lande g -factor*. For free electrons *in vacuo*, the cyclotron frequency is $\omega_c = eB/\hbar m_0$ which can also be expressed with the Bohr magneton $\mu_B = eh/(2m_0)$ as $\mu_c = 2\mu_B B/\hbar$. The corresponding frequency in an atom is the *Larmor frequency* $\omega_L = g\mu_B B/\hbar$, which is equal to ω_c for $g = 2$. For electrons orbiting within a semiconductor, g can deviate substantially from 2, depending on the effective mass and the spin-orbit splitting energy Δ_0 (Lax et al. 1959):

$$g \simeq 2 \left\{ 1 + \frac{m_n - m_0}{m_n} \left(\frac{\Delta_0}{E_g + 2\Delta_0} \right) \right\}, \quad (16.55)$$

and may even become negative ($g \cong -50$ for InSb). Since the effective mass has tensor properties, g is also a tensor. Some values of g are listed in Table 16.3—see also Roth and Lax (1959). Figure 16.5 illustrates the additional splitting of the Landau levels due to the spin.

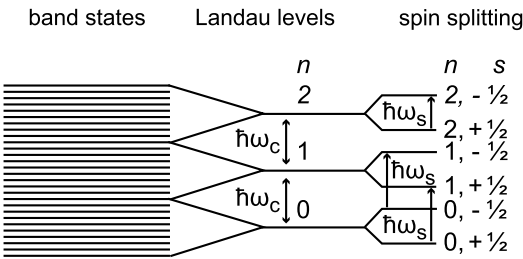
⁴In the k_z direction there are subbands; in the k_x and k_y directions, there are discrete levels in $E(k)$.

Table 16.3 Lande g -factor for selected semiconductors^a (after Roth and Lax 1959)

Material	g_c	Material	g_c	g_v^{so}	Material	g_c
Si	1.9989	GaSb	−7.68	−6.2	InSb	−50.6
Ge	−3.0	InP	1.48	−1.9	ZnSe	1.12
GaAs	−0.44	InAs	−15.6		CdTe	1.59
Material	$g_{c\parallel}$	$g_{c\perp}$	$g_{v\parallel}^A$	$g_{v\perp}^A$	$g_{v\parallel}^B$	$g_{v\perp}^B$
ZnS	2.2	1.9				
ZnTe	−0.4 [100]	−0.35 [110]				
CdS	1.774	1.787	1.25	0	1.8	1.8
CdSe	0.6	0.51	1.41			

^aIndices c and v for conduction and valence bands; indices A and B for the respective valence bands; $\parallel$ and $\perp$ with respect to the c axis

Fig. 16.5 Splitting of band states into Landau levels, considering diamagnetic interaction by orbiting electrons and, in addition, paramagnetic interaction with the electron spin resulting in further splitting



With a sufficient density of impurities with uncompensated spins, one can observe resonant absorption when flipping the spin by electromagnetic radiation of a frequency equal to the difference between states with parallel and antiparallel spin. This is an *electron paramagnetic resonance* (EPR), also called *electron spin resonance* (ESR) and occurs at

$$\hbar\omega_s = g\mu_B B. \tag{16.56}$$

These resonances provide information about the density of uncompensated spins through the strength of the resonance, and about the g factor through its resonance frequency.

The resonance absorption can be measured directly by interacting with an electromagnetic field of appropriate frequency (ω_g) or optically by observing changes in the intensity or polarization of laser-excited luminescence—see review by Cavenett (1981).

Further information about *defect centers* can be obtained from the paramagnetic interaction with nuclear spins, which can be measured by inducing spin-flipping by absorption of electromagnetic radiation (*nuclear spin resonance*). There is a wide variety of interactions involving the nuclear spin of defects that can be used for analyzing certain defect properties—see Bagraev and Mashkov (1986).

In addition to the paramagnetic interaction of electron spins, the *Pauli spin paramagnetism* at an impurity center, there is the diamagnetic part due to the orbital

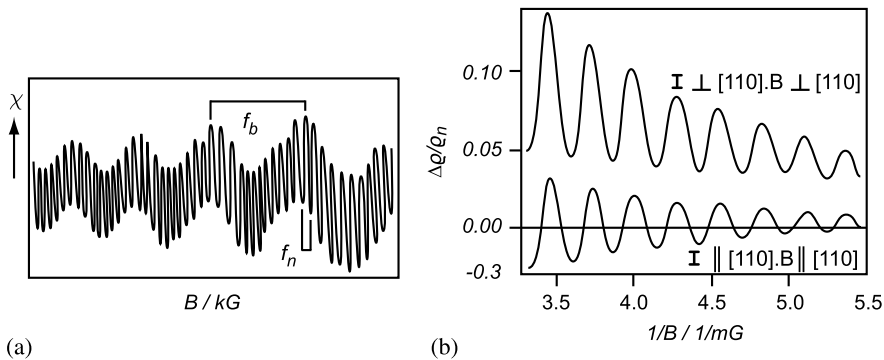


Fig. 16.6 (a) De Haas and van Alphen (1930) oscillation of magnetic susceptibility in silver with neck (high-frequency) and belly (low-frequency) oscillations when a Landau level passes through the Fermi surface (after Joseph and Thorsen 1965). (b) Shubnikov-DeHaas (1930) oscillations of the relative resistivity as a function of the magnetic field in GaSh at 4.2 K. Hall coefficient $R_H = -4.8 \text{ cm}^3/\text{As}$ (after Becker and Fan 1964)

quantization: for bound electrons, this is the *Landau diamagnetism* that is 1/3 the magnitude of the Pauli contribution. For more detail, see—Wilson (1954).

16.6 Density of States in Magnetic Fields

The modified $E(k)$ relation described in the previous section is shown in Fig. 16.6a and b with an applied magnetic field. The density of states depends on the Landau quantum number, and is given for each subband by

$$g(k_z \sim n_q) dk_z = \frac{2}{(2\pi)^2} \frac{m_n \omega_c}{\hbar} dk_z. \quad (16.57)$$

Using Eq. (16.53), one obtains the density of states as a function of the energy:

$$g(E, n_q) dE = \frac{1}{(2\pi)^2} \left(\frac{2m_n}{\hbar^2} \right)^{3/2} \frac{\hbar \omega_c}{\sqrt{E - (n_q + \frac{1}{2})\hbar \omega_c}} dE. \quad (16.58)$$

The total density of states is obtained by summation over all possible quantum numbers n_q within the band: near the bottom of it, lifted to $E_c + \hbar \omega_c/2$, for $E_c + 3\hbar \omega_c/2 < E < E_c + 5\hbar \omega_c/2$ with a summation over only one subband, for $E_c + 3\hbar \omega_c/2 < E < E_c + 5\hbar \omega_c/2$ over two, and so on for the conduction band. This density-of-state distribution is compared in Fig. 16.4c with the undisturbed distribution for vanishing magnetic induction (g_0).

16.6.1 DeHaas-Type Effects

In a metal or a degenerate semiconductor, the Fermi level lies within the conduction band. With increasing magnetic field, the spacing of the Landau levels increases and causes one after the other of these levels to cross E_F , thereby periodically changing the density of states (Fig. 16.4c) at E_F . This in turn causes the amplitude of certain properties which are determined near the Fermi surface to change periodically. These include the magnetic susceptibility, resulting in the *DeHaas-van Alphen effect*, shown in Fig. 16.6a, and the electrical conductivity, resulting in the *Shubnikov-DeHaas effect*, shown in Fig. 16.6b.

In actual materials, only rarely are the orbits at a spherical Fermi surface. In semiconductors, the orbits may be elliptical (in sidevalleys); in metals, they can have quite complicated shapes that make the oscillations more complex (Fig. 16.6a), and in turn provide information about the shapes of the Fermi surfaces (first suggested by Onsager 1952; see also Shoenberg 1969; Ziman 1972). As an example, the ratio of the wavelength of oscillation, shown in Fig. 16.6a, gives the ratio of the area of belly and neck (here 9).

16.7 Magneto-phonon Effects

When the spacing between the Landau levels coincides with the energy of longitudinal optical phonons, electrons can be transferred more easily by scattering with these phonons between different Landau levels.

$$\hbar\omega_{LO} = n_q \hbar\omega_c. \quad (16.59)$$

This causes a more pronounced change in magneto-resistance, with a period length

$$\Delta\left(\frac{1}{B}\right) = \frac{e}{m_n\omega_{LO}}, \quad (16.60)$$

which was first observed by Firsov et al. (1964) in InSb. The effect is small but observable at an intermediate range of the magnetic induction [Eq. (16.59)], temperature (to have sufficient optical phonons), and doping (the effect is sensitive to changes in scattering—Gurevich and Firsov 1964). It can be used to obtain information about the effective carrier mass.

When higher electric fields are applied in addition to the magnetic field, carrier heating takes place, and distinct multiphonon transitions can be observed—see the review by Stradling (1984).

16.8 The Quantized Hall Effect

The quantized Hall effect requires a two-dimensional electron system at high magnetic fields and low temperatures. Such a two-dimensional sample may be formed by

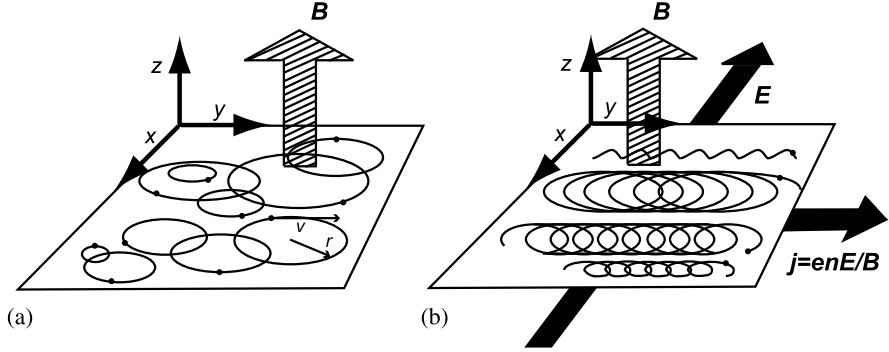


Fig. 16.7 (a) Two-dimensional electron gas with magnetic field only. (b) Movement of these electrons in the y direction when additional electric field acts in the z direction

a quantum well structure. It requires the third dimension to be $< 100 \text{ \AA}$. To facilitate an understanding of this effect, we will first review the electron motion in orthogonal electric (F_x) and magnetic (B_z) fields. Without scattering, electrons move in circles when exposed to Lorentz forces ($e\mathbf{v} \times \mathbf{B}$), with the radius, frequency, and energy given by

$$r_c = \frac{m_n v}{e B_z}, \quad \omega_c = \frac{e B_z}{m_n}, \quad E = \frac{m_n}{2} \omega_c^2 r_c^2. \quad (16.61)$$

With the addition of an electric field in the z direction, the electrons move perpendicularly to B_z and F_x in the y direction with constant velocity⁵ of the center of each circle, forming *trochoids* (a flat spiral) as shown in Fig. 16.7:

$$v_y = \frac{F_x}{B_z}, \quad \text{or} \quad \sigma_{xy} = \frac{en}{B_z} \quad (16.62)$$

while

$$v_x = 0 \quad \text{or} \quad \sigma_{xx} = 0. \quad (16.63)$$

With substantial scattering σ_{xy} decreases and σ_{xx} increases; the former is responsible for the Hall voltage, the latter for the magneto-resistance.

When the magnetic field is large enough to cause significant Landau-level splitting ($\hbar\omega > kT$), one has, instead of a continuum of states in the band, a set of discrete energy levels at

$$E_{nq} = E_c + \left(nq + \frac{1}{2}\right) \hbar\omega_c \quad \text{with } nq = 0, 1, 2, \dots \quad (16.64)$$

⁵In contrast to the case of vanishing magnetic induction where the motion proceeds in the x direction and, without scattering, is accelerated.

and with radii

$$r_{n_g} = \sqrt{\frac{2\hbar}{eB_z} \left(n_q + \frac{1}{2} \right)}. \quad (16.65)$$

Each of these Landau levels is degenerate, permitting occupation by

$$\tilde{n} = \frac{1}{2\pi r_{n_q=0}^2} = \frac{eB_z}{h} \text{ (cm}^{-2}\text{)} \quad (16.66)$$

electrons, which provides the highest packing without overlap for $n_q = 0$ of cyclotron orbits within the plane. Of n electrons in the conduction band, only n can fill the first Landau level; then n will fill the second level and so on, until all electrons are distributed, with the highest level at $T = 0$ partially filled, as long as n is not accidentally an integer multiple of n .

Scattering can only occur for electrons in the highest Landau level, and only if this level is incompletely filled or $kT \ll \hbar\omega$. Consequently, the electron ensemble will follow unperturbed trochoids as shown in Fig. 16.7b.

The filling of the Landau levels can be done by electron injection⁶ with increasing bias at constant magnetic induction, or by constant bias and increasing magnetic induction, which results in fewer Landau levels below E_F . This causes carrier rearrangement whenever a Landau level passes over the Fermi level, which tends to increase E_F and thereby changes the injection.

When the Fermi level coincides with a Landau level, the magneto-resistivity $\rho_{xx} = 1/\sigma_{xx}$ vanishes, and the Hall resistance $\rho_{xy} = 1/\sigma_{xx}$ shows a pronounced step (von Klitzing et al. 1980). This is measured by the voltage drop between the Hall probes of a two-dimensional sample—Fig. 16.8a. The results are shown in Fig. 16.8b.

From Eqs. (16.62) and (16.66), one can eliminate the incremental electron density per Landau step, and obtains a step distance of

$$\frac{1}{\Delta\sigma_{xy}} = \frac{B_z}{e\tilde{n}} = \frac{h}{e^2} = 25812.8 \, \Omega. \quad (16.67)$$

It is remarkable that the measured Hall resistance steps $\rho_{xy} = V_H/I$ are not influenced by layer geometry, defects, or by the carrier effective mass.

They are measured precisely to within 1 part in 10^8 , and can be used to define an absolute standard of resistance, or to update the value of h/e^2 , or the fine structure constant⁷ $a = hc/e^2$ (Tsui et al. 1982; von Klitzing 1981, 1986).

The rounding of the step edges and the step width is due to localized defect states in the gap between the Landau levels, and the broadening of the Landau levels into

⁶Electron injection relates to electrode properties not discussed in this book. It provides an experimental means of increasing the carrier density by simply increasing the bias, thereby injecting more carriers from an appropriate electrode. For a review, see Rose (1978b).

⁷The velocity of light contained in a is the best known of the three constants.

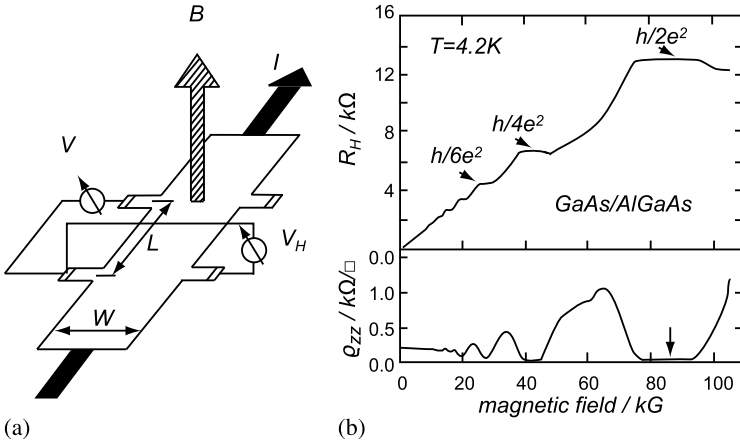


Fig. 16.8 (a) Experimental set-up to measure the quantized Hall effect. (b) Measured Hall resistance and magneto-resistance in a GaAs/Al_x-Ga_{1-x}As quantum well at 4.2 K as a function of the magnetic induction, with Landau level steps at $n_q = 2, 4$, and 6 indicated (after von Klitzing et al. 1980)

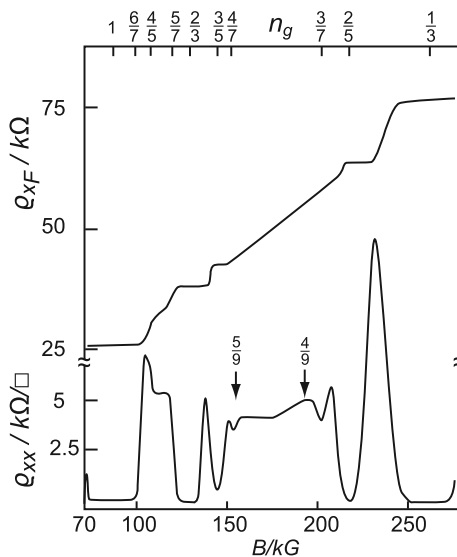
narrow Landau bands. The persistence of the plateau for a substantial width is more difficult to understand (Stormer and Tsui 1983).

16.8.1 Fractional Quantum Hall Effect

In high-quality GaAs/Al_x-Ga_{1-x}As quantum well samples at high magnetic induction and low temperatures, one can reach the quantum limit, the first Landau level. When T is decreased below 4 K, one observes that in addition to the integer n_q steps, fractional quantum numbers appear. The first is $n_q = 1/3$, which is identified at 0.09 K to better than 3 parts in 10^5 (Chang et al. 1984). Recently, more and more fractional steps have been identified by plateaus in the Hall resistance and are listed below (Tsui and Stormer 1986):

$$\begin{aligned}
 n_q &= \frac{1}{3}, \frac{2}{3}, \frac{4}{3}, \frac{5}{3}, \left(\frac{7}{3}\right), \left(\frac{8}{3}\right) \\
 n_q &= \left(\frac{1}{5}\right), \frac{2}{5}, \frac{3}{5}, \left(\frac{4}{5}\right), \left(\frac{6}{5}\right), \frac{7}{5} \\
 n_q &= \left(\frac{2}{7}\right), \frac{3}{7}, \frac{4}{7}, \left(\frac{9}{7}\right), \left(\frac{10}{7}\right), \left(\frac{11}{7}\right) \\
 n_q &= \left(\frac{4}{9}\right), \left(\frac{5}{9}\right), \left(\frac{13}{9}\right).
 \end{aligned}$$

Fig. 16.9 Fractional quantum Hall effect in GaAs/AhLeGaeAs quantum well structure at 0.09 K: curve 1 Hall resistance, and curve 2 magneto-resistance in the F_z direction (after Chang et al. 1984)



The numbers in parentheses, however, are obtained from only a slight dip of the magneto-resistance. Some of these steps are shown in Fig. 16.9.

The reason for such fractional numbers is not completely understood. It is remarkable, however, that for $n_q = p/q$, q must be odd (3, 5, 7, 9) while p is a positive integer (1 ... 13). With one exception, however $n_q = 5/2$ was recently observed at a GaAs/GaAlAs quantum well of exceptional perfection with $\mu_n > 10^6 \text{ cm}^2/\text{V s}$ (Willett et al. 1987). A theoretical explanation offered by Haldane and Rezayi (1988) indicates boson pairing of the electrons with mixed spin in the second Landau level.

It is likely that this experimental result reflects new, yet unexplained electron states in semiconductors at high magnetic fields, possibly with fractional filling of Landau levels, which are stabilized by strong mutual repulsion of the electrons. This in turn can be described with pseudo-particles of a fractional electron charge (*Laughlin states*).

Chapter 17

Carrier Scattering at Low Fields

Abstract Carrier scattering at low fields involve a large variety of scattering centers. Types of these scattering centers are intrinsic lattice defects with acoustic or optical phonons, intrinsic point defects, alloys, extrinsic point defects with charged or neutral impurities; line defects; surface defects at grain boundaries, outer surfaces; metal/semiconductor interfaces. Three dimensional defects as atomic clusters or micro crystalline or colloidal inclusions; and secondary defects such as electron–electron scattering, electron–hole scattering or electron–plasmon scattering. Matthiessen rule is given. Intervalley and intravalley scattering and; warped surface effects are described. Quasi-particles as polarons or exciton interaction is discussed. Elastic and inelastic scattering is evaluated. Each of these scattering mechanisms are theoretically described. Phonon generation and annihilation is introduced. Longitudinal acoustic scattering are analyzed. Deformation potential table is given. Acoustic scattering with piezo electric interaction is shown. Optical phonon scattering in polar and non polar semiconductors are enumerated. Scattering by intrinsic point defects and by neutral defects, as well as by ionic defects are evaluated. Coulomb scattering in anisotropic semiconductors is discussed. Quantum correction for ion scattering is introduced. Carrier–carrier scattering is identified.

Carrier scattering acts as a damping process for carrier motion. Both elastic and inelastic scattering influence the carrier transport and involve a large variety of scattering centers. Scattering determines the relaxation time, and with it, the carrier mobility.

Scattering at low fields will be discussed first. Here the deformation of the distribution function is very small and linearization, discussed in Sect. 28.3, is appropriate. The goal of this discussion is the estimation of the relaxation time, which is a measure of the carrier mobility.

When carriers are accelerated in an external electric field, their increased momenta and energies relax according to a multitude of scattering events. It is impossible to account for these events in a global fashion, and various approximations, which are different for different types of scattering centers, are required. We will first enumerate these centers, then will provide step by step some estimates of the various relaxation mechanisms, and will give the corresponding relation for the carrier mobilities.

17.1 Types of Scattering Centers

Any sufficiently large deviation from an ideal lattice periodicity can act as a scattering center. The more important ones are:

- (1) Intrinsic lattice defects
 - (a) phonons
 - (i) acoustic, with deformation potential or piezoelectric interaction
 - (ii) optical, with deformation potential (nonpolar) or polar interaction
 - (b) intrinsic point defects (interstitials, vacancies, substitutionals, and antisite defects)
 - (c) alloys (statistical distribution of lattice atoms)
- (2) Extrinsic point defects
 - (a) neutral impurities
 - (b) charged impurities
- (3) Line defects (dislocations)
- (4) Surface defects
 - (a) grain boundaries
 - (b) outer surfaces
 - (c) hetero-interfaces
 - (d) metal/semiconductor (electrode) boundaries
- (5) Three-dimensional defects
 - (a) small atomic clusters
 - (b) microcrystalline, or colloidal, inclusions
- (6) Secondary defects
 - (a) electron–electron scattering
 - (b) electron–hole scattering
 - (c) electron–plasmon scattering.

Each of these defects will shorten the relaxation time. When estimating the effect of several types of scattering centers, each related to a specific τ_i , the total time between independent scattering events can be estimated from *Mathiessen's rule*¹

$$\boxed{\frac{1}{\tau} = \sum_i \frac{1}{\tau_i}}, \quad (17.1)$$

¹An error up to 20 % can occur when applying Eq. (30.1) because of nonlinearities, interaction of different scattering events, as shown by Rode and Knight (1971).

since the collision term in the Boltzmann equation is additive. Consequently, the inverse mobilities calculated for single, independent types of scattering are also added to result in the inverse total carrier mobility—see also Debye and Conwell (1954)

$$\boxed{\frac{1}{\mu} = \sum_i \frac{1}{\mu_i}} \quad (17.2)$$

From Eq. (30.1), it is clear, however, that only the centers which influence the carriers the most need to be considered in an actual crystal under a given condition.

Depending on the type of crystal bonding, crystal preparation (growth and treatments), doping, temperature, and other external influences—such as light, strain, and electric and magnetic fields—the predominant scatterer may vary from sample to sample.

In addition, deviations from a simple lattice isotropy and other carrier-lattice interactions may create variations of the carrier scattering. For instance, one distinguishes:

- (7) Semiconductors with
 - (a) intravalley scattering
 - (b) intervalley scattering
 - (c) warped-energy surface effects
- (8) Quasi-particles, such as
 - (a) polarons directly contributing to the current instead of Bloch electrons and
 - (b) excitons (exciton-polaritons) contributing to the transport of energy and to the creation of free carriers at places different from the originations.

In the following sections, some of the more important scattering mechanisms will be discussed. A review by Nag (1984) summarizes the different scattering mechanisms and gives tables for the expressions of the relaxation times. See also Seeger (1973).

17.2 Intravalley Scattering

The scattering events described in the following sections leave the carrier within its valley. We will first assume that such scattering events take place with electrons near the r point.

17.3 Electron Scattering with Phonons

Most carriers have an energy near $(3/2)kT$. At low fields $F \ll V_{\text{rms}}/\mu$ they gain only a small fraction of additional energy compared to their thermal energy between scattering events. Carriers can interact with various types of phonons by absorbing

or emitting a phonon. Before discussing this scattering in detail, a few general remarks will provide some overall guidance.

The phonon dispersion relation of most semiconductors shows that optical phonons have an energy larger than kT at room temperature, and therefore are scarce. This makes the creation of optical phonons unlikely since most of the carriers do not have sufficient energy. Therefore, carriers scatter predominantly with the lower energy acoustic phonons, which are plentiful at room temperature. During such a scattering event, the electron energy is changed by only a small fraction; that is, the scattering is an essentially elastic event. In *semiconductors with a direct band gap*, only phonons near the center of the Brillouin zone have a high probability of scattering. During such events, substantial changes in the direction of motion can occur: k can easily change its sign.

In *semiconductors with indirect band gap*, electrons are in a valley of a relatively large k value.

Elastic scattering with low energy and momentum phonons tend to leave the electrons within their valley, with only small changes of their momentum, which changes their direction insignificantly. Intervalley scattering, which will be discussed in Sect. 30.3.1, requires a higher phonon momentum, i.e., higher energy acoustic or optical phonons except for Umklapp processes for electrons near the surface of the Brillouin zone where only small values of q are required to reverse the direction of the electron motion during scattering. This is most easily done in Ge, where the conduction band minimum lies at this surface, rather than in Si, where the minimum of $E(k)$ for conduction electrons lies at $0.8\pi/a$.

17.4 Elastic and Inelastic Scattering

When electrons scatter with phonons, energy and momentum conservation laws must be fulfilled. At room temperature, electrons have an average energy of $kT \cong 25$ meV). Near the r point, optical phonons are of the same order of magnitude, while acoustic phonons start from $\hbar\omega = 0$ at $q = 0$ and have energies $\ll kT$ in its vicinity. Therefore, almost no energy is exchanged when scattering with such acoustic phonons; hence, such scattering is an *elastic scattering* event.

In contrast, only the faster electrons have enough energy to create an optical phonon, and thereby lose almost all of their excess energy. This type of scattering is an *inelastic scattering* event.

One needs, however, to be careful when scattering with phonons of higher momentum is considered. Since at higher q the energy of acoustic phonons approaches in order of magnitude, that of optical phonons, both types of phonons cause *inelastic scattering*.

17.5 Phonon Generation and Annihilation

When interacting with electrons, phonons can be generated, thereby cooling the electron ensemble, or annihilated, thereby heating it. This interaction is determined by the ion-electron interaction potential in the Hamiltonian, which can be expressed as the sum over the individual contributions from each lattice atom:

$$H_{\text{ion,el}} \equiv V_{\text{ion,el}}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{r}_1, \mathbf{r}_2, \dots) = \sum V_{\text{ion,el}}(\mathbf{R}_i - \mathbf{r}_i). \quad (17.3)$$

This Hamiltonian is conventionally separated into one part that describes the electron-interaction with the periodic lattice $H_{\text{ion,el}}^{(0)}$ and another part that describes the interaction of the electron with the lattice oscillation $H_{\text{ph,el}}$

$$H_{\text{ion,el}} = H_{\text{ion,el}}^{(0)} + H_{\text{ph,el}}. \quad (17.4)$$

The second term involves the deviation from the periodic potential that causes the scattering. The simplest way of separating the periodic part of the potential from the oscillating perturbation is by an expansion of the potential, breaking it off after the linear term:

$$V_{\text{ion,el}}(\mathbf{R}_i - \mathbf{r}_i) = V_{\text{ion,el}}^{(0)}(\mathbf{R}_i^{(0)} - \mathbf{r}_i) - u_i \cdot \nabla V_{\text{ion,el}}(\mathbf{R}_i^{(0)} - \mathbf{r}_i), \quad (17.5)$$

where $u_i(t)$ is the displacement of the i th ion from its equilibrium position (see Sect. 5.1.1), which can be obtained from Eq. (5.3).

From the total Hamiltonian, one obtains the eigenvalues which, for the unperturbed system, are band states. With perturbation, transitions between the different eigenstates are initiated. The probability W for such transitions is proportional to the corresponding matrix elements [with ΔV given by the deviation from the periodic potential], and the population of initial and final states. For the absorption or emission of a phonon (see Sect. 28.2) one has:

$$W(\mathbf{k}, \mathbf{k} + \mathbf{q}) = \frac{2\pi}{\hbar} |M_{\mathbf{k}, \mathbf{k} + \mathbf{q}}|^2 f(\mathbf{k}) [1 - f(\mathbf{k} + \mathbf{q})] \{ f(\mathbf{q}) \delta[E(\mathbf{k} + \mathbf{q}) - E(\mathbf{k}) - \hbar\omega_{\mathbf{q}}] \\ + [1 - f(-\mathbf{q})] \delta[E(\mathbf{k} + \mathbf{q}) - E(\mathbf{k}) + \hbar\omega_{\mathbf{q}}] \}, \quad (17.6)$$

where f is the distribution function, and δ is the Dirac delta function. After integration over all possible transitions, one obtains the collision term of the Boltzmann equation [see Eq. (28.5)].

This integration, however, is difficult to perform for complex lattice oscillation. Therefore, the collision term is evaluated for one specific type of oscillation at a time, when approximations can easily be introduced. A simple example is the scattering of electrons on longitudinal acoustical phonons, which is discussed in the next section.

Fig. 17.1 (a) Undulation of the band edges due to “pressure waves,” e.g., in the long wave range of longitudinal acoustic phonons. (b) Step-like approximation of these undulations

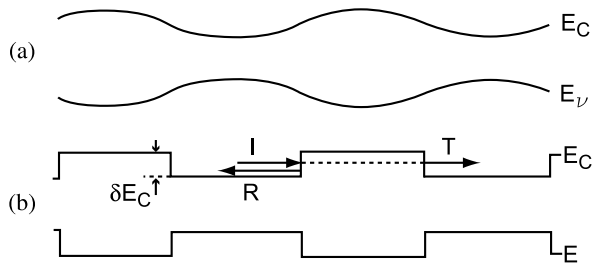


Table 17.1 Deformation potentials^a (eV)

Material					
Ge	$\mathcal{E}_u^X$	$\mathcal{E}_d^X$	$\mathcal{E}_u^L$	$\mathcal{E}_d^L$	
	10.4	0.53	16.4	−6.4	
GaAs	$\mathcal{E}_u^{\tau(111)}$	$\mathcal{E}_d^{\tau(111)}$		$\mathcal{E}_d^{\tau(100)}$	
	16.5	−8		−11.2	

^aSubscript u stands for pure shear, and d for the diagonal component of the deformation potential tensor

17.6 Longitudinal Acoustic Phonon Scattering

The interaction of electrons with longitudinal acoustic phonons can be analyzed in a variety of models. For reviews, see Mitra (1969), Seeger (1973), Nag (1980), Madelung (1978), and Zawadzki (1980/1982).

For pedagogical reasons, a classical approach is used with acoustic waves. In the acoustic branch at longer wavelengths, the lattice is alternately compressed and dilated. Consequently, the width of the band gap is modulated; it widens with compression. Electrons are scattered at a wave crest of the modulated band edge—Fig. 17.1a.

In a further simplified model, the deformation wave is approximated by a potential step in both bands—Fig. 17.1b and McKelvey (1966). An electron wave impinging on such a step is partially transmitted and partially reflected. The reflection probability is estimated from the solution of the Schrodinger equation as the difference between the impinging wave and the transmitted wave. Their energies are given in Table 17.1.

From continuity of the wavefunction and its derivatives at each step, we obtain for $k_i = k_T$ for the reflection probability $R = [(k_i - k_T)/(k_r + k_T)]^2$, which yields

$$R \simeq \left(\frac{m_n \delta E_c}{2\hbar^2 k_I^2} \right)^2, \quad (17.7)$$

where δE_c is the step-height and k_I is the wave vector of the impinging electron. The step-height is related to the lattice compression by

$$\delta E_c = -\mathcal{E} \frac{\delta \mathcal{V}}{\mathcal{V}}, \quad (17.8)$$

with $\mathcal{E}$ as the *deformation potential*,² V as the volume, and δV as its change, which is related to the thermal energy by a simple thermodynamic analogy:

$$\frac{1}{2}\delta p\delta\mathcal{V} = ckT, \quad (17.9)$$

where c is a proportionality factor on the order of 1. Replacing the pressure increment δp from the compressibility (K) relation

$$\kappa = \frac{1}{\mathcal{V}} \frac{\delta\mathcal{V}}{\delta p}, \quad (17.10)$$

we obtain for the probability of reflection, from Eqs. (17.7)–(17.10):

$$R \simeq \left(\frac{m_n}{2\hbar^2 k_l^2} \right)^2 \frac{ckkT}{\mathcal{V}} \mathcal{E}^2. \quad (17.11)$$

The probability of reflection can be connected with a mean free path Λ by $\lambda = l/R$, with l as the length of the sample (of volume $V = l^3$).

We obtain for $k_r\pi/l$, i.e., for long wavelength acoustic phonons:

$$\lambda \simeq \frac{h^4}{4m_n^2 c k T \mathcal{E}^2}. \quad (17.12)$$

A somewhat more rigorous treatment (Bardeen and Shockley 1950) yields a similar result:

$$\lambda = \frac{h^4 c_l}{m_n^2 k T \mathcal{E}^2}, \quad (17.13)$$

where c_l is the elastic constant for longitudinal deformation: $c_l = c_{11}$ for pressure in the (100) direction $c_l = 1/3(c_{11} + c_{12} + c_{44})$ in the (110) direction, $c_l = 1/3(c_{11} + 2c_{12} + c_{44})$ in the (111) direction. Here c_{ik} are components of the elastic tensor—see Sect. 4.1. Assuming an energy-independent $\lambda = \lambda$ using $\tau = \lambda/V_{\text{rms}}$, and replacing V_{rms} with Eq. (26.16), one obtains for the electron mobility due to acoustic phonon scattering

$$\mu_{n,\text{ac}} = \frac{\sqrt{8\pi}}{3} \frac{eh^4 c_l}{m_n^{5/2} (kT)^{3/2} \mathcal{E}^2}, \quad (17.14)$$

i.e., $=T^{-3/2}$ dependence at higher temperature, where this type of scattering is predominant. This is observed for direct, but not for indirect, band gap semiconductors.³ Intervalley scattering has a significant influence in indirect gap semiconductors.

²The deformation potential is defined as the change in band gap per unit strain, and is typically on the order of 10 eV. For a listing, see Table 17.1.

³The experimentally observed exponent of T is -1.67 for Ge (Conwell 1952) and not -1.5 . The exponent of T for Si is still larger (≈ 2.5). Inserting actual values for Si $c_l = 1.56 \cdot 10^{12}$ dyn/cm²,

The effective mass used in Eqs. (17.11)–(17.15) requires the proper mix of density-of-state and mobility effective masses:

$$m_n^{5/2} = m_{\text{nds}}^{3/2} m_{n\mu}. \quad (17.15)$$

The deformation potential used here has only slowly varying components in space. Another approach, suggested by Ginter and Mycielski (1970), contains a part of the potential varying with the lattice periodicity, which is more appropriate for shorter wavelength phonons.

This approach is a more general one; still, it gives similar results in a number of examples.

17.6.1 Acoustic Phonon Scattering with Piezoelectric Interaction

In piezoelectric crystals, ion oscillations cause a dipole moment that interacts with carriers rather effectively. A dipole moment can be generated by alternating lattice compression and dilatation, which in turn are caused by longitudinal acoustic phonons. These create an electric field parallel to the propagation direction which has a similar interaction with carriers, although slightly stronger than the acoustic deformation potential discussed above. The resulting mobility shows a somewhat similar behavior (Meyer and Polder 1953):

$$\mu_{n,\text{pe}} = \frac{16\sqrt{2\pi}}{3} \frac{\hbar^2 \varepsilon \varepsilon_0}{em_n^{3/2} K^2 (kT)^{1/2}}, \quad (17.16)$$

where K is the electromechanical coupling constant,⁴ which for most semiconductors is on the order of 10^{-3} . Numerically, one has

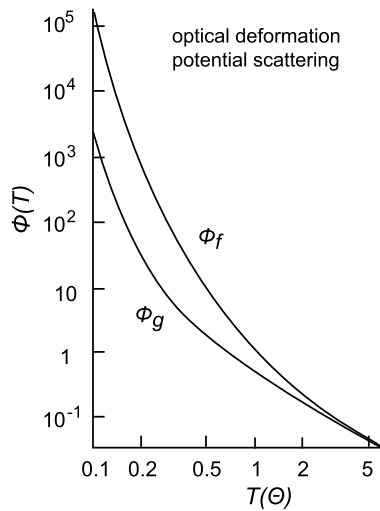
$$\mu_{n,\text{pe}} = 1.5 \cdot 10^4 \frac{\varepsilon}{10} \left(\frac{m_0}{m_n} \right)^{3/2} \left(\frac{10^{-3}}{K} \right)^2 \left(\frac{300 \text{ K}}{T} \right)^{1/2} (\text{cm}^2/\text{V s}). \quad (17.17)$$

At low temperatures (observe the $T^{-1/2}$ relation compared with a $T^{-3/2}$ relation for acoustic deformation potential scattering—see Fig. 18.4), piezoelectric phonon scattering can be an important scattering mechanism for low density of ionized impurities which otherwise predominate. See Seeger (1973) and Zawadzki (1980/1982); for an update, see Nag (1984).

$m_n = 0.2 m_0$ and $\mathcal{E} = 9.5 \text{ eV}$, one obtains $\mu_n = 5,900 \text{ cm}^2/\text{V s}$, a value that is larger by a factor of 4 than the measured $\mu_n = 1,500 \text{ cm}^2/\text{V s}$ at 300 K.

⁴ K^2 can be expressed as the ratio of the mechanical to the total work in a piezoelectrical material: $K^2 = (e_{\text{pz}}^2/c_l)/[\varepsilon \varepsilon_0 + e_{\text{pz}}^2/c_l]$, with e_{pz} the piezoelectric constant (which is on the order of 10^{-5} As/cm^2), and c_l the longitudinal elastic constant (relating the tension $\mathcal{T}$ to the stress $\mathcal{S}$ and the electric field F as $\mathcal{T} = c_l \mathcal{S} - e_{\text{pz}} F$).

Fig. 17.2 Auxiliary functions $\Phi_f(T)$ and $\Phi_g(T)$ for optical phonon scattering (after Seeger 1973)



17.7 Optical Phonon Scattering in Nonpolar Compounds

Low-energy electron scattering with optical phonons is predominantly elastic. This process can be understood as the annihilation of an optical phonon to create a high-energy electron, which in turn immediately creates an optical phonon in a highly probable transition.

Therefore, the electron energy is conserved in the turnaround, but not its momentum. When electrons have accumulated sufficient energy to create optical phonons, the scattering becomes very effective and is inelastic.

Optical phonon scattering in elemental nonpolar semiconductors couples both longitudinal and transverse optical modes with the scattering electron (Boguslawski 1975). It can be estimated by using a deformation potential formalism for longitudinal optical phonons (see also Conwell 1967). One obtains

$$\mu_{n,\text{opt}} = \frac{4\sqrt{2\pi}e\hbar^2\rho\sqrt{k\Theta}}{3m_n^{5/2}D_o^2}\phi(T), \quad (17.18)$$

where ρ is the density of the semiconductor, and D_o is the optical deformation potential (Meyer 1958):

$$\delta E_c = D_o\delta r, \quad (17.19)$$

with δr as the change in the interatomic distance, and $\Phi(T)$ is a function that contains the temperature dependence of μ and the density of phonons (Seeger 1973). At low temperatures, $\Phi(T)$ is large (typically 10^4 – 10^5 at $T = \theta/10$) and decreases rapidly to a value on the order of 1 near the Debye temperature θ .

The actual form of $\Phi(T)$ depends on the approximation used, and is plotted for two approximations Φ_f and Φ_g in Fig. 17.2. They show a nearly exponential

Table 17.2 Deformation potential^a at Γ points (in eV) (after Blacha et al. 1984)

	$a(\Gamma_1^c)$	$a(\Gamma_1^c)-a(\Gamma_{15}^v)$	b	d	$ d_o $
C					90
Si	-15.3	-10.0	-2.2	-5.1	40
Ge	-19.6	-12.6	-2.3	-5.0	34
AlSb		-5.9	-1.4	-4.3	37
GaP	-19.9	-9.3	-1.8	-4.5	44
GaAs	-17.5	-9.8	-2.0	-5.4	48
GaSb		-8.3	-1.8	-4.6	32
InP	-18.0	-6.4	-2.0	-5.0	35
InAs		-6.0	-1.8	-3.6	42
InSb	-14.6	-7.7	-2.0	-5.0	39
ZnS	-14.5	-4.0	-0.62	-3.7	4 ^a
ZnSe	-11.5	-5.4	-1.2	-4.3	12 ^a
ZnTe	-9.5	-5.8	-1.8	-4.6	23
CdS		-3.1			
CdSe		-3.0			
CdTe	-9.5	-3.4	-1.2	-5.4	22
CuCl			-0.7	0.43	7
CuBr			-0.25	-0.65	3.8
CuIn			-0.64	-1.4	1.1

^aThese deformation potentials are defined by *hydrostatic strain*

decrease with increasing temperature for $T < 0.3\theta$ (see actual values of the deformation potential for a number of semiconductors in Table 17.2).

Numerically, the mobility due to optical phonon scattering (Eq. (17.18)) can be expressed as

$$\mu_{n,\text{opt}} = 1.77 \cdot 10^3 \frac{(\frac{\rho}{\text{g cm}^{-3}})(\frac{\theta}{300 \text{ K}})^{1/2}}{(\frac{m_n}{m_0})^{5/2}(\frac{D_o}{10^8 \text{ (eV/cm)}})^2} \phi(T) \tag{17.20}$$

and shows a sufficiently low value near and above the Debye temperature, where $\Phi(T) \approx 1$, to become the determining factor in high-purity semiconductors.

Nonpolar optical phonon scattering is the only electron-optical phonon interaction in nonpolar semiconductors, such as Si and Ge. It is important for rs-bands, and, as was pointed out by Harrison

$$a_i = \frac{dE_i}{d \ln \mathcal{V}} = B \frac{dE_i}{dp} \tag{17.21}$$

With B as the bulk modulus by shear strain along [111] or [100]

$$d = \frac{\delta E}{2\sqrt{3}\varepsilon[111]} \quad \text{or} \quad b = \frac{\delta E}{6\varepsilon[100]} \tag{17.22}$$

where $\varepsilon[111]$ or $\varepsilon[100]$ is the strain in the $[111]$ or $[100]$ direction and by splitting of the Γ_{15} -state in the absence of spin-orbit interaction

$$d_0 = \frac{\delta E a_0}{u}, \quad (17.23)$$

with δE as the observed energy shift, a_0 as the lattice constant, and u as the atomic displacement. The parameter b is related to the optical deformation potential D_o by $D_o = -(3/2)b$.

Vanishes for the Γ_6 -band. Therefore, it is unimportant for n -type InSb, but important for hole scattering in p -type InSb (Costato and Reggiani 1972; Bir and Pikus 1974).

17.7.1 Optical Phonon Scattering in Polar Semiconductors

The scattering of carriers with longitudinal optical phonons (*Fröhlich interaction*) in a (partially) ionic lattice has a larger influence than the deformation potential interaction on the carrier mobility due to the larger dipole moment associated with such lattice vibration. This causes an induced field proportional to the polarization P :

$$F = -\frac{P}{\varepsilon \varepsilon_0}. \quad (17.24)$$

The polarization can be obtained from

$$P = \frac{e_c d_r}{\mathcal{V}_o}, \quad (17.25)$$

where d_r is the change in the interatomic distance, $\mathcal{V}_o$ is the volume of the unit lattice cell, and e_c is the Callen effective charge. The mobility was calculated by Ehrenreich (1961) using a variational method of Howarth and Sondheimer (1953), which accounts for the inelastic scattering. It yields for temperatures below the Debye temperature

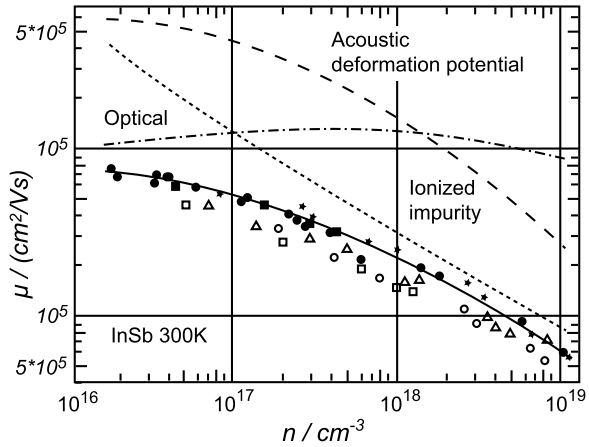
$$\mu_{n,\text{ion,opt}} = \frac{e\hbar}{2m_n \alpha_c k \Theta} \exp\left(\frac{\Theta}{T}\right), \quad (17.26)$$

where α_c is the coupling constant given in Eq. (17.6). The Debye temperature is used here to account for the LO phonon energy at $q = 0$ with $\hbar\omega_{\text{LO}} = k$. The mobility is numerically given by

$$\mu_{n,\text{ion,opt}} = 355 \frac{\exp(\frac{\Theta}{T})}{\alpha_c (\frac{m_n}{m_0}) (\frac{\Theta}{300 \text{ K}})} \text{ (cm}^2/\text{V s)}. \quad (17.27)$$

The mobility given by optical phonon scattering decreases linearly with increasing coupling constant. The mobility increases exponentially with decreasing temperature due to optical phonon freeze-out at lower temperatures.

Fig. 17.3 Electron mobility of n -InSb at 300 K as a function of the free-electron density. Dashed curves indicate the corresponding theoretical contributions (after Zawadzki 1972)



At temperatures $T \gg \Theta$, a different approximation (Seeger 1973) yields:

$$\mu_{n,\text{ion,opt}} = 1.5 \frac{e\hbar}{2m_n\alpha_c k\Theta} \sqrt{\frac{T}{\Theta}} \exp\left(\frac{\Theta}{T}\right) \simeq 533 \frac{\sqrt{\frac{T}{\Theta}} \exp(\frac{\Theta}{T})}{\alpha_c (\frac{m_n}{m_0}) (\frac{\Theta}{300 \text{ K}})}. \quad (17.28)$$

Zawadzki and Szymanska (1971) used a Yukawa-type screened potential that results in a reduced effectiveness of the optical phonon scattering. At higher temperatures they obtained

$$\mu_{n,\text{ion,opt}} = \frac{\sqrt{2}}{8\pi} \frac{M_r a^3 (k\Theta)^2}{ee_c^2 m^{3/2} kT} \frac{\sqrt{E - E_c}}{F_{\text{op}}}, \quad (17.29)$$

where F_{op} is a screening parameter⁵ that depends on the Debye screening length, and is on the order of 1 (Zawadzki 1980/1982). This results in an increased mobility by a factor of 3.5 for InSb at room temperature, and for $n = 10^{19} \text{ cm}^{-3}$. When the Fermi level is shifted into the conduction band, the mobility becomes explicitly electron-density-dependent:

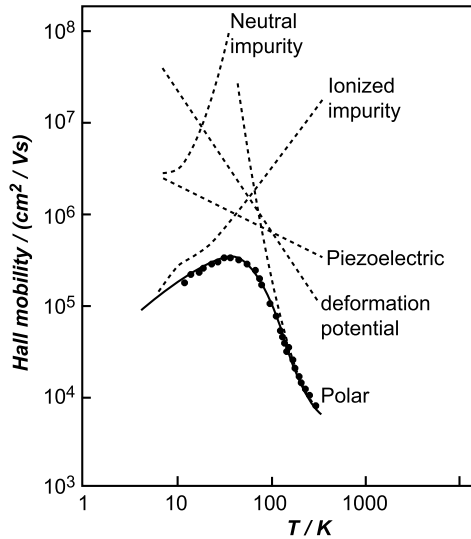
$$\mu_{n,\text{ion,opt}} = \frac{1}{4} \sqrt{\frac{3}{\pi}} \frac{M_r a^3 (k\Theta)^2 \hbar}{ee_c^2 kT m_n (E_F)} \frac{\sqrt[3]{n}}{F_{\text{op}}}. \quad (17.30)$$

Figure 17.3 shows the electron mobility of InSb as a function of the *electron density* at 300 K, and identifies the most important branches of scattering by longitudinal optical phonons at low densities, by ionized impurities at high density, and, of lesser importance, by acoustic phonons (after Zawadzki 1972).

Another example, shown in Fig. 17.4, gives the electron mobility as a function of the *temperature* for n -GaAs. It indicates major scattering at ionized impurities and

⁵Here, $F_{\text{op}} \simeq 1 + \frac{2}{\beta} \ln(\beta + 1) + 1/(\beta + 1)$, with $\beta = (2|\mathbf{k}|\lambda_D)^2$, and λ_D the Debye length given in Sect. A.3.

Fig. 17.4 Electron mobility in n -GaAs as measured by Stillman et al. (1970). *Dashed curve* indicates the corresponding theoretical contributions (after Fletcher and Butcher 1972)



by longitudinal optical phonons (high T); whereas scattering by acoustic phonons, piezoelectric scattering, and scattering at neutral impurities are of lesser importance, in this order.

17.7.2 Scattering by Intrinsic Point Defects

Carrier scattering by intrinsic point defects, such as by interstitials, vacancies, or antisite defects (an A atom on a B site), is caused by deviations from the periodicity of the lattice potential in the equilibrium position of the disordered atoms. These changes can be seen as a local deformation of the bands. The interaction potential responsible for the scattering may be approximated as a Coulomb potential at charged localized centers, or by using the central core potential if the defect is not charged relative to the lattice. The intrinsic defects are similar to foreign atoms with respect to their behavior as scattering centers, which is discussed in the following sections.

All such scattering events at atomic point defects are considered elastic: the electron momentum is changed, but not its energy; the fraction of energy transferred is $\propto: m_n/M \ll 1$. When its energy is changed, however, the electron becomes trapped.

17.8 Scattering by Neutral Lattice Defects

Neutral lattice defects have a scattering cross section that is about the size of the defect atom, typically 10^{-15} cm^2 . As described by Erginsoy (1950), they can be-

come important scattering centers at low temperatures (at $T < 100$ K), when the density of ionic impurities has decreased by carrier trapping due to carrier freeze-out and the phonon scattering has decreased due to phonon freeze-out. In analogy to the scattering of electrons by hydrogen atoms, the scattering cross section s_n is estimated as $\propto \pi a_{\text{qH}}^2$:

$$s_n = \pi a_{\text{qH}}^2 \cdot \frac{\lambda_{\text{DB}}}{a_{\text{qH}}} = 2\pi^2 \frac{a_{\text{qH}}}{|\mathbf{k}|}, \quad (17.31)$$

modified by a scattering correction factor $\lambda_{\text{DB}}/a_{\text{qH}}$ (Seeger 1973), where λ_{DB} is the De Broglie wavelength. Erginsoy estimated a similar relation $s_n \cong 20a_{\text{qH}}/|k|$. Using the gas-kinetic estimate for the collision time

$$\tau_n^\times = \frac{1}{N^\times s_n v_{\text{rms}}} \quad (17.32)$$

and $|k| = 2\pi/\lambda_{\text{DB}} = mv/h$, we obtain with $v \cong v_{\text{rms}}$ for the mobility due to neutral impurity scattering

$$\mu_n^\times = \frac{e}{m_n} \tau_n^\times = \frac{e}{2\pi^2 a_H \hbar} \frac{m_n/m_0}{\varepsilon_{\text{st}} N^\times} \quad (17.33)$$

or

$$\mu_n^\times = 1.46 \cdot 10^3 \left[\frac{10^{16}}{N^\times (\text{cm}^{-3})} \right] \left(\frac{10}{\varepsilon_{\text{st}}} \right) \left(\frac{m_n}{m_0} \right). \quad (17.34)$$

This mobility is independent of the temperature. The Erginsoy approximation is valid for temperatures $T > 20$ K. For lower temperatures, the screening depends on the energy; Blagosklonskaya et al. (1970) obtained

$$\mu_n = \frac{em_n^{3/2}}{\sqrt{2}\pi a_{\text{qH}}^2 N_n^\times \sqrt{E} \left(\frac{1}{E/E_i + 0.0275} + 10 \right)}, \quad (17.35)$$

where E_i is the ionization energy of the impurity.

The scattering is different if the spin of the incident electron is parallel or antiparallel to the electrons in the scattering atom (triplet or singlet state, respectively). In considering also the multivalley structure of the conduction bands, Mattis and Sinha (1970) arrived at results similar to Blagosklonskaya et al. (1970) at low temperatures, with only a slight mobility reduction at temperatures above 10 K, as shown in Fig. 17.5—also see Norton and Levinstein (1972).

17.9 Scattering on Ionic Defects

When scattering occurs on *charged* defects, the carriers interact with the *long-range Coulomb forces*, resulting in a substantially larger scattering cross section that is typically on the order of 10^{-13} cm^2 .

Fig. 17.5 Electron mobility (normalized to constant neutral impurity density) as a function of the temperature: (1) for $\varepsilon = 10$ and $m_n = m_0$ (after Erginsoy 1950); (2) (after Mattis and Sinha 1970); and (3) (after Blagosklonskaya et al. 1970). Experimental data for Ge (after Baranskii et al. 1975)

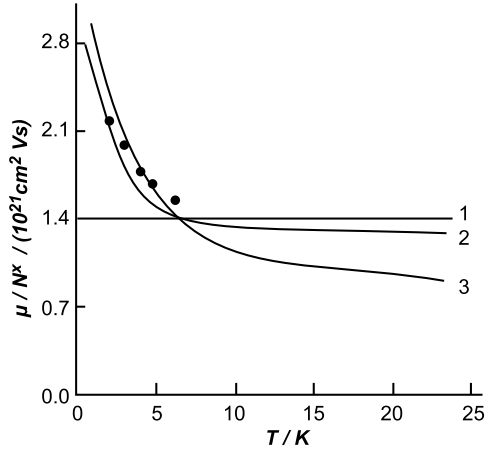
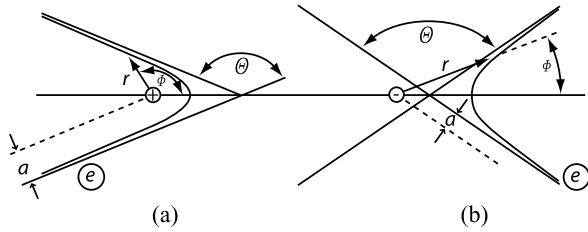


Fig. 17.6 Electron trajectories for (a) a Coulomb-attractive, and (b) a Coulomb-repulsive, scattering center



The original scattering analysis on charged particles was done by Rutherford (1911) for α -particles, and is easily adapted to carriers scattered by ions of charge z in a solid; that is after introducing the screening of this potential in the solid by using the dielectric constant ε_{st} and considering Bloch electrons by using the carrier effective mass. A differential cross section for the scattering of an electron of velocity v_{rms} under an angle θ into an element of solid angle $d\Omega = 2\pi \sin \theta d\theta$ (see Fig. 17.6) is then given (Leighton 1959) by

$$s_n(\theta)d\Omega = \left(\frac{Ze^2}{8\pi\varepsilon\varepsilon_0m_nv_{\text{rms}}^2} \right)^2 \sin^{-4} \frac{\theta}{2} d\Omega \quad (17.36)$$

with

$$\frac{\theta}{2} = \tan^{-1} \frac{Ze^2}{4\pi\varepsilon\varepsilon_0dm_nv_{\text{rms}}^2}, \quad (17.37)$$

which shows a rather slow decrease of the scattering angle θ with increasing minimum distance d from the center—see Fig. 17.6. In order to totally randomize the angle after collision, however, only a fraction of $(1 - \cos \theta)$ of all scatterings describes the number of *memory-erasing collisions* [Eq. (17.38)]:

$$dn = N_I v_{\text{rms}} s_n(\theta) (1 - \cos \theta) d\Omega = d \left(\frac{1}{\tau_m} \right). \quad (17.38)$$

This number is inversely proportional to the differential momentum-relaxation time.

Integration over all angles θ to obtain the total relaxation time requires a cutoff in order to avoid an infinite result, since $s_n(\theta = 0) = \infty$. Conwell and Weisskopf (1950) assumed that the closest distance d of the trajectory from the center to be considered must be smaller than a maximum distance, $d < d_{max} = 1/2N_I^{1/3}$, given by the average distance between ionized centers in the crystal. This yields for the time between collisions of carriers with velocity v_{rms} :

$$\tau = \frac{(4\pi\epsilon_{st}\epsilon_0)^2 m_n^2 v_{rms}^3}{2\pi Z^2 e^4 N_I} \frac{1}{\ln[1 + (\frac{\epsilon_{st}\epsilon_0 m_n v_{rms}^2}{2Ze^2 N_I^{1/3}})^2]}. \quad (17.39)$$

After averaging, one obtains the momentum-relaxation time T_m and with $v_{rms} = \sqrt{3}kT/m_n$, one has for the mobility, with $\mu_n = eT_m/m_n$,

$$\mu_n = \frac{8\sqrt{2}(4\pi\epsilon_{st}\epsilon_0)^2 (kT)^{3/2}}{\pi^{3/2} Z^2 e^3 m_n^{1/2} N_I} \frac{1}{\ln[1 + (\frac{3\epsilon_{st}\epsilon_0 kT}{2Ze^2 N_I^{1/3}})^2]}. \quad (17.40)$$

This mobility increases with temperature *ex*: $T^{3/2}$, i.e., faster electrons are less effectively scattered. The logarithmic dependence is usually neglected. As expected, μ decreases inversely with the density of scattering centers and with the square of their charge eZ .

A conversion of Eq. (17.40), using the definition of a scattering cross section as given in Chap. 18, reveals that, when disregarding the logarithmic term, s_n is given by

$$s_n = \frac{\pi^{3/2} Z^2 e^4}{8\sqrt{6}(4\pi\epsilon_{st}\epsilon_0)^2 (kT)^2} = \pi r_i^2, \quad (17.41)$$

where r_i is the “scattering radius” of the ion. This scattering radius can be compared with r_c , the radius of a Coulomb well at a depth of kT :

$$\frac{Ze^2}{4\pi\epsilon_{st}\epsilon_0 r_c} = kT \quad \text{or} \quad r_c = \frac{Ze^2}{4\pi\epsilon_{st}\epsilon_0 kT}. \quad (17.42)$$

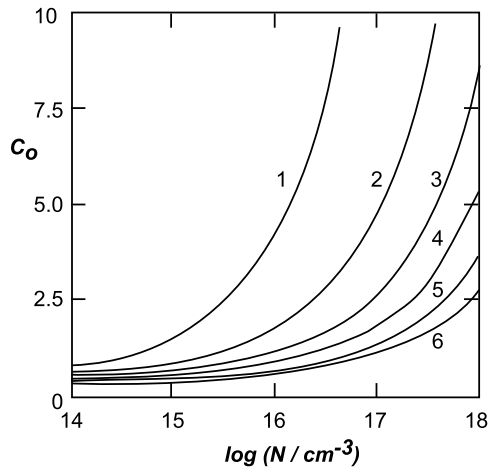
We now relate the scattering radius defined in Eq. (17.41) with the above defined Coulomb radius by

$$r_i = c_c r_c \quad (17.43)$$

where c_c is a correction factor. By comparison with Eq. (17.40), now including the logarithmic term, we obtain:

$$c_c = 2 \left(\frac{2\pi}{3} \right)^{\frac{1}{4}} \frac{1}{\ln[1 + (\frac{3\epsilon_{st}kT}{2Ze^2 N_I^{1/3}})^2]}, \quad (17.44)$$

Fig. 17.7 Correction factor for the Conwell-Weisskopf formula from the simple classical Coulomb well scattering of a cross section corresponding to a depth of kT/e , with the temperature as family parameter: $T = 100, 200, \dots, 600$ K for curves 1–6, respectively



which is on the order of 1—see Fig. 17.7. One thereby sees that, except for this correction factor, the scattering cross section is equal to the square of the Coulomb radius at $E = E_c - kT$. Therefore, the cross section decreases $r_c \propto 1/T^2$, or the increase in mobility is directly related to a decrease of r_c with T . This relationship is closely associated with the trapping of a charge at a Coulomb-attractive center when energy is dissipated. For such inelastic events to occur, the carrier must penetrate to $r < r_c$.

With the Coulomb radius introduced above, the Conwell-Weisskopf formula can be rewritten as the classical scattering relation

$$\mu_n = \frac{e}{m_n} \frac{c_c}{v_n s_n N_I}. \quad (17.45)$$

A somewhat refined approach was suggested by Brooks and Herring (Brooks 1955). They assumed a cut off in the integration over θ by replacing the Coulomb potential with a screened Yukawa potential, and used the Debye length λ_D as the screening length. In addition, they replaced the electron density in Eq. (17.9) with $n + (n + N_a)[1 - (n + N_a)/N_d]$, considering partial compensation.

The ensuing result is similar to Eq. (17.40):

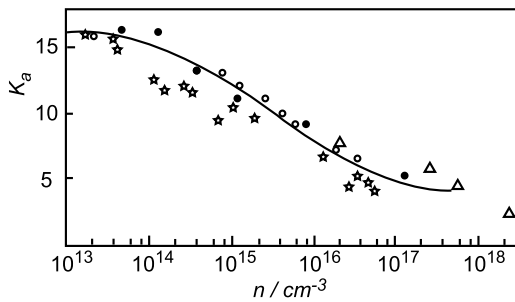
$$\mu_n = \frac{8\sqrt{2}(4\pi\epsilon_{st}\epsilon_0)^2(kT)^{3/2}}{\pi^{3/2}Z^2e^3m_n^{1/2}N_I} \frac{1}{\ln(1 + \beta - \frac{\beta}{1+\beta})} \quad \text{with} \quad \beta = (2|k|\lambda_D)^2. \quad (17.46)$$

Comparing the cut-off by Brooks and Herring with that of Conwell and Weisskopf, we observe a simple relation:

$$r_c \lambda_D^2 = n^{-1}, \quad (17.47)$$

which introduces the carrier density dependence into the scattering. For a review, see Zawadzki (1980/1982), and Chattopadhyay and Queisser (1981).

Fig. 17.8 Mobility anisotropy factor measured at 77 K in i-Ge (after Baranskii et al. 1975) and calculated curve (after Dakhovskii and Mikhai 1964)



17.10 Coulomb Scattering in Anisotropic Semiconductors

Ionized impurity scattering is sensitive to the anisotropy of the band structure, since low-angle scattering events dominate and interfere with randomizing electron velocities (Herring and Vogt 1956).

One also requires that the screening length be substantially smaller than the mean free path in order to prevent successive collisions from occurring in the same defect-potential region.

The anisotropy of the effective mass and of the density of states, which are largest along the long axes of the valley ellipsoids, influences the mobility (Boiko 1959). The mobility can be expressed as Samoilovich et al. (1961)

$$\mu = e \left(\frac{2}{3} \frac{\langle \tau_{\perp} \rangle}{m_{\perp}^*} + \frac{1}{3} \frac{\langle \tau_{\parallel} \rangle}{m_{\parallel}^*} \right) \quad (17.48)$$

with $m_{n\parallel}/m_{n\perp} = 19$ or 5.2 for Ge or Si, respectively.

With a screened Yukawa potential, the anisotropy factor $K_a = \mu_{\parallel}/\mu_{\perp}$ decreases with increasing carrier density as shown in Fig. 17.8. A smaller cross section of the scattering centers with higher carrier densities is caused by a decreasing $\lambda_D \cong 1/\sqrt{n}$; it also renders ion scattering more randomizing with increasing n .

17.10.1 Quantum Corrections for Ion Scattering

Several assumptions of the Brooks-Herring approximation are often not fulfilled (Moore 1967). Corrections obtained by dropping these assumptions may be expressed in a linearized form:

$$\mu = \mu_0 \frac{1}{1 + \delta_B + \delta_m + \delta_d}, \quad (17.49)$$

with three correction contributions:

1. The Born approximation, used to estimate the scattering probability, requires $s|k|\lambda_D > 1$ with the average wave vector $|k| = m_n v_{\text{rms}}$.

When this condition is not fulfilled, a Born correction component δ_B is introduced with

$$\delta_B = \frac{2Q(\beta)}{k^2 \lambda_D a_{qH}} \propto \begin{cases} \text{const.} & \text{for low } T \\ \sqrt{n}/T^{\frac{3}{2}} & \text{for high } T \end{cases} \quad (17.50)$$

with $Q(\beta)$ a slowly varying function: $0.2 < Q < 0.8$. One estimates $0.1 < \delta_B < 1$ for ion densities between 10^{16} and 10^{19} cm^{-3} . It is a more important correction for lower temperatures ($T < 100 \text{ K}$; Moore 1967).

2. When coherent scattering occurs from more than one ion, the mean free path becomes comparable to the screening length. The multiple-scattering correction factor δ_m has been estimated by Raymond et al. (1977), and is of minor importance at low temperatures.
3. A dressing effect can be expected to take care of the chemical individuality of the scattering center. The effect of the electron wavefunction of the scattering ion is rather small: δ_d is about 30–50 % of δ_m . However, the defect individuality is observed at higher impurity densities for InSb doped with Se or Te (Demchuk and Tsidilkovskii 1977), and for Si or Ge doped with As or Sb (Morimoto and Tani 1962). It is suggested that the stress field surrounding the impurity of different sizes is the reason for the individuality of the scattering probability of such ions rather than central cell potential corrections (Morgan 1972).

17.11 Carrier-Carrier Scattering

The scattering of carriers by other carriers within the same band does not change the total momentum of the carrier gas. Therefore, it does not influence the momentum relaxation time. Combined with other scattering mechanisms, however, it causes an accelerated relaxation. This results in a *slight* decrease in mobility, which is usually on the order of only a few percent. Estimates made by Appel (1961) for covalent semiconductors, and by Bate et al. (1965) for ionic semiconductors, indicate a mostly negligible effect of low-field electron-electron scattering.

Some larger effects in energy relaxation are discussed by Dienys and Kancleris (1975), and by Nash and Holm-Kennedy (1974). When a subgroup of electrons is excited to higher energies, electron-electron is important, as it tends to restore thermal electron distribution.

Chapter 18

Carrier Mobility Influenced by Larger Defects

Abstract Carrier mobility influenced by larger defects, such as dislocations, defect clusters; microcrystalline boundaries, external surfaces, metal/semiconductor boundaries, are all discussed quantitatively in this chapter.

Carriers are scattered, or their path is severely perturbed, when they have to pass through regions of the semiconductor that are disturbed by larger lattice defects. There are three types of large lattice defects that have a significant effect on carrier transport:

- dislocations, i.e., line defects,
- clusters, i.e., larger associates of point defects, and
- surfaces, such as grain boundaries between the same or different phases, or external surfaces.

The influence of these defects on carrier transport will be discussed briefly in this chapter.

18.1 Scattering at Dislocations

The edge dislocation presents a major disturbance in carrier transport within the lattice because of the surrounding stress field and the charging of the reconstructed core states. Another disturbance can be expected from the charges induced in piezoelectric crystals, and caused by the strain field around edge and screw dislocations (Levinson 1965; Podor 1977). These core states attract electrons or holes, depending on the position of the Fermi level, and are screened by free carriers surrounding the line as a cylinder of a radius equal to the Debye Length [$L_D = \sqrt{\epsilon_{st}\epsilon_0 kT/(e^2 p_0)}$, where p_0 is the hole density in the bulk of the semiconductor, when electrons are attracted to the dislocation core]. Core states in Ge and Si are positively charged at low temperatures and negatively charged at higher temperatures.

Bonch-Bruевич and Kogan (1959) discussed the carrier scattering at a charged cylinder. By treating the scattering cylinder similarly to a scattering center of spher-

ical symmetry, Podor (1966) obtained an expression for the mobility due to dislocation scattering:

$$\mu_{\text{disl}} = \frac{75\sqrt{p_0}a_l^2(\epsilon_{\text{st}}\epsilon_0)^{3/2}}{e^2Nm_n^{1/2}}kT, \quad (18.1)$$

where N (cm^{-2}) is the dislocation density, and a_l is the distance between charged defect centers along the dislocation core line. Even without charge of the dislocation core at a “neutrality temperature” between negative and positive core charges, a lower mobility in deformed Ge is observed. This is caused by the scattering at the strain field.

A more refined theory takes into consideration the influence of the deformation potential, and the anisotropy, of the scattering for the dislocation fields with a preferred orientation (Düster and Labusch 1973). The mobility, measured parallel to an array of aligned dislocations, is nearly equal to the mobility without dislocations; whereas when it is perpendicular to the array, the mobility is substantially reduced. This was experimentally confirmed by Schroter (1969) and Podor (1974). For a short review, see Zawadzki (1980/1982).

18.2 Scattering at Defect Clusters

Larger clusters of defects, such as associates of defects or small inclusions of a different phase, can interfere with the carrier transport beyond their own occupied volume via a space-charge cloud surrounding the defect. Depending on the charge, size, and distribution of these defects, the interaction can be modeled by a simple neutral center of a larger effective diameter, or by a charged center with a surrounding space charge extending up to a distance of several Debye lengths.

The charge of the defect associate may be due to carrier trapping. The charge of a different phase inclusion can be estimated from the difference in electron affinity between inclusion and host.

In addition, the strain field surrounding such a defect cluster influences the band edge via the deformation potential, and as such can act as an extended scattering center.

The influence on carrier transport may range from the scattering similar to that at point defects to the carrier repulsion from areas comparable to or larger than the mean free path.

18.3 Carrier Influence of Microcrystallite Boundaries

This influence is important for carrier transport in most microcrystalline semiconductors. A substantial reduction in mobility is observed when carriers must pass through the interface between crystallites on their way from one electrode to the

Fig. 18.1 Soap-bubble model of a two-dimensional crystal with grain boundaries, indicating a high defect density at these grain boundaries

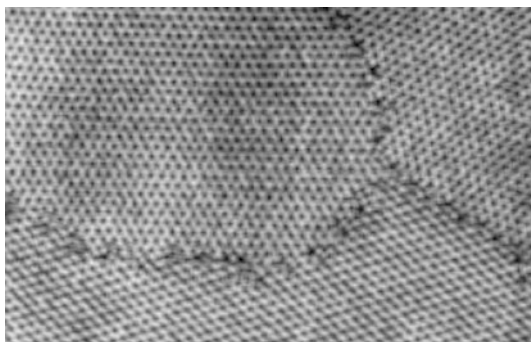
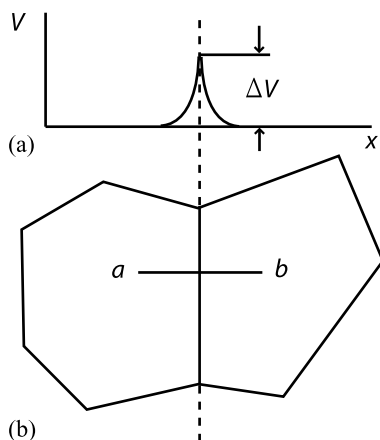


Fig. 18.2 (a) Crystallite boundary and (b) potential barrier along line *a-b*, as indicated in (a)



other. These interfaces contain a high density of lattice defects, such as dislocations along small-angle grain boundaries and vacancies or clusters of defects with substantial lattice relaxation along other grain boundaries—see Fig. 18.1. Carrier transport through the interfaces is therefore subject to a high degree of scattering. For a first approximation, one may assume that a free path ends at such interfaces, with a consequent reduction of the effective mobility: the smaller the crystallite grains, the more the mobility is reduced compared with the mobility in large single crystals.

Usually, interfaces have a high density of traps, which can become occupied by carriers. As a consequence, interfaces are often charged. Screening charges are located on both sides of the interface, causing a space-charge triple layer (Fig. 18.2), which produces a potential barrier between each of the crystallites. The height of the barrier can be estimated from the integrated Poisson equation

$$\Delta V_b \simeq \frac{e}{\epsilon \epsilon_0} \Sigma_i L_D, \quad (18.2)$$

where Σ_i is the surface charge density at the interface, and L_D is the Debye length. The actual surface charge density, however, is usually insufficiently known to make such an estimate meaningful.

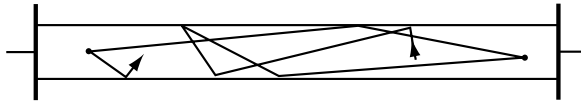


Fig. 18.3 Specular and nonspecular scattering limited by surfaces in a thin platelet of high carrier mobility

The barrier height eV_b is deduced from experimental data. With such a barrier, an exponential dependence of the mobility vs. $1/T$ is observed:

$$\mu_b = \mu_0 \exp\left(-\frac{e\Delta V_b}{kT}\right), \quad (18.3)$$

when carriers must pass over these inter-grain barriers, i.e., when the grain size is smaller than the distance between the electrodes.

The mobility μ_b is an effective mobility. Within each grain, the carrier mobility (μ_0) is larger than the effective mobility.

In the last three decades, carrier transport through grain boundaries has received much attention. However, as this topic deals with the inhomogeneous semiconductor, it is not a subject of this book. For a review, see Seeger (1999).

18.4 Influence of External Surfaces

External surfaces interact with carriers as perfect scattering surfaces, as surfaces for carrier recombination, and via their space charge. The space charge compensates the surface charge and extends into the bulk by a few Debye lengths. These space-charge effects are of technical importance, e.g., in field-effect transistors, and are discussed by Anderson (1970), Sze (1981), and others. Surface scattering with Influence by External Surfaces uses the mean free path to be on the order of the crystal dimensions (see below). It also plays a role at low temperatures in high-mobility semiconductors, where the mean free path becomes comparable to at least one of the crystal dimensions, e.g., in thin platelets—Fig. 18.3.

In *homogeneous* thin semiconductor platelets, a simple treatment of the influence of both platelet surfaces is rather transparent when one distinguishes between specular and nonspecular scattering at the surfaces.¹ The first has no influence on the mobility; the second causes a reduction in the average carrier relaxation time:

$$\frac{1}{\bar{\tau}} = \frac{1}{\tau_B} + \frac{1}{\tau_S}, \quad (18.4)$$

with the surface-induced relaxation time τ_s given by (see Many et al. 1965)

$$\tau_S \simeq \frac{\delta}{\lambda} \tau_B. \quad (18.5)$$

¹More sophisticated estimates (e.g., Fuchs 1938; Sondheimer 1952) are applied for thin metal layers, where surface-induced effects are less complex. These yield results on the same order of magnitude as given here.

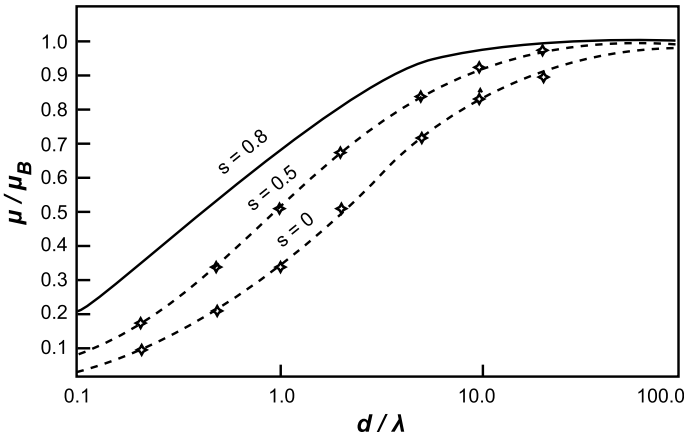


Fig. 18.4 Carrier mobility as a function of the ratio of platelet thickness to mean free path with specular surface scattering fraction s as the family parameter. x Is the result of the approximate theory (after Anderson 1970). Curves calculated from Sondheimer (1952)

Here, T_B is the bulk relaxation time, λ is the mean free path, and δ is the mean carrier distance from the surface. From Eqs. (19.4) and (19.5), one obtains for the ratio of actual-to-bulk mobility

$$\frac{\mu}{\mu_B} = \frac{\bar{\tau}}{\tau_B} = \frac{1}{1 + \frac{\lambda}{\delta}}. \quad (18.6)$$

Setting $2\delta = d$, where d is the platelet thickness, and using s as the fraction of the specular scattering events at the platelet surfaces, one obtains

$$\mu = \mu_B \frac{d}{d + 2(1-s)\lambda}, \quad (18.7)$$

which is shown in Fig. 18.4 with s as the family parameter.

18.5 Influence of Metal-Semiconductor. Boundaries

These boundaries are essential for semiconductor devices, for they serve as electrical contacts. Their electrical properties are determined by space-charge effects, and will be discussed extensively in *Transport Properties in Inhomogeneous Semiconductors*. For extensive reviews on this subject, see Henisch (1957), Spenke (1958), Rhoderick (1978), Sze (1981).

Chapter 19

Electron at High Fields

Abstract Electrons at high fields are discussed, including tunneling through barriers of different shape; band to band tunneling, tunneling in a three dimensional lattice. Tunneling currents are calculated. Tunneling spectroscopy is introduced. Tunneling with phonon assistance, and with trap assistance is evaluated. Tunneling with photon assistance, the Franz-Keldysh effect is defined. The influence of the electric field on defect levels is shown as Stark effect. Field effect in superlattices are identified. The ionization via energetic particles is discussed.

19.1 Electron Tunneling

Electrons can penetrate potential barriers if these barriers are thin and low enough, as pointed out by Oppenheimer (1928), Fowler and Nordheim (1928), and others. This quantum-mechanical phenomenon can easily be understood by recognizing that the wave-function of an electron cannot immediately stop at a barrier, but rather decreases exponentially into the barrier with a slope determined by the barrier height. If the barrier is thin, there is a nonzero amplitude of the wavefunction remaining at the end of the barrier, i.e., a nonzero probability for the electron to penetrate. For a comprehensive review, see Duke (1969) or Wolf (1976). This phenomenon, called *electron tunneling*, that will first be discussed for a simple one-dimensional rectangular barrier.

19.1.1 Tunneling Through Rectangular Barrier

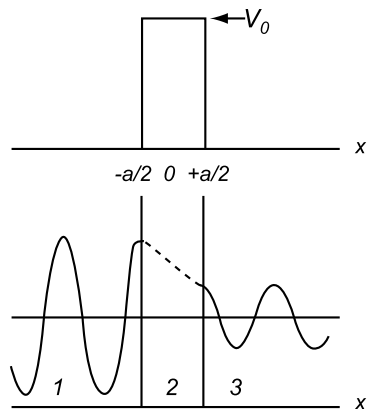
When an electron wave with an energy E impinges on a rectangular barrier with height eV_0 and width a , one distinguishes three wavefunctions in the three regions: before, in, and after the barrier—see Fig. 19.1:

$$\psi_1 = A_1 \exp(ik_0x) + B_1 \exp(-ik_0x) \quad \text{for } x < -\frac{a}{2} \quad (19.1)$$

for

$$\psi_2 = A_2 \exp(k_1x) + B_2 \exp(-k_1x) \quad \text{for } -\frac{a}{2} < x < \frac{a}{2} \quad (19.2)$$

Fig. 19.1 One-dimensional rectangular barrier with incoming and attenuated transmitted waves



$$\psi_3 = A_3 \exp(ik_0x) \quad \text{for } x > \frac{a}{2} \quad (19.3)$$

with amplitude coefficients A_i , for the incoming wave, and B_i , for the reflected wave at $-a/2$ and $+a/2$, respectively. The wave numbers k_0 and k_1 outside and inside the barrier are given by

$$k_0^2 = \frac{2m_n}{\hbar^2} E \quad \text{and} \quad k_1^2 = \frac{2m_n}{\hbar^2} (eV_0 - E). \quad (19.4)$$

Continuity of ψ and $d\psi/dx$ at $x = -a/2$ and at $+a/2$ provides four conditions for the coefficients A_i and B_i , from which one derives an expression for the transmission and reflection probabilities $\mathcal{T}_e$ and R_i

$$\mathcal{T}_e = \left(\frac{A_3}{A_1} \right)^2 \quad \text{and} \quad R = B_1^2 = 1 - \left(\frac{A_3}{A_1} \right)^2. \quad (19.5)$$

After solving the set of condition equations for A_i and B_i , one obtains

$$\mathcal{T}_e = \frac{1}{1 + \left(\frac{k_0^2 + k_1^2}{4k_0k_1} \right)^2 \sinh^2\left(\frac{k_1 a}{2}\right)} \simeq \left(\frac{4k_0k_1}{k_0^2 + k_1^2} \right)^2 \exp(-k_1 a); \quad (19.6)$$

this approximation is for $k_1 a \gg 1$. After introducing the expressions for k_0 and k_1 , one obtains for the transmission probability:

$$\mathcal{T}_e \sim 16 \left(\frac{E}{eV_0} \right)^2 \left(\frac{eV_0}{E} - 1 \right) \exp \left(-a \sqrt{\frac{2m_n}{\hbar^2} (eV_0 - E)} \right). \quad (19.7)$$

For a barrier height eV_0 much larger than the kinetic energy of the tunneling electrons, Eq. (19.7) can be approximated as

$$\mathcal{T}_e \simeq 16 \frac{E}{eV_0} \exp \left(-0.512a(\text{\AA}) \sqrt{\frac{m_n}{m_0} (eV_0 - E)} \right). \quad (19.8)$$

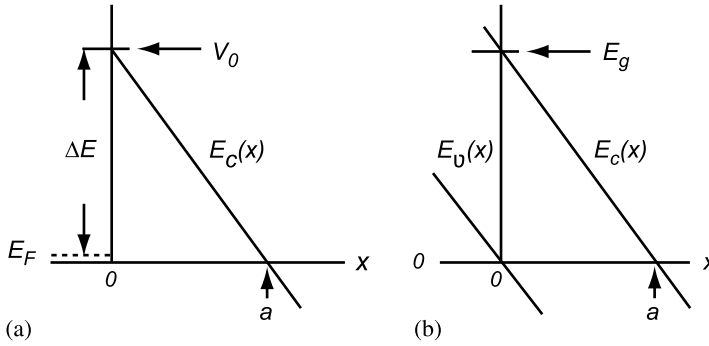


Fig. 19.2 Triangular potential barrier at (a) a metal-semiconductor contact neglecting image forces, and (b) for a band-to-band transition

For example, thermal electrons [$E = kT$ (300 K)] are attenuated by a factor of 2.2×10^{-3} when impinging on a $10 \text{ \AA}$ thick barrier of 1 Volt height. The transmission probability also depends on the shape of the barrier.

19.1.2 Tunneling Through Triangular or Parabolic Barrier

In semiconducting devices, the potential barrier often can be approximated by a *triangular shape*, for instance, at a simplified metal-semiconductor (Fig. 19.2a) or heterojunction interface, or for a band-to-band transition (Fig. 19.2b). At sufficiently high fields, tunneling through such a barrier can become important.

The transmission probability $\mathcal{T}_e$ for a wide class of barriers is given in the WKB approximation by:

$$\boxed{\mathcal{T}_e \simeq \exp \left\{ - \int_0^a |k(x)| dx \right\}}, \quad (19.9)$$

neglecting the pre-exponential factor which is on the order of 1, and with the shape of the barrier contained in the wave vector:

$$k(x) = \sqrt{\frac{2m}{\hbar^2} (eV_0 - E(x))}. \quad (19.10)$$

For the triangular barrier, $k(x)$ is given by

$$k(x) = \sqrt{\frac{2m}{\hbar^2} (\Delta E - eFx)}. \quad (19.11)$$

Integration of Eq. (19.10) with Eq. (19.11) yields

$$\int k(x) dx = \sqrt{\frac{2m}{\hbar^2}} \cdot \frac{2}{3} \frac{(\Delta E - eFx)^{3/2}}{eF/2} \Big|_0^a. \quad (19.12)$$

For a Parabolic barrier one obtains the lowering of a triangular barrier from E_g to $E_{\max}$ and with $\Delta E - eF \cdot 0 = \Delta E$, and $\Delta E - eF \cdot a = 0$, one obtains

$$\mathcal{T}_{e\Delta} = \exp \left\{ -\frac{4}{3} \sqrt{\frac{2m}{\hbar^2}} \frac{(\Delta E)^{3/2}}{eF} \right\} \quad (19.13)$$

or

$$\mathcal{T}_{e\Delta} \simeq \exp \left\{ -6.828 \cdot 10^7 \frac{[\Delta E(V)]^{3/2}}{F(\text{V/cm})} \right\}. \quad (19.14)$$

The pre-exponential factor is similar in form to that given in Eq. (19.7); compared with the exponential, its ΔE - and F -dependencies are usually neglected. The barrier height/field relation is superlinear; thus, doubling the barrier height requires $2^{3/2} = 2.83$ times the field to result in the same tunneling probability.

19.1.3 Band-to-Band Tunneling

For band-to-band tunneling, ΔE in Eq. (19.13) is replaced by the band gap E_g :

$$\mathcal{T}_{eg} \simeq \exp \left\{ -\frac{4}{3} \sqrt{\frac{2m}{\hbar^2}} \frac{E_g^{3/2}}{eF} \right\}. \quad (19.15)$$

Although this transmission probability is multiplied by a large density of electrons acting as candidates for tunneling from band to band, one needs very high fields ($> 10^6$ V/cm) to produce significant tunneling currents, except for very narrow gap semiconductors.

A parabolic barrier is better suited as an approximation for barriers in which two fields overlap, e.g., the Coulomb-attractive field of a center or the image force of a metal-semiconductor barrier and the external field. The corresponding wave vector is given by

$$k(x) = \sqrt{\frac{2m}{\hbar^2}} \sqrt{\frac{(\Delta E)^2 - (eFx)^2}{\Delta E}}, \quad (19.16)$$

and yields after integration

$$\int_0^a k(x) dx = \sqrt{\frac{2m}{\hbar^2}} \frac{\pi}{8} \frac{(\Delta E)^{3/2}}{eF/2}. \quad (19.17)$$

Therefore, the transmission probability for a parabolic barrier is given by

$$\mathcal{T}_{e\cap} = \exp \left\{ -\frac{\pi}{4} \sqrt{\frac{2m}{\hbar^2}} \frac{(\Delta E)^{3/2}}{eF} \right\} \quad (19.18)$$

with an exponent that is reduced by a numerical factor of $3\pi/16 = 0.589$ from the expression for the triangular barrier.

19.2 Tunneling in a Three-Dimensional Lattice

In the one-dimensional model, one is concerned only with the momentum in the direction of the barrier, which decreases exponentially during the tunneling transition.

In a three-dimensional lattice, however, there is a three-dimensional distribution of momenta. Assuming a planar barrier, only the component in the direction of tunneling is influenced by the tunneling process; the two components perpendicular to the tunneling are not: *these components are conserved*. The total transition probability is therefore reduced by a factor given by the fraction of electrons having a favorable momentum component to the ones that do not. This fraction η was calculated by Moll (1964):

$$\eta = \exp\left(-\frac{E_{\perp}}{\bar{E}}\right) \quad (19.19)$$

with $E_{\perp}$ the energy associated with the momentum perpendicular to the direction of tunneling, equal to $\hbar^2 k_x / (2m)$, and with E given by

$$\bar{E} = \sqrt{\frac{\hbar^2}{2m_n} \frac{eF}{\pi \sqrt{\Delta E}}} = 6.19 \sqrt{\frac{m_0}{m_n} \frac{F(\text{V/cm})}{10^6}} \frac{1}{\sqrt{\Delta E}} \text{ (meV)}. \quad (19.20)$$

Hence, for the tunneling probability through a flat plate barrier of parabolic shape, one obtains

$$\mathcal{T}_{e\cap,3} = \eta T_{e\cap} = \exp\left(-\frac{E_g + 4E_{\perp}}{4\bar{E}}\right). \quad (19.21)$$

19.3 Tunneling Currents

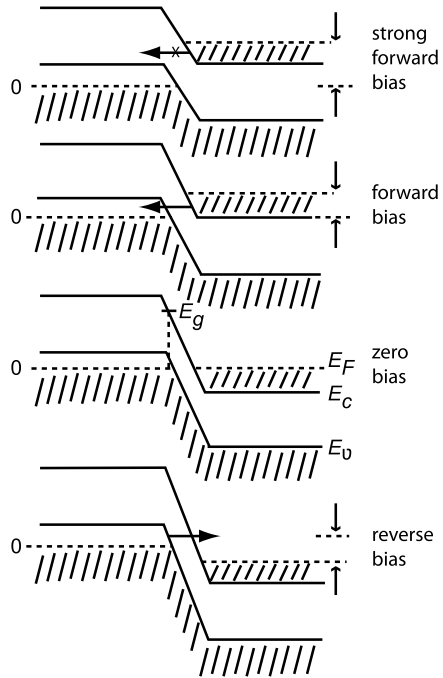
The current is proportional to the product of the tunneling transmission probability and the incident carrier flux. As an example, an idealized n^+p^+ -junction is shown in Fig. 19.3 for various bias conditions.

Depending on the bias, the current can flow across this junction from filled states in the valence to empty states in the conduction band with reverse bias, or from filled states in the conduction band to the empty states in the valence band with forward bias. The net current is the difference of both (Moll 1964):

For any given bias, one has

$$\vec{j}_n = j_{n,vc} = A \int_{E_{cr}}^{E_{vl}} \{N_v(E) f_n(E)\}_l \{N_c(E) f_p(E)\}_r \mathcal{T}_{e\Delta,3} dE \quad (19.22)$$

Fig. 19.3 Band model with idealized tunnel junction for four different bias conditions. Current flow is indicated by a horizontal arrow



$$\overleftarrow{j}_n = j_{n,cv} = A \int_{E_{cr}}^{E_{vl}} \{N_c(E) f_n(E)\}_r \{N_v(E) f_p(E)\}_l \mathcal{T}_{e\Delta,3} dE, \quad (19.23)$$

with $T_{\Delta,3} = \eta T_{e\Delta}$ from Eqs. (19.13) and (19.19). The subscripts l and r stand for the left and right sides in Fig. 19.3; $N_v(E)$ and $N_c(E)$ are the respective density-of-state distributions in the valence and conduction bands; and f_n and $f_p = 1 - f_n$ are the Fermi distributions for electrons and holes. The first factor in parentheses under the integral identifies the density of available electrons; the second factor gives the density of holes into which tunneling can proceed. One therefore obtains

$$j_n = A \int_{E_{cr}}^{E_{vl}} N_v(E) N_c(E) \{f_{nr}(E) - f_{nl}(E)\} \mathcal{T}_{e\Delta,3} dE. \quad (19.24)$$

The proportionality constant A can be obtained by accounting for the charge and the velocity of electrons in k space; with these, the current density is

$$j_n = \frac{em_n}{2\pi^2\hbar^3} \exp\left(\frac{\pi m_n^{1/2} E_g^{3/2}}{2\sqrt{2}e\hbar F}\right) \iint \{f_{nr}(E) - f_{nl}(E)\} \exp\left(-\frac{2E_{\perp}}{\bar{E}}\right) dE dE_{\perp}. \quad (19.25)$$

assuming the same isotropic effective mass at the left and right sides of the junction. After integrating over $E_{\perp}$, which yields E_{l2} , and approximating the integral over E ,

one obtains

$$j_n = \frac{e^3 m_n^{1/2} d}{2\sqrt{2}\pi^3 \hbar^2 E_g^{1/2}} F^2 \exp\left(-\frac{\pi m_n^{1/2} E_g^{3/2}}{2\sqrt{2}e\hbar F}\right), \quad (19.26)$$

for $V_a \gg kT/e$ and $V_a \gg E/e$; V_a is the applied voltage across the barrier. Equation (19.26) has the field dependence given by the Fowler-Nordheim formula (Fowler and Nordheim 1928): $j_e \cong F^2 \exp(-F_0/F)$. Thus, Eq. (19.26) has the numerical value of

$$j_n = 1.011 \cdot 10^{-8} \left(\frac{F}{10^6}\right)^2 \left(\frac{m_n}{m_0}\right)^{1/2} \left(\frac{d}{100 \text{ \AA}}\right) \frac{1}{\sqrt{E_g}} \exp\left(-\frac{F_0}{F}\right) (\text{A/cm}^2) \quad (19.27)$$

with

$$F_0 = 4.04 \cdot 10^7 \left(\frac{m_n}{m_0}\right)^{1/2} E_g^{3/2} (\text{V/cm}), \quad (19.28)$$

which indicates substantial tunneling ($>10^{-3} \text{ A/cm}^2$) is expected for fields in excess of $1.5 \cdot 10^6 \text{ V/cm}$ for the given parameters. A reduced effective mass lowers the critical field by a factor of 3 for $m_n = 0.1m_0$.

19.4 Tunneling Spectroscopy

The dependence of the tunneling current on the level density distribution [Eq. (19.24)] permits the use of this current for obtaining information about the distribution. There are several methods available; they involve a similar principle in shifting the Fermi-level or quasi-Fermi level on one side of a barrier with respect to the Fermi level on the other side (see Fig. 19.3), thereby permitting the tunneling of carriers through the barrier at variable energies. Thus, the level distribution is profiled near the top of the valence band or in the conduction band, depending on forward or reverse bias, respectively: the increment in tunneling current becomes larger when more levels become available.

The probing side of the barrier can be either a highly doped semiconductor, a metal electrode, or a superconductor.

A higher sensitivity of the probing can be achieved by the derivative technique (Thomas and Rowell 1965; Adler and Jackson 1966; Adler et al. 1971). In this method, a small ac-signal is applied on top of a varying dc-bias $V(t) = V_0 + \Delta V \cos \omega t$, resulting in a current

$$I = I_0 + \frac{dI}{dV} \Delta V \cos(\omega t) + \frac{d^2 I}{dV^2} \left(\frac{\Delta V}{2}\right)^2 [1 + \cos(2\omega t)] + \dots, \quad (19.29)$$

which permits detection of first and second derivatives at ω and 2ω , respectively.

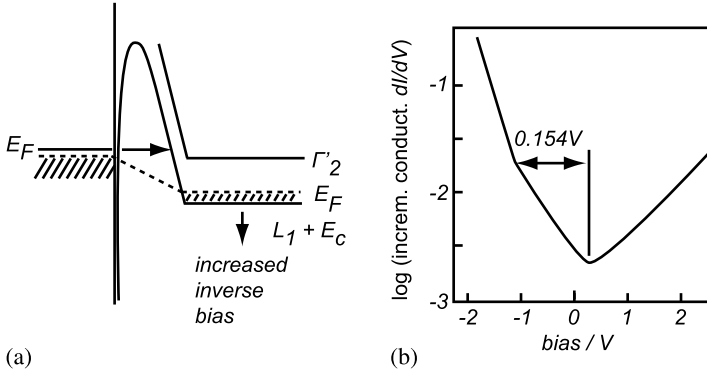


Fig. 19.4 Incremental tunneling conduction of an Au/*n*-type Ge barrier at 4.2 K: (a) band model, and (b) experimental curve (after Conley and Tiemann 1967)

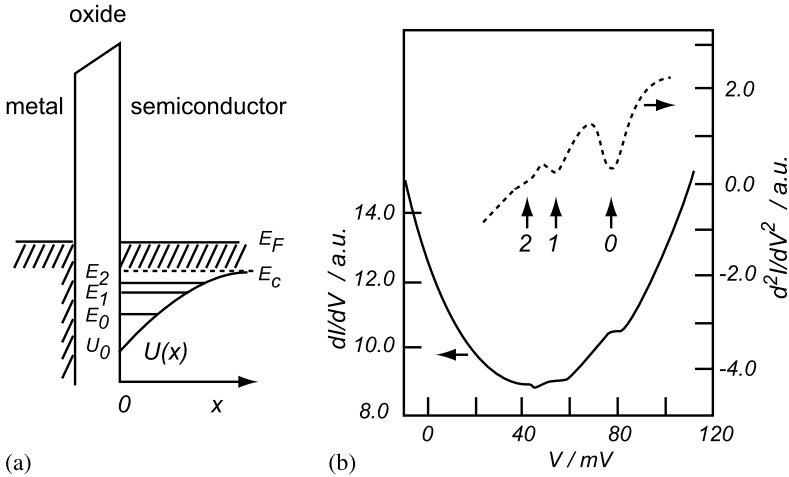
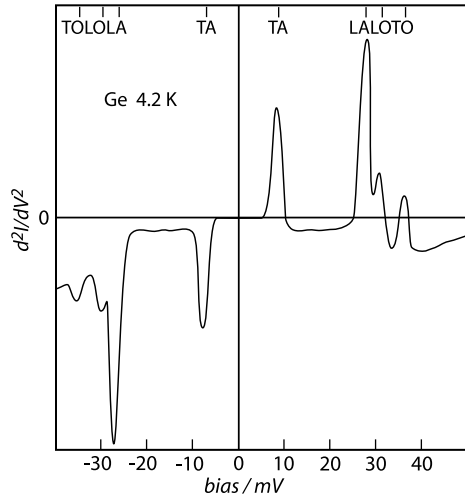


Fig. 19.5 (a) Band diagram of an MOS (metal-oxide-semiconductor) junction with surface states in a potential well of depth U_0 . (b) First and second derivatives of the tunneling current, showing transitions into the eigenstates of the surface well [indices correspond to those of the energy shown in subfigure (a)] for a Pb-oxide- n^+ -PbTe junction (after Tsui et al. 1974)

An example of probing the conduction band of Ge with a gold contact is shown in Fig. 19.4. Here, dI/dV , the incremental conduction, is plotted. It shows an increase in conduction as more states in the L1-conduction band become available with increased reverse bias; it shows another edge at 154 meV above the conduction band edge when additional direct transitions into the T2'-band become possible.

Another example is the incremental current obtained by tunneling from a metal contact into the eigenstates of a quantum well, which is created at the surface of an n^+ -PbTe semiconductor connected by an oxide interlayer to a Ph-electrode—see Fig. 19.5a.

Fig. 19.6 Second derivative of tunnel current to emphasize the structure for a Ge tunnel diode, indicating the phonon spectrum (after Payne 1965)



There are three identifiable bound states below the continuum E_c . These states are best seen in d^2I/dV^2 at $V = 78, 55$, and 42 mV for E_0, E_1 , and E_2 , respectively, and are counted from the Fermi-level, which is 36 mV above E_c ; hence, the binding energies of the states in the surface well are $42, 19$, and 6 mV, respectively—see Fig. 19.5b. The insert of Fig. 19.5b shows this more clearly in an enhanced scale. Other examples of tunnel spectroscopy are listed in the following sections (see also Tsui 1980; Hayes et al. 1986).

19.5 Tunneling with Phonon Assistance

Indirect band-gap materials show a much lower band-to-band tunneling probability, since an indirect transition requires an additional phonon to accomplish the change in momentum. An estimate of the tunneling probability by Keldysh (1958a) shows a similar functional behavior as given by Eq. (19.15), but reduced by a factor on the order of 10^{-3} .

Other changes in the tunneling probability are seen when the phonon energy is used in addition to the electron energy to bridge the barrier:

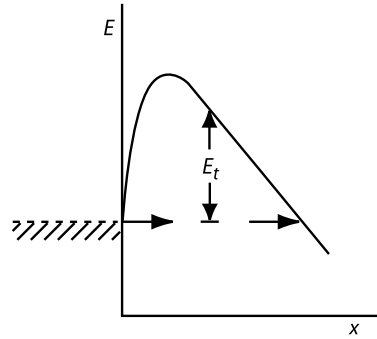
$$\mathcal{T}_e = \exp \left\{ -\frac{4}{3} \sqrt{\frac{2m}{\hbar^2}} \frac{(E_g - \hbar\omega_0)^{3/2}}{eF} \right\}. \quad (19.30)$$

When the bias V reaches the phonon energy,

$$V \geq \frac{\hbar\omega_0}{e}, \quad (19.31)$$

the tunneling current increases measurably. This change can be used to identify the corresponding phonon energies as shown in Fig. 19.6 for Ge.

Fig. 19.7 Tunneling from a contact into a semiconductor, which becomes marked when the trap level is lowered by the field to coincide with the Fermi-level of the metal



19.5.1 Tunneling with Trap Assistance

Tunneling through a barrier into the conduction band can be assisted by tunneling first into a trap and then from the trap into the conduction band—a *two-step tunneling* process—as indicated in Fig. 19.7. When defect centers are spaced close enough to an interface, and are present at sufficient densities, the two-step tunneling can substantially increase the overall tunneling probability, which is calculated from the sum of the reciprocal individual probabilities:

$$\mathcal{T}_{e,2st} = \left(\frac{1}{\mathcal{T}_{e1}} + \frac{1}{\mathcal{T}_{e2}} \right)^{-1}. \quad (19.32)$$

19.6 Tunneling with Photon Assistance (Franz-Keldysh Effect)

The Franz-Keldysh effect is an important tunneling phenomenon in which only a small fraction of the energy is supplied from the electric field. Most of the energy comes from an optical excitation from a state in the gap near the valence band edge to a symmetrical state close to the conduction band edge—Fig. 19.8a.

This three-step process was suggested by Franz (1958) and Keldysh (1958a), and was observed first by Böer et al. (1958a); see also Böer and Kümmel (1960). It results in a shift of the absorption edge towards lower energies. The amount of the shift can be estimated from the photon-assisted tunneling—compare with Eq. (19.30):

$$\mathcal{T}_e = \exp \left\{ -\frac{4}{3} \sqrt{\frac{2m^*}{\hbar^2}} \frac{(E_g - \hbar\nu)^{3/2}}{eF} \right\}. \quad (19.33)$$

As a result, the optical absorption edge is shifted (Fig. 19.8b) by the same amount:

$$\alpha_o = \alpha_{o0} \exp \left\{ -\frac{4}{3} \sqrt{\frac{2m^*}{\hbar^2}} \frac{(E_g - \hbar\nu)^{3/2}}{eF} \right\}. \quad (19.34)$$

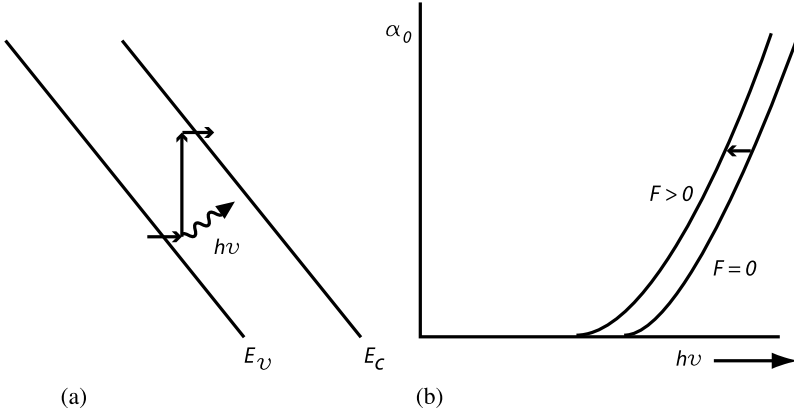


Fig. 19.8 Franz-Keldysh effect: **(a)** photon-assisted tunneling from band to band; **(b)** resulting shift of the band edge

The shift $\Delta E_{g,\text{opt}}$ can be obtained from the condition that the exponent remains constant and $\cong 1$, resulting in

$$\Delta E_{g,\text{opt}} = E_g - h\nu = \left(\frac{3}{4} eF \sqrt{\frac{\hbar^2}{2m^*}} \right)^{2/3} \quad (19.35)$$

or

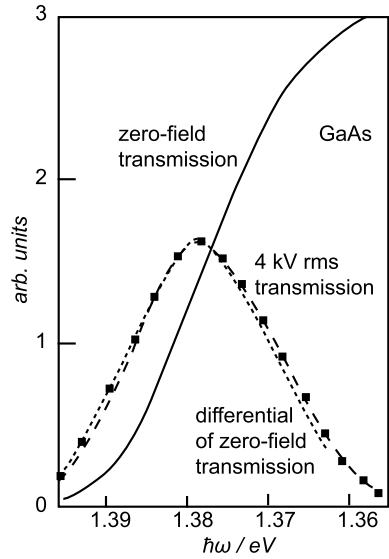
$$\Delta E_{g,\text{opt}} = 7.25 \cdot 10^{-6} [F \text{ (V/cm)}]^{2/3} \text{ (eV);} \quad (19.36)$$

that is, for a band edge shift of 10 meV, equivalent to $100 \text{ \AA}$ at a band gap of 2 eV, one needs a field of 50 kV/cm.

The photon-assisted tunneling is not restricted to the transition from the valence to conduction band near its principal edge; one can optically excite an electron to a state close to any higher band and complete the transition via tunneling. The Franz-Keldysh effect thereby provides a relatively simple method for measuring the energy of characteristic points in the $E(k)$ behavior of any band (Seraphin 1964; Aspnes 1967). At first view, this may suggest no advantage over a purely optical transition. When applying an ac-electric field, the maximum modulation signal of the optical response is observed where the absorption edge has the highest slope, i.e., at the inflection point of $\kappa(\lambda)$, as shown in Fig. 19.9. With overlapping higher bands, the optical absorption itself is not very structured. In contrast, however, the Franz-Keldysh modulation is highly structured and shows unusually sharp features with characteristic oscillations toward higher frequencies (Fig. 19.10), which have attracted numerous investigations. For reviews, see Frova and Handler (1965), Seraphin and Bottka (1965), and Aspnes (1980).

A quantum mechanical treatment reveals the characteristic features of the dielectric function. For a transition to an isotropic M_0 critical point, the imaginary part the

Fig. 19.9 Optical transmission at the absorption edge and ac-component of the optical transmission with an ac-field applied to GaAs (after Moss 1961a, 1961b)



dielectric constant is given by

$$\varepsilon''(h\nu, F) = \frac{2\pi^2 e^2}{m^{*2} \nu^2} |\hat{\mathbf{e}} \cdot \mathbf{M}_{\text{ev}}|^2 J_{\text{ev}}(h\nu, F), \quad (19.37)$$

where $\mathbf{e}$ is the unit polarization vector of the light, $\mathbf{M}_{\text{ev}}$ is the momentum matrix element, and J_{ev} is the joint density of states for transitions from the valence to the conduction band under the influence of a homogeneous electric field. Tharmalingam (1963) and Aspnes (1966) obtain for the change in the complex dielectric function

$$\Delta \bar{\varepsilon}(h\nu, F) = \frac{2e^2 \hbar^2 |\hat{\mathbf{e}} \cdot \mathbf{M}_{\text{ev}}|^2}{m^{*2} E^2} \left(\frac{2m_{\parallel}}{\hbar^2} \right)^{3/2} \sqrt{h\nu_F} [\bar{G}(\eta) + i \bar{F}(\eta)] \quad (19.38)$$

with the characteristic energy for the Franz-Keldysh effect (Cardona 1969)

$$h\nu_F = \left(\frac{e^2 F^2 \hbar^2}{2m_{\parallel}} \right)^{1/3} \quad (19.39)$$

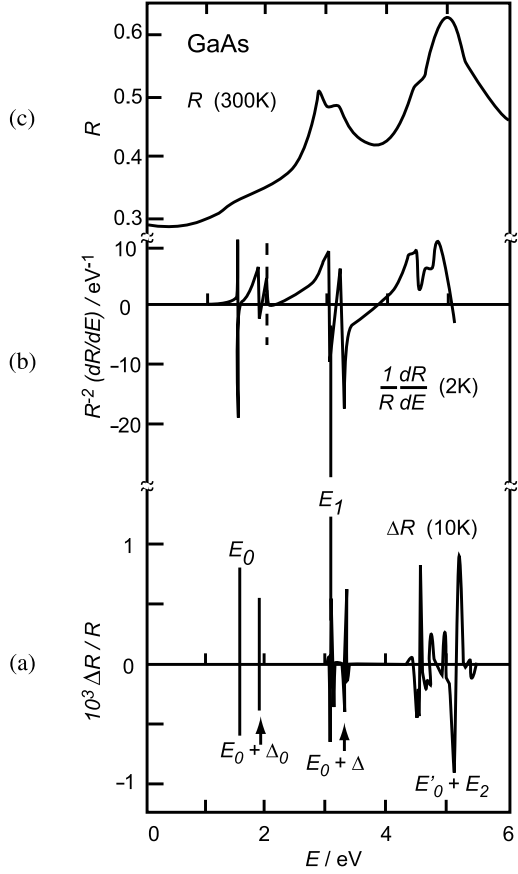
and with

$$\bar{F}(\eta) = \pi [\text{Ai}'^2(\eta) - \eta \text{Ai}^2(\eta)] - \sqrt{-\eta} u(-\eta). \quad (19.40)$$

$$\bar{G}(\eta) = \pi [\text{Ai}'(\eta) \text{Bi}'(\eta) - \eta \text{Ai}(\eta) \text{Bi}(\eta)] + \sqrt{\eta} u(\eta). \quad (19.41)$$

Here, Ai, Bi, and the primed functions are the Airy functions (Antosiewicz 1972), $\eta = (E_g - h\nu)/(h\nu_F)$; u is the unit step function; and m is the projection of the effective mass in the field direction. F and G are proportional to the real and imaginary parts of the dielectric constant, i.e., proportional to reflection and absorption,

Fig. 19.10 Comparison of reflectance (a), energy derivative reflectance (b), and low-field Franz-Keldysh reflectance (c) of GaAs, measured by Philipp and Ehrenreich (1963), Sell and Stokowski (1970), and Aspnes and Studna (1973), respectively (after Aspnes 1980)



respectively (see Bassani 1975), and in Fig. 19.11a are plotted against a reverse η abscissa to indicate electric-field modulation. This figure also shows a sharp spike at the transition energy followed by typical *Franz-Keldysh oscillations* toward higher energies, which increase in amplitude and in period length (line width) with the electric field as

$$\text{Period} = \left(\frac{3\pi}{2} \right)^{2/3} h\nu_F = \left(\frac{3\pi}{2} \frac{e\hbar}{\sqrt{2m_{\parallel}}} F \right)^{2/3}. \quad (19.42)$$

Near the absorption edge (for $h\nu \ll E_g$), one obtains from Eq. (19.38)

$$\varepsilon''(\nu, F) = \frac{\sqrt{2}e^2}{2\pi\sqrt{m_{\parallel}}(h\nu^2)^2} |\hat{\mathbf{e}} \cdot \mathbf{M}_{\text{ev}}|^2 \frac{\sqrt{h\nu_F}}{2(E_g - h\nu)} \exp \left[-\frac{4}{3} \left(\frac{E_g - h\nu}{h\nu_F} \right) \right], \quad (19.43)$$

which indicates the typical exponential extension of the optical absorption edge obtained by Franz (1958) and Keldysh (1958a); this is shown in Fig. 19.12. The field

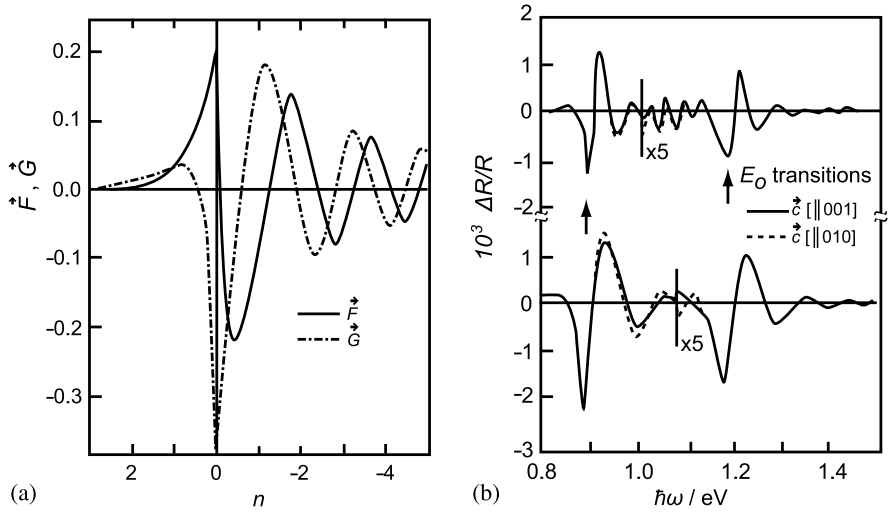
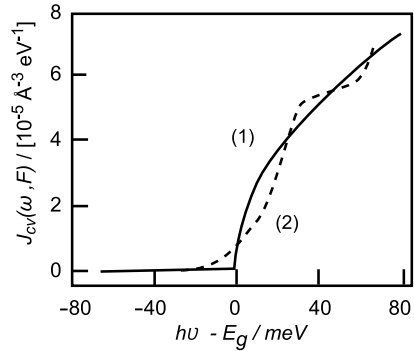


Fig. 19.11 (a) Franz-Keldysh line shapes $F(\eta)$ and $G(\eta)$ [Eqs. (19.40) and (19.41)] plotted against $-\eta (\propto E_g - h\nu)$ for transition to an M_0 -type critical point (after Aspnes 1967). (b) Electro-reflectance of Ge at 10 K for $F = 46$ and 115 kV/cm for the upper and lower parts of the figure, respectively (after Aspnes 1975)

Fig. 19.12 Joint density of states for a transition near an M_0 transition edge. Curve 1 for zero field; curve 2 calculated for $F = 5 \cdot 10^4$ V/cm and $m_n = 0.1m_0$ (after Aimerich and Bassani 1968)



dependence can in turn be used to probe for an electric field inside a semiconductor (Böer 1960).

The electro-reflectance $\Delta R/R$, which is proportional to G and is shown in Fig. 19.11b for Ge, has well-separated extrema and permits a comparison to the single-band transition computed in Fig. 19.11a (Aspnes 1975).

The increased amplitude and period length with increasing field is seen by comparison of the two parts of Fig. 19.11b. Some interferences above the characteristic points, identified by arrows, are due to the contributions from light- and heavy-hole bands, and are used to determine the complete set of interband effective masses (Hamakawa et al. 1968).

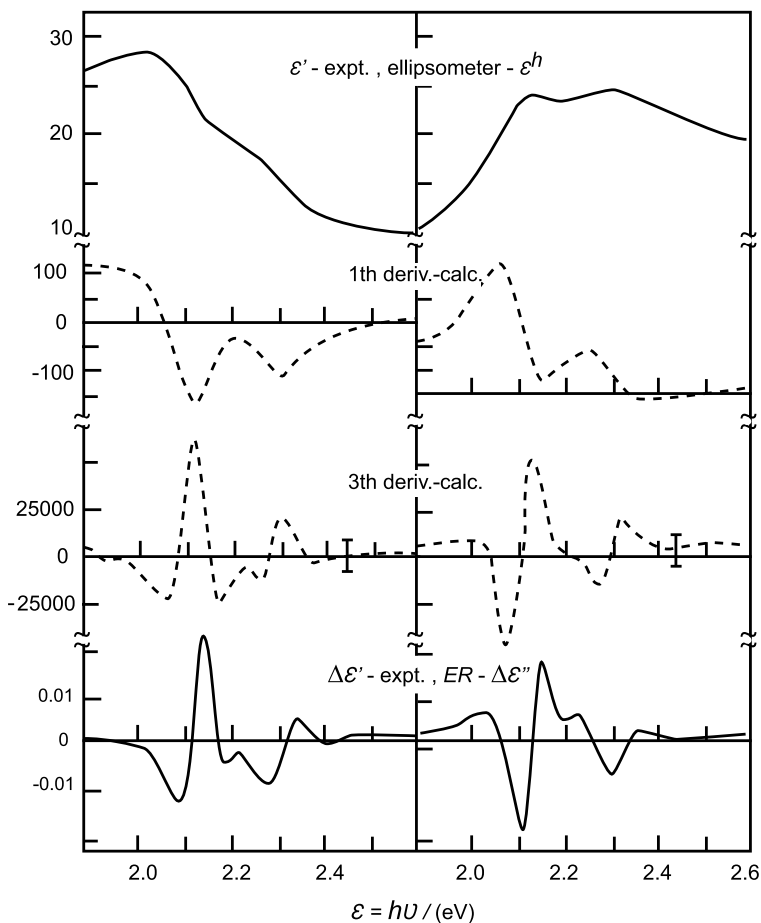


Fig. 19.13 Comparison of the ε -spectrum and derivative line shape between experiment (*top* and *bottom* from electro-reflectance) and derivatives taken from independent ellipsometer data (*top*) (after Aspnes 1972)

Further analysis of the Franz-Keldysh effect indicates the existence of three field ranges with substantially different behavior:

- (1) the low-field range where the modulation of reflection $\Delta R/R$ is smaller than 10^{-3} and is employed for line-shape studies using a third-derivative analysis—Fig. 19.13;
- (2) a medium-field range where the electron acceleration predominates¹ and determines line-shape broadening; and

¹The electron is accelerated in the electric field and occupies a range of k states, thereby losing translational invariance, i.e., resulting in the loss of k as a good quantum number. Different k -state mixing can describe the behavior and causes k -state broadening.

- (3) a high-field range where additional band-edge changes due to the *Stark effect* must be considered.

19.6.1 Influence of the Electric Field on Defect Levels

Impurity levels and *strongly bound Frenkel excitons* show a field effect that closely resembles the atomic Stark effect—see Grassano (1977), Boyn (1977). In semiconductors, the eigenstates are less localized, rendering the discussion of the Stark-effect more complex because of mixing between localized and band states (Vinoogradov 1973; Bauer 1978). Valuable information about the defect center, relating to its surroundings, symmetry, and crystal field splitting, can be deduced from the field-dependent absorption spectrum.

19.7 Field Effects in Superlattices

When the field is applied in the direction parallel to the superlattice layers, its effect on impurity states or excitons is similar to that in the bulk material; with the exception, however, that a_{qH} and R_H refer to the two-dimensional hydrogen problem with confinement in the direction normal to the superlattice plane.

Field ionization of hydrogen-like defects takes place when the energy gain across the hydrogen-like defect radius becomes larger than the binding energy

$$eFa_{qH} \gtrsim E_{qH}, \quad \text{or} \quad F \gtrsim 2.76 \cdot 10^4 \left(\frac{m_n/m_0}{0.1} \right)^2 \left(\frac{10}{\varepsilon_{st}} \right)^3 \text{ (V/cm)}. \quad (19.44)$$

Typical ionization fields for this Frenkel-Poole type of ionization in good semiconductors are on the order of 10 kV/cm (Miller et al. 1985)—see also Eq. (19.24).

In the direction normal to the superlattice plane, one has to consider confinement that permits much higher fields (typically $> 10^5$ V/cm) before ionization takes place (Bastard et al. 1983). Before ionization, two types of *quantum-confined Stark effects* (Miller et al. 1985) are observed: a *quadratic Stark shift*, in which the binding energy changes as

$$\Delta E_1 \propto m^* l^4 F^2 \quad (19.45)$$

where l is the width of the quantum well; and a *Stark shift*, where the binding energy changes with a lesser slope

$$\Delta E_1 \propto F^\alpha \quad \text{with } \alpha < 2. \quad (19.46)$$

At still higher fields, tunneling out of the well becomes important (Bastard et al. 1983).

Fig. 19.14 Influence of an electric field on the ground state of a quantum well with sequentially increasing field strength

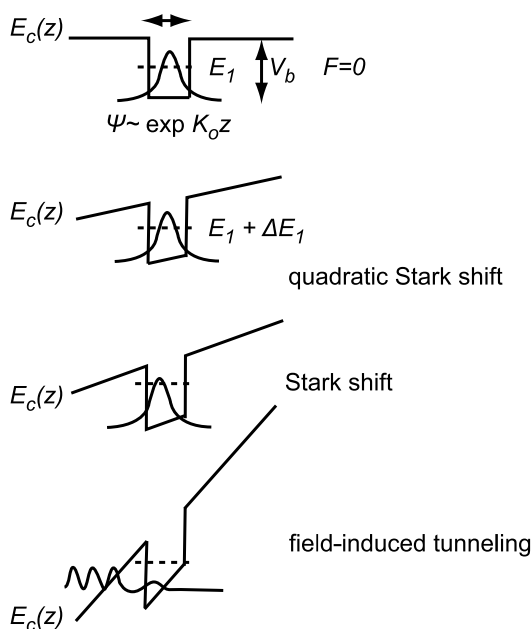


Figure 19.14 shows these cases schematically. The field-induced shift of the binding energy depends significantly on the position of the Coulomb-attractive defect within the well and is given in Fig. 19.15a. Changes in the exciton energy with field are more substantial and are given in Fig. 19.15b (see Brum and Bastard 1985; Miller et al. 1985).

Summaries on the field effect in superlattices are given by Bastard and Brum (1986), and by Miller et al. (1986).

19.8 Ionization via Energetic Particles

Carriers can be generated by a wide variety of high-energy particles, such as X-ray photons, fast electrons, and various nuclear particles. Consequently, the use of certain solids, e.g., CdS, for the detection of such particles and for dosimetry was proposed early (Frerichs and Warminski 1946; Fassbender and Hachenberg 1949; Broser et al. 1950).

In all of these excitation processes with high-energy particles, a large number of carriers are produced per incident particle. In addition, however, lattice damage is also produced depending on the energy and the mass of the particle. Such damage varies in severity from photochemical reactions with X-rays (Böer et al. 1966) to severe impact damage with protons and α -particles.

The excitation process depends on the type of particle. It may occur in the bulk via X-rays or γ -rays, or near the surface by fast electrons or α -particles; it may also

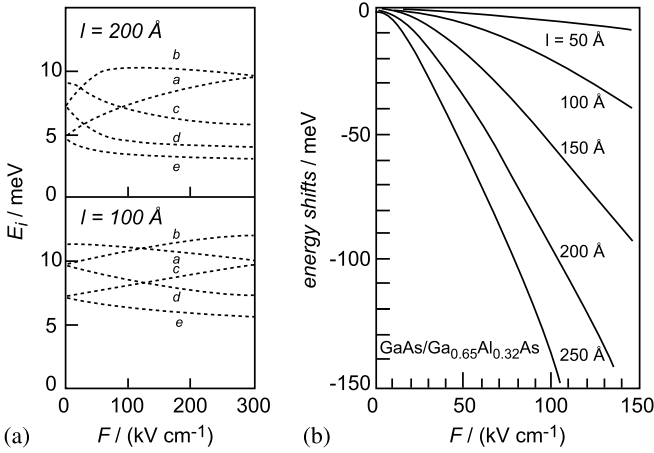


Fig. 19.15 (a) Influence of an electric field on the impurity binding energy for wells of different widths and different positions of the defect within the well, identified by letters referring to the defect position at $-l/2$, $l/4$, 0 , $l/4$, and $l/2$ for a–e, respectively. (b) Influence of an electric field on the binding energy of excitons. The field direction is normal to the well plane; family parameter is the well width (after Brum and Bastard 1985)

be of a cascade character, i.e., the initially generated fast carriers may in turn create secondary carriers of sequentially lower energy. For another review, see Hayes and Stoneham (1984).

Part III

Photons

Chapter 20

Basics of Optical Spectroscopy

Abstract Interaction with light is described by Maxwell's equations, yielding in a phenomenological theory of reflection, transmission and absorption. Semiconductors with optical absorption are discussed. Optical constants and refraction index for element and II–V compound semiconductor are tabulated. Complex electrical conductivity tensor is given. The dielectric constant tensor and dielectric polarization is tabulated for such compounds. The measurement of optical parameters, such as reflection and transmission in dielectrics, and in semiconductors is described. The Abac chart is introduced. Modulation spectroscopy is described. Absorption constant and reflection table for element and III–V semiconductors are given. Band to band transitions are discussed.

The interaction of light with matter is described by Maxwell's equations from which the basic optical material parameters can be obtained. The interaction of electromagnetic radiation (photons) with semiconductors provides major insight into the electronic and phononic structure of these solids. Such interactions can be described as resonant and nonresonant.

Resonant absorption concerning ions is observed in the infrared part of the spectrum; resonant absorption dealing with bound electrons is observed at shorter wavelengths and is usually separated from the ionic component by a wavelength range with low optical absorption, except for semiconductors with almost zero band gap. Both types of absorption describe *intrinsic* properties of the semiconductor. In addition, a large variety of *extrinsic* ionic and electronic resonance transitions of semiconductor defects can be distinguished. These optically induced transitions are extensively used for the identification of such defects.

Nonresonant interactions can be observed between photons and free electrons, except at high densities of free electrons when they act jointly as plasmons.

The interaction between photons and the semiconductor can be *elastic*, without absorption, or *inelastic*, with absorption. The latter requires damping of the excited state, by either absorption or emission of phonons or by collisions with electrons or other quasi-particles.

The resonant transitions will be described for ions in Sect. 20.2 and for electrons in Chap. 21. The description in this chapter is based on solutions of Maxwell's equations, which deal with the resonant transitions in a *phenomenological* way.

Comparison with the experiment requires the transformation of experimentally accessible quantities, such as reflectance and optical transmissivity, into quantities obtained as a result of a theoretical analysis, such as the set of optical constants. This relationship is summarized in Sect. 10.2.

20.1 Phenomenological Theory

In this section, the interaction of electromagnetic radiation with a semiconductor is described in a classical model. Beginning with *Maxwell's equations* one obtains the dispersion equation, yielding the optical parameters of the semiconductor (its complex dielectric constant) as a function of the frequency of the electromagnetic radiation (the energy of the photons). For more information, see Moss (1961a), or Palik (1985).

20.2 Reflection, Transmission, and Absorption

Light impinging on a semiconductor is subject to a number of optical interactions before it is absorbed. First, a fraction of the light is reflected at the outer surface; another fraction is scattered by crystal imperfections, phonons, and other quasi-particles; then a fraction of the light within the semiconductor is absorbed by various elementary excitation processes. The unabsorbed fraction is transmitted and exits through the semiconductor's surfaces after partial reflection.

Initially, let us regard the semiconductor as a continuum, represented by four parameters which can be measured macroscopically μ , ε , ϱ and σ , the magnetic permeability, the dielectric constant, the space charge density, and the electric conductivity, respectively.

With these parameters, the relationship between absorption, reflection, and transmission can be obtained from *Maxwell's equations* with the proper boundary conditions:

$$\nabla \times \mathbf{E} = -\mu\mu_0 \frac{\partial \mathbf{H}}{\partial t} \quad (20.1)$$

$$\nabla \times \mathbf{H} = \varepsilon\varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} + \sigma \mathbf{E} \quad (20.2)$$

$$\nabla \cdot \mathbf{E} = \frac{\varrho}{4\pi\varepsilon\varepsilon_0} \quad (20.3)$$

$$\nabla \cdot \mathbf{H} = 0. \quad (20.4)$$

Here $\mathbf{E}$ is chosen as the electric field vector rather than $\mathbf{F}$ as in other chapters of this book; $\mathbf{H}$ is the magnetic field vector.

20.2.1 Nonabsorbing Dielectrics

For homogeneous, non-magnetic, nonconductive dielectrics, one obtains with $\mu = 1$, $\mu_0 = 1/(\epsilon e^2)$ from Eqs. (20.1) and (20.2):

$$\begin{aligned}\nabla \times \nabla \times \mathbf{E} &= \nabla(\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} = -\nabla \times \left(\frac{1}{\epsilon_0 c^2} \frac{\partial \mathbf{H}}{\partial t} \right) \\ &= -\frac{1}{\epsilon_0 c^2} \frac{\partial}{\partial t} (\nabla \times \mathbf{H}),\end{aligned}\quad (20.5)$$

which yields the undamped wave equation for the electric vector

$$\nabla^2 \mathbf{E} = \frac{\epsilon}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} \quad (20.6)$$

and a similar one for the magnetic vector. Assuming a plane wave entering the dielectric in the x -direction with linear polarization in the y -direction, one has with $\mathbf{E} = (0, E_y, 0)$ from Eq. (20.6)

$$\frac{\partial^2 E_y}{\partial x^2} = \frac{\epsilon}{c^2} \frac{\partial^2 E_y}{\partial t^2}, \quad (20.7)$$

which can be solved with the trial solution

$$E_y = f(x) \exp(-i\omega t), \quad (20.8)$$

where $f(x)$ is the amplitude function. Substitution of Eq. (20.8) into Eq. (20.7) yields

$$\frac{d^2 f}{dx^2} + \frac{\epsilon \omega^2}{c^2} f = 0 \quad (20.9)$$

with the solution

$$f(x) = A \exp \left[\pm i \left(\frac{\omega x}{v} \right) \right]. \quad (20.10)$$

Here $n_r = \sqrt{\epsilon}$ the index of refraction and c is the light velocity in vacuo. Thus, with the $+$ sign in Eq. (20.10), Eq. (20.8) describes a plane wave traveling in $+$ -direction

with a phase velocity v and amplitude A :

$$\begin{aligned}
 E_{\parallel r} &= E_{\parallel i} \frac{n_{r2} \cos \phi_i - n_{r1} \cos \phi_t}{n_{r2} \cos \phi_i + n_{r1} \cos \phi_t} \\
 E_{\perp r} &= E_{\perp i} \frac{n_{r1} \cos \phi_i - n_{r2} \cos \phi_t}{n_{r1} \cos \phi_i + n_{r2} \cos \phi_t} \\
 E_{\parallel t} &= E_{\parallel i} \frac{2n_1 \cos \phi_i}{n_{r1} \cos \phi_t + n_{r2} \cos \phi_i} \\
 E_{\perp t} &= E_{\perp i} \frac{2n_{r1} \cos \phi_i}{n_{r2} \cos \phi_t + n_{r1} \cos \phi_i}
 \end{aligned} \tag{20.11}$$

$$E_y = A \exp \left[i \omega \left(\frac{x}{v} - t \right) \right] = A \exp \left[i \omega \left(\frac{n_r}{c} x - t \right) \right]. \tag{20.12}$$

The energy flow in this wave is given by the *Poynting vector* (a vector in the direction of the wave propagation)

$$\mathbf{S} = \mathbf{E} \times \mathbf{H}. \tag{20.13}$$

Here, we assume $E = (0, E_y, 0)$ and $H = (0, 0, H_z)$. The energy density is given by

$$W = \frac{1}{2} (\varepsilon \varepsilon_0 E^2 + \mu \mu_0 H^2). \tag{20.14}$$

With an equal amount of energy in the electrical and magnetic component, one obtains for the total energy density twice the energy represented by the electrical vector:

$$W = \varepsilon \varepsilon_0 E_y^2. \tag{20.15}$$

20.3 Semiconductors with Optical Absorption

The introduction of a finite conductivity $\sigma = \sigma(\omega)y$ produces a damping contribution [second term of Eq. (20.16)] on the electromagnetic wave in a semiconductor, resulting in a finite optical absorption.¹ From Eqs. (20.2) and (20.5), we obtain the *damped wave equation* for the electric vector

$$\nabla^2 \mathbf{E} = \frac{\varepsilon}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} + \frac{\sigma}{\varepsilon_0 c^2} \frac{\partial \mathbf{E}}{\partial t}. \tag{20.16}$$

¹One can understand this by equating damping with transfer of energy into heat, and optical absorption with extraction of this energy from the radiation field. Such absorption occurs even outside a specific electronic or ionic resonance absorption.

Using the same trial solution as given in the previous section for $f(x)$ we obtain

$$\frac{d^2 f}{dx^2} + \frac{\omega^2}{c^2} \left(\varepsilon - i \left(\frac{\sigma}{\varepsilon_0 \omega} \right) \right) f = 0 \quad (20.17)$$

which has a solution that can be written exactly as Eq. (20.10). This yields a plane wave traveling in the x -direction

$$E_y = A \exp \left[i \omega \left(\frac{\tilde{n}}{c} x - t \right) \right], \quad (20.18)$$

except that the index of refraction used to describe the ratio c/v (Eq. (20.11)) is now complex and is identified as n . This *complex index of refraction*

$$\tilde{n} = \frac{c}{v} = \sqrt{\tilde{\varepsilon}} = n_r + i\kappa \quad (20.19)$$

is related to the complex dielectric constant ε in a similar fashion as given in Eq. (20.11), and contains as its real part the previously defined index of refraction and as its imaginary part the *extinction coefficient*. The *complex dielectric constant* ε is given by

$$\tilde{\varepsilon} = \varepsilon' + i\varepsilon'' \quad \text{with} \quad \varepsilon' = \varepsilon \quad \text{and} \quad \varepsilon'' = \frac{\sigma}{\varepsilon_0 \omega}, \quad (20.20)$$

with its imaginary part related to the conductivity. From Eqs. (20.19) and (20.20), we obtain the important relations for an optically absorbing (damping) homogeneous continuum:

$$\begin{array}{l} \boxed{\begin{array}{l} \varepsilon' = n_r^2 - \kappa^2 \\ \varepsilon'' = \frac{\sigma}{\varepsilon_0 \omega} = 2n_r \kappa \end{array}} \quad \text{or} \\ \boxed{\begin{array}{l} n_r^2 = \frac{1}{2} [\varepsilon' + \sqrt{\varepsilon'^2 + \varepsilon''^2}] \\ \kappa^2 = \frac{1}{2} [-\varepsilon' + \sqrt{\varepsilon'^2 + \varepsilon''^2}]. \end{array}} \end{array} \quad (20.21)$$

The optical parameters for a number of typical semiconductors are listed in Tables 20.1 and 20.2. The temperature-dependence of n_r is shown for the example of GaAs in Fig. 20.1.

Using Eq. (20.19), the wave equation can be rewritten as

$$E_y = A \exp i \omega \left(\frac{n_r}{c} x - t \right) \exp \left(-\frac{\omega \kappa}{c} x \right) \quad (20.22)$$

and shows the damping factor in the second exponential. Using a more conventional expression $\exp(-\alpha_o x)$ for the damping of the energy flux, with α_o as the optical

Table 20.1 Optical constants for element and III–V compound semiconductors for $E > E_g$

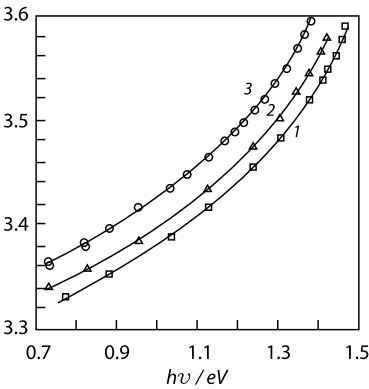
$h\nu$	Crystals						$h\nu$			
	Si	Ge	GaP	GaAs	GaSb	InP	InAs	InSb	ZnSe	CdTe
ϵ'	13.488	21.500	10.102	13.435	19.135	11.904	13.605	19.105	6.4	11.5
	= 1.5 eV									= 1.5 eV
	15.254	30.361	11.114	14.991	25.545	12.493	15.558	14.448	6.0	12.2
	2.0 eV									2.0 eV
	18.661	13.153	12.996	18.579	13.367	14.313	15.856	7.811	6.8	13.2
	2.5 eV									2.5 eV
	27.197	12.065	16.601	16.536	9.479	17.759	6.083	7.354	7.7	15.0
	3.0 eV									3.0 eV
	22.394	9.052	24.833	8.413	7.852	6.400	5.973	5.995	7.8	14.5
	3.5 eV									3.5 eV
ϵ''	12.240	4.123	9.652	9.279	−1.374	6.874	7.744	−6.722	8.5	17.0
	4.0 eV									4.0 eV
	−19.815	−14.655	11.073	6.797	−8.898	8.891	−1.663	−6.297	9.5	10.2
	4.5 eV									4.5 eV
	−10.242	−8.277	0.218	−11.515	−5.693	−7.678	−5.923	−4.250	8.0	7.5
	5.0 eV									5.0 eV
	−9.106	−6.179	−10.266	6.705	−5.527	4.528	−3.851	−4.325	5.6	4.6
	5.5 eV									5.5 eV
	−7.443	−6.648	−5.521	−4.511	−4.962	−2.681	−2.403	−3.835	6.5	—
	6.0 eV									6.0 eV
	0.038	2.772	0.000	0.589	3.023	1.400	3.209	5.683	0	0.2
	1.5 eV									1.5 eV
	0.172	10.427	0.000	1.637	14.442	2.252	5.062	14.875	0	0.8
	2.0 eV									2.0 eV
	0.630	20.695	0.046	3.821	19.705	3.904	15.592	15.856	0.5	2.1
	2.5 eV									2.5 eV
	2.807	17.514	1.832	17.571	15.738	10.962	13.003	13.421	1.5	2.4
	3.0 eV									3.0 eV
	33.818	21.442	8.268	14.216	19.267	12.443	10.550	17.673	1.9	7.6
	3.5 eV									3.5 eV
	35.939	26.056	16.454	13.832	25.138	10.871	11.919	19.443	2.2	11.0
	4.0 eV									4.0 eV
	24.919	16.782	17.343	22.845	10.763	16.161	22.006	8.351	3.8	13.8
	4.5 eV									4.5 eV
	11.195	8.911	26.580	18.563	7.529	14.896	8.752	6.378	8.5	14.8
	5.0 eV									5.0 eV
	8.846	7.842	10.974	8.123	6.410	7.308	6.008	4.931	6.2	6.5
	5.5 eV									5.5 eV
	5.877	5.672	7.041	6.250	4.520	5.644	6.005	3.681	7.8	—
	6.0 eV									6.0 eV

^aSensitive to preparation and hydrogen content. Values of CdTe and α -Si from Palik (1985)

Table 20.2 Refractive index as a function of the photon wavelength for some semiconductors at 300 K for $E < E_g$ (from *American Institute of Physics Handbook*, 1963—for more extensive data, see Palik 1985)

	λ (μm)	n_r	λ (μm)	n_r	λ (μm)	n_r
Si	1.3570	3.4975	2.4373	3.4408	5.50	3.4213
	1.3673	3.4962	2.7144	3.4358	6.00	3.4202
	1.3951	3.4929	3.00	3.4320	6.50	3.4195
	1.5295	3.4795	3.3033	3.4297	7.00	3.4189
	1.6606	3.4696	3.4188	3.4286	7.50	3.4186
	1.7092	3.4664	3.50	3.4284	8.00	3.4184
	1.8131	3.4608	4.00	3.4255	8.50	3.4182
	1.9701	3.4537	4.258	3.4242	10.00	3.4179
	2.1526	3.4476	4.50	3.4236	10.50	3.4178
	2.3254	3.4430	5.00	3.4223	11.04	3.4176
Ge	2.0581	4.1016	2.998	4.0452	8.66	4.0043
	2.1526	4.0919	3.3033	4.0369	9.72	4.0034
	2.3126	4.0786	3.4188	4.0334	11.04	4.0026
	2.4374	4.0708	4.258	4.0216	12.20	4.0023
	2.577	4.0609	4.866	4.0170	13.02	4.0021
	2.7144	4.0552	6.238	4.0094		
GaAs	0.78	3.34	13.0	2.97	17.0	2.59
	8.0	3.34	13.7	2.895	19.0	2.41
	10.0	3.135	14.5	2.82	21.9	2.12
	11.0	3.045	15.0	2.73		
InSb	7.87	4.00	12.98	3.91	17.85	3.85
	8.00	3.99	13.90	3.90	18.85	3.84
	9.01	3.96	15.13	3.88	19.98	3.82
	10.06	3.95	15.79	3.87	21.15	3.81
	11.01	3.93	16.96	3.86	22.20	3.80
	12.06	3.92				

Fig. 20.1 Refractive index of GaAs as a function of the photon energies with the temperature as family parameter: $T = 103, 187$, and 300 K for curves 1–3, respectively (after Marple 1964)



absorption coefficient for the energy density, we obtain by comparison with the second exponential in Eq. (20.22)

$$\alpha_o = \frac{2\omega\kappa}{c} = \frac{4\pi}{\lambda}\kappa; \quad (20.23)$$

here the energy flow is given by the product of the electric and magnetic vectors, thus producing a factor of 2 in the exponent. However, H_z is phase-shifted by δ with $\tan \delta = \kappa/n_r$. From Eqs. (20.21) and (20.22), we also obtain

$$\alpha_o = \frac{\sigma}{\varepsilon_0 n_r c}, \quad (20.24)$$

which shows the direct connection of α_o with the electrical conductivity. This conductivity is to be taken at the optical frequency and needs further explanation.

20.4 The Complex Electrical Conductivity

The right-hand side of Eq. (20.2) of Maxwell's equations is considered as total current

$$\mathbf{j} = \sigma \mathbf{E} + \varepsilon \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} = (\sigma + i\omega \tilde{\varepsilon} \varepsilon_0) \mathbf{E}. \quad (20.25)$$

The second term is obtained after Fourier transformation from the time into the frequency domain. When introducing for $i\omega \varepsilon \varepsilon_0$ a *complex conductivity*, we obtain

$$\tilde{\sigma} = \sigma' + i\sigma'' = \varepsilon_0 \omega (\varepsilon'' - i\varepsilon') \quad (20.26)$$

or

$$\begin{aligned} \sigma' &= \varepsilon'' \varepsilon_0 \omega = \sigma_d \\ \sigma'' &= -\varepsilon' \varepsilon_0 \omega = -(n_r^2 - \kappa^2) \varepsilon_0 \omega. \end{aligned} \quad (20.27)$$

Observe that the real part of σ is proportional to the imaginary part of ε and vice versa. The conductivity σ_d is proportional to the *displacement current*, caused by bound electrons surrounding each atom core, which are slightly displaced and oscillate out of phase with the acting electric field.

The current can now be rewritten. When expressed by the dielectric function, Eq. (20.25) reads

$$\begin{aligned} \mathbf{j}(\omega) &= \{\sigma_0 + \omega \varepsilon_0 \varepsilon''(\omega) + i\omega \varepsilon_0 \varepsilon'(\omega)\} (\mathbf{E})\omega \\ &= \{\sigma_0 + \sigma_d(\omega) + i\omega \varepsilon_0 (n_r^2 - \kappa^2)\} (\mathbf{E})\omega. \end{aligned} \quad (20.28)$$

20.4.1 Dielectric Polarization

For later discussions of microscopic models, it is advantageous to introduce the dielectric polarization. The electric displacement $\mathbf{D}$, field strength $\mathbf{E}$, and polarization $\mathbf{P}$ are related by

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \quad (20.29)$$

and

$$\mathbf{P} = \varepsilon_0 \tilde{\chi} \mathbf{E} = \varepsilon_0 (\tilde{\varepsilon} - 1) \mathbf{E} \quad (20.30)$$

with $\tilde{\varepsilon}$ as the complex dielectric constant. Here, only a linear relationship between $\mathbf{P}$ and $\mathbf{E}$ is given. Higher terms are of importance at higher fields and give rise to nonlinear optical effects, and defines the susceptibility χ ; i as the proportionality constant between the polarization $\mathbf{P}$ and the electric field $\mathbf{E}$. From Eqs. (20.29) and (20.30) we have

$$\mathbf{D} = \varepsilon_0 \tilde{\varepsilon} \mathbf{E} = \varepsilon_0 (1 + \tilde{\chi}) \mathbf{E}. \quad (20.31)$$

In an anisotropic material, ε and χ have tensor form with components

$$P_i = \varepsilon_0 \chi_{ij} E_j \quad \text{and} \quad D_i = \varepsilon_0 \varepsilon_{ij} E_j. \quad (20.32)$$

This matrix relationship must be used when applying Maxwell's equations to an anisotropic medium. For instance, from *Poisson's equation* $\nabla \cdot \mathbf{E} = \rho / (\varepsilon \varepsilon_0)$, we have for the ij -component

$$\varepsilon_0 \varepsilon_{ij} \frac{\partial E_j}{\partial x_i} = \rho. \quad (20.33)$$

Depending on the crystal symmetry, the dielectric constant tensor can be reduced, and contains at most six independent coefficients—see Table 10.3. This dielectric constant will be the subject of further discussion.

20.5 Measurement of Optical Parameters

The parameters obtained from an analysis of the optical phenomena are the complex dielectric constant (or index of refraction) and the complex conductivity, as well as the amplitude and polarization of electromagnetic waves after interacting with the semiconductor (the dielectric constant tensor is shown for different crystal systems in Table 20.3).

On the other hand, the parameters measured directly are the intensities of reflected and transmitted radiation and its change of the state of polarization. It is the purpose of this section to summarize briefly the most relevant interrelation of these two sets of parameters, thereby permitting a quantitative comparison between theory and experiment. For more detail, see Stern (1985), or Palik (1985).

Table 20.3 Dielectric constant tensor

Crystal system	Characteristic symmetry	Number of independent coefficients	Form of tensor showing independent coefficients
Cubic	4 3-fold axes	1	$\begin{pmatrix} \varepsilon & 0 & 0 \\ 0 & \varepsilon & 0 \\ 0 & 0 & \varepsilon \end{pmatrix}$
Tetragonal	1 4-fold axis	2	$\begin{pmatrix} \varepsilon_1 & 0 & 0 \\ 0 & \varepsilon_1 & 0 \\ 0 & 0 & \varepsilon_3 \end{pmatrix}$
Hexagonal	1 6-fold axis		
Trigonal	1 3-fold axis		
Orthorhombic	3 mutually perpendicular 2-fold axes; no axes of higher order	3	$\begin{pmatrix} \varepsilon_1 & 0 & 0 \\ 0 & \varepsilon_2 & 0 \\ 0 & 0 & \varepsilon_3 \end{pmatrix}$
Monoclinic	1 2-fold axis	4	$\begin{pmatrix} \varepsilon_{11} & 0 & \varepsilon_{13} \\ 0 & \varepsilon_{22} & 0 \\ \varepsilon_{13} & 0 & \varepsilon_{33} \end{pmatrix}$
Triclinic	A center of symmetry or no symmetry	6	$\begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{12} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{13} & \varepsilon_{23} & \varepsilon_{33} \end{pmatrix}$

20.6 Reflectance and Transmissivity in Dielectrics

The index of refraction, as well as the extinction and absorption coefficients can be related to the amplitude and polarization of reflected and transmitted optical waves which can be measured directly. The relationship between these waves can be obtained from the wave equation and the boundary conditions at the interface between two media (see Moss 1961a).

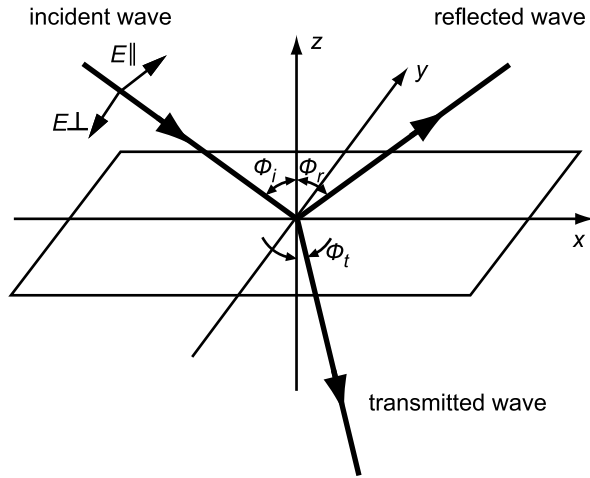
The electric vector of the incident wave (denoted by subscript i) can be described by its two components normal and parallel to the plane of incidence at $z = 0$ (Fig. 20.2):

$$(E_y, E_z)_i = (E_\perp, E_\parallel)_i \exp \left[i\omega \left\{ \frac{n_{r1}}{c} (x \sin \phi_i + z \cos \phi_i) - t \right\} \right], \quad (20.34)$$

with the corresponding components of the reflected (index r) and transmitted (index t) waves

$$(E_y, B_z)_r = (E_\perp, E_\parallel)_r \exp \left[i\omega \left\{ \frac{n_{r1}}{c} (x \sin \phi_r + z \cos \phi_r) - t \right\} \right] \quad (20.35)$$

$$(E_y, E_z)_t = (E_\perp, E_\parallel)_t \exp \left[i\omega \left\{ \frac{n_{r2}}{c} (x \sin \phi_t + z \cos \phi_t) - t \right\} \right]. \quad (20.36)$$

Fig. 20.2 Coordinate system with light beams and interface

The coordinate system is chosen so that the interface is normal to the z -axis and cuts z at $z = 0$. The x - and y -axes are chosen so that the normal-to-the-incident wavefront lies in the xz -plane; the angles are identified in Fig. 20.2.

From the condition that at the plane of incidence ($z = 0$) the tangential component of the electrical field of all three waves must be the same, we require that the corresponding exponents must be equal $n_{r1} \sin \Phi_i = n_{r1} \sin \Phi_r := n_{r2} \sin \Phi_t$ from here, *Snell's law* can be deduced:

$$\begin{aligned} \phi_i &= \phi_r \\ n_{r1} \sin \phi_i &= n_{r2} \sin \phi_t. \end{aligned} \quad (20.37)$$

For $n_{r1} > n_{r2}$ this yields an angle of total reflection (i.e., for $\Phi_t = 90^\circ$), with $\Phi_i = \Phi_c$ the critical angle,² given by

$$R_0 = R_\perp = R_\parallel = \frac{(n_r - 1)^2 + \kappa^2}{(n_r + 1)^2 + \kappa^2}. \quad (20.39)$$

$$\sin \phi_c = \frac{n_{r2}}{n_{r1}}. \quad (20.40)$$

²A *Brewster angle* is defined as the angle under which no component Eu is reflected. Here $\sin \Phi_i = \cos \Phi_t$ hence

$$\tan \phi_B = \frac{n_{r1}}{n_{r2}}. \quad (20.38)$$

Total reflection is sometimes used in photosensing devices for light trapping by properly shaping the surface in order to increase the optical path within the device for more optical absorption, and thereby increasing the photosensitivity.

The amplitudes of the tangential components of the reflected and transmitted waves must be continuous when passing through $z = 0$; hence

$$(E_{\parallel i} - E_{\parallel r}) \cos \phi_i = E_{\parallel t} \cos \phi_t \quad (20.41)$$

$$E_{\perp i} + E_{\perp r} = E_{\perp t} \quad (20.42)$$

$$n_{r1}(E_{\perp i} - E_{\perp r}) \cos \phi_i = n_{r2} E_{\perp t} \cos \phi_t \quad (20.43)$$

$$n_{r1}(E_{\parallel i} + E_{\parallel r}) = n_{r2} E_{\parallel t}. \quad (20.44)$$

The first set of two equations is obtained from the electric vector-components; the second set is obtained from the magnetic vector components.

After solving this set of four equations for the four components of the electric vector, we obtain Fresnel's equations:

$$\begin{aligned} E_{\parallel r} &= E_{\parallel i} \frac{n_{r2} \cos \phi_i - n_{r1} \cos \phi_t}{n_{r2} \cos \phi_i + n_{r1} \cos \phi_t} \\ E_{\perp r} &= E_{\perp i} \frac{n_{r1} \cos \phi_i - n_{r2} \cos \phi_t}{n_{r1} \cos \phi_i + n_{r2} \cos \phi_t} \\ E_{\parallel t} &= E_{\parallel i} \frac{2n_1 \cos \phi_i}{n_{r1} \cos \phi_t + n_{r2} \cos \phi_i} \\ E_{\perp t} &= E_{\perp i} \frac{2n_{r1} \cos \phi_i}{n_{r2} \cos \phi_t + n_{r1} \cos \phi_i} \end{aligned} \quad (20.45)$$

which are generally valid and are the basis for all following discussions.

All measurable quantities are related to the energy flux, i.e., for the incident and reflected waves to the Poyntings vector. For the incident and reflected waves we have

$$W_a = \varepsilon_0 n_{r1}^2 E_a^2 \quad \text{for } a = i, r. \quad (20.46)$$

For the transmitted wave we have

$$W_t = \varepsilon_0 n_{r2}^2 E_t^2. \quad (20.47)$$

The reflectance³ and transmittance are defined by the ratios of the energy flux to the incident energy flux normal to the interface:

³Reflectance (etc.) is used rather than reflectivity since it is not normalized to the unit area; this is similar to the use of the word resistance (not normalized) vs. resistivity, distinguishing between the suffixes -ance and -ivity.

$$R = \left(\frac{E_r}{E_i} \right)^2 \quad \text{and} \quad T = \left(\frac{E_t}{E_i} \right)^2 \frac{\cos \phi_t}{\cos \phi_i}, \quad (20.48)$$

which can be computed from the normal and parallel components given by the Fresnel equations. The resulting formulae become rather lengthy and confusing. Some simplified cases better demonstrate the typical behavior. These simplifications include

- (1) air as the first medium with $n_{r1} = 1$ and $\sigma_1 = 0$;
- (2) a nonabsorbing second medium with $\sigma_2 = 0$; and
- (3) that the incident wave is normal to the interface.

With assumptions (1) and (2), we obtain from Eqs. (20.48) and (20.45) for the two components of the reflected beam

$$R_{\perp} = \frac{\sin^2(\phi_t - \phi_i)}{\sin^2(\phi_t + \phi_i)} \quad \text{and} \quad R_{\parallel} = \frac{\tan^2(\phi_t - \phi_i)}{\tan^2(\phi_t + \phi_i)} \quad (20.49)$$

and the transmitted beam

$$T_{\perp} = \frac{\sin 2\phi_i \sin 2\phi_t}{\sin^2(\phi_i + \phi_t)} \quad \text{and} \quad T_{\parallel} = \frac{\sin 2\phi_i \sin 2\phi_t}{\sin^2(\phi_i + \phi_t) \cos^2(\phi_i + \phi_t)}. \quad (20.50)$$

When assumptions (2) and (3) hold, we obtain the well-known relations for the reflected and transmitted beams:

$$R = R_{\perp} = R_{\parallel} = \left(\frac{n_{r1} - n_{r2}}{n_{r1} + n_{r2}} \right)^2 \quad (20.51)$$

$$T = T_{\perp} = T_{\parallel} = \frac{4n_{r1}n_{r2}}{(n_{r1} + n_{r2})^2}.$$

20.7 Reflectance and Transmittance in Semiconductors

In semiconductors, condition (2) of the previous section no longer holds; there is absorption. However, in spectral ranges in which n_r is much larger than K , we obtain still rather simple approximations, which for the reflected wave are:

$$R_{\perp} \simeq \frac{(n_r - \cos \phi_i)^2 + \kappa^2}{(n_r + \cos \phi_i)^2 + \kappa^2} \quad \text{and} \quad R_{\parallel} \simeq R_{\perp} \frac{(n_r - \sin \phi_i \tan \phi_i)^2 + \kappa^2}{(n_r + \sin \phi_i \tan \phi_i)^2 + \kappa^2}. \quad (20.52)$$

These reflectance components are shown for a set of n_r and κ in Fig. 20.3. There is a substantial amplitude difference for low angles of incidence between the parallel and perpendicular polarized components. The ratio of these components shows a maximum at the *Brewster angle* given by

$$\tan^2 \phi_B \simeq n_r^2 + \kappa^2. \quad (20.53)$$

Fig. 20.3 Polarized components of the reflectance parallel and perpendicular to the semiconductor surface as a function of the incident angle, computed for $n_r = 3$ and $\kappa = 1$ (Moss 1961a)

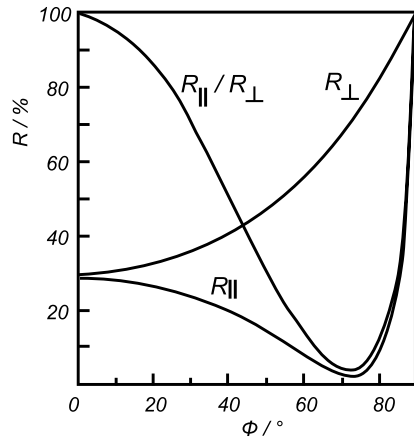
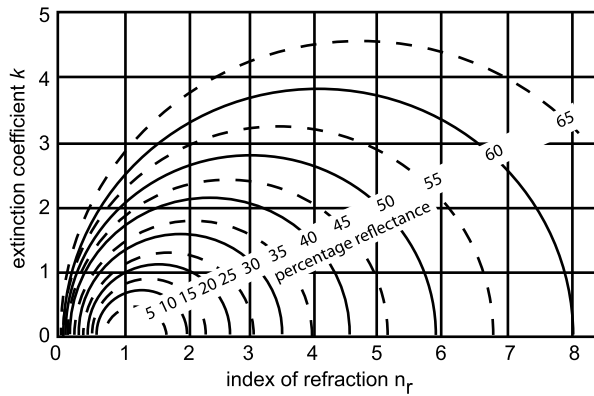


Fig. 20.4 Relation between the normal reflectance and the optical constants for a single surface reflectance



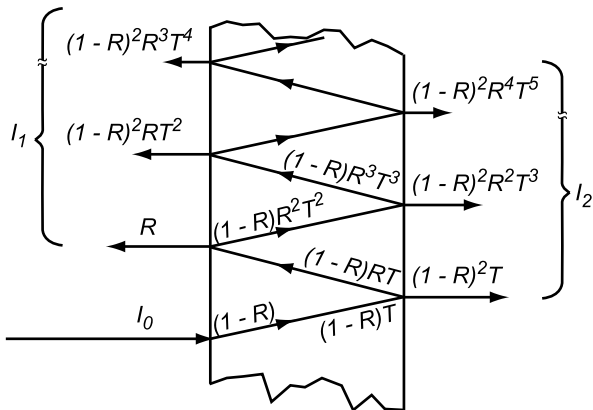
Reflection at this angle can be used to obtain nearly linearly polarized light from the normal component (the amplitude of the parallel component is negligible)—see Fig. 20.3.

For normal incidence, parallel or normal components can no longer be distinguished in reflectance:

$$R_0 = R_{\perp} = R_{\parallel} = \frac{(n_r - 1)^2 + \kappa^2}{(n_r + 1)^2 + \kappa^2}. \quad (20.54)$$

Equation (20.54) is the equation of a circle centered at $n = (1 + R_0)/(1 - R_0)$ with a radius of $2\sqrt{R_0/(1 - R_0)}$, as shown in Fig. 20.4.

For a semiconductor plate with two planar surfaces separated by a distance d , we must consider reflection from both surfaces, as shown in Fig. 20.5. The result of the

Fig. 20.5 Multireflection in a semitransparent slab

series of sequential reflections, indicated by the subscript Σ , is

$$R_{\Sigma} = R_0 \left[1 + \frac{T_0^2 (1 - R_0)^2}{1 - R_0^2 T_0^2} \right] \quad \text{and} \quad T_{\Sigma} = T_0 \left[\frac{(1 - R_0)^2}{1 - R_0^2 T_0^2} \right], \quad (20.55)$$

with T_0 as the transmittance through the slab at its first pass under normal incidence without reflection. For a perfectly transmitting slab, we consequently obtain

$$R_{\Sigma} = \frac{2R_0}{1 - R_0} \simeq 2R_0. \quad (20.56)$$

In a more precise analysis, a phase shift δ between both reflected waves must be included, which, for normal incidence, is given by

$$\delta_o = \frac{2\pi n_r d}{\lambda}. \quad (20.57)$$

The total reflectivity of this plate at normal incidence is given by

$$R_{\Sigma} = \frac{\sinh^2(\alpha_o d/2) + \sin^2 \delta_o}{\sinh^2(\alpha_o d/2 + \gamma_o) + \sin^2(\delta_o + \psi_o)}, \quad (20.58)$$

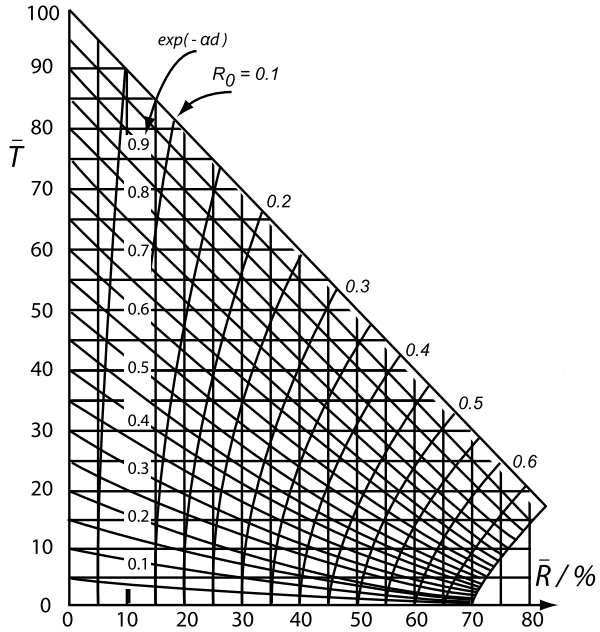
where the auxiliary functions γ_o and ψ_o are given by $\gamma_o = \ln \sqrt{1/R_0}$, with R_0 from Eq. (20.54), and $\psi_o = \tan^{-1}(2\kappa/[n_r^2 + \kappa^2 - 1])$; α_o is the optical absorption coefficient. The transmissivity through this plate is given by

$$T_{\Sigma} = \frac{\sinh^2 \gamma_o + \sin^2 \psi_o}{\sinh^2(\alpha_o d/2 + \gamma_o) + \sin^2(\gamma_o + \psi_o)}. \quad (20.59)$$

For vanishing absorption ($\kappa = 0$, $\psi_o = 0$), we confirm from Eqs. (20.58) and (20.59) that the sum of transmissivity and reflectivity is 1.

The interference pattern from the superposition of front and back reflections makes an evaluation of κ (or α_o) in thin planar layers difficult.

Fig. 20.6 Abac chart for obtaining α_o and R_0 from measured values of T and R



However, one can deduce the index of refraction from the ratio of maximum to minimum amplitudes of the transmitted light for adjacent extrema

$$\frac{T_{0,\max}}{T_{0,\min}} = \frac{(n_r^2 + 1)^2}{4n_r^2} \quad (20.60)$$

as long as the absorption term can be neglected—see Moss (1961a, 1961b), for inclusion of α_o .

In order to determine the absorption coefficient, compromises must be made to average out the interference pattern by making either the surfaces slightly nonplanar (rough), or the light slightly polychromatic. This yields an “average” reflectivity

$$\boxed{\bar{R} = R_0(1 + \bar{T} \exp(-\alpha_o d))} \quad (20.61)$$

and an “average” transmissivity

$$\boxed{\bar{T} = \frac{(1 - R_0)^2 \exp(-\alpha_o d)}{1 - R_0^2 \exp(-2\alpha_o d)} \simeq (1 - R_0)^2 \exp(-\alpha_o d),} \quad (20.62)$$

with R_0 given by Eq. (20.54). From the measured values of T and R , the more relevant values of α_o and R_0 , and hence of κ and n_r , can be obtained. This is done most easily with an Abac chart, as shown in Fig. 20.6.

The reflectance and absorption coefficient of some typical semiconductors is given in Table 20.4.

20.8 Modulation Spectroscopy

For analytical purposes, modulating one of the parameters of a semiconductor while investigating the optical response is a very powerful technique. The light itself (frequency or intensity), temperature, pressure, mechanical stress (uniaxial), and electric or magnetic field have all been employed as parameters to be modulated. As optical response, the reflectance is most often used by measuring its relative change $\delta R/R_0$ or its higher derivatives as a function of the wavelength. Absorption within the band is too strong to be observed, except for extremely thin platelets.

The modulation is detected with a phase-sensitive lock-in technique, which is extremely sensitive and permits detection of rather small signals ($<10^{-5}$)—see Cardona (1969), Seraphin (1973), and Enderlein (1977).

With this technique it is relatively easy to detect changes in spectral ranges of high optical absorption. For instance, one can measure the energy difference between the critical points within the valence and conduction bands. This method is analyzed below.

From the reflectance equation [Eq. (20.51)]

$$R_0 = \left(\frac{n_r - n_{ra}}{n_r + n_{ra}} \right)^2, \quad (20.63)$$

we obtain the modulated signal of the reflected light beam, which is proportional to the changes in the complex dielectric constant n_{ra} is the index of refraction for an external medium in contact with the semiconductor.

Using the Maxwell relation

$$n_r^2 = \varepsilon_{\text{opt}} = \varepsilon \quad \text{and} \quad n_{ra}^2 = \varepsilon_{a,\text{opt}} = \varepsilon_a, \quad (20.64)$$

such changes can be expressed as (Re = real part)

$$\frac{\Delta R}{R_0} = \text{Re} \left[\frac{2n_{ra}}{n_r(\varepsilon - \varepsilon_a)} \Delta \varepsilon \right]. \quad (20.65)$$

Equation (20.64) can also be written as

$$\frac{\Delta R}{R_0} = \text{Re}[(\alpha_S - i\beta_S)\Delta\tilde{\varepsilon}] = \alpha_S\Delta\varepsilon' + \beta_S\Delta\varepsilon'', \quad (20.66)$$

where α_S and β_S are the *Seraphin coefficients* (Seraphin and Bottka 1965) and $\Delta\varepsilon = \Delta\varepsilon' + i\Delta\varepsilon''$ is the change in the complex dielectric constant due to the modulation.

A more useful equation for comparing the experimental results with a theoretical analysis is the inverse relation

$$\Delta\varepsilon = \frac{\frac{\Delta R}{R_0} + 2i\Delta\theta}{\alpha_S - i\beta_S} \quad (20.67)$$

with

$$\Delta\theta = -\frac{\omega}{\pi} P \int_0^\infty \left[\frac{\Delta R}{R_0}(\omega') \right] \frac{d\omega'}{\omega'^2 - \omega^2}, \quad (20.68)$$

where P indicates the principal part of the integral. The integral can be evaluated by a Kramers-Kronig analysis—see Aspnes (1980).

20.9 Relation to Band-to-Band Transitions

The analysis of the modulation reflection spectrum is involved. It permits identification of the energy and type of critical points. As an example, below is given a short outline of how the energy difference from the valence band to an extremum of an upper conduction band can be obtained from typical reflection signals.

The complex dielectric constant for band-to-band excitation in a one-electron approximation is given by, e.g., Petroff (1980), Aspnes (1980):

$$\varepsilon(E, \gamma) = 1 + \frac{4\pi e^2 \hbar^2}{m_0^2 E^2} A_0^2 \sum_{k,e,v} |\mathbf{e} \cdot \mathbf{M}_{ev}(k)|^2 \left[\frac{1}{E_c(\mathbf{k}) - E_v(\mathbf{k}) - h\nu - i\gamma} + \frac{1}{E_e(\mathbf{k}) - E_v(\mathbf{k}) + h\nu + i\gamma} \right], \quad (20.69)$$

with M_{ev} as the momentum matrix element, e is the electric vector of the impinging electromagnetic wave A_0 as its amplitude, and γ as an empirical damping parameter. Equation (20.68) can be simplified for a direct transition into one parabolic band to

$$\varepsilon(E, \gamma_d) = \frac{e^2 \hbar^2 A_0^2}{\pi^2 m_0^2 E^2} |e \cdot \mathbf{M}_{ev}|^2 \int \frac{d^3k}{E_e(k) - E_v(k) - h\nu - i\gamma} \quad (20.70)$$

with

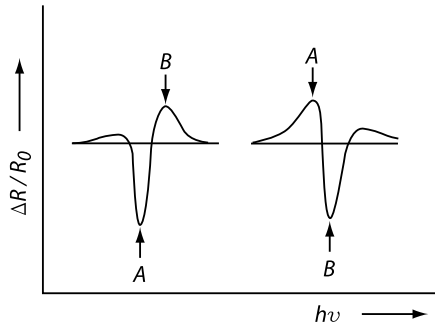
$$E_e(\mathbf{k}) - E_v(\mathbf{k}) = E_g + \frac{\hbar^2}{2} \left(\frac{k_x^2}{m_{xx}} + \frac{k_y^2}{m_{yy}} + \frac{k_z^2}{m_{zz}} \right). \quad (20.71)$$

From Eq. (20.70) we deduce that an isolated critical point (of the type M_0 or M_3) can be described by

$$\varepsilon(E, \gamma) - A\gamma^{-n} \exp(i\theta)(E - E_g + i\gamma)^n \quad (20.72)$$

where A is an amplitude factor, θ is a phase projection factor, and n is an exponent which is $-1/2$, 0 (logarithmic), or $1/2$ for one-, two-, or three-dimensional critical points. The gap E_g , i.e., the energy difference between critical points in any of the valence and conduction bands related to the initiated transition and the damping γ can be determined from the line shape, which typically shows three extrema near the critical point (Fig. 20.7). With subscripts A and B identifying the two largest

Fig. 20.7 Typical line shape of a reflection signal caused by a simple band-to-band transition



extrema, E_g and γ , can be estimated according to (Aspnes 1980)

$$E_g = E_A + (E_B - E_A)f(\xi) \quad (20.73)$$

and

$$\gamma = (E_B - E_A)g(\xi) \simeq E_B - E_A, \quad (20.74)$$

with $0.8 < g(\xi) < 1.2$ and $f(\xi)$ monotonically increasing from 0 to 1 with increasing $\xi = (\Delta R/R_0)_A/(\Delta R/R_0)_B$. Hence, E_g always lies closest to the largest peak in the reflection spectrum: the closer to the peak, the larger the ratio of their magnitude.

Chapter 21

Photon Interaction with Carriers

Abstract The optical carrier generation from band-to-band and from defect centers is described. The density of state and the band structure diagram is given for Si. The oscillation strength for transition of a hydrogen atom is tabulated. Photo-ionization cross section measurements are described. Reaction kinetics for these transitions is briefly indicated.

Free carriers, generated by light and causing an increase in electrical conductivity, provide an important means of detecting light or measuring light-transmitted signals. This photoconductivity also permits a convenient analysis of carrier excitation and relaxation processes. When the electric conductivity is *significantly* increased because of an increased *majority* carrier *density* as a result of an optical excitation, the resulting raised conductivity is called *photoconductivity*. With excitation from the valence to the conduction band, it is termed *intrinsic photoconductivity*; with excitation involving levels in the band gap, it, is called *extrinsic photoconductivity*. Semiconductors that show strong photoconductivity are called *photoconductors*.

First the different intrinsic and extrinsic carrier-generation processes will be reviewed. Then, an overview of a reaction-kinetic analysis will be given, which is the basis for a quantitative description of the change in carrier distribution due to optical excitation. Finally, some typical examples will be given for the various processes of photon-induced changes in conductivity. For reviews see, Bube (1970, 1978), Mort and Pai (1976), and Rose (1978a, 1978b), as well as Vols. 5 and 12 of *Semiconductors and Semimetals* (R.K. Willardson and A.C. Beer (eds.) Academic Press, New York).

21.1 Carrier Generation

Band-to-band excitation was discussed in Sect. 13.1, in which most attention was given to an excitation near the fundamental edge. Photoconductivity with excitation beyond the band edge, i.e., extrinsic excitation, is rather homogeneous throughout the volume of the semi conductor.

At higher photon energies, however, the optical absorption becomes large and consequently the carrier generation occurs closer to, and often within the first

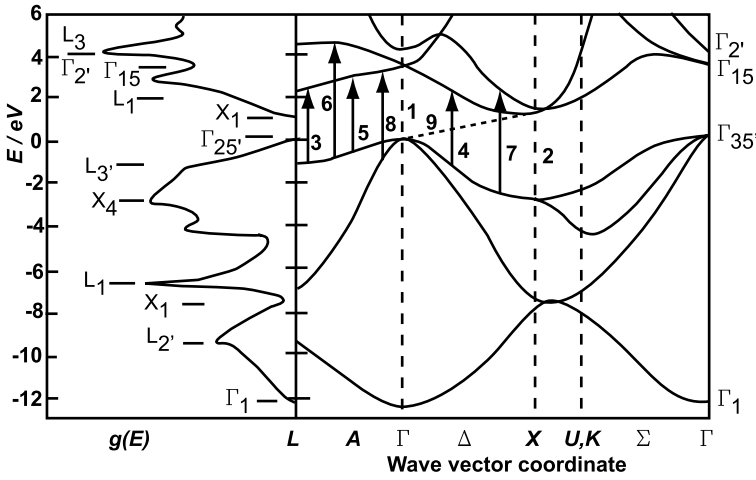


Fig. 21.1 Band structure and density-of-state distribution of Si with competing direct electron transitions indicated at characteristic points (1, 2, and 3) along $E(k)$ -ranges with parallel bands and comparatively high joint density of states (4 and 5), transitions into higher conduction bands (6 and 7), and from the light-hole valence band (8). The indirect band edge transition (9) is indicated by a dotted arrow

100, ..., 1000 Å of the front surface. Most intrinsic transitions are direct (vertical) transitions which can proceed from any point in k -space with the appropriate photon energy—Fig. 21.1.

The generation rate is proportional to the impinging light flux Φ_0 (photon/cm² s) normal to a platelet surface (z), the square of the matrix element for each of the transitions at a given energy and the joint density of states (neglecting reflection it is included in Eq. (21.7)). When expressing these in terms of the optical absorption coefficient, one has

$$g_o(\lambda)d\lambda = \phi_o(\lambda)\alpha_o(\lambda)\exp(-\alpha_o z)d\lambda \quad (21.1)$$

with

$$\alpha_o(\lambda) = \frac{e^2 \lambda}{6\epsilon_0 n_r c^2 m_0^2 \nu} |M_6|^2 J_{c,v}. \quad (21.2)$$

Integration over the energy range, given by the specific optical excitation, e.g., a band-to-band excitation, yields the total generation rate with electrons distributed in certain regions of the k space—see Fig. 21.1. From this deformed distribution, the electrons will relax to approach a Boltzmann distribution, with most of the electrons near the lower edge of the conduction band, or the upper edge of the valence band for holes. Most of the photoconductivity occurs near the band edges.

Defect-to-band excitation was extensively discussed in Sect. 20.2; here, again, excitations into higher states of the band need to be considered. Excitation from deeper centers shows a wider distribution, since they are more localized in real

space. Hence, their eigenfunctions are more spread out in k space, and they offer a broad range of vertical transitions; whereas for shallow-level centers, the direct transitions are restricted closer to $k = 0$.

Ground-to-excited state excitation can act as the precursor to photoconductivity when a secondary process completes the excitation into the band. Such secondary processes can be

- tunneling,
- impact ionization,
- thermal ionization, or
- an excitation by additional photons.

Finally, an excitation of free carriers, from states near the band edge to higher states, influences the photoconductivity by changing the effective mass and relaxation time. Devices based on this effect are referred to as *free-electron bolometers*.

21.2 Photo-Ionization Cross Section

The excitation of electrons from deep-level centers into the conduction band can be described as transitions into resonant states. Such transitions are possible when the excited state contains Bloch functions of the same k value as the ground state—conservation of momentum. The cross section of localized deep centers extends over a large range in k -space; it therefore extends to a wide energy range of the band continuum. This cross section can be approximated by:

$$s_0(h\nu) \propto \frac{h\nu - |E_i|}{(h\nu)^3} g(h\nu - |E_i|), \quad (21.3)$$

where E_i is the ionization energy, and $g(h\nu - |E_i|)$ is the density of states, which, for a simple parabolic band near its edge, can be expressed as

$$g(h\nu - |E_i|) \propto \sqrt{h\nu - |E_i|}. \quad (21.4)$$

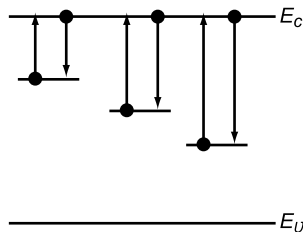
The cross section can be calculated when the deep center potential is known. When it is approximated by a square well function (Lucovsky 1965), one obtains

$$s_0(h\nu) = \frac{1}{n_r} \left(\frac{F_{\text{eff}}}{F} \right)^2 \frac{32\pi^2 e^2 \hbar \sqrt{E_i} (h\nu - |E_i|)^{3/2}}{3m^*(h\nu)^3}; \quad (21.5)$$

where F_{ff}/F is the ratio of the effective local field (Eq. (20.24)) to the electromagnetic radiation field, which takes into consideration the local screening by charges near the defect center. This ratio is typically on the order of 1 for shallow levels; s_0 is on the order of 10^{-16} cm^2 near the band edge. Further from the band edge, the expression becomes more complicated, causing a rapid reduction of the cross section (Jaros 1977). Equation (21.5) describes rather well the IR absorption of GaAs: Au or GaAs: Ag (Queisser 1971).

Table 21.1 Oscillator strength (f_{ba}) for transitions of a hydrogen atom

$1s \rightarrow 2p$	0.4162	$1s \rightarrow 5p$	0.0139
$1s \rightarrow 3p$	0.0791	$1s \rightarrow 6p$	0.0078
$1s \rightarrow 4p$	0.0290	$1s \rightarrow \text{contin.}$	0.436

Fig. 21.2 Photoionization from three independent centers into the conduction band

For excitation into an excited state, one obtains for the cross section

$$s_0(h\nu) = \frac{1}{n_r} \left(\frac{F_{\text{eff}}}{F} \right)^2 \frac{2\pi^2 e^2 \hbar}{m^* e} f_{ba} \simeq 1.1 \cdot 10^{-16} \frac{1}{n_r} \left(\frac{F_{\text{eff}}}{F} \right)^2 \frac{m_0}{m^*} f_{ba} \quad (21.6)$$

with f_{ba} as the oscillator strength that is given for a hydrogen atom in Table 21.1 and applies to a quasi-hydrogen defect.

21.3 Photo-Ionization Cross Section Measurement

The relative cross section of different impurities can be easily obtained by a constant-photoconductivity method developed by Grimmeiss and Ledebro (1975).

One can show from detailed balance that the photo-ionization cross section is inversely proportional to the intensity of light ($I(h\nu)_\sigma$) required to produce, with light of different photon energies, the same photoconductivity

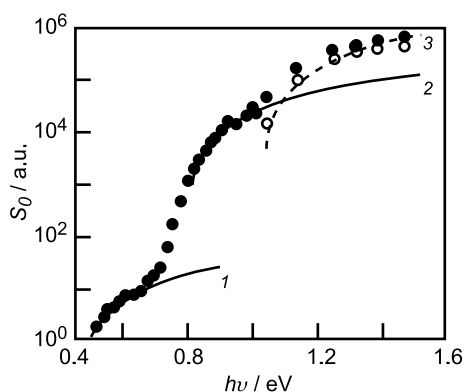
$$s_0(h\nu) = \frac{\text{const}}{I(h\nu)_\sigma}. \quad (21.7)$$

This assumes that, with changing photon energy, photo-ionization occurs from different deep defect levels into the same band, and results in carriers with the same mobility. One must also assume that these levels do not communicate with other levels or bands; this is indicated in Fig. 21.2.

An example of results obtained from this method is given in Fig. 21.3, which shows the photo-excitation from three deep impurity levels into the conduction band of GaAs:O. The deepest level is at an energy of 1.03 eV below the conduction band edge, with a cross section almost 105 times larger than the shallowest level at 0.46 eV below E_c . The middle level, with a cross section close to the deepest level, lies at 0.79 eV below E_c .

Careful checking as to whether all of the assumptions used are fulfilled is imperative. The *photo-Hall effect* can be used to detect competing transitions involving the opposite carrier.

Fig. 21.3 Relative photo-ionization cross section for excitation of three deep impurity centers into the conduction band of GaAs (after Grimmeiss and Ledebro 1975)



21.4 Reaction-Kinetics Evaluation

The density of carriers in the respective bands and in levels in the band gap is changed from thermal equilibrium with optical excitation. These densities can be obtained from reaction-kinetic arguments.

First, the carrier density in the respective bands is discussed for a number of rather simple reaction-kinetic models in order to identify the specific influence of certain defect levels.

Chapter 22

Carrier Recombination

Abstract Carriers that were excited into one of the bands can recombine by radiative or non-radiative means. Non-radiative recombination can occur by single photon emission (luminescence), by mission of phonons, by simultaneous emission of multi phonons, or by an accelerated carrier (Auger emission). Recombination can start from the band edge at $k = 0$, from a higher band edge, or from an excited state of a defect center, and proceed to another band or from a higher to a lower excited state, or to the ground state of another defect level. Recombination also can proceed after diffusion into the same level (geminate recombination) or after migration to another site. Table of capture cross sections in Si and CdS is given. Recombination at Coulomb attractive centers is discussed. Geminate recombination, especially recombination in amorphous semiconductors is discussed. Non-radiative recombination at deep traps is identified. Competition between radiative and non-radiative recombination is evaluated. Non-radiative multi phonon recombination is explained. Auger recombination is discussed. Statistics of recombination is introduced at recombination centers, with demarcation lines defined. Thermal equilibrium and steady state are distinguished. The Hall-Shockley-Read center is introduced.

Carriers can return immediately or after scattering to their original pre-excitation state (geminate recombination), or they can recombine with another state after diffusion away from their site of origin. On the average, for each act of generation there must be one in verse act of recombination. Carrier recombination is the opposite process to carrier generation, which was discussed the previous chapter. For reasons of detailed balance, a process of recombination must occur for every process of generation in equilibrium. Although, there is a wide variety of such recombinations, depending on the type of energy released during recombination, one can distinguish two principle types

- radiative recombination

and

- nonradiative recombination.

Radiative recombination releases a photon, is of great technical importance, and is discussed as *luminescence* in Sect. 22.5. Non-radiative recombination is discussed below.

22.1 Nonradiative Recombination

Nonradiative recombination is usually an undesired effect, since it converts high electronic energy into heat; that is, it increases the entropy of the system. It thereby decreases the performance of all but a few devices—such as bolometers, which are designed to measure the incident total energy; this is best accomplished by converting it into heat. Nonradiative recombination can occur by:

- single-phonon emission when recombining with a shallow level,
- a cascade emission of phonons,
- simultaneous multi-phonon emission, and
- Auger generation of an accelerated carrier.

Recombination can occur from a band edge at

- $k = 0$, or at
- $k \neq 0$, or from an
- excited state of a defect level. Recombination can proceed
- to another band,
- from a higher to a lower excited state, or
- to the ground state of a defect level.

Finally, recombination can proceed either

- directly back, or
- after some scattering back into the same state (geminate recombination), or
- after migration to another site.

22.2 Capture Cross Section

A carrier, ignoring its kinetic energy, will be captured at a defect center with a phonon ladder if, while colliding with the center, it dissipates energy of at least kT . Its probability of reemission would be equal to its probability of further emitting a phonon, however, multiplied with the probability of finding a phonon for the reemission.

This probability is < 1 .

The capture cross section of such a center is

$$s_{\text{nr}} = \pi r_0^2, \quad (22.1)$$

where r_0 is the radius of the electron eigenstate at kT below the band edge. In the following section, we will present an estimate of r_0 for a Coulomb-attractive center.

Capture occurs with high probability when, during its Brownian path within a band, a carrier approaches the center

- (a) within kT of the band edge *and*
- (b) within a distance of less than r_0 of the recombination center.

The first condition is usually fulfilled (it occurs for carriers in thermal equilibrium), and only the second condition needs to be considered. Therefore, using a gas-kinetic model, carrier capture, like ordinary scattering, takes place after the electron has traveled a distance

$$\lambda_r = v_{\text{rms}} \tau_r, \quad (22.2)$$

where τ_r is the lifetime of a carrier between generation and capture and is given by

$$\tau_r = \frac{1}{v_{\text{rms}} s_{\text{nr}} (N_r - n_r)}, \quad (22.3)$$

with $N_r - n_r$ as the density of free recombination centers. A listing of capture cross sections for electrons or holes for some defect centers is given in Table 22.1. When nonequilibrium conditions are involved at higher fields or with optical excitation, energy-dependent capture cross section must be considered that involves relaxation processes within the band.

22.2.1 Recombination at Coulomb-Attractive Centers

The energy spectrum of a Coulomb-attractive center is given by

$$E_{\text{qH}} = \frac{m^*/m_0}{\varepsilon_{\text{st}}^2 n_q^2} R_H \quad (22.4)$$

where n_q is the quantum number. For capture to take place, one identifies a quantum number $n_k T$ as the closest integer of n_q , for which $E_{n=\infty} - E_n > kT$. Then

$$\hat{n}_{kT}^2 \simeq \frac{m^*/m_0}{\varepsilon_{\text{st}}^2 kT} R_H; \quad (22.5)$$

one obtains as the radius of the corresponding eigenstate

$$r_{kT} = a_H \frac{\varepsilon_{\text{st}} m_0}{m^*} \hat{n}_{kT}^2. \quad (22.6)$$

Table 22.1 Electron and hole capture cross sections of deep level impurities at room temperature in cm^2 and level depth in eV (collected from Landolt and Börnstein 1982a, 1982b)

Dopant	Host lattice	
	Si	CdS
Cu		$s_n(E_c - 0.09) = 4 \cdot 10^{-18}$ $s_n(E_c - 0.2) = 3 \cdot 10^{-17}$ $s_n(E_v + 1.1) = 3 \cdot 10^{-21}$ $s_p(E_v + 0.34) \geq 10^{-15}$
Ag	$s_n(77 \text{ K}) = 10^{-12}$	$s_n(E_c - 0.23) = 10^{-13}$
Au	$s_p(E_c - 0.55) = 10^{-15}$ $s_n(E_v + 0.35) = 10^{-14}$	$s_n(E_c - 0.065) = 10^{-19}$ $s_n(E_c - 0.15) = 10^{-17}$
Zn	$s_p(E_v + 0.26) = 10^{-10}$	
S	$s_n(E_c - 0.59) = 2 \cdot 10^{-15}$	
W	$s_n(E_c - 0.22) = 10^{-16}$ $s_n(E_c - 0.3) = 6 \cdot 10^{-17}$ $s_n(E_c - 0.37) = 3 \cdot 10^{-18}$	
Co	$s_p(E_v + 0.29) = 2 \cdot 10^{-16}$ $s_p(E_v + 0.4) = 10^{-16}$	
Ni	$s_n(E_c - 0.35) = 10^{-15}$ $s_n(E_v + 0.23) = 10^{-15}$	$s_n = 10^{-17}$ $s_p(E_v + 1.44) = 10^{-15}$
Rh	$s_n(E_c - 0.31) = 7 \cdot 10^{-16}$ $s_p(E_v + 0.52) = 6 \cdot 10^{-16}$	
Pd	$s_n(E_c - 0.22) = 3 \cdot 10^{-15}$ $s_p(E_c - 0.19) = 10^{-16}$	
Pt	$s_n(E_c - 0.23) = 5 \cdot 10^{-15}$ $s_p(E_v + 0.32) = 10^{-15}$	

Usually, the ground state is only slightly below kT at room temperature. Thus, $n_q = 1$ is often used for the quasi-hydrogen recombination radius, yielding the well-known approximation

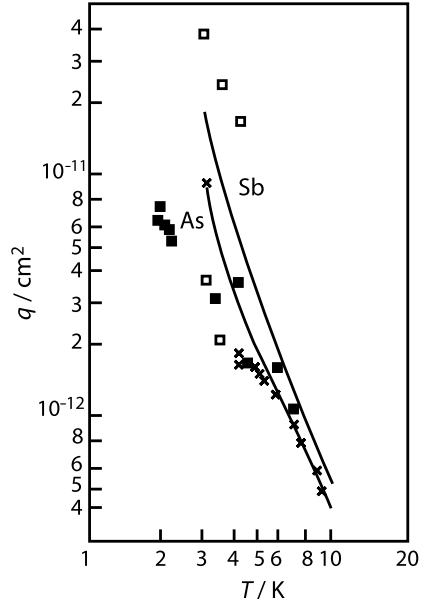
$$r_{kT} = a_H \frac{\varepsilon_{\text{st}} m_0}{m^*}. \quad (22.7)$$

From Eqs. (22.5) and (22.6) one obtains

$$r_{kT} = a_H \frac{R_H}{\varepsilon_{\text{st}} kT} = \frac{e^2}{8\pi \varepsilon_{\text{st}} \varepsilon_0 kT} = 27.8 \cdot \left(\frac{10}{\varepsilon_{\text{st}}} \frac{300}{T} \right) (\text{\AA}). \quad (22.8)$$

Except for a factor of $3/2$, this is the same result as obtained by setting a random-walk velocity away from the center equal to a drift velocity due to the Coulomb potential (Bube 1974, p. 488). The derivation presented here is not limited to lower-

Fig. 22.1 Giant capture cross section for electrons by positively charged donors in As- or Sb-doped Si as a function of temperature (after Ascarelli and Rodriguez 1961)



mobility semiconductors, which are implicitly required ($\lambda > r_{kT}$) in the velocity criterion.

The resulting recombination cross section is independent of m^* ,

$$s_{nr} = \frac{e^4}{64\pi(\epsilon_{st}\epsilon_0 kT)^2} = 2.42 \cdot \left(\frac{10^3}{\epsilon_{st} T}\right)^2 \cdot 10^{-13} \text{ (cm}^2\text{)}, \quad (22.9)$$

and decreases with increasing temperatures $\propto 1/T^2$. It becomes very large at low temperatures, e.g., $4 \cdot 10^{-12} \text{ cm}^2$ at 70 K, or $6 \cdot 10^{-10} \text{ cm}^2$ at $T = 5 \text{ K}$. Measured capture coefficients are only slightly smaller (Fig. 22.1), possibly because of some overlap of the giant cross sections.

From Eq. (22.8), one obtains for the Coulomb potential:

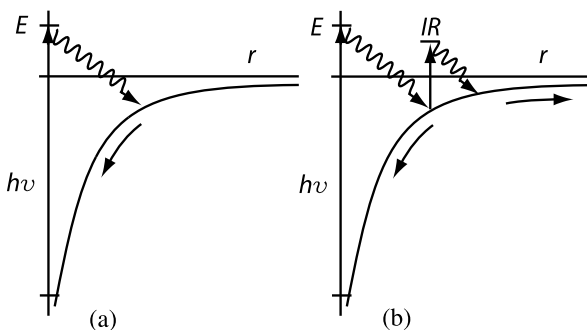
$$2r_{kT} = \frac{e^2}{4\pi\epsilon_{st}\epsilon_0 kT}; \quad (22.10)$$

i.e., the radius of the Coulomb well for $E_n \cong kT$, is just twice the corresponding quasi-Bohr radius.

22.2.2 Geminate Recombination

In semiconductors with a relatively short mean free path, the excitation from a Coulomb-attractive center higher up into the band is followed by a number of scattering processes until the carrier is within kT of the band edge. If the carrier reaches

Fig. 22.2 (a) Geminate recombination after excitation from a Coulomb-attractive center. (b) Out-diffusion after excitation with an additional IR excitation. The wavy arrow pointing down symbolizes scattering with phonon emission



the band edge within the same Coulomb funnel, it will recombine with the same center from which it was generated—see Fig. 22.2a. Such recombination is referred to as *geminate recombination*. It is observed in organic crystals and plays an important role in some of the amorphous semiconductors.

A similar process also holds for geminate band-to-band recombination.

With an additional IR excitation, it is possible to increase the probability for out-diffusion and thereby reduce geminate recombination—Fig. 22.2.

22.3 Recombination in Amorphous Semiconductors

After optical excitation higher into the bands of amorphous semiconductors, inelastic scattering will relax these carriers into the tailing states, which extend from the band edges. Near the mobility edge (Sect. 22.4), the carriers continue to diffuse, thereby losing energy and consequently being trapped at deeper and deeper centers until thermal reemission and tunneling from center to center is no longer possible, as the deeper centers are more widely spaced.

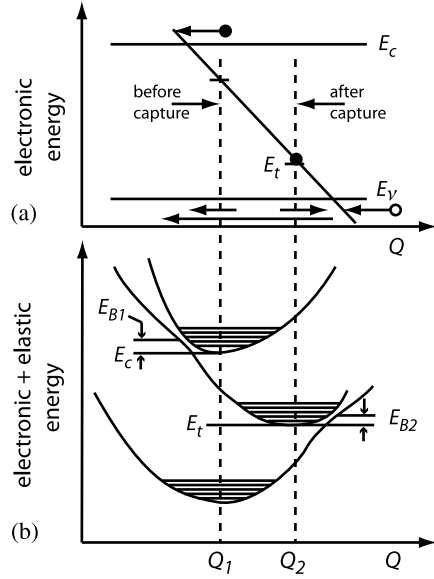
22.4 Nonradiative Recombination at Deep Centers

Electron eigenfunctions in deep centers are strongly coupled with lattice oscillations. The energy of such a defect level depends on the relative position of the defect atom with respect to its surrounding lattice atoms. With vibrations of these atoms, the defect level moves up and down in the band gap about its equilibrium position.

One mechanism of nonradiative capture is related to a sufficiently large lattice vibration, which moves the defect level into the conduction band. Here it can accept an electron from the conduction band. After the capture, the lattice is far from the equilibrium position, considering the recharging of the defect. This causes a violent vibration, which quickly relaxes with the emission of many phonons.

If the relaxation is very large, the defect level can move from the upper to the lower half of the band gap. Here, it can act now as a similar trap for holes, thereby

Fig. 22.3 (a) Electron energy vs. configuration coordinate of a deep center before and after relaxation. (b) Electron plus elastic energy vs. coordination coordinate, shown for the deep level between valence and conduction bands (after Henry and Lang 1977)



completing the process of band-to-band recombination (Henry and Lang 1977). This mechanism was alluded to in Sects. 22.1 and 23.3, and is pictured schematically in Fig. 22.3a. The equilibrium position of the defect after electron capture is given by Q_2 . The extent of average oscillations before and after capture (short arrows), as well as the extent of the giant oscillation directly after electron capture but before relaxation (large arrow), are indicated at the bottom of part (a) of this figure. The corresponding configuration coordinate diagram is redrawn here for convenience—Fig. 22.3b. The diagram identifies the activation energy E_{B1} for the electron trapping transition, and E_{B2} for hole trapping. The thermal binding energy of the electron in the center is $E_c - E_t$.

As an important consequence of this model, one obtains a temperature-dependent capture cross section:

$$s_n = s_\infty \exp\left(\frac{E_c - E_{B1}}{kT}\right). \quad (22.11)$$

The pre-exponential factor s_∞ , obtained from detailed balance arguments, relates capture and emission, as shown in Eq. (22.8) for an unrelaxed trap. With lattice relaxation, care must be taken to account for the different activation energies; one then obtains (Sumi 1983)

$$e_{tc} = \frac{v_c}{v_t} e_{ct} \exp\left(-\frac{S\hbar\omega_r}{kT}\right), \quad (22.12)$$

where v_c is the number of equivalent valleys in the conduction band, v_t is the degeneracy of the deep trap level, and S is the number of phonons emitted (Huang-Rhys

factor) during the relaxation process after electron capture. Here, w_r is the relevant defect eigenfrequency of a breathing mode.

With e_{tc} also given by (see Fig. 22.3b)

$$e_{tc} = \frac{\omega_r}{2\pi N_c} \exp\left\{-\frac{E_c - E_t}{kT}\right\}, \quad (22.13)$$

one obtains with $C_{ct} = v_{rms}s_n$ and Eq. (22.13), setting $E_c - E_t = S\hbar\omega$, for the pre-exponential factor of the capture cross Sect. (22.11):

$$s_\infty = \frac{v_t}{v_c} \frac{\omega_r}{2\pi} \frac{1}{N_c v_{rms}} \simeq 6.5 \cdot 10^{-15} \left(\frac{\hbar\omega_r}{40 \text{ meV}}\right) \left(\frac{300 \text{ K}}{T}\right)^2 \left(\frac{0.1}{m_n/m_0}\right) \text{ cm}^2. \quad (22.14)$$

A more careful consideration of the approximations used to compute the capture requires the introduction of a factor η into Eq. (22.14), yielding a modified $s'_\infty = \eta s_\infty$. The correction factor η can be approximated as (Sumi 1983)

$$\eta = \begin{cases} \frac{3\pi}{4} \gamma & \text{for } \gamma \ll 1 \\ 1 - \frac{5\pi}{9\sqrt{3}} \gamma^{-2/3} \simeq 1 & \text{for } \gamma \gg 1 \end{cases} \quad (22.15)$$

with the material parameter

$$\gamma = \frac{4\alpha_c kT \sqrt{\Delta E_c}}{3\hbar\omega_r} (E_c - E_t)^{3/2} \quad (22.16)$$

and ΔE_c as the width of the conduction band (see also Kayanuma and Fukuchi 1984). Peuker et al. (1982) have given a short review of the different approaches to obtain transition probabilities between the states in the adiabatic approximation. Such probabilities are proportional to the capture cross section discussed here.

The pre-exponential factor s_∞ for deep centers is on the order of 10^{-15} cm^2 and depends on the effective mass and degeneracies in agreement with measurements in typical III–V compounds (Henry and Lang 1977). The thermal activation energies vary between a few meV and 0.6 eV for different defects; the larger energies represent a significant fraction of the level depth, and require substantial thermal activation for recombination. Such activation was observed in some early TS C measurements of deep centers in CdS (Böer and Borchardt 1953).

22.5 Competition Between Radiative and Nonradiative Recombination

For transitions *within* a deep center, there is a simple rule as to whether radiative recombination from the upper minima to the lower curves in Fig. 22.4, or radia-

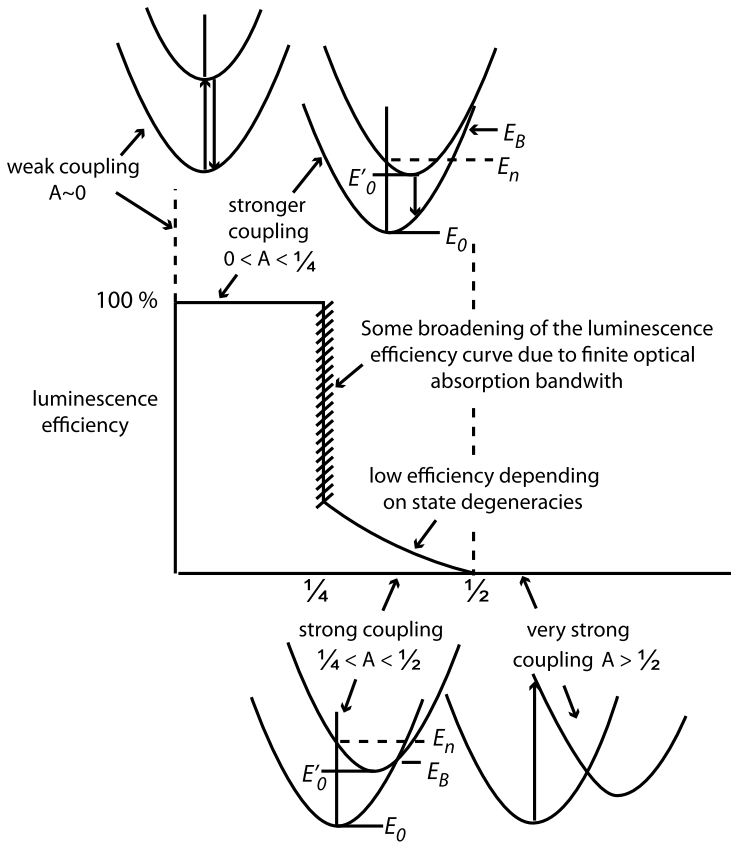


Fig. 22.4 Luminescence efficiency as a function of the electron-lattice coupling expressed as parameter A [Eq. (22.17)]; with four typical configuration coordinate diagrams for ground and excited states of a deep level center shown in the insets for various degrees of coupling (after Hayes and Stoneham 1984). John Wiley & Sons, Inc.

tionless recombination from the upper curve via crossover to the lower curve is preferred. The Dexter-Klick-Russell rule (Dexter et al. 1956b) states that radiative recombination occurs if the optical excitation E_n ends above the crossover E_B , i.e., for relatively weak coupling. Otherwise, the electron will cross over to the lower curve and reach the ground state in a nonradiative process via multiphonon emission. Depending on the strength of the coupling, such a crossover for nonradiative recombination may or may not require thermal activation; the nonthermal part is accomplished by tunneling to the lower curve.

This rule can be translated into the ratio of measurable energy

$$E_B = \frac{(E'_0 - E_n)^2}{4(E_n - E_0)}. \quad (22.17)$$

22.5.1 Nonradiative Multiphonon Recombination

Nonradiative recombination into tightly bound centers, or from band to band with simultaneous *emission* of multiple phonons, i.e., typically, ..., 30 phonons for a 1 eV band gap transition, are comparatively rare transitions. Haug (1972) estimates the transition probability for band-to-band recombination as

$$P_{\text{cvl}} \simeq A \exp\left(-\frac{(h\nu_l - S\hbar\omega_0)^2}{CkT}\right), \quad (22.18)$$

where $h\nu_l$ is the electron energy to be dissipated, $\hbar\omega_0$ is the relevant phonon energy, and S , the Huang-Rhys factor, gives the average number of phonons emitted in the recombination process. From Eq. (22.18), one sees that P_{cvl} increases exponentially with temperature and decreases with increasing energy dissipation. A comparison with a similar equation for the radiative transition, which shows only minor temperature dependence, indicates that non-radiative transitions will predominate at higher temperatures. There is a large body of investigation dealing with non-radiative transitions, which is based on non-adiabatic approximations, rather than the static approach used by Haug. For an advanced discussion, see Gutsche (1982).

Other types of non-radiation transitions are required to explain the observed large rate of nonradiative recombination at elevated temperatures. These include the involvement of deep centers with large lattice relaxation or the acceleration of free carriers in the proximity of a recombination center, which take up part of the energy set free during a recombination transition. This process is described in the following section.

22.6 Auger Recombination

An electron in the conduction band will lose a large amount of energy while recombining with a defect center or a hole in the valence band if it can transmit this energy to another nearby electron. The second electron is thereby excited high into the band and can easily return to the bottom of the band by sequential LO phonon scattering. The process is called *Auger recombination*, and is the inverse process to the impact ionization. It was originally proposed by Beattie and Landsberg (1958). For a review, see Landsberg (1987) and Haug (1988).

Energy and momentum need to fit the excited state higher in the band. When a phonon is provided to facilitate the momentum match, one speaks of phonon-assisted Auger transitions (Lochmann and Haug 1980), which typically have a factor of 5 higher probabilities.

Several types of Auger recombination are possible, depending on whether the recombination occurs into an ionized defect center or into the valence band. The energy set free during the Auger recombination can be used to accelerate a second

Fig. 22.5 Comparison between Auger recombination and impact ionization involving (a) a second electron or (b) a second hole (open circles), with an additional phonon indicated for momentum matching

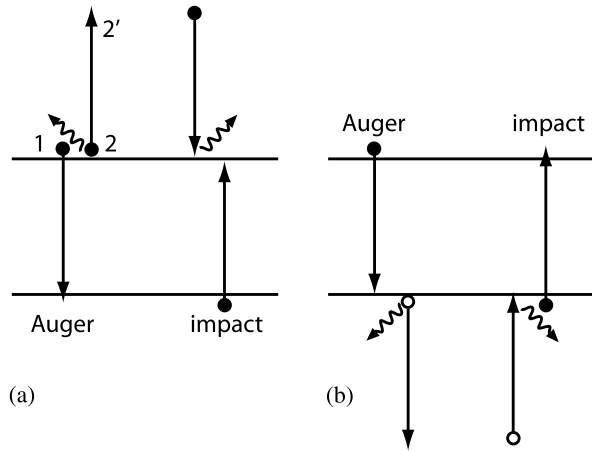
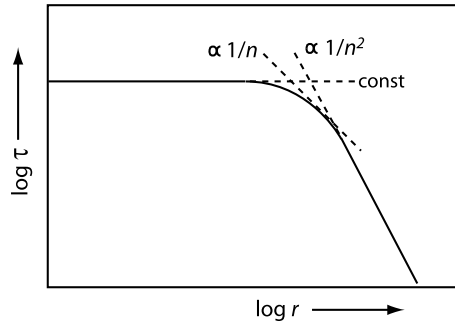


Fig. 22.6 Schematic of the dependence of carrier lifetime on the carrier density



electron or a hole—Fig. 22.5. The smaller electron mass is the reason for a preference for the acceleration of a second electron (Landsberg and Willoughby 1978; Landsberg 1987).

A typical electron lifetime as a function of the electron density is given in Fig. 22.6; it shows three ranges. At low densities, τ is independent of n , then it decreases $\propto 1/n$, and finally $\propto 1/n^2$. We will concentrate first on the final range, which is determined by band-to-band Auger recombination.

The recombination rate and the electron lifetime, which are limited by Auger recombination, are given by:

$$C_{cv}^{(A)} = Bn^2p \quad \text{and} \quad \tau_A = \frac{1}{Bn^2}; \quad (22.19)$$

B is typically on the order of $10^{-30} \dots 10^{-22} \text{ cm}^6 \text{ s}^{-1}$.

A quantum-mechanical derivation of the Auger recombination rate for band-to-band transition from thermally produced intrinsic carriers is given by

$$C_{cv}^{(A)} = 2 \frac{2\pi}{h} \frac{\mathcal{V}^3}{(2\pi)^9} \iiint |M|^2 f(E_1) f(E_2) |1 - f(E'_1)| |1 - f(E'_2)|$$

$$\times \delta(E_1 + E_2 + E'_1 - E'_2) d^3 k_1 d^3 k_2 d^3 k'_1 \quad (22.20)$$

with the Auger matrix

$$M = \iint \phi_{k_1}^*(\mathbf{r}_1) \phi_{k_2}^*(\mathbf{r}_2) V(|\mathbf{r}_1 - \mathbf{r}_2|) \phi_{k'_1}(\mathbf{r}_1) \phi_{k'_2}(\mathbf{r}_2) d^3 r_1 d^3 r_2; \quad (22.21)$$

where Φ is the Bloch function, and $V(r)$ is the screened Coulomb potential

$$V(\mathbf{r}) = \int \frac{d^3 q}{(2\pi)^3} \frac{4\pi e^2}{\varepsilon(q)(q^2 + \lambda^2)} \exp(\mathbf{q} \cdot \mathbf{r}). \quad (22.22)$$

Here λ is the electron screening factor, and $\mathbf{q} = |\mathbf{k}' - \mathbf{k}|$ is the momentum transfer. Assuming parabolical isotropic bands and $m_n \ll m_p$, Haug (1972) obtains for the electron lifetime

$$\tau_A = \frac{\pi \hbar (4\pi \varepsilon_{\text{opt}} \varepsilon_0 \hbar)^2}{24 e^4 m_n} \frac{\Delta E}{kT} \frac{\sqrt{2}}{0.01} \exp\left(\frac{\Delta E}{kT}\right). \quad (22.23)$$

Haug's formula also contains two overlap integrals, the values of which are estimated (Beattie and Landsberg 1958) as $I_1 = 1$ and $I_2 = 0.1$, resulting in $(I_1 I_2)^2 = 0.01$, and as such are included in the denominator of Eq. (22.23). Further research is currently being done to obtain better estimates. For comments, see Haug (1988) and Laks et al. (1988).

$\Delta E = [(2m_n + m_p)/(m_n + m_p)]E_g$ is the energy dissipated in the Auger process. With an increasing band gap, the Auger-determined electron lifetime increases rapidly,¹ and reaches values not attained in a semiconductor with a band gap $E_g > 0.35$ eV; here, one eliminates $\tau_A = 10^{-6}$ s.

Intrinsic Auger recombination at room temperature for thermally excited carriers is important only for narrow gap semiconductors. With high doping densities, however, sufficient carrier densities can be created to obtain Auger recombination rates in wider gap semiconductors. Such Auger recombination then dominates.

For larger band-gap materials, however, the approximations used are too coarse. Recent computations, using the empirical pseudo-potential method with self-consistent calculation plus Thomas-Fermi screening and $e = e(g)$, resulted in much improved results, as shown in Fig. 22.7 for n -type Si (Laks et al. 1988).

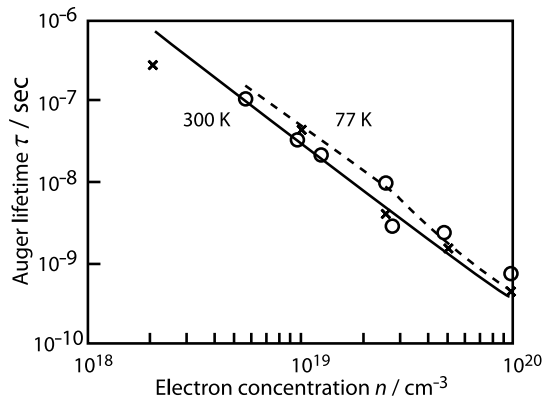
Similar results are obtained for Auger recombination with ionized defects, where again only shallow defects influence the observed lifetime.

¹It is interesting to see that Eq. (22.23) can be rewritten, using the quasi-hydrogen energy E_{qH} , as

$$\tau_A \simeq \frac{h}{E_{\text{qH}}} \cdot \frac{E_g}{kT} \exp\left(\frac{E_g}{kT}\right). \quad (22.24)$$

The first part of Eq. (22.24) represents the Heisenberg uncertainty relation, indicating that τ_A cannot be smaller than the Heisenberg uncertainty time for an exciton, $\tau_A > 1.6 \cdot 10^{-13}$ s. This presents a lower limit for $E_g > kT$ for the approximation used.

Fig. 22.7 Auger lifetime in n -type Si as function of the electron density n and x experimental points at 77 and 300 K (after Dziewior and Schmid 1977), and computation for the corresponding temperatures (by Laks et al. 1988)



With additional excitation, e.g., high-intensity optical carrier generation, sufficient carriers are available to render Auger recombination important. The Auger lifetime for recombination via recombination centers is given by (Haug 1981a, 1981b)

$$\tau_A = \frac{1}{B N_r n} = \frac{v_{\text{rms}}}{N_r n} \frac{m_n^2}{8\pi^2 e^4 \hbar^3} \frac{Q}{R} \sqrt{\frac{m_p}{m_n}} (E_c - E_r)^3, \quad (22.25)$$

with $Q = 0.5(m_0/m_n)^{3/2}(1 + m_n/m_0)^2$ and where $R = 2.6$ is an enhancement factor; E_r is the energy of the recombination center. This yields for typical values of $E_c - E_r = 0.5$ eV and $m_n = 0.1m_0$ an Auger coefficient $B = 10^{-26} \text{ cm}^6 \text{ s}^{-1}$. Somewhat lower values have also been suggested by Robbins and Landsberg (1980). For a density of recombination centers $N_r = 10^{17} \text{ cm}^{-3}$ and $n = 10^{14} \text{ cm}^{-3}$ one obtains an Auger lifetime of 10^{-5} s .

The Auger coefficient at recombination centers can be estimated from rough formulae with simple power law dependences in $E_c - E_r$ (Landsberg and Pimpale 1976). In particular, for GaAs as (Haug 1980)

$$B = \frac{2.5 \cdot 10^{-25}}{Q(E_c - E_r)^3} (\text{cm}^6 \text{ s}^{-1}) \quad (22.26)$$

The capture cross section for Auger recombination is given as

$$s_n = \frac{Bn}{v_{\text{rms}}} \quad (22.27)$$

and is on the order of 10^{-11} cm^2 for shallow traps and 10^{-18} cm^2 for deep traps, when $n = 10^{14} \text{ cm}^{-3}$.

Evidence of intrinsic Auger recombination can be obtained from the dependence of the lifetime of minority carriers on the square of the density of majority carriers (Haynes and Hornbeck 1955; Dziewior and Schmid 1977).

22.7 Plasmon-Induced Recombination

At very high excitation rates, the carrier density becomes high enough so that the plasmon energy $\hbar\omega_p$ equals the band gap energy; the recombination is much enhanced by such resonance transitions. Typical critical densities for a band gap of 1 eV are on the order of 10^{20} – 10^{21} cm⁻³ [see Eq. (22.4)]. This *plasmon-induced recombination* can exceed the Auger recombination, which is also effective at high carrier densities (Malvezzi 1987).

22.8 Statistics of Recombination

Except for stimulated lasing luminescent transitions, all recombination transitions are spontaneous and follow the rules of statistics.

In a statistical description of the recombination, one is not interested in how the carrier loses its energy, but rather with what state it recombines and what changes in carrier densities occur with changing rates of generation and temperature. The probability of recombination is described by a capture rate, which is linked to the capture cross section by Eq. (22.12).

22.9 Trapping or Recombination

When a carrier returns to an ionized state, one speaks of *recombination*. When a carrier is captured by a shallow level from which it can.

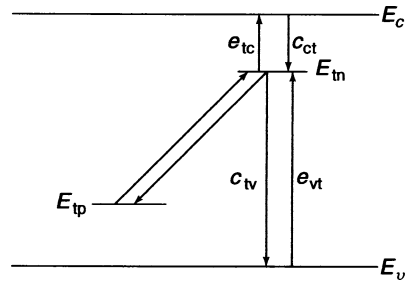
A more precise way to distinguish between trapping and recombination is given in the following section.

22.10 Electron and Hole Traps

There are several transitions possible between any center and other states. All such transitions are described by their corresponding rates. These rates are additive and describe the change in the population of the center. For instance, the change of the electron density in an electron trap is determined by excitation from the trap into the conduction band, by electron capture from the band, by recombination with holes from the valence band, and by electron transfer to other localized states of nearby defects to which such transitions are sufficiently probable.

For reasons of detailed balance, there are always pairs of transitions between two states (Fig. 22.8), which must be equal to each other in thermal equilibrium. The magnitude of transition rates *varies from pair to pair over a wide* range. For example, thermal excitation of an electron from the more distant valence band into an electron trap is much less probable than thermal excitation of a trapped electron into the closer conduction band.

Fig. 22.8 Various possible transitions to and from a localized state be thermally reemitted into the band before it finally recombines, the process is called *trapping*



In steady state (see Sect. 22.2.2), the total rate of transition from the center must equal the total rate into the center. Usually, one can *neglect all transitions compared to the one pair with the highest transition probability*. These pairs can now involve different states (see below). Thereby, one can identify different classes of centers according to the predominant types of transitions.

Centers close to the conduction band are identified as *electron-traps*, and centers close to the valence band as *hole-traps*, when these centers communicate predominantly with the adjacent bands.

22.10.1 Recombination Centers

Centers close to the middle of the band gap readily communicate with both bands, since it is easier for a captured electron to recombine with a hole in the valence band than to be reemitted into the conduction band. These centers are called *recombination centers*.

Relaxation of the center after trapping a carrier is not included here. Such relaxation can assist significantly in bridging the band gap during recombination—see also Henry and Lang (1977).

22.11 Demarcation Lines

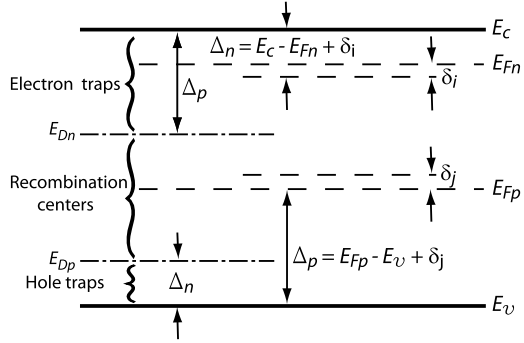
A demarcation line between electron traps and recombination centers is defined (Rose 1951) when the transition rates of electrons from these centers to the two bands become equal:

$$n_t e_{tc} N_c = n_t c_{tv} p. \quad (22.28)$$

Using the expression for e_{tc} and p ,

$$e_{tc} = v_{rms} s_{tv} \exp\left(-\frac{E_c - E_t}{kT}\right) \quad \text{and} \quad p = N_v \exp\left(\frac{E_v - E_{Fp}}{kT}\right), \quad (22.29)$$

Fig. 22.9 Band model with quasi-Fermi potentials and demarcation lines for one kind of electron trap, with corresponding capture cross sections for electrons and holes (s_{ni} , s_{pi}) and hole trap (s_{nj} , s_{pj})



one obtains an equation for this *electron demarcation line* from Eq. (22.27), defining a specific E_t [Eq. (22.29)] = E_{Dn} :

$$E_c - E_{Dn} = E_{Fp} - E_v + \delta_i, \quad \text{with} \quad \delta_i = kT \ln \frac{m_n s_{ni}}{m_p s_{pi}}. \quad (22.30)$$

Although possible confusing at first glance, the reference to the hole quasi-Fermi level for determining the *electron demarcation line* is understandable, since the recombination path, competing with thermal ionization, depends on the availability of free holes. Figure 22.9 may help to clarify this dependency: the distance of the demarcation line for electrons from the conduction band, identified as Δ_p , is the same as the distance of the quasi-Fermi level for holes from the valence band plus a corrective δ_i or δ_j —see below. These correction terms are logarithmically related to the ratio of the capture cross sections for electrons and for holes at this center. The electron demarcation line defines the energy border between electron traps above, and recombination centers below, this center.

A similar relationship holds for the *hole demarcation line*:

$$E_{Dp} - E_v = E_c - E_{Fn} + \delta_j, \quad \text{with} \quad \delta_j = kT \ln \frac{m_p s_{pi}}{m_n s_{ni}}; \quad (22.31)$$

this line is also shown in Fig. 22.9. For *n*-type material with narrow $E_c - E_{Fn}$, there is a wide range of electron traps and a narrow range of hole traps, and vice versa.

The correction terms δ_i and δ_j depend on the ratio of capture cross sections for electrons and holes that change with the occupancy of the center. As an illustration, let us assume a simple example of a center that is neutral without an electron in it, having a cross section for an electron on the order of 10^{-16} cm^2 . After it has captured the electron, it is negatively charged; its capture cross section for a hole has thus increased, say to 10^{-14} cm^2 . For this example s_{ni}/s_{pi} 10^{-2} and $5i - 0.12 \text{ eV}$. For a similar type of hole trap, the charge character changes from neutral to positive after hole capture, making s_{nj}/s_{pj} 100 and $\delta_i = +0.12 \text{ eV}$. The shifts δ_i and δ_j in Fig. 22.9 have been chosen accordingly.

Since the capture cross section varies from center to center, typically from 10^{-12} to 10^{-22} cm^2 , δ_i varies for these different centers by as much as 0.6 eV at room temperature. Hence, the demarcation lines of these centers are spread over a wide range within the band gap. Therefore, it is not customary to plot demarcation lines of all the possible centers, while it is still instructive to discuss those that provide the most important transitions in the given model.

Neglect of the other centers is often justified, because all transitions enter additively, spanning many orders of magnitude; therefore, usually only one kind of transition is important to each type of trap or recombination center for a given situation.

22.12 Thermal Equilibrium and Steady State

Thermodynamic (thermal) *equilibrium* is present when a semiconductor without any external excitation is kept long enough at a constant temperature to reach such equilibrium. Deviations from thermal equilibrium can occur because of nonthermal, additional excitation by light or an electrical field. When such deviations occur but have become stationary, a nonequilibrium *steady state* is reached.

22.12.1 Thermal Equilibrium

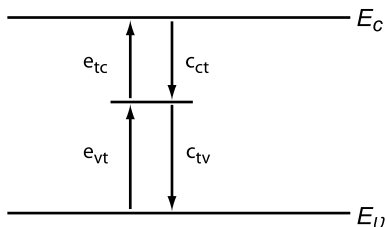
In a semiconductor at constant temperature without optical or electrical excitation, thermal equilibrium becomes established. Electrons and holes are generated by thermal excitation alone. The same number of carriers which are generated in any volume element must recombine in the same volume element except for statistical fluctuations. There is no net transport of carriers. This also holds for space-charge regions, e.g., in a *pn*-junction, in which *n* and *p* are rapidly changing functions of the spatial coordinate, whereas j_n and j_p vanish independently in every volume element.

For thermal equilibrium the carrier distribution is uniquely described by the Fermi-level E_F . Consequently, when formally using quasi-Fermi levels, they must collapse to $E_{Fn} = E_{Fp} = E_F$. One sees from Eqs. (22.30) and (22.31) that the resulting demarcation lines then coincide: $E_{Dn} = E_{Dp} = E_d$, i.e., electron and hole traps join borders with no recombination center range in between. Here, thermal ionization (generation) and recombination on the average attain a balance within each volume element of the semiconductor.

22.12.2 Steady State

When non-thermal carrier generation is introduced, the equilibrium density distribution is altered. As a consequence, the Fermi energy splits into two quasi-Fermi

Fig. 22.10 Hall-Shockley-Read center with transitions to both bands



levels, and sets of two demarcation lines for each type of defect center appear. Thus, some levels, which previously acted as traps, will now act as recombination centers. Much of the content of the following sections deals with this steady-state condition.

22.13 The Hall-Shockley-Read Center

Changing the external excitation will alter the demarcation lines between traps and recombination centers. Therefore, one needs to include all four transitions between the level and the two bands for such centers when variations of carrier distributions are considered (Hall 1951, 1952; Shockley and Read 1952).

For a center in the band gap that interacts only with the bands, the four transition rates are $e_{tc}n_t p_c$, $e_{vt}n_v(N_t - n_t)$, and $c_{tv}n_t p$ —see Fig. 22.10. In *equilibrium*, the sum of each pair of transitions to each band must vanish. In *steady state*, this is no longer necessary; there may be a net flow of carriers from one band through such a center to the other band, which is balanced with another transition, e.g., an optical band-to-band generation of carriers. The sum of all four transition rates, however, must vanish to maintain a time-independent electron population in the center:

$$c_{ct}n(N_t - n_t) - e_{tc}n_t p_c = c_{tv}n_t p - e_{vt}n_v(N_t - n_t). \quad (22.32)$$

Equation (22.32) can be used to determine this population. After using Eq. (22.10) and an analogous condition for holes to convert e_{tc} and e_{vt} into the respective capture coefficients, and with the parameters $n_1 = N_c \exp[(E_t - E_c)/(kT)]$ and $p_1 = N_v \exp[(E_v - E_t)/(kT)]$, one obtains

$$n_t = \frac{N_t(c_{ct}n + c_{tv}p_1)}{c_{ct}(n + n_1) + c_{tv}(p + p_1)}. \quad (22.33)$$

Introducing this steady-state density of the trapped electrons into the net rate equation, permitting a net flow U of electrons through such a center, yields

$$U = c_{ct}n(N_t - n_t) - e_{tc}n_t N_c = c_{tv}n_t p - e_{vt}n_v(N_t - n_t), \quad (22.34)$$

and the equivalent rate equation for the same net rate of carrier transfer from the center to the valence band. By eliminating n_t from the net carrier flow rate, one

obtains

$$U = \frac{c_{\text{ct}}c_{\text{tv}}N_t(np - n_1p_1)}{c_{\text{ct}}(n + n_1) + c_{\text{tv}}(p + p_1)}. \quad (22.35)$$

Using the condition

$$n_1p_1 = n_i^2 \quad (22.36)$$

and introducing the *intrinsic level* E_i

$$E_i = \frac{E_c - E_v}{2} + \frac{kT}{2} \ln \frac{N_v}{N_c}, \quad (22.37)$$

one obtains the well-known expression for the net carrier flow through a Hall-Shockley-Read center:

$$U = \frac{c_{\text{ct}}c_{\text{tv}}N_t(np - n_i^2)}{c_{\text{ct}}[n + n_i \exp(\frac{E_t - E_i}{kT})] + c_{\text{tv}}[p + n_i \exp(\frac{E_i - E_t}{kT})]}. \quad (22.38)$$

From Eq. (22.38), one sees immediately that U vanishes for thermal equilibrium, i.e., for $np = n_i^2$. In steady state, however, with optical generation and the Hall-Shockley-Read center acting as a dominant recombination center, U must equal the generation rate g_o in a homogeneous semiconductor.

Equation (22.38) becomes very valuable when deviations from the thermal equilibrium are analyzed. A separation into thermal generation rates

$$g_n = g_p = \frac{c_{\text{ct}}c_{\text{tv}}N_t n_i^2}{c_{\text{ct}}(n + n_i^+) + c_{\text{tv}}(p + n_i^-)}, \quad (22.39)$$

and recombination rates

$$r_n = r_p = \frac{c_{\text{ct}}c_{\text{tv}}N_t np}{c_{\text{ct}}(n + n_i^+) + c_{\text{tv}}(p + n_i^-)}, \quad (22.40)$$

is helpful. For brevity, the expression

$$n_i^\pm = n_i \exp\left(\pm \frac{E_t - E_i}{kT}\right) \quad (22.41)$$

is used above.

A deviation from thermal equilibrium may be caused by optical excitation. With band-to-band excitation, the optical generation term g_o is simply added to Eq. (22.39), yielding

$$g_{n,o} = g_{p,o} = \frac{c_{\text{ct}}c_{\text{tv}}N_t n_i^2}{c_{\text{ct}}(n + n_i^+) + c_{\text{tv}}(p + n_i^-)} + g_o \quad (22.42)$$

the necessarily increased recombination in steady state is automatically included in Eq. (22.40) through the increase in n and p .

In *homogeneous* semiconductors, and for steady-state conditions, the generation rate will always be equal to the recombination rate; therefore, U will vanish.

Deviations from $U = 0$ will occur during kinetics and when spatial inhomogeneities are considered. In space-charge regions, such as in Schottky barriers or pn -junctions, this formalism becomes most valuable. One aspect of such inhomogeneity deals with the current continuity in photoconductors.

Chapter 23

Kinetics of Electron Distribution in Defects

Abstract The electron distribution in defects is based on widely different mechanisms such as creation of atomic lattice defects and their electronic defect levels, carrier redistribution over these defects, phonon relaxation, orientation relaxation, carrier-carrier scattering relaxation of momentum and energy, and electron spin relaxation. These changes can be initiated by changes in optical excitation yielding rise and decay of photoconductivity (reaction kinetics). The method of controlled excitation is introduced. Photoconductivity time constants are defined. Kinetics that is influenced by trap distributions are evaluated. Ultrafast photo detectors are described. Competing excitation processes are evaluated. Optical quenching is introduced. Orientation relaxation is discussed. The changes in thermal excitation, yielding glow curves and thermally stimulated currents are evaluated. The residence time of carriers in deep traps is tabulated. Changes in field ionization and field stimulated current curves are given.

Six kinetic effects can be distinguished in semiconductors that permit separate access to different solid-state processes with substantially different time constants (relaxation times), and thus reveal predominant interactions. Major systems with vastly different relaxation times can be distinguished:

- creation of atomic lattice defects with associated electronic levels,
- carrier redistribution over these defect levels,
- phonon relaxation,
- orientation relaxation of anisotropic states,
- carrier-scattering relaxation (momentum and energy relaxation), and
- electron spin relaxation.

The corresponding relaxation times span from geologic times down into the femtosecond range. The entire time range is now accessible to experimental observation.

The creation of lattice defects was discussed in Chaps. 2 and 3. The electronic *eigenstates* of the corresponding levels can easily be identified when lying in the band gap. The redistribution of carriers over these levels is the subject of this chapter, since they influence the quasi-Fermi level distribution and thereby the solar cell performance and will be the subject of this chapter.

Kinetic effects are used to measure the transition coefficients and level densities critical for cell performance and therefore analyzed here in more detail. More transparent results are obtained in homogeneous single crystals with sufficient examples available for CdS platelets presented here. The selection of CdS was done in recognition of the importance of this material in hetero-junction solar cells, earlier in CdS/Cu_xS and more recently in CdS/CdTe and CdS/CIS cells.

23.1 Changes of Optical Excitation

Changes in the optical generation rate is used to initiate the kinetic behavior.

23.2 Rise and Decay of Photoconductivity

The kinetics of a photoconductor is determined by the set of reaction-kinetic equations, one for each of the electron densities in a given level or band; we will neglect a redistribution of carriers within the band, and assume here that all transition coefficients are independent of such redistribution. In a homogeneous semiconductor, the kinetic expressions are of the form

$$\frac{dn_i}{dt} = g_i - r_i, \quad i = 1, 2, \dots, \quad (23.1)$$

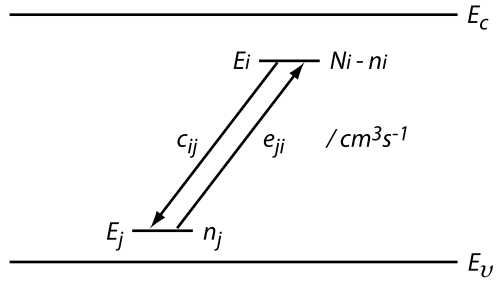
where g_i and r_i are the generation and recombination rates for the i th level, respectively. The bands are represented by levels at their band edges with an effective density of N_c and N_v , disregarding an energy distribution of the carriers within the band. The generation term contains all contributions that cause an increase in the population of this level; the recombination term combines all contributions that cause a decrease of the population. They can be written as

$$g_i = \sum_j n_j e_{ji} (N_i - n_i) \quad \text{and} \quad r_i = \sum_j n_i c_{ij} (N_j - n_j), \quad (23.2)$$

where e_{ji} and c_{ij} are the transition coefficients between level i and level j , N_i is the density of level i , and n_i is the density of electrons in the level, assuming single occupancy of each level; e transitions are upward (excitation) transitions within the band diagram, while c transitions are downward (capture) transitions with release of energy—Fig. 23.1.

Equation (23.1) represents a set of first-order, nonlinear differential equations, which usually cannot be solved in closed form except for some simple cases, examples of which are given below.

Fig. 23.1 Electronic transition between two defect levels with the transition coefficient identified in the figure



23.2.1 Rise and Decay of Intrinsic Photoconductivity

The kinetics of an intrinsic photoconductor with electron transitions between the bands only is given by

$$\frac{dn}{dt} = g_{vc} - c_{cv}np \quad (23.3)$$

and by a similar equation for holes. With $g_{vc} = g_o$ (optical generation rate) and for sufficiently high generation with $n = p$, this equation has the solution

$$n(t) = \sqrt{\frac{g_o}{c_{cv}}} \tanh[\sqrt{g_o c_{cv}}(t - t_o)], \quad (23.4)$$

with $n = g = 0$ for $t < t_o$ and $g = g_o$ for $t > t_o$. This shows a nearly linear rise of n for $t_o < t < t + \tau_o$ with τ_o as the photoconductive rise time,

$$\tau_o = \frac{1}{\sqrt{g_o c_{cv}}}. \quad (23.5)$$

According to the tanh function, the electron density approaches its steady state-value

$$n_0 = \sqrt{\frac{g_o}{c_{cv}}} \quad (23.6)$$

It seems to offer a simple method to determine the transition coefficient for electron and hole recombination across the band gap and with $c_{vc} = s_{np} v_{rms}$ the recombination cross section for electrons and holes. However, there are many other processes involved that can change these results substantially.

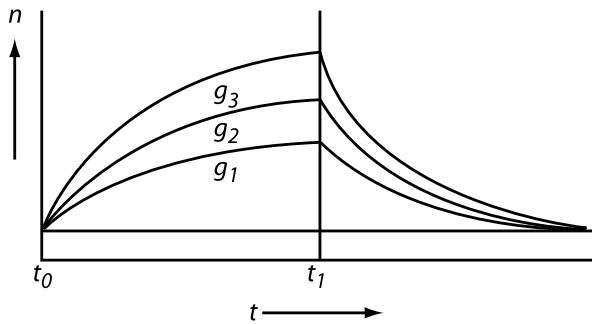
When, after reaching steady state, the optical excitation is switched off, the decay of the photoconductivity follows:

$$\frac{dn}{dt} = -c_{cv}n^2. \quad (23.7)$$

and is hyperbolic:

$$n(t) = \frac{1}{c_{cv}(t - t_1)} = n_0 \frac{\tau_1}{t - t_1} \quad (23.8)$$

Fig. 23.2 Rise and decay of intrinsic photoconductivity with the optical generation rate as the family parameter ($g_3 > g_2 > g_1$)



with a decay time constant of

$$\tau_1 = \frac{1}{n_0 c_{cv}}. \quad (23.9)$$

Introducing n_0 from Eq. (23.6), one sees that both the rise and decay time constants are equal (see Fig. 23.2):

$$\tau_1 = \tau_0. \quad (23.10)$$

Rise and decay proceed faster at higher light intensities and in materials with larger recombination cross sections $c_{cv} = s_{cv} v_{rms}$.

23.2.1.1 The Influence of Traps on Photoconductivity Kinetics

With traps present, there are competing transitions. For instance, with electron traps, one obtains

$$\frac{dn}{dt} = g_o - \frac{dn_t}{dt} - c_{cv}n(n + n_t) \quad (23.11)$$

and

$$\frac{dn_t}{dt} = c_{ct}n(N_t - n_t) - e_{tc}N_c n_t. \quad (23.12)$$

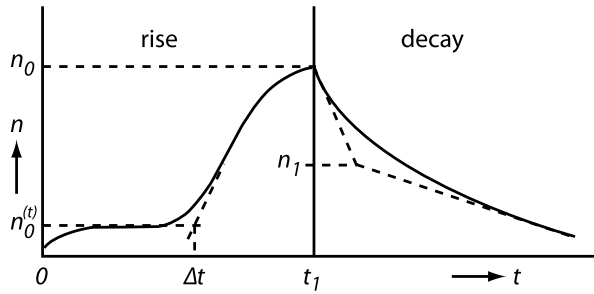
Here, quasi-neutrality requires $p = n + n_t$. The transitions of electrons into traps compete with transitions into the valence band. As long as traps are mostly empty, the first transition predominates: with $n_t \ll N_t$, one has

$$\frac{dn_t}{dt} \simeq c_{ct}nN_t; \quad (23.13)$$

hence,

$$\frac{dn}{dt} \simeq g_o - c_{ct}nN_t \quad (23.14)$$

Fig. 23.3 Rise of the photoconductivity at medium intensity optical excitation, which shows a plateau until deep traps are filled. In the decay of photoconductivity, two slopes are indicated



as long as $c_{ct}N_t \gg c_{cv}p(n + n_t)$. After separation of variables, Eq. (23.14) can be solved, yielding

$$n = n_0 \left\{ 1 - \exp\left(-\frac{t - t_0}{\tau_t}\right) \right\} \quad \text{with} \quad \tau_t = \frac{1}{c_{ct}N_t}, \quad (23.15)$$

and with τ_t as the time constant for trap-filling.

The quasi-steady state between generation and trapping into nearly empty traps yields for the density of electrons in the conduction band while the traps are being filled:

$$n_0^{(t)} = \frac{g_o}{c_{ct}N_t}. \quad (23.16)$$

When the traps become filled, the trapping transition becomes clogged (see Fig. 23.4). Consequently, n rises again until steady state between generation and recombination is reached. With $N_t \gg n$, i.e., for low-generation rate, one obtains for the second rise

$$\frac{dn}{dt} = g_o - c_{cv}nN_t. \quad (23.17)$$

The kinetics for trap-filling is similar to the first rise of the electron density, except for a somewhat longer time constant, since usually $c_{ct} \gg c_{cv}$:

$$\tau_1 = \frac{1}{c_{cv}N_t}. \quad (23.18)$$

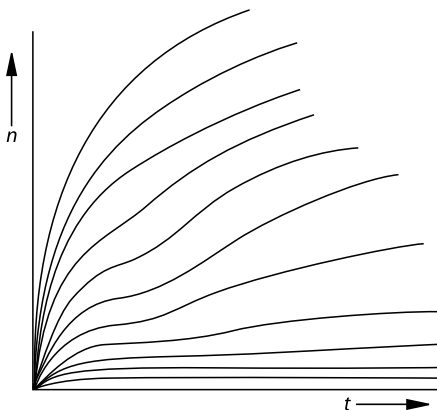
This behavior is presented in Fig. 23.3, which shows a first rise to a plateau while trap-filling occurs, and then another rise to reach a steady-state value at

$$n_0 = \frac{g_o}{c_{cv}N_t}. \quad (23.19)$$

The ratio of $n_o/n_o^{(t)}$ can be used to determine the ratio of capture cross sections of electron traps and band-to-band transitions:

$$\frac{n_0^{(t)}}{n_0} = \frac{s_{ct}}{s_{cv}}. \quad (23.20)$$

Fig. 23.4 Rise of the photoconductivity with trap-filling; light intensity as the family parameter. It shows an intermediate intensity range in which a plateau develops (after Böer and Vogel 1955)



The length of the plateau Δt can be used to estimate the density of traps

$$g_o \Delta t \simeq N_t \quad (23.21)$$

if recombination can be neglected during trap-filling (Böer and Vogel 1955).

The decay after switching off the light proceeds inversely, first with a time constant given by the recombination transition, obtained from which yields an exponential decay

$$\frac{dn}{dt} = -c_{cv} n N_t, \quad (23.22)$$

$$n = n_0^{(t)} \exp\left(-\frac{t - t_1}{\tau_1}\right), \quad (23.23)$$

where τ_1 is given by Eq. (23.18). Later, electrons are supplied by the emission from traps ($e_{tc} N_c n_t$), which determines the slow tail of the decay of n . From

$$\frac{dn}{dt} = e_{tc} N_c N_t - c_{cv} n N_t \quad (23.24)$$

for the first part of the decay, as long as n_t is still $\sim N_t$ one obtains the onset of the slow decay when $n = n_1$ is reached, with a condition for

$$n_1 \simeq N_c \frac{e_{tc}}{c_{cv}} = N_c \frac{e_{tc}}{c_{ct}} = \frac{c_{ct}}{c_{cv}} N_c \exp\left(-\frac{E_c - E_t}{kT}\right), \quad (23.25)$$

i.e., when the quasi-Fermi level just passes through the trap level. The decay is then determined by the slow depletion of the traps with a time constant given by the net emission from traps, i.e., emission minus retrapping.

23.2.2 The Method of Controlled Excitation

The discussion of the reaction-kinetic behavior can be substantially simplified when the experiment is designed to eliminate one of the differential equations. Böer and Oberländer (1958) developed a method in which, after starting a rise of photoconductivity, the optical excitation rate is changed so that the electron density is kept constant. Experimentally, this can be done automatically by using a feedback mechanism to control the light intensity so that, from a preselected time on, the photocurrent does not change. Instead of $n(t)$, one now measures $g(t)$ to determine the parameters of interest. This converts the set of differential equations into the set

$$\frac{dn}{dt} = g(t) - \frac{dn_t}{dt} - c_{cv}n(n + n_t) \equiv 0 \quad (23.26)$$

$$\frac{dn_t}{dt} = c_{ct}n(N_t - n_t) - e_{tc}N_cn_t. \quad (23.27)$$

The order of this set is reduced by one, and it has the solution

$$g(t) = A + B \exp\left(-\frac{t - t_k}{\tau_k}\right), \quad (23.28)$$

with t_k as the start of the controlled optical excitation, and

$$\tau_k^{-1} = e_{tc}N_c + c_{ct}n_k, \quad (23.29)$$

$$A = c_{cv}n_o^2(1 + \tau_k c_{ct}N_t), \quad (23.30)$$

$$B = \left(\frac{1}{\tau_k} - c_{cv}n_o\right)(\tau_k n_k c_{ct}N_t - n_t(t_k)), \quad (23.31)$$

where n_k is the electron density for $t \cong t_k$. For $t > t_k$, the electron density is kept constant by changing the optical generation rate as necessary—Fig. 23.5b.

When the initiation time t_k is varied, the reciprocal time constant τ^{-1} of the changing generation rate varies linearly with the electron density nk . From the slope of $n_k(\tau_k^{-1})$, one obtains the trapping coefficient C_{ct} , and from the intercept of the ordinate, the trap emission probability $e_{tc}N_c$ —see Fig. 23.5c.

This method is useful when one set of traps predominates. Then the capture cross section of traps ($S_{et} = c_{ct}/v_{rms}$) can be obtained and, when the experiment is done at different temperatures, the ionization energy and frequency factor of these traps can be determined:

$$e_{tc}N_c = \nu_t \exp\left(-\frac{E_c - E_t}{kT}\right). \quad (23.32)$$

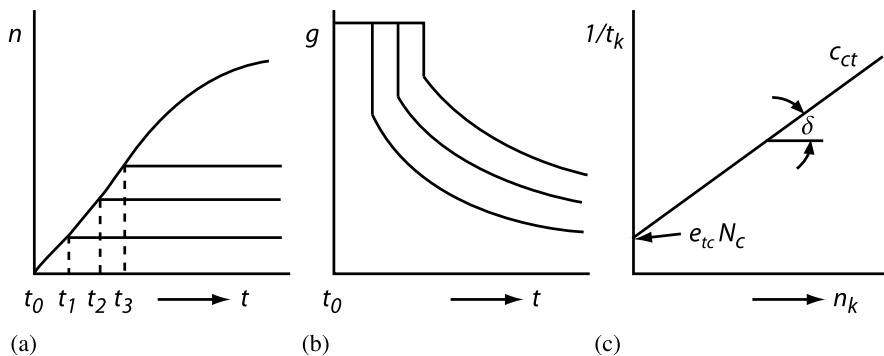


Fig. 23.5 Method of controlled excitation. (a) Rise to a constant photoconductivity stopped at $t = t_1, t_2, \dots, t_k$ by changing the light intensity from this time on, according to (b) in three experiments. (b) Variation of the light intensity in order to achieve a constant photoconductivity. (c) Reciprocal time constant for changing light intensity as a function of constant electron density

23.2.3 Photoconduction Time Constants

The electron life-time in the conduction band is an important parameter in the discussion of photoconductivity:

$$\tau_n = \frac{n}{g_o}. \quad (23.33)$$

This lifetime depends on the electron distribution over levels in the band gap_o and thus depends on the light intensity $\tau_n(g_o)$. When only small changes from steady-state values are considered, one may set this lifetime, here for extrinsic photoconductivity as a constant

$$\tau_n \sim -(c_{ca} p_a)^{-1} \simeq (c_{ca} N_a)^{-1}, \quad (23.34)$$

and obtains from Eq. (23.11)

$$\frac{dn}{dt} = g_o - \frac{n}{\tau_n} - \frac{dn_t}{dt}. \quad (23.35)$$

Assuming an exponential decay function for the photoconductivity, one has for the *photoelectron decay time* τ which may be an implicit function of the electron density

$$\frac{dn}{dt} = -\frac{n}{\tau}, \quad (23.36)$$

and with it, one obtains from Eq. (23.35) with $g_o = 0$

$$\frac{dn}{dt} = -\frac{n}{\tau_n} - \frac{dn_t}{dt} = -\frac{n}{\tau}. \quad (23.37)$$

This presents an instructive relation between the decay time τ and the carrier lifetime τ_n :

$$\tau = \tau_n \left(1 + \frac{dn_t}{dn} \right). \quad (23.38)$$

The decay time is always longer than the carrier lifetime. It is increased by the change of trap population, which is caused by a changing electron density.

This is also an example for demonstrating the existence of *two* relaxation *times* for *the two subsystems*: conduction band/activator and conduction band/ electron traps. When additional trap levels become involved, more relaxation times will appear.

23.2.4 Small Sinusoidal Excitation

Another method designed to obtain reaction-kinetic parameters is based on the linearization of solutions, which can be applied if a small light signal is superimposed on top of a constant bias light:

$$g = g_o(1 + m \cos \omega t) \quad \text{with} \quad m \ll 1. \quad (23.39)$$

The constant light moves the quasi-Fermi level to a position around which the trap distribution is to be investigated, and the modulated light signal probes these trap levels. The method was originally used by Fassbender and Lehmann (1949) and further developed by Niekisch (1955).

As a result of this oscillating light signal, one obtains an electron density modulation

$$n = n_0 + n_1 \cos(\omega t - \phi). \quad (23.40)$$

Introducing the *Ansatz* (23.40) into the reaction-kinetic differential equation, one obtains the trap density from the phase shift:

$$N_t = \frac{g_o \tan \phi}{\omega}. \quad (23.41)$$

The coefficients are given by

$$n_0 = g_o \tau_n, \quad n_1 = \frac{g_o m \tau_n}{\sqrt{1 + \omega^2 \tau^2}}, \quad \text{and} \quad \tan \phi = \omega \tau. \quad (23.42)$$

From the amplitude of the photo current modulation, one obtains the ratio of the time constants for $\omega \tau \gg 1$

$$n_1 = \frac{m g_o}{\omega} \frac{\tau_n}{\tau}. \quad (23.43)$$

By changing the constant bias light, one can now move the quasi-Fermi level and probe a wide range of the trap distribution—see the following section. For the measured dc- and ac-photocurrent components, one consequently obtains

$$j_{dc} = e\mu_n g_o \tau_n F \quad \text{and} \quad j_{ac} = e\mu_n \frac{g_o \tau_n m}{\sqrt{2}\omega\tau} F. \quad (23.44)$$

When the light intensity is high enough to fill all traps, dn_t/dn vanishes or the quasi-Fermi level falls in between two trap levels so that $dn_t/dn \ll 1$ —see Eq. (23.38). Then τ_n becomes equal to τ , and Eq. (23.44) can be used to determine the carrier mobility:

$$\mu_n = j_{ac} \frac{\sqrt{2}\omega}{e g_o m F}. \quad (23.45)$$

23.3 Kinetics Influenced by Trap Distribution

The competition between trapping and thermal reemission tends to fill (or deplete) a distribution of traps from lower to higher (or from higher to lower) traps for traps of similar capture coefficients. For sufficiently high temperatures and light intensities, a quasi-stationary approximation is justified; that is, one can use quasi-Fermi levels for the description of the gradual filling or depletion of the trap distribution

$$n(t) \simeq N_c \exp\left(-\frac{E_c - E_{Fn}(t)}{kT}\right) \quad (23.46)$$

when changes in $n(t)$ proceed slowly enough so that the degree of trap-filling can follow. The total trapped-electron density within such a trap distribution $N_t(E)$ [measured in $\text{cm}^{-3} (\text{eV})^{-1}$] is then given by

$$n_t = \int_{E_F}^{E_{Fn}} N_t(E) dE. \quad (23.47)$$

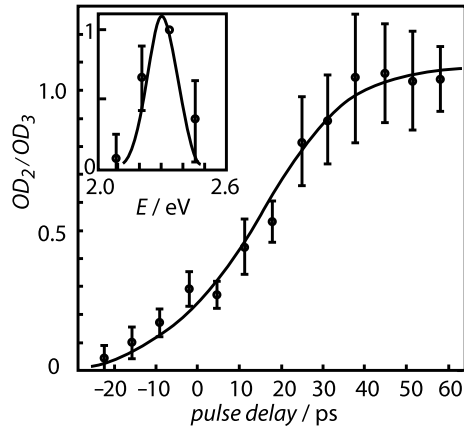
The change of trapped electrons within a trap distribution as a function of the electron density can be calculated from

$$\begin{aligned} \frac{dn_t}{dn} &= \int_{E_F}^{\infty} \frac{dn_t(E)}{dn} dE = \frac{1}{n} \int_{E_F}^{\infty} N_t(E) \frac{\exp(-\frac{E-E_{Fn}}{kT})}{\{1 + \exp(-\frac{E-E_{Fn}}{kT})\}^2} dE \\ &= \frac{kT}{n} \left\{ N_t(E_{Fn}) + \frac{(\pi kT)^2}{6} \frac{d^2 N_t}{dE^2} \bigg|_{E_{Fn}} + \dots \right\}. \end{aligned} \quad (23.48)$$

Therefore, the relation between decay time and electron lifetime can be written as

$$\frac{\tau}{\tau_n} \simeq 1 + \frac{N_t(E_{Fn})kT}{n}. \quad (23.49)$$

Fig. 23.6 Decay of photo-conductance in *p*-Si, indicating three distinct ranges of decay involving band-to-band recombination, and reemission from shallow and from deep traps (after Hornbeck and Haynes 1955)



This presents a relatively direct method for measuring the trap distribution, by obtaining τ_0 from n/g_0 and τ from the decay immediately after switching off the optical excitation, provided the temperature and light intensity are high enough for the quasi-Fermi level to follow the changes in n in a quasi-steady-state condition or in a more elegant way, from the methods discussed in the previous section.

A good example for the sequential depletion of shallow and deep traps is shown in Fig. 23.6, measured for *p*-Si. Here, the decay of the photoconductivity shows the typical ranges of substantial slowdown while the depletion of a specific level takes place.

For n distinct groups of levels, one would expect $n - 1$ relaxation times (Landsberg and Cole 1966). Thus, one observes one relaxation time for the band-to-band transition, plus *several relaxation times* for the transitions between bands and different trap levels. A differentiation into distinct trap-related relaxations becomes possible when groups of trap levels are substantially separated from each other with only a few traps in between, as given in the example of Fig. 23.6.

23.3.1 Ultrafast Photodetectors

For many applications, such as in pattern recognition, fiber optics communications, and electro-optical computers, one desires sensitive and very fast photoconductive devices. Fast rise and decay times can be achieved by avoiding traps near the portion of the quasi-Fermi level under operating conditions, and by providing fast recombination centers. This reduces the lifetime, but also the photosensitivity, which can be partially compensated by selecting photoconductors with high carrier mobility.

An example of a reasonably sensitive ultrafast photoconductive detector is GaAs, when deposited at low temperatures (200 °C) by molecular beam epitaxy, which results in high dark resistivity and rise and decay times of ≈ 1.5 ps in response to a short laser flash (Smith et al. 1988).

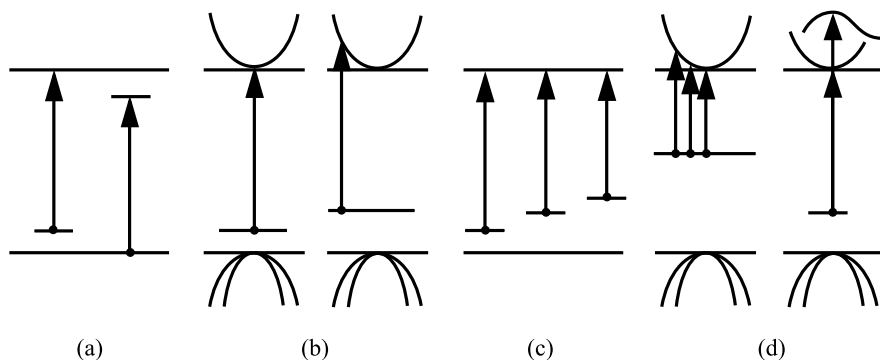


Fig. 23.7 Various extrinsic excitations as described in the text

23.4 Competing Excitation Processes

The competing effects of optical excitation from different levels can be separated by a kinetic analysis whenever their relaxation times are sufficiently different from each other.

We will briefly review the various competing optical transitions first:

- Transitions with the same photon energy can proceed from an activator into the conduction band or from the valence band into electron trap—Fig. 23.7a; or it can proceed from different deep levels into higher energies ($k \neq 0$) of the band when the deep center extends over a wider k range (Fig. 23.7b).
- Transitions with different photon energies can proceed from different sets of deep levels to the band edge—Fig. 23.7c, or from the same deep center into different parts of the same or a different band—Fig. 23.7d.

The resulting carrier distribution usually shows substantially different relaxation, depending on whether valence or conduction bands are involved, or carrier relaxation occurs from higher to lower band states. The latter will be discussed in Sect. 25.2.

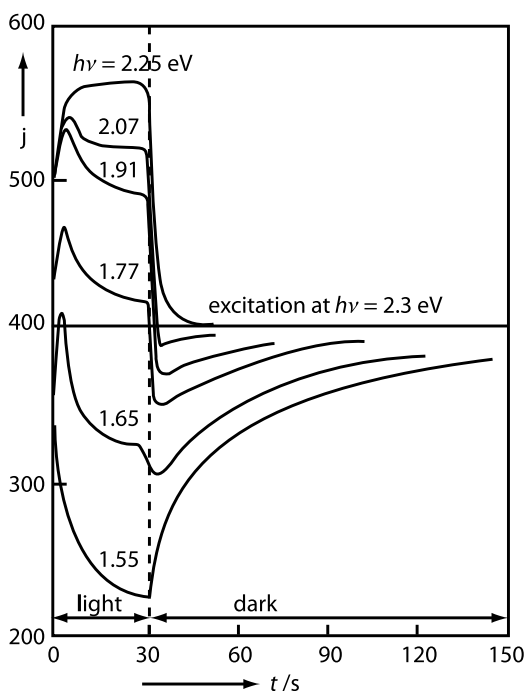
A typical two-beam excitation, involving competing excitations into conduction and valence bands, is referred to as the *quenching transition* and will be discussed in the following section.

23.5 Optical Quenching

When one light beam induces sensitized photoconductivity and another causes desensitization, one speaks of *optical quenching*. Both processes proceed with a substantially different time constant: desensitization is usually the slower process.

A typical example is the quenching of the photoconductivity in CdS, as described in Sect. 23.5. Here, the primary photogeneration with an excitation at 2.3 eV from

Fig. 23.8 Rise and decay of the photocurrent in CdS with two light beams (primary beam at $h\nu = 2.25$ eV), indicating competition between electron generation and quenching when a nonmonotonic behavior becomes visible (after Taft and Hebb 1952)



a fast center into the conduction band shows a fast rise of the photo current. When a steady state is reached, a second light pulse of 30 s duration and variable photon energy is added as shown in Fig. 23.8. A monotonic rise shows the additional excitation of conduction electrons when the photon energy is close to that of the primary beam. With decreasing photon energy of the secondary beam, however, an increasing contribution of the quenching transition is observed by a pronounced nonmonotonic behavior. For photon energies above ≈ 1.75 eV, such a contribution is hidden in stationary measurements—Sect. 23.2: the resulting stationary photoconductivity is still larger when the second beam is applied in addition to the initial excitation at 2.3 eV—see Fig. 23.8.

However, the nonmonotony observed in kinetic measurements indicates some quenching for energies below 2.1 eV.

The nonmonotonic behavior can also be observed in the decay of the additional photoconductive component that is induced by the second light beam at energies between 1.65 and 2.07 eV, resulting in an undershoot below the stationary value. The different relaxation times for the two subsystems, electrons/holes and holes/sensitizing centers, permit a distinction between the different processes.

In addition to the optical excitation described in the previous sections, there is a preferred excitation of anisotropic lattice defects with polarized light that relaxes by recombination. We will now briefly discuss this recombination relaxation.

23.6 Orientation Relaxation

The use of polarized light results in an excited state of anisotropic centers that is created in a subset of such centers with preferential orientation; the symmetry axis of the excited centers points in the direction of the electric vector of the exciting light. These excited states may involve, e.g., donor-acceptor pairs, other defect associates. The population of anisotropically excited states can be measured by observing bleaching, i.e., increased transmission, as soon as the population of the ground state becomes significantly reduced, while the population of the excited state approaches saturation. This bleaching is anisotropic and relaxes with a time constant given by the lifetime of the excited states. In addition, such anisotropic excitation can cause secondary effects which facilitate observation of its time evolution (Oudar et al. 1985a, 1985b), such as Faraday rotation i.e., a polarization rotation. The relaxation of these anisotropic excited states occurs by recombination, except for rare cases in which resonance excitation of adjacent centers with similar energy states is possible.

23.7 Changes in Thermal Ionization

Changes in temperature cause an exponential change of the thermal ionization of carriers from traps into the respective bands. The free carriers obtained from thermal ionization contribute to an increased conductivity and luminescence. In addition, other transitions cause changes in sensitization or quenching. In a variety of experimental methods, the changes in temperature are usually made with a constant heating rate. An analysis of the resulting current or luminescence as a function of time permits a distinction of the different ionization effects.

23.7.1 Thermally Stimulated Luminescence

When a luminophore has deep traps, carriers are trapped at room temperatures and are frozen-in over long time periods. An estimate of the residence time in such traps can be made from the thermal emission probability

$$e_{tc} = V_t \exp[-(E_c - E_t)/kT]. \quad (23.50)$$

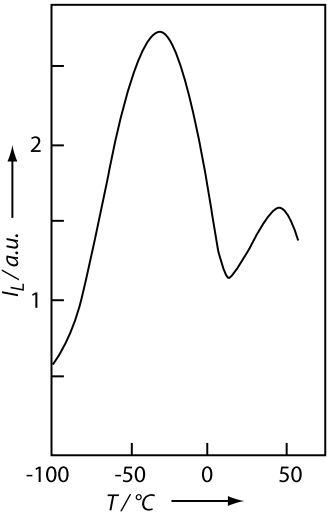
A trap with an ionization energy of 1.5 eV, located close to the middle of the band gap in a wide gap luminophore (e.g., ZnS with $E_g = 3.6$ eV), has a residence time of millions of years at room temperature—see Table 23.1. Heating the luminophore to 600 K reduces this residence time t_o only a few minutes.

A luminophore with deep traps which store carriers for more than a second is called a *phosphorescent material* or a *phosphor*. Slowly released luminescence by electrons emitted from deep traps is called *phosphorescence*.

Table 23.1 Residence time of carriers in deep traps with an attempt to-escape frequency $\nu = 10^{10} \text{ s}^{-1}$

Trap depth	$T = 200 \text{ K}$	$T = 300 \text{ K}$	$T = 450 \text{ K}$	$T = 600 \text{ K}$
0.6 eV	1.3 d	1.2 s	$5 \cdot 10^{-4} \text{ s}$	$1 \cdot 10^{-5} \text{ s}$
0.8 eV	390 y	43 min	$8.5 \cdot 10^{-2} \text{ s}$	$5 \cdot 10^{-4} \text{ s}$
1 eV	$4.1 \cdot 10^7 \text{ y}$	0.5 y	15 s	$2.5 \cdot 10^{-2} \text{ s}$
1.2 eV	$4.3 \cdot 10^{12} \text{ y}$	430 y	43 min	1.2 s
1.5 eV		$5 \cdot 10^7 \text{ y}$	65 d	6.3 min

Fig. 23.9 Glowcurve of a ZnS phosphor with two deep trap levels at 0.4 and 0.75 eV, resulting in peaks of the luminescence at -30 and $+45 \text{ }^\circ\text{C}$, respectively (after Urbach 1930)



When the temperature is increased, the amount of phosphorescence will rapidly increase as more electrons are released from deep traps. It will then go through a maximum, and decrease again when the deep traps become depleted. Such an emission curve is called a *glowcurve* (Urbach 1930)—Fig. 23.9. Glowcurves are easily obtained.

Usually, the phosphor is cooled down and illuminated in order to fill traps. Then the temperature is increased according to

$$T = T_0 + a_T t, \tag{23.51}$$

where a_T is the heating rate, and T_0 is the starting temperature.

The luminescence intensity is then measured as a function of time. Plotting the intensity, one observes one or more maxima, which indicates a more or less structured trap distribution, which in turn can be obtained by deconvolution, as shown in Fig. 23.10. For a review, see Braunlich (1979).

An instructive picture about the complexity of thermally stimulated luminescence is given in Fig. 23.11, which shows three peaks at 320, 360, and 530 K, plus a broad saddle between 360 and 480 K. The 360 and 530 peaks show three emission maxima near 3000, 3500, and 5000 Å.

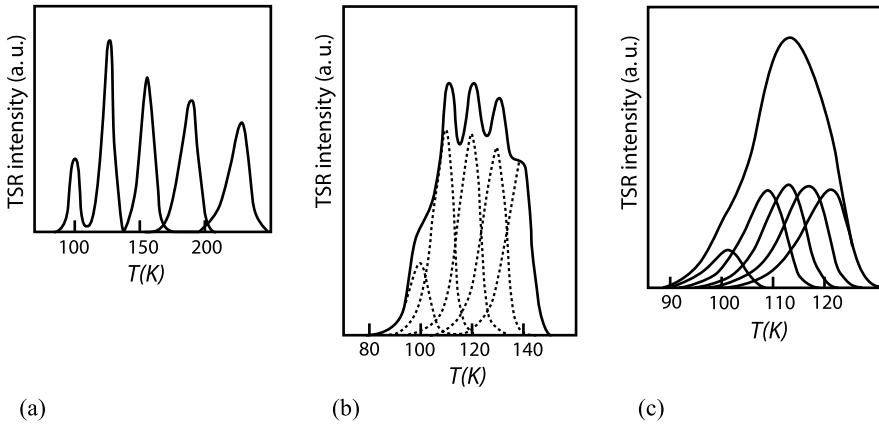
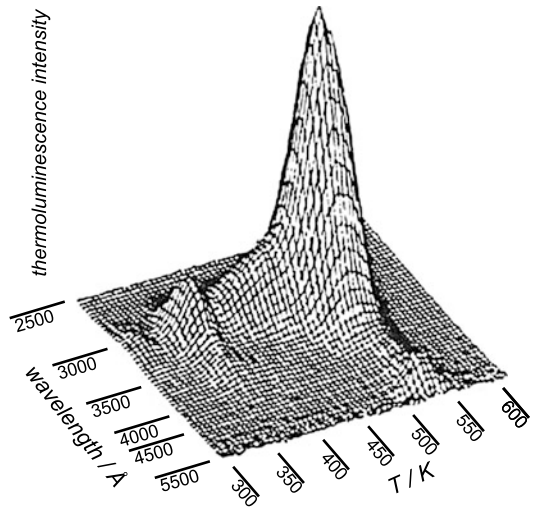


Fig. 23.10 Glowcurves caused by several traps of different energy separation, resulting in (a) resolved or (c) unresolved glowcurve structures; (b) representation of an intermediate case (after Simmons and Taylor 1971)

Fig. 23.11 Thermoluminescence of KCl:Ti, showing its temperature and spectral distribution (after Mott and Massey 1965)



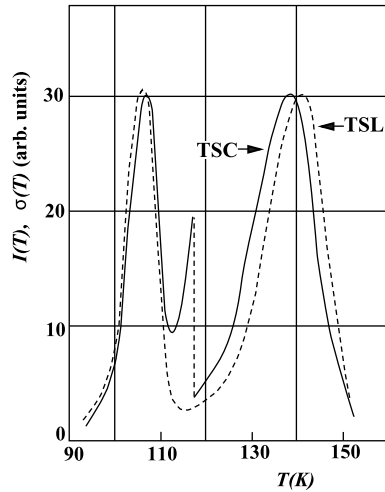
An estimate about the trap depth in relation to the temperature of the glow maximum $T_{\max}$ was derived by Randall and Wilkins (1945) from the simple one-trap model by introducing $T(t)$ into the exponent of the trap-ionization coefficient:

When we set the trap-ionization rate etc. $n_t N_c$ equal to the luminescence transition rate $c_{ca} n p_a$, we obtain for the time-dependent luminescence intensity

$$I_L = e_{tc} n_{t0} N_c \exp\left(-\int_0^t e_{tc}(t) dt\right), \quad (23.52)$$

which can be solved for $E_c - E_t$:

Fig. 23.12 Example of a glow spectrum showing similar behavior between TSC and TSL for a LiF single crystal that was exposed to X-rays at 85 K and subsequently heated at a rate of approximately 0.05 degrees per second (after Bohm and Scharmann 1969)



where the function $f(t, a_T)$ for this simple model is small compared to 1, and D_v is a dimension factor on the order of 1. With traps of a frequency factor of 10^{10} s^{-1} , Eq. (23.54) simplifies to the often-used estimate

$$E_c - E_t \simeq 25kT_{\text{max}}. \quad (23.53)$$

Phosphors with very deep traps have an important technical application for dosimetry; for instance, these phosphors can be excited by X-rays. The effect of such irradiation is a cumulative trap-filling. Trapped electrons can be stored over long time periods, and later checked by performing a glowcurve experiment. The area under the glowcurve is a measure of the dosage. See the review by DeWerd (1979).

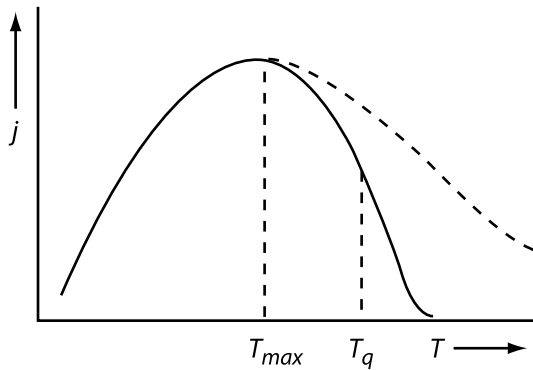
One such dosimeter is the CaF:Mn phosphor, which shows linearity of the thermoluminescence peak after X-ray exposure over five orders of magnitude of the dosage from 0.1 to 10^4 R .¹

23.8 Thermally Stimulated Currents

While the trapped carriers are released by an increase in temperature, one also observes an increase in electrical conductivity which shows a behavior similar to the glowcurves—Fig. 23.12. The corresponding current is called the *thermally stimulated current* (TSC).

¹R = Roentgen; 1 R is the amount of X-ray (or γ -ray) irradiation that produces 1 esu of charges ($2.08 \cdot 10^9$ ions) per cm^3 of air. Natural background radiation is 120 mR per year. Diagnostic single X-ray exposures lie between 50 and 500 mR per exposure. Skin reddening occurs near 500 R.

Fig. 23.13 Competition of trap release centering at $T_{\max}$ and quenching at T_q



When only one trap level is involved, both glow and TSC maxima occur at the same temperature, since both are proportional to the free carrier density. When other levels are involved, however, there are some differences in curve shape as well as the position of the maxima between TSC and thermally stimulated luminescence (TSL). There is competition between radiative and nonradiative transitions, and this competition is influenced by the temperature, most severely during thermal quenching.

A cut-off of luminescence or current occurs at a temperature at which a quenching transition becomes significant. This is shown in Fig. 23.13, where a broad donor spectrum is assumed; the resulting TSC curve is shown as a dashed line. The steep decrease at T_q is caused by the release of holes from hole traps, causing a desensitization, i.e., a lowering of the carrier lifetime. Without additional information, such a decrease could be misinterpreted as a missing part in the electron-trap distribution.

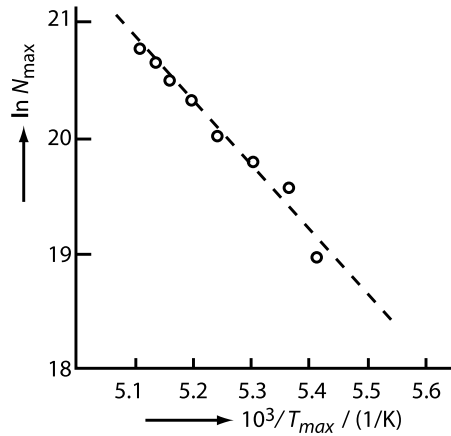
A more detailed analysis shows that the logarithmic factor in Eq. (23.54) needs to be modified (Böer and Vogel 1955; Böer et al. 1958a, 1958b), which yields

$$E_c - B_t = kT_{\max} \ln \left(\frac{\nu_t k T_{\max}}{a_T (E_c - E_t)} \frac{\eta}{(1 - \eta)^2} \frac{c_{ca}}{c_{ct}} \right), \quad (23.54)$$

with η as the relative trap-filling at $T_{\max}$. The result of the correction is twofold: it shows the influence of the competing recombination transitions, and the degree of trapping. When these traps are partially depleted,² the amplitude and temperature of the maximum change. When the carrier density at the TSC maximum, after sequentially increased fractional depletion, is plotted on a semilogarithmic scale as a function of $1/T_{\max}$, one obtains the trap depth from the slope (Fig. 23.14), providing only a single trap level is involved.

²This can be done by a preceding, incomplete glowcurve run, which proceeds from run to run to progressively higher temperatures, followed by cooling to the starting temperature for the following run.

Fig. 23.14 Current at the maximum of a TSC curve in CdS as a function of the temperature for partially depleted traps before starting the TSC (after Böer et al. 1958a, 1958b)



This relationship can be written as

$$j_{\max} = e\mu_n F N_c \frac{1-\eta}{\eta} \exp\left(-\frac{E_c - E_t}{kT}\right). \quad (23.55)$$

23.9 Changes in Field Ionization

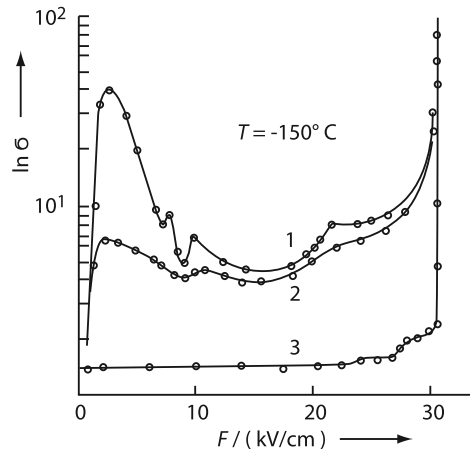
In semiconductors with sufficiently low conductivity to avoid heating, trapped carriers can be freed by a high electric field. At relatively low fields, one observes impact ionization of shallow levels at low temperatures, and then preferential depletion of Coulomb-attractive traps caused by Frenkel-Poole ionization.

When the field is increased, the carrier distribution is changed very similarly to the rise and decay of photoconductivity after changing the optical generation rate. Depending on the magnitude of the applied field, traps of various nature and depths are influenced, which causes the current to change with different time constants. Relatively slow rise or decay can be observed with a successive trap depletion by changing the applied voltage stepwise.

23.9.1 Field-Stimulated Current Curves

When increasing the bias as a function of time after previous trapfilling, one obtains nonstationary currents similar to TSC curves. Figure 23.15 shows a family of such curves of the electric conductivity with large maxima between 10 and 60 kV/cm, after the traps were filled by previous optical excitation. When shallow traps are

Fig. 23.15 Field-stimulated conductivity curves (1 after filling traps, 2 after 2 min wait at 150 K, 3 after previous run of curves 1 or 2 without filling of traps), measured at CdS platelets (after Böer and Kümmel 1954)



partially depleted by thermal ionization, the first, low-field maximum is much reduced. After the *field-stimulated conductivity curve* is traversed, the traps are depleted: a second curve does not show any significant increase in conductivity until 80 kV/cm is reached. The steep increase here in conductivity indicates the onset of the pre-breakdown range; FB is the breakdown field.

Chapter 24

Photoconductivity

Abstract One distinguishes intrinsic and extrinsic photoconductivity. The influence of traps on photoconductivity is discussed. Shallow traps and trap distributions are distinguished and evaluated. The influence of recombination centers in photoconductors are evaluated. Thermal excitation of activators is discussed. Sensitization of photoconductors is introduced. Super linear photoconductivity is discussed. Photosensitivity and gain factor are identified. Photo detector figures of merit, responsivity, frequency response are discussed. Current continuity and in ambipolar non-conductors is introduced. Persistent photoconductivity is identified

24.1 Intrinsic Photoconductivity

The intrinsic photoconductivity involves only electrons and holes in the conduction and valence bands. They are generated at the same rate g_o and recombine directly with each other (*intrinsic recombination*—Fig. 24.1a). The incremental carrier densities are equal. The change in carrier densities is given by the difference between generation (g) and recombination (r) rates:

$$\frac{dn}{dt} = g - r = g_o - c_{cv}np = \frac{dp}{dt}; \quad (24.1)$$

for parameter identification in this chapter. Equation (24.1) is written for high generation rates when the incremental carrier densities Δn and Δp are large compared to the thermally generated densities n_0 and p_0

$$\Delta n = n - n_0 \simeq n \quad \text{and} \quad \Delta p = p - p_0 \simeq p. \quad (24.2)$$

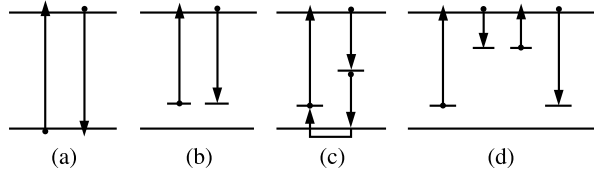
In steady state, with $dn/dt = dp/dt = 0$, one obtains with $n = p$, from Eq. (24.1)

$$n = \sqrt{\frac{g_o}{c_{cv}}}, \quad (24.3)$$

which is usually referred to as the *bimolecular recombination* relation. Intrinsic recombination occurs at high generation rates when other recombination paths are saturated.¹

¹That is, the Hall effect measured for photogenerated majority carriers.

Fig. 24.1 (a) Intrinsic photoconductivity; 24.4(b) extrinsic photoconductivity involving only one defect center, (c) involving a different recombination center, and (d) involving traps



The intrinsic photoconductivity is *ambipolar* and is given by

$$\sigma_a = e(n\mu_n + p\mu_p) = en(\mu_n + \mu_p). \quad (24.4)$$

24.2 Extrinsic Photoconductivity

Extrinsic photoconductivity involves levels in the band gap. It is either *n*- or *p*-type. A deep defect center from which carrier generation occurs is called an *activator*. One can distinguish three types of extrinsic photoconductivities involving such activators:

- excitation from an activator with direct recombination into the same type of level—Fig. 24.1b;
- excitation from an activator with carrier recombination through another level—Fig. 24.1c; and
- excitation into a band from which major trapping occurs before recombination—Fig. 24.1d.

When generation and direct recombination involve the same type of activator, and this activator is separated far enough from the valence band (Fig. 24.4) so that thermal ionization of the optically generated hole can be neglected, the carrier density follows the same bimolecular relationship as that for intrinsic carrier generation:

$$\frac{dn}{dt} = g_o - c_{ca}np_a = \frac{dp_a}{dt}, \quad (24.5)$$

where the density of holes in activators is represented by p_a and the quasi-neutrality condition by

$$p_a = n. \quad (24.6)$$

In steady state one obtains

$$\boxed{n = \sqrt{\frac{g_o}{c_{ca}}}} \quad (24.7)$$

reflecting *monomolecular recombination*. The photoconductivity is *n*-type with

$$\sigma_n = en\mu_n. \quad (24.8)$$

At high intensities, depletion of these activators causes saturation of the photoconductivity induced by high-intensity lasers, which were pulsed in order to avoid

thermal destruction of the material. This saturation has been observed, e.g., by Bube and Ho (1966) and Celler et al. (1975).

The following sections will analyze the two other types of extrinsic photoconductivity shown in more detail in Fig. 24.3.

24.3 Influence of Traps on Photoconductivity

When photo-generated carriers are trapped intermittently before they re-combine, the carrier balance is shifted and three balance *equations* must be considered:

$$\frac{dn}{dt} = g_o - c_{ct}n(N_t - n_t) + e_{tc}N_cn_t - c_{ca}np_a, \quad (24.9)$$

$$\frac{dn_t}{dt} = c_{ct}n(N_t - n_t) - e_{tc}N_cn_t, \quad (24.10)$$

$$\frac{dp_a}{dt} = g_o - c_{ca}np_a, \quad (24.11)$$

plus the quasi-neutrality *condition*:

$$n + n_t = p_a. \quad (24.12)$$

In steady state, all time derivatives vanish. As a consequence, the two terms related to trapping drop out of Eq. (24.9); hence, it becomes identical to the balance equation that was discussed in the previous section—Eq. (24.5):

$$g_o = c_{ca}np_a. \quad (24.13)$$

The influence of the traps enters through the neutrality condition, yielding

$$g_o = c_{ca}n(n + n_t). \quad (24.14)$$

Deep traps tend to be completely filled, i.e.,

$$n_t \simeq N_t. \quad (24.15)$$

Introducing Eq. (24.15) into Eq. (24.14), one obtains for the electron density

$$n = \frac{1}{2} \left(-N_t + \sqrt{N_t^2 + 4 \frac{g_o}{c_{ca}}} \right); \quad (24.16)$$

for small optical generation rates, i.e., for $g_o < N_t^2 c_{ca}/4$. Here, Eq. (24.16) reduces to

$$\boxed{n = \frac{g_o}{c_{ca}N_t}}, \quad (24.17)$$

which is referred to as a *monomolecular recombination relation*, and indicates that each electron finds a constant density of available recombination sites with $p_a \cong N_t$. For high optical generation rates, Eq. (24.16) converts back to Eq. (24.7); p_0 increases and becomes $> N_t$ and therefore $n \cong p_0$. Figure 24.2 shows the dependence of n on g_o , with a break between the linear and square-root branches at $n \cong N_t$, permitting a determination of the trap density in a photoconductor with one dominating deep trap level.

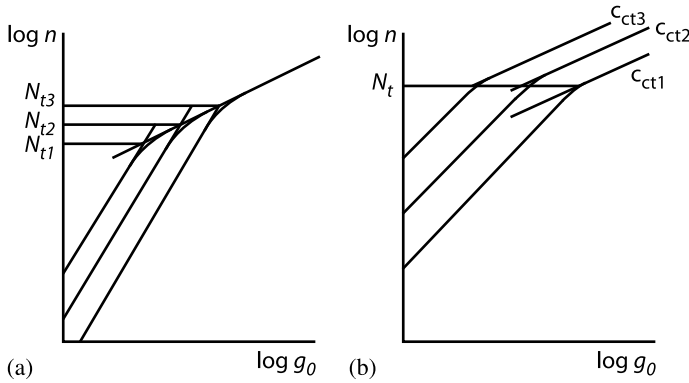


Fig. 24.2 Electron density as a function of the optical generation rate with one deep trap level: (a) trap density as the family parameter; and (b) recombination coefficient as the family parameter (with $c_{ct1} > c_{ct2} > c_{ct3}$)

24.3.1 Shallow Traps

When the interacting electron trap is shallow, its degree of filling is incomplete; thus Eq. (24.15) must be replaced by the equation obtained from Eq. (24.10) in steady state:

$$n_t = \frac{c_{ct} n N_t}{c_{ct} n + e_{tc} N_c}, \quad (24.18)$$

which yields Eq. (24.15) for high optical generation rates ($c_{ct} n \gg e_{tc} N_c$), and decreases proportionally to n for lower excitation rates:

$$n_t \simeq n \frac{c_{ct} N_t}{e_{tc} N_c}. \quad (24.19)$$

The transition rates c_{ct} and etc. can be replaced from detailed balance arguments [Eq. (4.10)], yielding

$$n_t = n \frac{N_t}{N_c} \exp\left(\frac{E_c - E_t}{kT}\right), \quad (24.20)$$

i.e., an exponential increase of electrons in traps with trap depth until saturation occurs. Then, Eq. (24.20) becomes identical to Eq. (24.15).

By introducing Eq. (24.20) into Eq. (24.14), one obtains, in the range of incomplete trap-filling, a quasi-bimolecular relationship

$$g_o - c_{ca} n^2 (1 + \eta_t^*), \quad (24.21)$$

With $\eta_t^* = n_t/n$ as an effective *trap availability factor*

$$\eta_t^* = \frac{N_t}{N_c} \left(\frac{E_c - E_t}{kT} \right); \quad (24.22)$$

thus, for higher generation rates, one obtains

$$n = \sqrt{\frac{g_o}{c_{ca}(1 + \eta_t^*)}}. \quad (24.23)$$

Since $\eta_t^* > 0$, one can see that the introduction of traps usually leads to a reduced photoconductivity:² part of the otherwise photoelectrically active electron population is stored in localized states, while the holes remain available for increased recombination.

24.3.2 Trap Distribution

In many photoconductors, more than one trap level actively influences the photoconductivity. The successive filling of these traps with increasing optical generation causes a successive spread of the two quasi-Fermi levels, and provides increasing storage capacity for carriers. This causes a successively increased recombination rate, since p_a increases with increasing n_t . The carrier density can be written similarly to Eq. (24.23) as

$$n = \sqrt{\frac{g_o}{c_{ca}[1 + \eta_t(g_o)]}}, \quad (24.24)$$

where $\eta_t(g_o)$ is a monotonically increasing function indicating the increasing availability of traps:

$$\eta_t(g_o) = \frac{kT}{E_c - E_{Fn}} \int_{E_F}^{E_{Fn}} \frac{N_t(E)}{N_c} \exp \frac{E_c - E}{kT} dE. \quad (24.25)$$

The degree of filling can be described by the position of the quasi-Fermi level, which is given by the electron density according to

$$E_{Fn} = E_c - kT \ln \frac{N_c}{n(g_o)}, \quad (24.26)$$

rendering Eq. (24.24) an implicit equation. The trap distribution can be reconstructed from the slope of $\eta_t(g_o)$ or $n(g_o)$. When a high-density trap level is being filled with increasing optical excitation, the quasi-Fermi level shifts by only a small amount; thus, $\eta_t(g_o)$ changes little, and the slope of n remains close to the square-root slope. When this level is filled, E_{Fn} moves rapidly up with increasing g_o until the next level closer to the conduction band starts to become filled. This causes the slope of $n(g_o)$ first to increase, until it decreases again; E_{Fn} remains near the next-higher level when it is being filled, causing another square-root

²Except when carrier excitation takes place from filled trap levels.

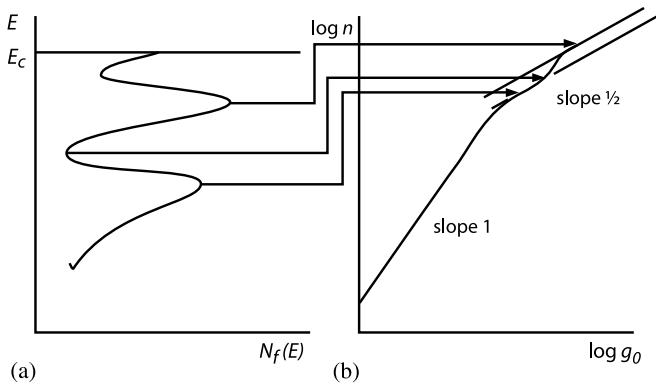


Fig. 24.3 (a) Trap distribution with two trap levels of high density. (b) Carrier density as a function of the optical generation rate with linear and square-root branches and indication of the transition from the higher to the lower square-root branch when the quasi-Fermi level, with continuing trap depletion, moves through the minimum in $N_t(E)$

branch. Figure 24.3 illustrates qualitatively this behavior for a distribution with two trap levels.

In actual photoconductors, the trap-level distribution is less structured, and thus the $n(g_0)$ behavior has less pronounced steps. In addition, other interactions with different recombination centers interfere; this makes $n(g_0)$ an unattractive method for determining $N_t(E)$.

24.4 Recombination Centers in Photoconductors

Recombination of photogenerated carriers proceeds mostly via recombination centers. The activators from which the conduction electrons are optically generated can act as such centers. Their effectiveness as recombination centers depends on their capture cross section, which is affected by the charge character before and after photo-ionization. Such recombination can be very strong, e.g., into Coulomb-attractive centers, resulting in a low carrier lifetime; or weak, e.g., into Coulomb-repulsive centers, or centers with strong lattice coupling, resulting in a long lifetime. A photoconductor with a long carrier lifetime is called a *sensitive photoconductor*.

An *n*-type photoconductor with doubly negatively charged activators, which become singly negatively charged when photo-ionized, is an example of a sensitive photoconductor in which a small intensity of light causes a large change in carrier densities. Such repulsive recombination centers have a very small cross section of 10^{-22} cm^2 , as observed in sensitized CdS resulting in $c_{cr} = s_{nr} v_{rms} \cong 10^{-15} \text{ cm}^2 \text{ s}^{-1}$. With a density of recombination centers of $N_r = 10^{17} \text{ cm}^{-3}$, and

for a generation rate³ of $10^{18} \text{ cm}^{-3} \text{ s}^{-1}$, one obtains from Eq. (24.17) an increase in carrier densities of

$$n = \sqrt{\frac{g_o}{c_{ca}N_a}} \simeq 10^{16} \text{ cm}^{-3}. \quad (24.27)$$

This increment is much larger than the carrier concentration of $<10^{10} \text{ cm}^{-3}$ in the dark for a wide gap material. Such a large ratio of carrier densities is typical of a *sensitive* photoconductor.

A photoconductor with neutral activators that becomes positively charged when ionized is an example of an *insensitive* photoconductor. A large recombination cross section prevents the buildup of a substantial density of photogenerated electrons.⁴

Insensitive photoconductors with a recombination cross section of $s_{nr} = 10^{-13} \text{ cm}^2$, and the same density of recombination centers of $N_r = 10^{17} \text{ cm}^{-3}$ at a generation rate of $10^{18} \text{ cm}^{-3} \text{ s}^{-1}$, yields an increment of

$$\Delta n \simeq 10^7 \text{ cm}^{-3}, \quad (24.28)$$

which is usually only a small fraction of the already present carrier concentration in the dark.

Sensitive photoconductors typically have a carrier lifetime

$$\tau_n = \frac{1}{c_{cr}N_r} \quad (24.29)$$

of $10^{-5} \dots 10^{-2} \text{ s}$, whereas the carrier lifetime of insensitive photoconductors is on the order of $10^{-12} \dots 10^{-8} \text{ s}$.

24.5 Thermal Ionization of Activators

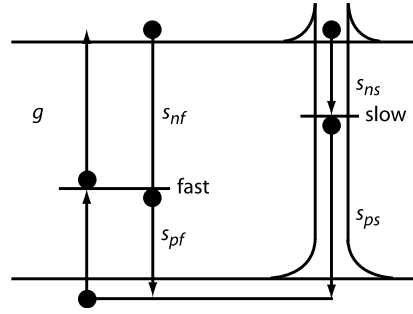
When the activator lies close enough to the valence band, the hole created by light in the activator can be thermally emitted into the valence band, from where it is redistributed with a shift of its population toward Coulomb-attractive hole traps—Fig. 24.4.

This redistribution causes a shift of the recombination of electrons from the activator to the center, which has the largest density times cross section product. This process has the tendency to decrease the electron recombination in sensitized photoconductors, and thus to increase the sensitivity, since it preferentially selects defects for hole storage that are more negatively charged than the activator. These centers then become the predominant recombination centers.

³For an extrinsic photoconductor with an absorption constant of 10 cm^{-1} this is equivalent to a photon flux of $10^{16} \text{ cm}^{-2} \text{ s}^{-1}$ for photons with an energy of 1 eV, this is also equivalent to an illumination of 1 mW/cm^2 , i.e., about 1 % of solar radiation of 100 mW/cm^2 ; this example should be interpreted to obtain a rough estimate only, since monochromatic light is inappropriately compared here with polychromatic sunlight.

⁴This recharging of recombination centers is given as a simple example of the sensitizing or desensitizing of a photoconductor. In actuality, deep centers with different degrees of lattice coupling must be considered.

Fig. 24.4 Competing recombination between slow and fast recombination centers



The carrier lifetime is determined by competition of recombination through the different centers—Fig. 24.4. Labeling the different recombination centers with an index f (fast) or s (slow) to indicate their speed of electron capture, one has, neglecting electron traps in this example:

$$\frac{dn}{dt} = g_o - c_{crs}np_{rs} - c_{crf}np_{rf} = 0, \quad (24.30)$$

$$\frac{dp_{rs}}{dt} = -c_{crs}np_{rs} + c_{rsv}(N_{rs} - p_{rs})p = 0, \quad (24.31)$$

$$\frac{dp_{rf}}{dt} = g_o - c_{crf}np_{rf} + c_{rfv}(N_{rf} - p_{rf})p - e_{vrf}N_v p_{rf} = 0, \quad (24.32)$$

$$\frac{dp}{dt} = -c_{rfv}n_{rf}p + e_{vrf}N_v p_{rf} + e_{vrs}N_v p_{rs} = 0, \quad (24.33)$$

with the quasi-neutrality condition

$$n = p_{rf} + p_{rs} + p. \quad (24.34)$$

For a moderate generation rate, one obtains

$$n = g_o \tau_\infty \left(1 + \frac{N_{rf}}{p_v} \frac{c_{crs}}{c_{crs} + c_{rsv}} \right) \quad \text{and} \quad p = \frac{n}{1 + \frac{N_{rf}}{p_v}}, \quad (24.35)$$

and

$$p_v = N_v \exp\left(-\frac{E_{rf} - E_v}{kT}\right) \quad \text{and} \quad \tau_\infty = \frac{1}{N_{rs}} \left(\frac{1}{c_{crs}} + \frac{1}{c_{rsv}} \right). \quad (24.36)$$

For a higher generation rate, one can approximate

$$n = g_o^2 \frac{1}{p_v c_{rsv}^2 N_{rs}^2} \frac{c_{crs} + c_{rsv}}{c_{crs}} \quad \text{and} \quad p = \frac{g_o}{c_{rsv} N_{rs}}, \quad (24.37)$$

and for very high generation rates, one obtains

$$n = p = g_o \tau_\infty. \quad (24.38)$$

Equation (24.37) presents an intermediate range in which the carrier density increases *superlinearly* with the generation rate between two linear branches—Eqs. (24.35) and (24.38), as shown in Fig. 24.5. When traps are included, an additional sublinear branch at high intensities will appear.

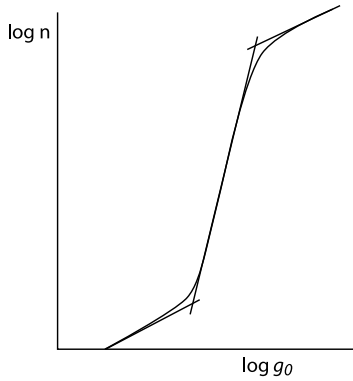


Fig. 24.5 Carrier density as a function of the optical generation rate. At low intensities the photoconductor is not sensitized, so a low lifetime and a linear relationship hold. At high intensities the photoconductor is sensitized; here a long lifetime and a linear relationship shifted to higher electron densities hold. In the transition range the carrier density increases superlinearly with g_0 .

The density of holes in slow centers controls the transition between the different ranges, with p_{rx} increasing for moderate generation rates related to p_v as

$$p_{rs} \simeq \frac{N_{rs}}{\frac{N_{rf}}{c_{rsv} p_v} + \frac{c_{cvs} + c_{rsv}}{c_{crs} c_{rsv}}}, \quad (24.39)$$

and for higher generation rates related to p_v and n as

$$p_{rs} \simeq c_{rsv} N_{rs} \sqrt{\frac{p_v}{c_{crs}(c_{crs} + c_{rsv})n}}; \quad (24.40)$$

for very high excitation levels p_{rs} saturates at

$$p_{rs} \simeq \frac{c_{rsv} N_{rs}}{c_{rsv} + c_{crs}}. \quad (24.41)$$

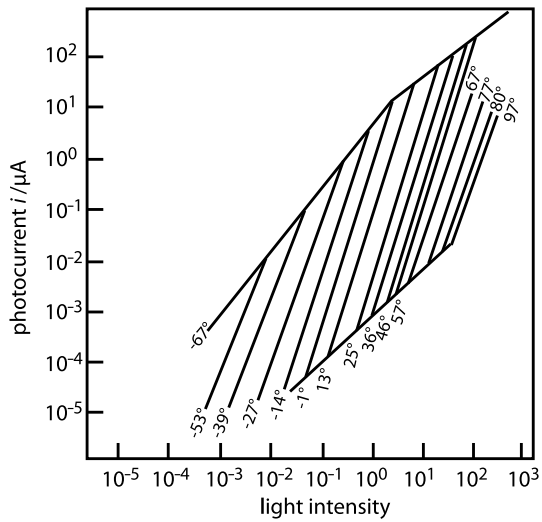
24.6 Sensitization of Photoconductors

Sensitization is accomplished by doping an n -type photoconductor with centers that have a large capture cross section for holes but, even after hole capture, only a very small cross section for electrons. Such centers, for example, could be doubly negatively charged defects or negatively charged tightly bound defects with large lattice coupling, requiring a large activation energy for electron capture.

Doping with such centers causes an increase in the photogenerated carrier lifetime: it *sensitizes* the photoconductor.

An example of such sensitization is the doping of CdS with Cu. Copper on a lattice site, Cu_{Cd} , acts as a Coulomb-attractive center for holes and as a Coulomb-repulsive, slow recombination center for electrons. It produces CdS with an electron lifetime typically on the order of $10^{-4} \dots 10^{-3}$ s.

Fig. 24.6 Shift of the superlinear range to higher optical generation rates with decreasing temperatures (in °C) as the family parameter (after Bube 1957)



24.6.1 Superlinearity of Photoconductivity

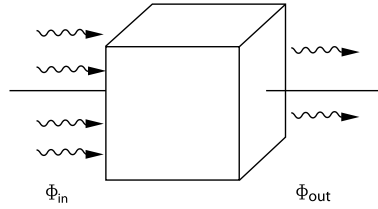
The sensitization obtained by doping with a higher density of sensitizing centers can also be obtained electronically if such centers are already present but their sensitizing action is yet inactive. This can best be seen by following the competing interaction of slow and fast recombination paths. With little optical excitation, only the fast path is open: every electron finds its hole at the fast recombination center.

With increasing excitation, the quasi-Fermi level for holes moves closer to the valence band; as the holes from the fast recombination centers are removed by thermal ionization, more and more holes are stored at slow centers. An equal density of electrons now has an increased lifetime, causing the average lifetime to increase with an increasing generation rate. This causes a transition range in which the current increases faster than linearly with an increasing generation rate, as is shown in Fig. 24.5. Such a superlinear range is observed for sufficiently sensitized photoconductors. It shifts to higher generation rates for lower temperatures, since thermal ionization becomes more difficult and must be counteracted by a higher degree of filling. Thus, the quasi-Fermi level for holes is shifted closer to the valence band. Such a shift is shown in Fig. 24.6 for sensitized CdS.

24.7 Photosensitivity and the Gain Factor

When photoconductors are used as sensitive devices to detect small amounts of light, the introduction of *photosensitivity* is sometimes instructive. It describes the changes of an electrical current in relation to the optical generation rate.

Fig. 24.7 Schematics of a volume element with light from the left for gain-factor evaluation text



In the previous sections, such changes were discussed in terms of the majority carrier density. In n -type homogeneous photoconductors, one obtains for the incremental photocurrent

$$\Delta j_n = e g_o \mu_n \tau_n \frac{V}{d}, \quad (24.42)$$

where V is the bias applied across the distance d between the electrodes, assuming ohmic contacts. Equation (24.42) shows the importance of a high $\mu\tau$ -product to distinguish between sensitive and insensitive photoconductors: the increase in current Δj_n is directly proportional to the increase in carrier density

$$\Delta n = g_o \tau_n \quad (24.43)$$

and to the mobility.

Another description is sometimes used to indicate similarities $\Delta\tau$ between a photoconductor and a vacuum photodiode or a photomultiplier, where each photon produces electrons according to the quantum efficiency and, in the latter, to a gain. In a photoconductor, the flux of electrons (per $\text{cm}^{-2}\text{s}^{-1}$) traversing the distance from cathode to anode is given by $n v_{Dr} = n \mu_n F$. The flux of photons ($\text{cm}^{-2}\text{s}^{-1}$) absorbed in the volume of the photoconductor is given by $\Delta\Phi = \Phi_{in} \Phi_{out}$ (see Fig. 24.7); hence, the *gain of a photoconductor* can be defined as

$$G_o = \frac{n \mu_n F}{\Delta\Phi}. \quad (24.44)$$

Replacing n with $\Delta\tau_n/d$, assuming homogeneous carrier generation [see Eq. (24.12)], and F with V/d , we obtain

$$G_o = \mu_n \tau_n \frac{V}{d^2}, \quad (24.45)$$

which again shows the importance of the pT -product for sensitive photoconductors. However, the influence of V/d^2 , indicating a higher gain with increased V and decreased d , is intuitively unsatisfactory.

A better way to describe the gain involves the transit time of electrons from cathode to anode, $\tau_n = d/v_{Dr} = d^2/(\mu_n V)$ introducing τ_n into Eq. (24.45), we obtain

$$\boxed{G_o = \frac{\tau_n}{t_n}}. \quad (24.46)$$

This relation can be readily interpreted as *chains of electrons* traversing the photoconductor, with each chain starting as an act of generation and terminating after

τ_n with the act of recombination, i.e., assuming unhindered replenishment of electrons from an ohmic cathode. One can also regard τ_n as the lifetime of the immobile trapped hole, which is simultaneously created during the generation of an electron. Thus, after the initial electron has traveled to the anode, a new electron is pulled in from the cathode in order to maintain quasi-neutrality. This process continues until one of these electrons recombines with the immobile hole, thereby ending the chain of traversing electrons. This means that the gain factor compares the distance a photogenerated carrier can travel in a similar but longer photoconductor in the acting field before it recombines,

$$l_n = \mu_n F \tau_n, \quad (24.47)$$

with the distance d between the electrodes of the actual device:

$$G_o = \frac{l_n}{d}. \quad (24.48)$$

The length l_n is the *drift length*, and is an important parameter for various devices.

The use of the gain factor is limited, as is the similarity to the vacuum photodetector (diode or multiplier); the conduction mechanisms are different. A more useful quantity is the *photodetectivity*, which identifies the smallest light signal that can be detected with a photoconductor against the background of dark semiconductivity and its electronic noise. This will be discussed in the following sections.

24.8 Photodetector Figures of Merit

Photoconductors are used to detect light signals. Most of these require amplification. For this purpose the light signal is usually chopped, resulting in an ac-signal at chopping frequency ν_s , which in turn is amplified within a frequency band width $\Delta\nu$. The resulting power output is often referred to as root-mean-square amplitude ($=\sqrt{2}^3$ of the peak-to-peak amplitude of the fundamental component).

For comparison between different photodetectors, certain Figures of merit are used, the most important of which are the responsivity, the detectivity, and the frequency response or time constant.

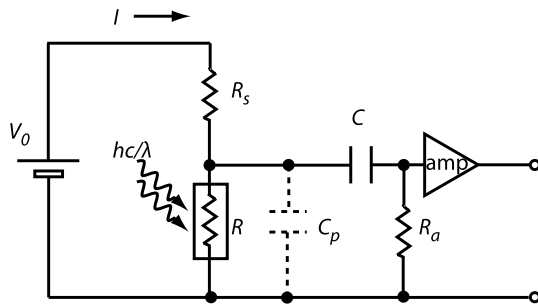
24.8.1 Responsivity

The responsivity $\mathcal{R}$ is defined as the ratio of the output signal, i.e., voltage V across the photoconductor in series to a load resistor, to the incident radiation power

$$\mathcal{R} = \frac{V}{\phi A h c / \lambda} \left(\frac{\text{V}}{\text{W}} \right). \quad (24.49)$$

Here, A is the photoconductor area exposed to light, λ is the wavelength of incident light flux Φ , and $h\nu/\lambda$ is the photon energy.

Fig. 24.8 Schematic for a typical photodetector circuit. R is the photodetector



The voltage across a photoconductor in series with a load resistor and a battery (see Fig. 24.8) is proportional to $I \Delta n / n$, where I is the dc-current, and Δn and n are the photo-induced and dark carrier densities, respectively. Hence, the responsivity can be expressed as

$$\mathcal{R} = \frac{I \Delta n \lambda}{\phi A h c n}, \quad (24.50)$$

where Δn is a function of the chopping frequency ν_s due to the sluggishness $f(\nu_s, \tau)$ of rise and decay; assuming a sinoidal photon flux variation, Δn is given by

$$p_{rs} \simeq \frac{c_{rsv} N_{rs}}{c_{rsv} + c_{crs}}. \quad (24.51)$$

Ψ is the phase shift between n and g . With $\Delta g_0 \cong \frac{\eta \Phi}{d}$ and η as the fraction of light absorbed. d is the optical device thickness; this yields

$$\mathcal{R} = \frac{I \eta \lambda \tau}{A d h c n} \frac{1}{\sqrt{1 + (2\pi \nu_s \tau)^2}}. \quad (24.52)$$

The responsivity is a function of the wavelength of light, also contained in I , η , and τ , chopper frequency, bias (contained in I), device geometry, and temperature that is contained in n , I , and τ .

24.8.2 Detectivity

For practical purposes, the output signal has to be compared with the total electronic noise. The *detectivity* usually referred to a D^* , is the signal-to-noise ratio per Watt of radiation influx, normalized to unit area (1 cm^2) and band width ($\Delta \nu = 1 \text{ Hz}$):

$$D^*(\nu_0) = \frac{\mathcal{R}(\nu_0)}{N(\nu_0)} \sqrt{A \Delta \nu} \left(\sqrt{\frac{\text{cm}}{\text{s}}} / \text{W} \right), \quad (24.53)$$

where N is the root-power noise that is composed of generation/recombination, flicker ($1/f$), thermal (Johnson-Nyquist), and photon-noise.

The photon noise is caused by the random arrival of photons generating the free electrons in the device. It has the same form as the generation/recombination noise. The photon noise will become important only for very long wavelength IR light detectors when competing background radiation needs to be considered (see van Vliet 1958b, 1967).

In the frequency range generally used for light detection with better detectors, the noise can be described by the generation/recombination component

$$\mathcal{N} = \sqrt{\bar{i}^2 g - r} = 2I \sqrt{\frac{\tau \Delta v}{ndA[1 + (2\pi v_s \tau)^2]}}. \quad (24.54)$$

With Eq. (24.53), one obtains for the detectivity a rather simple expression:

$$D^* = \frac{\eta \lambda}{2hc} \sqrt{\frac{\tau}{nd}}. \quad (24.55)$$

For more information—see Bratt (1977).

24.9 Frequency Response

The frequency response $V(v_s)$ for ac-light signals depends on the photoconductor time constant τ . It is given by

$$V(v_s) = \frac{1}{\sqrt{1 + 2\pi v_s \tau}}. \quad (24.56)$$

24.10 Current Continuity

The generation, recombination, extraction, and replenishment of carriers, described in Sect. 24.5, require a more detailed analysis of the current within the photoconductor. When an electric field is acting, electrons generated in one volume element are carried into another one by the current drift, where they recombine.

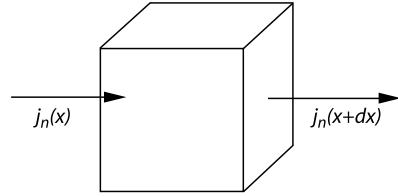
Consequently, the net change of the population in this volume element is given by the difference between birth (generation) and death (recombination) rates plus the net difference between the incoming and outgoing traffic (current density) from electrode to electrode in x direction—Fig. 24.9:

$$j_n(x + dx) = j_n(x) + eU dx, \quad (24.57)$$

with U as the net flow rate per unit volume of carriers between valence and conduction bands—see Eq. (24.53). Therefore, one has for electron or holes

$$\boxed{\frac{dn}{dt} = g_n - r_n - \frac{1}{e} \frac{dj_n}{dx}} \quad \text{or} \quad \boxed{\frac{dp}{dt} = g_p - r_p - \frac{1}{e} \frac{dj_p}{dx}}. \quad (24.58)$$

Fig. 24.9 Current continuity with net generation/recombination within the volume element



These are the basic equations⁵ that permit an analysis of the reaction-kinetic behavior. For steady state, one obtains the *steady-state current continuity equations*

$$\boxed{\frac{1}{e} \frac{dj_n}{dx} = g_n - r_n} \quad \text{and} \quad \boxed{\frac{1}{e} \frac{dj_p}{dx} = g_p - r_p}. \quad (24.60)$$

24.10.1 Current Continuity in Ambipolar Photoconductors

In the previous sections, it was assumed that only one of the photogenerated carriers is mobile and that the other is trapped. The charge neutrality requires current continuity of the photo-generated carrier; therefore, for an n -type photoconductor,

$$\frac{dj}{dx} = \frac{dj_n}{dx} \equiv 0. \quad (24.61)$$

Here, all generated carriers must recombine within the photoconductor, typically after passing several times through the external circuit.

In actuality, some of the generated holes are mobile, e.g., between thermal ionization from activators and trapping in recombination centers, although with substantially different lifetimes: for an n -type photoconductor with $\tau_p \ll \tau_n$. With any bias, some of these holes can be pulled into the electrode and recombine outside of the photoconductor in the external circuit with electrons supplied from the other electrode, thereby maintaining neutrality.

This renders $dj_n/dx \neq 0$. In order to make the total current divergence-free, it requires a finite dj_p/dx of the same magnitude and opposite sign:

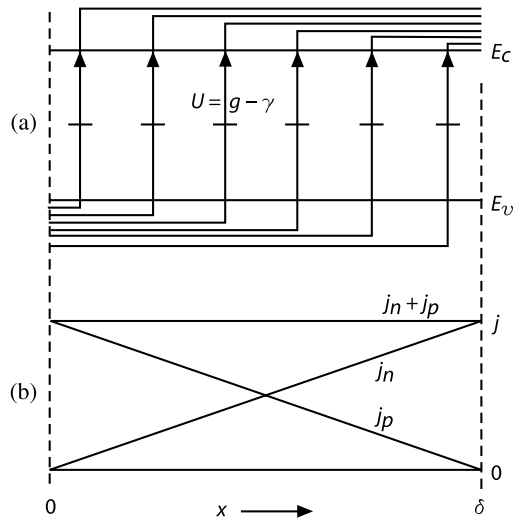
$$\frac{dj_n}{dx} + \frac{dj_p}{dx} \equiv 0. \quad (24.62)$$

⁵These relate to the basic Maxwell's equation with its condition for the conservation of electrons

$$\nabla \cdot \mathbf{j} = -\frac{\partial \rho}{\partial t}; \quad (24.59)$$

for equilibrium, with $\delta\rho/\partial t \equiv 0$, it follows $\nabla \cdot \mathbf{j} \equiv 0$. In semiconductors, with the introduction of holes, one has two types of currents, j_n and j_p , and expects with $g_n = g_p$ and $r_n = r_p$ that $\nabla \cdot (\mathbf{j}_n + \mathbf{j}_p) \equiv 0$; the sign dilemma in comparing this equation with Eq. (24.58) can be resolved by replacing the conventional $e = |e|$ with $-e$ for electrons and $+e$ for holes. This is the condition for the conservation of charges. In actuality, however, only a fraction of the electrons and holes are mobile, others are trapped and do not contribute to the currents while participating in the total neutrality account.

Fig. 24.10 Current generation with sufficient bias to render $g \gg r$ for an ambipolar photoconductor with resulting current increments. (a) Band model with continuous current lines; (b) current distribution



For further explanation, we assume first an extreme case of symmetrical, ambipolar photoconductivity, $\tau_n = \tau_p$ and sufficient field, resulting in a drift length much larger than the distance between the electrodes. Starting from the cathode, the electron current increases linearly with distance as increasingly more carriers are created on the way to the anode (see Fig. 24.10—with $r \ll g_o$).

$$\boxed{\frac{dj_n}{dx} = eg_o.} \quad (24.63)$$

Similarly, the hole current increases linearly with increasing distance from the anode with the same magnitude of the slope g_o , but with opposite sign. Although each carrier current is no longer constant, the sum must be constant in order to fulfill current continuity:

$$j = j_n(x) + j_p(x) = \text{const}, \quad (24.64)$$

as shown in Fig. 24.10, neglecting the dark current. At the electrodes, each current has also risen to the same value, and thus provides an equal flux of electrons and holes for recombination within the external circuit.

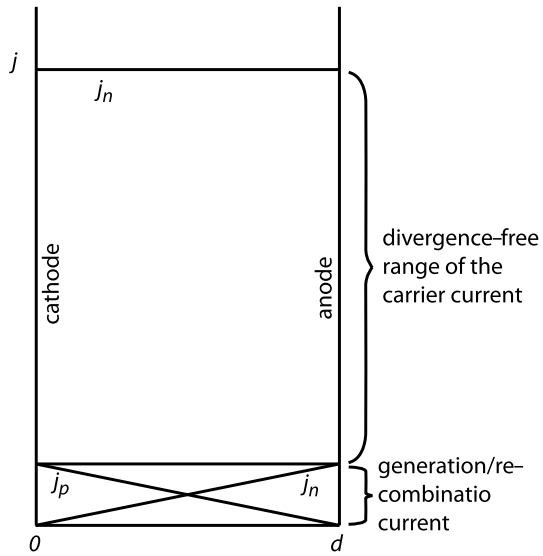
When the condition of a large drift length is not fulfilled, a similar increase of the current of each carrier within the photoconductor still holds, except that the slope is no longer constant but somewhat lower, as some of the electrons have recombined before leaving the photoconductor:

$$\frac{dj_n}{dx} = -e[g_o - r(n)] = -eU \quad (24.65)$$

and consequently for holes

$$\frac{dj_p}{dx} = e[g_o - r(n)] = eU. \quad (24.66)$$

Fig. 24.11 Current distribution in a photoconductor with dominant (n) majority carrier current indicating two current contributions: a divergence-free majority current, and a generation/recombination current



This current is called the *generation/recombination current*.

When recombination inside the photoconductor is no longer negligible, the slopes of the currents are no longer constant, since the recombination rate depends on n , or when there are inhomogeneities in doping.

When one carrier becomes the majority carrier, each current is composed of two components. One component is equal to the minority carrier current that exits the electrode; it is the generation/recombination current as given in Fig. 24.11. The other component is the divergence-free part of the majority carrier current, and contains the dark current caused by thermal ionization. Its magnitude is equal to the total current minus the maximum of the minority carrier current. This behavior is illustrated in Fig. 24.11.

In cases in which the minority carrier current is negligible, the generation/recombination current is also negligible, and Eq. (24.61) holds: all carriers generated also recombine within the semiconductor. With bias, carrier recombination in the external circuit of such photoconductors can be neglected.

24.11 Persistent Photoconductivity

An interesting consequence of current continuity in photoconductors with activators of extremely small capture cross section is a *persistent photoconductivity*. At low temperatures, photoconductivity has been observed which persists for days or even months after the optical excitation is terminated. The initially generated carriers are extracted from the photoconductor, and are repeatedly replenished.

The current continues in order to maintain neutrality, since recombination is extremely slow. In CdTe:Cl at 77 K, the photocarrier lifetime can exceed 10^6 hours

(Dmowski et al. 1977). Other examples include a donor at a thermal depth of 0.1 eV and an optical depth of 1.3 eV, thus with a giant lattice relaxation of 1.2 eV in $\text{Al}_\xi\text{Ga}_{1-\xi}\text{As}$, which shows a recombination cross section of $<10^{-30} \text{ cm}^2$ at 77 K (Lang and Logan 1977).

Such extremely small recombination cross sections are difficult to explain with Coulomb-repulsive centers. With large impurity–lattice coupling, however, a very large relaxation, e.g., for some $D - X$ centers, is possible when the charge state of the impurity is changed. Such relaxation causes a large effective barrier for carrier capture, which cannot be overcome at low temperatures by thermal excitation. The tunneling probability through this barrier is sufficiently small to explain $s_n < 10^{-30} \text{ cm}^2$. For a recent review, see Bhattacharya and Dhar (1988).

Part IV

Photovoltaics

Chapter 25

Creation of Space-Charge Regions in Solids

Abstract Examples of space charges created in semiconductors are given. Abrupt changes in donor densities is evaluated. The governing system of equations, current and Poisson equation is given and the field is defined. One carrier abrupt step junction is the introduced and evaluated. Computation for a semiconductor with listed parameters is performed, with computed electron density, space charge and field distribution. Current voltage characteristics are calculated. Electron surface charges are identified. Electrostatic and Fermi potentials are distinguished. Currents. External and built-in fields are distinguished. Penalties are identified for using the simple transport model. Distribution of built-in and external field ranges in junction devices are identified. Mobilities in built-in and in external fields are distinguished. Current rectification is explained. Dependence on doping step size for solutions of the set of transport equations are evaluated. Space charge limited currents are introduced as valid approximation.

The relations of the creation of space-charge regions that is caused by inhomogeneous doping can best be studied in a semiconductor with an abrupt step in the density of shallow donors (an nn^+ -junction). The interrelations to electric fields and currents are transparent and present the foundation to discuss more complex space-charge effects.

Space-charge regions occur normally in solids as a consequence of inhomogeneous doping or of the boundary conditions at the contact.

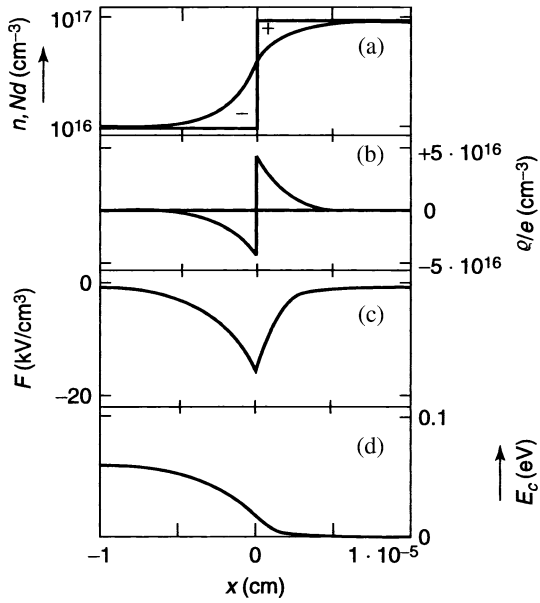
Here carriers can *leak out* from a region of higher carrier density into a region of lower carrier density. Since the average electron density in thermal equilibrium is equal to the density of ionized uncompensated donors in a homogeneous n -type solid, the leaking out of electrons into an adjacent region creates a positive space charge

$$\rho = e(N_{d2} - n) \quad (25.1)$$

in the higher doped region a negative space charge is created:

$$\rho = e(N_{d1} - n), \quad (25.2)$$

Fig. 25.1 Step-like doping distribution in an nn^+ -junction with higher doping density at right, and resulting carrier density (a), space charge (b), field (c) and band edge (d) distributions



with an abrupt flip¹ of sign of the space charge at the doping boundary, as shown in Figs. 25.1a and 25.1b.

This doping step produces a space charge double layer and a field spike at the interface. The distribution is drawn for zero bias and provides neutrality over the junction.

The shape of these distributions for different bias can be computed from the transport equation, considering diffusion out of the highly doped region ($x > 0$), counterbalanced by carrier drift in the opposite direction, due to the field induced that can be computed from the Poisson equation:

The governing set of differential equations are:

$$j_n = e\mu_n n F + \mu_n k T \frac{dn}{dx} \quad (25.3)$$

$$\frac{dF}{dx} = e \frac{\rho}{\epsilon \epsilon_0} \quad (25.4)$$

$$\frac{d\psi_n}{dx} = F. \quad (25.5)$$

Equation (25.3) is given to show the relation between electron potential and field. These equations determine the electrical behavior of any junction in which only one carrier is mobile.

¹The left-hand region is identified with a parameter index 1, the right-hand region with an index 2.

These idealized nn^+ -junction,² illustrate the main behavior that, in a modified form is the basis for the carrier transport in all other barriers or junctions.

Such junctions have technical relevance as high-low junctions, or nn^+ -junctions in many devices. The notation n^+ is used to identify a highly doped, or often degenerate region in which the Fermi-level is close to, or inside the conduction band.

25.1 One Carrier Abrupt Step-Junction

In rewriting Eqs. (25.3)–(25.5) one obtains set of four simultaneous nonlinear differential equations:

$$\frac{dn}{dx} = \frac{j_n - e\mu_n n F}{\mu_n kT} \quad (25.6)$$

$$\frac{dF}{dx} = \frac{e(N_{d1} - n)}{\epsilon\epsilon_0} \quad \text{for } x < 0 \quad (25.7)$$

$$\frac{dF}{dx} = \frac{e(N_{d2} - n)}{\epsilon\epsilon_0} \quad \text{for } x \geq 0 \quad (25.8)$$

$$\frac{d\psi_n}{dx} = F. \quad (25.9)$$

With $x = 0$ at the interface between materials 1 and 2. The density of positively charged donors $p_d = N_d - n$ is approximately equal to the total density of these donors N_d when they are shallow enough to be fully ionized: $p_{d1} \approx N_{d1}$ and $p_{d2} \approx N_{d2}$.

Equations (25.6)–(25.9) cannot be integrated in closed form. Therefore, the solution curves are obtained by numerical integration, requiring six boundary conditions for selecting the set of physically meaningful solution curves. To illustrate such solutions, we will first assume very thick slices of materials 1 and 2 so that the solutions approach the *singular point* far away from the interface:

$$\frac{dn}{dx} = \frac{dF}{dx} \equiv 0 \quad (25.10)$$

i.e., the electron density and the electric field become constant:

$$n(x \rightarrow -\infty) = n_{10} \rightarrow N_{d1} \quad (25.11)$$

$$n(x \rightarrow \infty) = n_{20} \rightarrow N_{d2} \quad (25.12)$$

$$F_{(x \rightarrow -\infty)} \rightarrow \frac{j_n}{e\mu_n N_{d1}} \quad (25.13)$$

²Many other doping inhomogeneities also need consideration of minority carriers and require the current continuity equation. This will be discussed in Chap. 27.

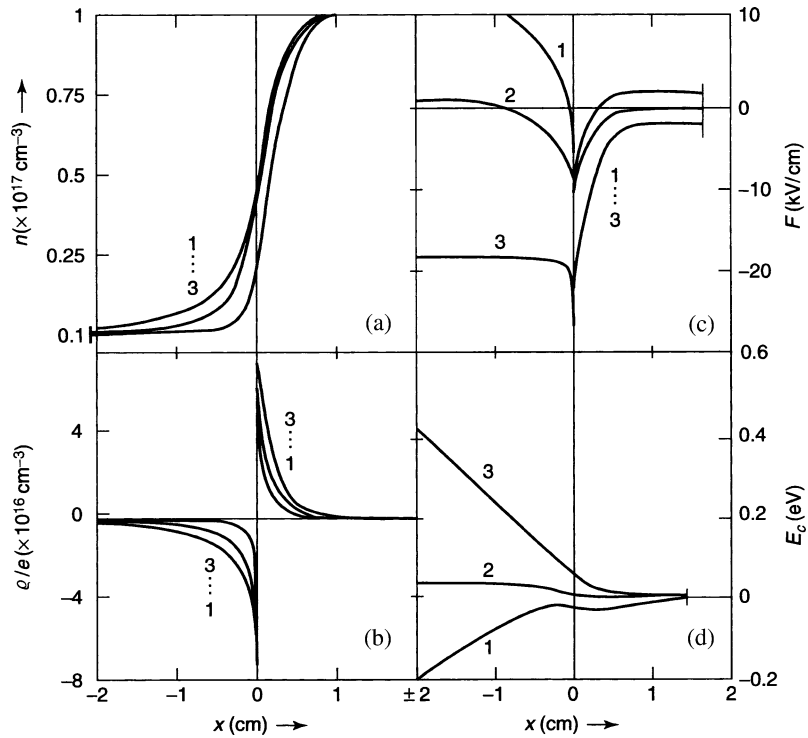


Fig. 25.2 *nn*-junction with a small doping step of a factor of 10; with resulting electron density, $n(x)$, space charge $Q(x)$, electric field $F(x)$, and conduction band $E_c(x)$ distributions, as a function of the distance from the junction interface, for the net current as family parameter: curves 1–3 for $j_n = 3.0$, and -3 kA/cm², respectively (observe the large current densities assumed here in order to obtain a significant changes in these distributions)

Table 25.1 Parameters used for Fig. 25.2

Parameters	μ_n	T	ε	N_{d1}	N_{d2}	d_1	d_2
Values	100	300	10	10 ¹⁶	10 ¹⁷	$-2 \cdot 10^{-5}$	10 ⁻⁵
Dimensions	cm ² /V s	K	–	cm ⁻³	cm ⁻³	cm	cm

$$F_{(x \rightarrow \infty)} \rightarrow \frac{j_n}{e\mu_n N_{d2}}. \tag{25.14}$$

The initial value for the electrostatic electron potential is set arbitrarily to zero for $x = d_2$ in this section.

The results of the numerical integration of Eqs. (25.6)–(25.9) for an *nn*-junction with relatively low doping step and with the set of parameters given in Table 25.1 are shown in Fig. 25.2.

The family parameter is the current density. The center curve is obtained for zero current, i.e., for thermodynamic equilibrium. For each selected current one obtains

the corresponding potential difference between both electrodes. With these one can derive the *current-voltage characteristics* (see following section).

In an experiment, however, one supplies the voltage difference (bias) to both electrodes and measures the resulting current. We should emphasize this difference between the mathematical analysis and the experiment.

25.1.1 Electron Density, Space Charge, and Field Distribution

The set of solution curves given in Fig. 25.2 show the difference of the polarity of the bias: With the anode at the left (forward bias), the electrons in the higher doped region (2) are blown from the junction interface into region (1), making this a *surplus* or *accumulation* space charge region.

With the cathode at the left side (reverse bias) more electrons are pulled away from the junction making region (2) a slightly wider region charge region.

In series connection, the accumulation layer dominates, as it reduces the resistance of region (1) while the slight depletion of region (2) has little influence since it does not change the resistance of this region markedly with changing applied voltage.

The total positive space charge, is equal to the total negative space charge in the junction for vanishing net current, i.e., quasi-neutrality in the entire device is maintained.

When a bias is applied, quasi-neutrality no longer holds. With forward bias the negative charge becomes larger while the positive one decreases, resulting in a negative net charge. Inversely, with reverse bias a positive net charge of the double layer results—see Fig. 25.2b. This typical behavior holds as long as the influence of the electrodes are neglected (as will be discussed below).³

25.1.2 Electrode-Surface Charges

The corresponding “missing” charges, to render the total device neutral, are located at the two electrodes (not shown⁴ in Fig. 25.2b). These charges are split between both electrodes so that the fields (Fig. 25.2c) created by these charges provide drift current continuity in the bulk of regions 1 and 2.

The current outside of the space-charge region is given by drift alone:

$$j = \sigma F \approx e\mu N_d F = \text{const}, \quad (25.15)$$

³When an inhomogeneous semiconductor is held between two electrodes and, after a current has passed, it is dropped into the beacher of an electrometer without the electrodes, these net charges can be measured and give an indication of the inhomogeneities (Böer and Kümmel 1957).

⁴Three boundary conditions for Eqs. (25.6)–(25.9) in region 1, and three conditions for the same equations in region 2.

hence current continuity requires:

$$\frac{F_{20}}{F_{10}} = \frac{\sigma_1}{\sigma_2} = \frac{N_{d1}}{N_{d2}} \quad (25.16)$$

(=0.1 for the parameters used in this example). From the integration of Poisson's equation one obtains for the left electrode a surface charge

$$\Omega_1 = \rho \delta x = \varepsilon \varepsilon_0 F_{10} \quad (25.17)$$

with $\rho \delta x$ as the surface charge in a layer of thickness δx (a few Å). After eliminating F_{10} from Eq. (27.17) using the drift current equation, one obtains for the surface charges at the left and right electrodes respectively

$$\Omega_1 = -\frac{|j_n| \varepsilon \varepsilon_0}{\sigma_1}; \quad \Omega_2 = +\frac{|j_n| \varepsilon \varepsilon_0}{\sigma_2}. \quad (25.18)$$

For the given parameters and a current density of 2,000 A/cm², the surface charge at the right electrode is $\approx 10^{-9}$ A s/cm², or $\approx 10^{10}$ electrons/cm², i.e. the charge of widely dispersed electrons with 1,000 Å average distance between the right electrode. At the left electrode the charge is 10 times higher since $\sigma_2 = 10\sigma_1$.

Surface charges adjacent to bulk semiconductors are common in many application, including external surfaces and semiconductor insulator interfaces. As an example, see for an analysis of surface charge between semiconductor and insulator: Kamieniecki (1990).

25.1.3 Field Distribution

The field distributions shows a nearly constant range in region (1) in forward bias (Fig. 24.2c, curve 3), that is a linear change of the conduction band in this range. With further increased forward bias the entire region (1) would become swamped from electrons of region (2) and the field spike disappears: the double layer becomes a single space charge layer with compensating charge at the left electrode.

With reverse bias the slope to the field spike increases and the conduction band flattens out.

25.1.4 Electrostatic and Fermi Potentials

The electrostatic electron potential distribution⁵ for the *nn*-junction shows the typical potential step down for a (+−) space-charge double layer and is shown in

⁵Its use is permissible also in an *nn*⁺-junction and to some extent throughout some Schottky barriers, provided that the carrier depletion in the Schottky barrier remains "moderate", i.e., even within this range, the electron density remains larger than the free hole density.

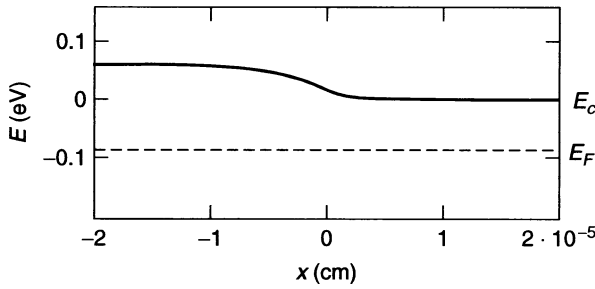


Fig. 25.3 Shows the Fermi level as *horizontal straight dashed line* and the conduction band edge computed from Eqs. (25.7)–(25.10) corresponding to Fig. 25.2 for thermodynamic equilibrium. The distance between band and Fermi level reflects the electron density distribution

Fig. 24.2d with j_n as family parameter. This potential distribution represents the shape of the edge of the conduction band $E_c(x)$

$$e\psi_n(x) = E_c(x) + c_1, \quad (25.19)$$

as shown in Fig. 25.3 for zero bias, indicating a larger distance from the horizontal Fermi level in region (1) than in region (2), hence a smaller electron density there.

The electrostatic electron potential follows the conduction (or valance band) distribution, but has the opposite sign of the electrostatic potential which conventionally is taken as the potential energy of a positively charged particle:

$$\psi_n(x) = -\psi(x). \quad (25.20)$$

In thermodynamic equilibrium the potential step between regions 1 and 2 (Fig. 25.3) can be obtained from the integration of the transport equation [Eq. (25.3)] (without involving the Poisson equation).⁶

$$e\mu_n n \frac{d\psi_n}{dx} - \mu_n kT \frac{dn}{dx}, \quad (25.21)$$

permitting separation of variables,

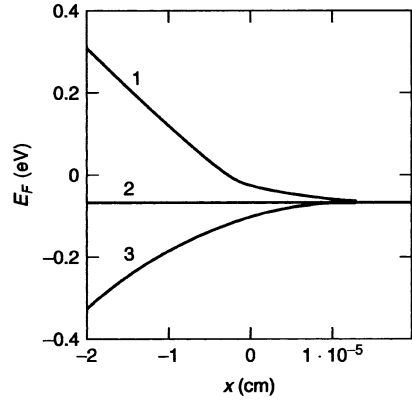
$$\frac{e}{kT} d\psi_n = \frac{1}{n} dn. \quad (25.22)$$

After integration this yields:

$$\boxed{\psi_{n,D} = \psi_{n,10}(j=0) - \psi_{n,20}(j=0) = \frac{kT}{e} \ln\left(\frac{n_{20}}{n_{10}}\right)}. \quad (25.23)$$

⁶See Eqs. (25.7) and (25.8).

Fig. 25.4 Fermi-energy distribution using Eq. (25.24) with j_n as family parameter as in Fig. 25.2; compare these with $E_c(x)$ given in part (d) of that figure



The potential difference $\psi_{n,D}$ for zero currents is called the *electron diffusion potential*. For the given parameters with a donor density ratio of 10, it is approximately 60 mV (one should observe that such ratio is limited by the band gap).

In addition to the electrostatic electron potential $\psi_n(x)$, one recognizes as very useful variable the *electrochemical potential*, also referred to as the *Fermi potential*, $(1/e)E_F$, which relates to the electrostatic electron potential and the free electron density in the classical approximation, here expressed as *Fermi energy*:

$$E_F = E_c(x) - kT \ln \left[\frac{N_c}{n(x)} \right]. \quad (25.24)$$

This relation can be derived from the equation for the equilibrium electron density at the lower edge of the conduction band, using Fermi-Dirac statistics:

$$n = \frac{N_c}{1 + \exp\left(\frac{E_c - E_F}{kT}\right)} \quad (25.25)$$

or, for $(E_c - E_v) > 3kT$

$$n \simeq N_c \exp\left(-\frac{E_c - E_F}{kT}\right), \quad (25.26)$$

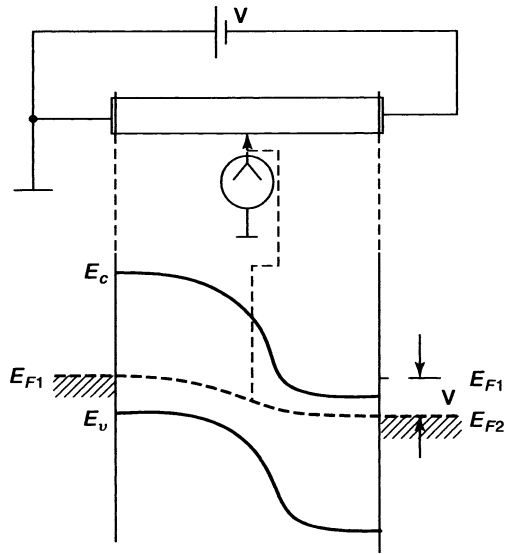
where N_c is the *effective density of states* at the lower edge of the conduction band, given by

$$N_c = 2 \left(\frac{m_n kT}{2\pi \hbar^2} \right) = 2.5 \times 10^{19} \left(\frac{m_n}{m_o} \frac{T(\text{K})}{300} \right)^3 / 2 \quad (25.27)$$

and m_n is the effective mass of electrons at the edge of the conduction band. Eq. (25.26) holds in thermal equilibrium throughout the entire crystal, including the space-charge region.

With non vanishing bias, the Fermi level will split into two quasi-Fermi levels. However, in a sufficiently doped device the majority carrier quasi-Fermi level

Fig. 25.5 Probing of the Fermi-level distribution along the surface of a semiconductor with a metal point contact



remains so close to the Fermi level, that the latter suffices as a reasonable approximation, even for non vanishing bias. With bias then E_F becomes space-dependent $E_{F_n}(x)$, here $\cong E_F(x)$.

With bias the Fermi levels are essentially straight line segments in slab 1 and slab 2 with the slopes proportional to the inverse conductivity of these slabs to keep the current continuous (Fig. 25.4). The distribution of the Fermi levels is similar to the distribution of the band edge, except the influence of the junction causing more curvature extending further into the bulk (Fig. 25.5).

The distribution of the Fermi level can be measured with a thin metal probe (Fig. 25.5). With j_n as a family parameter it is shown in Fig. 25.4 for the nn -junction given in Fig. 25.2. The two slopes in bulk regions 1 and 2 are directly proportional to the different conductivities there (see below).

The difference of the Fermi potentials at the interfaces to the two electrodes is equal to the applied voltage difference:

$$\Delta V = \frac{1}{e} [E_F(x = -d_1) - E_F(x = d_2)]. \quad (25.28)$$

While the electrochemical potential of the semiconductor is measurable by outside probing (Fig. 25.5), *the electrostatic potential distribution is not accessible to outside probing.*

The constant c_1 of Eq. (25.21) can be determined by using the electron density in the bulk, thereby fixing the distance $E_c - E_F$ according to Eq. (25.24), e.g., with the ratio N_c/n_{20} , and using the applied voltage at the corresponding electrode to determine E_F .

25.1.5 Currents

The *total current*, including drift and diffusion is given by the product of the conductivity and *slope of the Fermi level* $E_F(x)$. This can be seen by differentiating the Fermi-distribution [Eq. (25.25)] with respect to the spatial coordinate:

$$\frac{d}{dx}(E_c - E_F) = kT \frac{d}{dx} \left[\ln \left\{ \frac{N_c}{n(x)} \right\} \right], \quad (25.29)$$

yielding

$$\frac{dE_c}{dx} - \frac{dE_F}{dx} = -kT \frac{1}{n} \frac{dn}{dx}, \quad (25.30)$$

which, after multiplying with μ_n and rearranging, yields:

$$\mu_n n \frac{dE_F}{dx} = n \mu_n \frac{dE_c}{dx} + \mu_n kT \frac{dn}{dx}. \quad (25.31)$$

After replacing dE_c/dx with e times the electric field,⁷ the right-hand side of Eq. (25.31) gives the *sum of drift and diffusion current*. Therefore, the *total current is given by the product of conductivity with the gradient of the electrochemical potential*.⁸

$$\boxed{j_n = \frac{\sigma_n}{e} \frac{dE_F}{dx}}. \quad (25.32)$$

This is a similar expression to the drift current, which is given by the product of conductivity with the gradient of the *electrostatic electron potential*:

$$\boxed{j_{n,\text{Drift}} = \frac{\sigma_n}{e} \frac{dE_c}{dx} = \sigma_n \frac{d\psi_n}{dx}}. \quad (25.33)$$

In the *bulk* of regions 1 and 2, the *drift currents are*

$$j_{n,\text{Drift}} = e\mu_n n_{10} F, \quad \text{or} \quad = e\mu_n n_{20} F \quad (25.34)$$

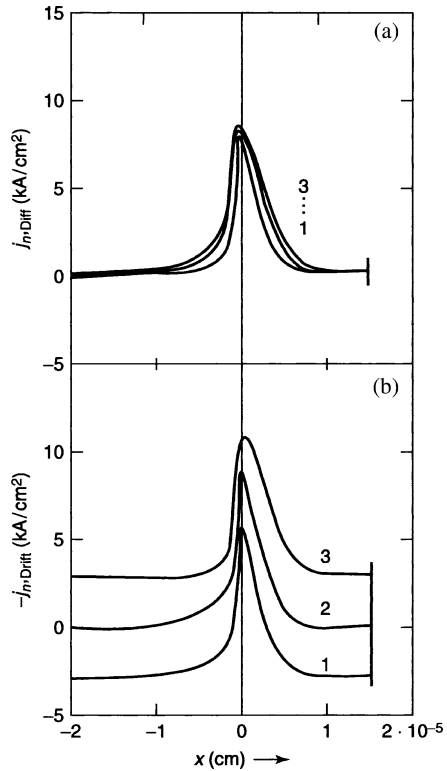
The diffusion current becomes very large at the doping interface (Fig. 25.6). It is typically on the order of 10^4 A/cm^2 and changes little with applied bias.⁹ The drift current distribution, shown in Fig. 25.6b matches the diffusion current, however, is shifted parallel to the current axis resulting in the constant net current. *For $j_n = 0$, both currents are exactly equal in magnitude and cancel each other.*

⁷This holds strictly only for electron-fields, but, except for graded band gap semiconductors or highly doped regions with inhomogeneous dopant distribution, this distinction need not be made.

⁸The Fermi-level is often described as the electrochemical potential.

⁹Its distribution is slightly deformed, according to the changes in $n(x)$ with applied bias, while its amplitude remains nearly unchanged. This reflects the fact that at a first approximation the electron distribution is pushed “sideways” (in the x -direction) with changing bias, with little deformation at the point of its steepest slope, as shown Fig. 25.2a.

Fig. 25.6 Values of the drift currents (*lower graph*) and the diffusion currents (*upper graph*) within the nn -junction, with the net current as family parameter are shown in Fig. 25.2. Both currents act in opposite direction, so that, e.g., for vanishing bias, they compensate each other exactly



25.2 External and Built-in Fields

The distinction between electrostatic potential (the band edge) and the electrochemical potential (the Fermi Potential) leads to a distinction between the external and the built-in field; there are substantial differences. The most significant being that an external field can heat a carrier gas, while a built-in field cannot.

As we discussed the space charge, we described the creation and influence on the field and the potential distribution within a device. When in addition a voltage is applied to the electrodes one observes the consequent changes in space charge, field and potential distribution. We have, however, not distinguished between the important difference between the part of the electric field that is induced by the applied voltage, the external field, that is then superimposed on the built-in field that is due to the space charge without an external voltage. We will now point out this difference as it applies to the device heating and, as we later will see to the entropy production.

The external field is created by an external bias resulting in a surface-charge on the two electrodes with no space-charge within the semiconductor. Within a typical semiconductor, however, space-charge regions exist because of intentional or unintentional inhomogeneities in the distribution of charged donors or acceptors. This charge density f_2 causes the development of an internal field according to the

Poisson equation:

$$\boxed{\frac{dF_i}{dx} = \frac{\rho}{\epsilon\epsilon_0}}. \quad (25.35)$$

The acting field is the sum of both internal, subscript i , and external, subscript e , fields:

$$F = F_i + F_e. \quad (25.36)$$

External and internal fields result in the same slope of the bands. Therefore, this distinction between internal and external fields is usually not made, and the subscripts at the fields are omitted.

We will indicate here the basic differences between external and internal fields as they relate to carrier transport.

25.2.1 Penalties for a Simple Transport Model

There are, however, penalties one must pay for a general description of fields, which can best be seen from carrier heating in an electric field. *Carrier heating* is used to describe the field dependence of the mobility (see Böer 1985a) in a microscopic model. Carriers are shifted up to higher energies within a band. Consequently, their effective mass changes, it usually increases, and the scattering probability changes—most importantly, due to the fact that it becomes easier to create phonons. For all of these reasons, the mobility becomes field-dependent; it usually decreases with increasing field.

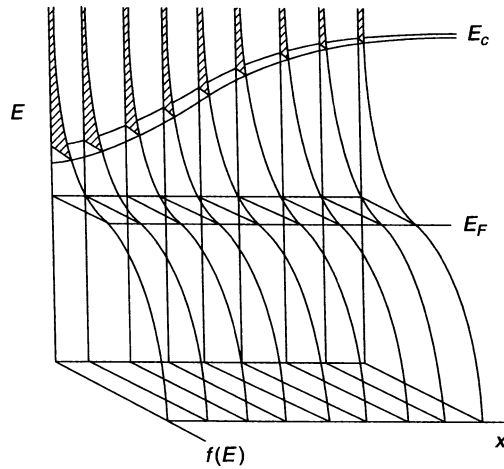
The heating is *absent in thermal equilibrium*: the carrier gas and the lattice with its phonon spectrum is in equilibrium within each volume element; thus, carrier and lattice temperatures remain the same (Stratton 1969). *No energy can be extracted from an internal field*, i.e., from a sloped band, due to a space charge in equilibrium.¹⁰

This situation may be illustrated with an example replacing electrical with gravitational forces: a sloping band due to a space-charge region looks much like a mountain introduced on top of a sea-level plane, the Fermi level being equivalent to the sea level. As the introduction of the mountain does little to the distribution of molecules in air, the introduction of a sloping band does little to the distribution of electrons in the conduction band. Since there are fewer molecules above the mountain, the air pressure is reduced, just as there are fewer electrons in a band where it has a larger distance from the Fermi level (Fig. 25.7).

However, when one wants to conveniently integrate over all altitudes (energies) in order to arrive at a single number, the air pressure (or the electron density), one

¹⁰This argument no longer holds with a bias, which will modify the space-charge; partial heating occurs, proportional to the fraction of external field. This heating can be related to the tilting of the quasi-Fermi levels (Böer 1985a).

Fig. 25.7 Fermi distribution for different positions in a semiconductor with a built-in field region (junction) and zero-applied bias



must consider additional model consequences to prevent winds from blowing from the valleys with high pressure to the mountain top with low pressure by following only the pressure gradient. Neither should one expect a current of electrons from the regions of a semiconductor with the conduction band close to the Fermi level, which results in a high electron density, to a region with low electron density in the absence of an *external field*.

To prevent such currents in the electron-density model, one uses the *internal fields*, i.e., the built-in fields, and balances the diffusion current with an exactly compensating drift current. The advantage of this approach is the use of a simple carrier density and a simple transport equation. The penalty is the need for some careful definitions of transport parameters, e.g., the mobility, when comparing external with built-in fields, and evaluating the ensuing drift and diffusion currents when the external fields are strong enough to cause carrier heating—see for an example Liou et al. (1990).

25.2.2 Built-in or External Fields

The carrier distribution and mobility are different in built-in or external fields, as discussed by e.g., Green (1997).

25.2.3 Distributions in Built-in or External Fields

The carrier distribution is determined relative to the Fermi level. For vanishing bias, the distribution is independent of the position; the Fermi level is horizontal. The distribution remains unchanged when a junction with its built-in field is introduced

(Böer 1985a). (For measurements of built-in fields see e.g., Neugroschel and Sah 1996; Mioc et al. 1996.) The sloping bands cut out varying amounts from the lower part of the distribution, much like a mountain displaces its volume of air molecules at lower altitudes (Fig. 25.7). The carrier concentration n becomes space-dependent through the space dependence of the lower integration boundary, while the energy distribution of the carrier $n(E)$ remains independent in space:

$$n(x) = \int_{E_c(x)}^{\infty} n(E) dE. \quad (25.37)$$

This is similar to the velocity distribution of air molecules, which is the same at any given altitude, whether over a mountain or an adjacent plane; whereas the integrated number, i.e., the air pressure near the surface of the sloping terrain, is not. This does not cause any macroscopic air motion, since at any stratum of constant altitude the molecular distribution is the same; hence, the molecular motion remains totally random.

In a similar fashion, electrons at the same distance above the Fermi level are surrounded by strata of constant electron density; within such strata their motion must remain random. During scattering in thermal equilibrium, the same amount of phonons are generated as are absorbed by electrons, except for statistical fluctuations: on the average, all events are randomized. Electron and hole currents both vanish in equilibrium for every volume element. Figure 25.8a gives an illustration of such a behavior.

In an external field, however, Fermi level and bands are tilted parallel to each other; that is, with applied bias, the carrier distribution becomes a function of the spatial coordinate (Fig. 25.8b). When electrons are accelerated in the field, they move from a region of higher density $n(E_1 - E_F)x_1$ to a region of lower density $n(E_1 - E_F)x_2$. These electrons can dissipate their net additional energy to the lattice by emitting phonons and causing lattice (Joule's) heating. In addition, while in net motion, electrons fill higher states of the energy distribution, thereby causing the carrier temperature to increase. The carrier motion in an external field is therefore no longer random; it has a finite component in field direction; the drift velocity $v_D = \mu F$ and the collisions with lattice defects are at least partially inelastic. A net current and lattice heating result.

25.2.4 Mobilities in Built-in or External Fields

At higher fields the carrier mobility becomes field-dependent. The difference between the built-in and the external fields relates to the influence of carrier heating on the mobility, since the averaging process for determining the mobility uses the corresponding distribution functions.

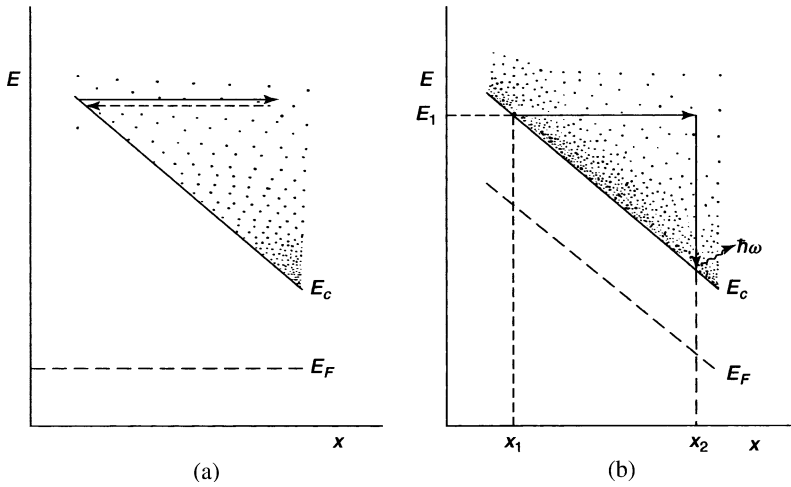


Fig. 25.8 Sloping band due to (a) an internal (built-in) field with horizontal Fermi level; and (b) due to an external field with parallel sloping bands and Fermi level. The electron distribution is indicated by a dot distribution, and the action of field and scattering by arrows

For instance, with an electric field in the x -direction, one obtains for the drift velocity of electrons

$$v_D = \mu_n F_x = \bar{v}_x = \frac{\iiint v_x f(v) g(v) d^3 v}{\iiint f(v) g(v) d^3 v}, \quad (25.38)$$

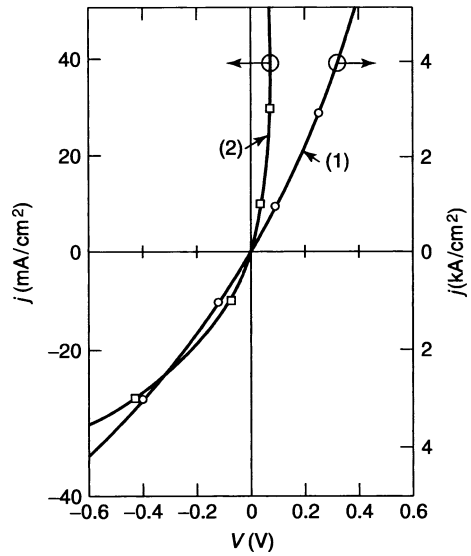
where $g(v)$ is the density of states in the conduction band per unit volume of velocity space, and $d^3 v$ is the appropriate volume element in velocity space. If F_x is the built-in field F_i , then the distribution function is the Boltzmann function $f_B^{(v)}$. If F_x is the external field F_e , the distribution function is modified due to carrier heating according to the field strength $f_{F_e}^{(v)}$.

The averaging process involves the distribution function, which is modified by both scattering and effective mass contributions. This is addressed in numerous papers dealing with external fields (for a review, see Conwell 1967; Nag 1980; see also Jacobini et al. 1977; Seeger 1999). In contrast, when only a built-in field is present, the averaging must be done with the undeformed Boltzmann distribution, since lattice and electron temperatures remain the same at each point of the semiconductor.

25.3 Current Rectification

Current voltage characteristics are obtained from the solution of the transport and Poisson equations. Curve 1 in Fig. 25.9 is obtained from the solutions of $E_F(x)$ given in Fig. 25.4 for the described nm -junction. This curve shows a non-ohmic behavior due to the expansion or contraction of the more resistive region 1 in reverse or

Fig. 25.9 Current-voltage characteristic for an nn -junction corresponding to the solutions shown in Fig. 27.4 as curve 1 with the right current scale. For a higher step ($N_d = 10^{17}$ to 10^{11} cm^{-3}) of an nn^+ -junction, obtained from their solution curves shown in Fig. 25.10. Observe the different scales with mA/cm^2 on the left and kA/cm^2 on the right and the much stronger curvature (rectifying shape) of curve 2



forward bias respectively. This asymmetry is also reflected in the difference of the distributions of field, conduction band and Fermi levels caused by an asymmetric shrinkage of expansion of the electron distribution and becomes more pronounced with higher step size as shown in curve 2 of Fig. 25.9.

Such a characteristic is easily obtained experimentally. It presents the key information to judge the performance of many semiconductor devices.

The nonlinearity of such a current-voltage characteristic can be used for rectification of an ac (alternating current) input. Such a characteristic is, therefore, also referred to as a *rectifying characteristic*.

Rectification occurs when a sinusoidal voltage bias is supplied to a device in which the current in forward bias is larger than in reverse bias, thereby causing a net forward dc component (Fig. 25.10).

There is a large body of publication dealing with devices designed for efficient current rectification. For a more exotic device involving a p/p^+ -diamond diode that is capable to operate at high temperatures and high current rectification ratios, see Ebert et al. (1994).

25.3.1 Dependence on the Doping Step-Size

In Fig. 25.10 a set of solution curves is shown for a substantially higher step-size of an nn^+ -junction:¹¹ the donor density in region 1 is reduced by a factor of 10^5 from

¹¹We are using the denotation as an nn^+ -junction somewhat loosely in this chapter, merely to indicate that the electron density in the n^+ -region is orders of magnitude larger than in the n -region.

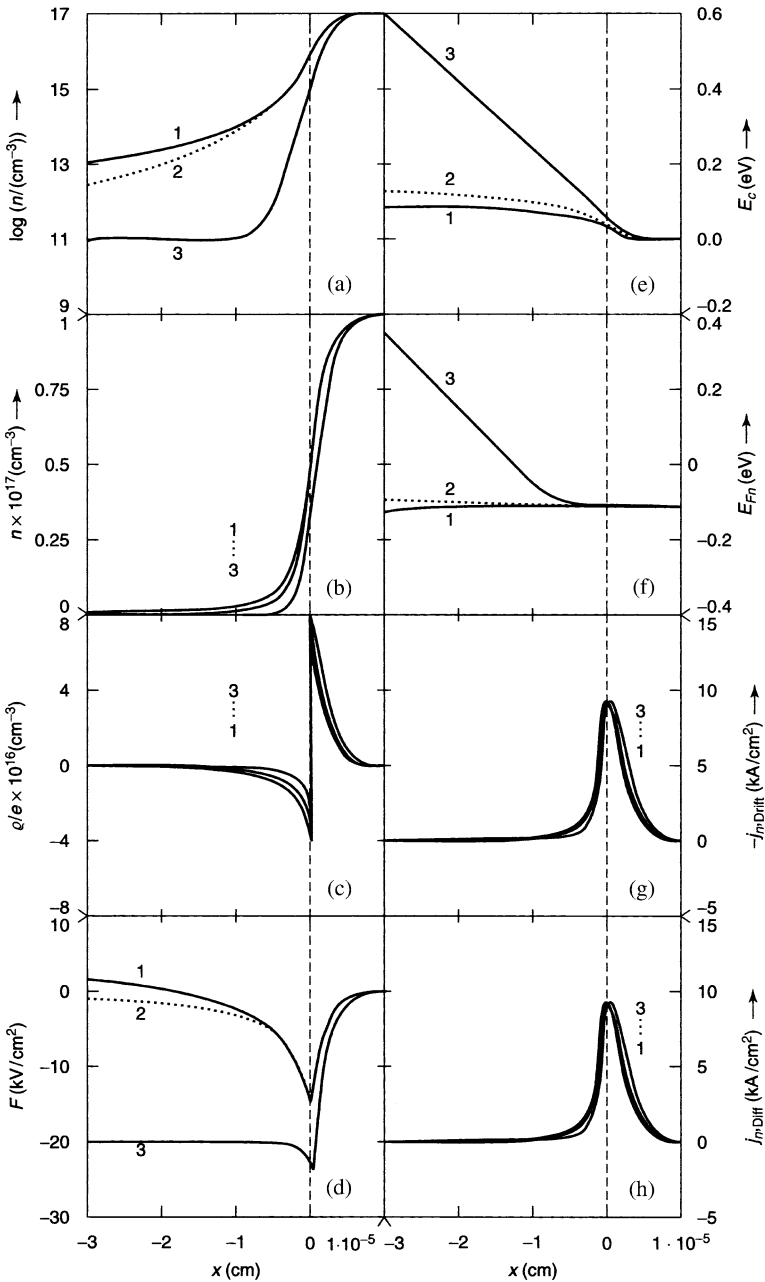


Fig. 25.10 nn^+ -junction with a large doping step, of 10^5 with resulting distributions: $n(x)$, $Q(x)$, $F(x)$, $\psi(x)$, $E_F(x)$, $j_{n,Drift}(x)$, and $j_{n,Diff}(x)$ for j_n as family parameter; curves 1–3 for 30, 0, and -30 mA/cm ^{2} , respectively (for the lower step size we used a spread of the family parameter in kA instead and reduced the scale of the abscissa also by a factor of 10^5). The curve set shows similar shapes as the curve set for the nn -junction, except that the asymmetry for different bias is larger

the value in Fig. 27.4 to $N_{d1} = 10^{11} \text{ cm}^{-3}$, while all other parameters remain the same as in Fig. 25.4, except for the current densities that also are correspondingly reduced by a factor of 10^5 to obtain a set of curves for forward, zero, and reverse bias that can be more easily compared with solution curves shown in Fig. 27.4 for the nn -junction.

The general behavior depicted in Fig. 25.10 is similar to the one shown for the much smaller step-size; (106 vs. 10), however, with a scale factor equal to the step size relation.

As more carriers are swept from the higher to the lower doped region with forward bias, the substantial increase in carrier density, as seen in Fig. 25.10a, permits a much increased current in region 1. The higher the N_{d2}/N_{d1} ratio, the higher is the ratio of forward to reverse current; the lower N_{d1} , the lower is the current at which rectification becomes noticeable. However, if the lightly doped region is too wide, so that the limited number of carriers swept into it¹² cannot sufficiently raise the average free carrier concentration there, then the current in the nn^+ -junction is series-resistance limited. This similarity relates to the fact that we left the donor density in the highly doped region unchanged.

In most practical devices, nn -junctions are caused by unintentional doping inhomogeneities or by intentional boundary layer doping. The influence of such junctions on the current-voltage characteristics is small, except for extreme cases involving high current densities or extremely high doping density ratios.

25.4 Space-Charge Limited Current

In an nn^+ -junction of sufficient step size, the electron density in the entire lowly doped region can become much larger than the donor density with sufficient forward bias. Then the current through the device becomes controlled by the surplus carriers originating from the highly doped region. This current behaves much like the current in a vacuum diode¹³ in which electrons are injected from the cathode and carried to the anode following the electric field, although limited by the space charge near the injecting cathode. This current is therefore often referred to as an *injected* current, or as a space-charge limited current¹⁴ (Mott and Gurney 1940; Lampert 1956; Rose 1978a).

With space charge limited currents the trap distribution in the low doped region can be determined. For the theory of space-charge limited currents in materials with

¹²We will see later that the distance to which such carriers can be swept into the lowly doped region is given by the diffusion length or at higher fields by the drift length (Sect. 5.3.2) which may be smaller than the device thickness.

¹³Though modified by the scattering of electrons in the semiconductor.

¹⁴This is distinctly different from the influence of a Schottky barrier or a pn -junction on the current voltage characteristic, which introduce *new*, more highly resistive regions that expand or contract with bias.

an exponential distribution of capture coefficients. The temperature dependence of space-charge limited currents in amorphous and disordered semiconductors is discussed by Schappe et al. (1996).

Space-charge limited currents were first discussed in semiconductors with injecting (non-blocking) electrodes. Here we have chosen the injection from a highly doped (n^+) region since it presents less ambiguities near the junction than neighboring an electrode (see the discussion later in this section).

For $n \gg N_{d1}$ in the entire region 1, with sufficient forward bias the space charge in the lower doped region can be approximated by

$$\rho = e(N_{d1} - n) = -en. \quad (25.39)$$

Consequently, the Poisson equation becomes independent of the doping in this region:

$$\frac{dF}{dx} = -\frac{en(x)}{\varepsilon\varepsilon_0}. \quad (25.40)$$

In addition, the drift current becomes much larger than the diffusion current in this region. This permits, with sufficient forward bias, an approximation of the total current by the drift current alone:

$$j_n = e\mu_n n(x) F(x). \quad (25.41)$$

After replacing $n(x)$ in Eq. (25.39) with the Poisson equation [Eq. (25.40)] one obtains

$$j_n - \varepsilon\varepsilon_0\mu_n F(x) \frac{dF}{dx} \quad (25.42)$$

which can be integrated after separating variables, yielding

$$(x_0 - x)j_n - \varepsilon\varepsilon_0\mu_n \frac{[F(x) - F_0]^2}{2}. \quad (25.43)$$

Whenever $F_0 \ll F(-d_1)$, one can evaluate Eq. (25.43) at $x = -d_1$ for sufficient forward bias and directly obtain with¹⁵ $F(d_1) = V/d_1$ an analytical expression for the current-voltage characteristic:

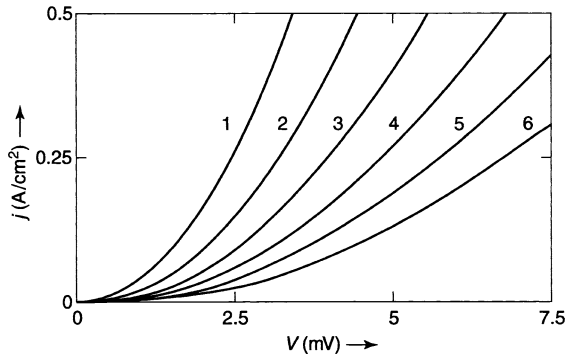
$$j_n \sim \varepsilon\varepsilon_0 \frac{\mu_n V^2}{2d_1^3}; \quad (25.44)$$

that is, *the current increases proportionally to the square of the applied voltage and decreases with the third power of the width of the low conductivity region.*

Therefore space-charge-limited currents occur with sufficient forward bias in devices that have a *thin enough* region 1 sufficient to have the entire low-conducting

¹⁵Neglecting the voltage drop in the highly conducting region 2. A somewhat better approximation yields $F(-d_1)(3/2)V/d_1$, yielding 9/8 as numerating factor in Eq. (25.41).

Fig. 25.11 Space-charge-limited currents calculated from Eq. (25.44) with $\mu_n = 100 \text{ cm}^2/\text{Vs}$, $\varepsilon = 10$, and the device thickness as family parameter with $L = 1, 1.2, 1.4, 1.6, 1.8$, and $2 \cdot 10^{-5} \text{ cm}$ for curves 1–6, respectively (the thinner the device, the steeper is the increase of the current with bias, the more electrons are swept through the entire device)



region swamped with electrons, and have a density of carriers at the injecting boundary which lies sufficiently above the bulk carrier density in region 1 of the device. Such a device may alternatively consist of a homogeneous semiconductor of length L with an injecting contact; its current follows the same, well-known *space-charge-limited current equation*:

$$j_n = \varepsilon \varepsilon_0 \frac{\mu_n V^2}{2L^3}. \quad (25.45)$$

From the relation $n \gg N_{d1}$ throughout the device, that is used to evaluate the space charge [Eq. (25.45)] and the characteristics given in Fig. 25.11, one sees that the space-charge-limited current equation holds only for “thin devices” in which the entire low-doped region can be swept over by electrons from the n^+ -region. The injected currents then become rather large in such thin devices even in the mV bias range as shown in Fig. 25.11 and, in the given approximation do not depend on the doping density or the step size beyond a minimum range.

However, one should recognize that the space-charge-limited currents are part of the ordinary current-voltage characteristic in forward bias discussed in the previous section. The often-cited majority carrier injection¹⁶ presents no special, new mechanism, but describes the normal “blowing over” of surplus carriers from the region of high carrier density into the region of lower doping. Under the given approximation, it permits explicit integration of the transport and Poisson equations and results in an analytical expression of the current-voltage characteristics.

¹⁶It is an expression coined to indicate similarity to the current in a vacuum diode.

Chapter 26

The Schottky Barrier

Abstract The classical Schottky barrier is introduced. The Schottky approximation is initially used with parameters listed and $F(x)$ and $\Psi(x)$ are given. The zero current solution for $n(x)$. Diffusion potential and junction field is given. The Debye length and barrier width are defined. The accuracy of the Schottky approximation is discussed. $n(x)$ for non vanishing currents are evaluated. The Dobson integral is given. The Boltzmann term is shown to be independent of the current. Current voltage characteristics are calculated. A modified Schottky barrier is introduced. Schottky barrier with current dependent Interface density is identified. Metal/semiconductor boundary conditions are given. Richardson-Dushman emission is identified. Current voltage characteristic in modified Schottky barriers are computed. The ideal diode equation is given. The shape factor is given. DRO and DO ranges are identified. A modified Boltzmann range is shown. Electrostatic and electrochemical potential in the Schottky barrier are identified.

A metal of sufficiently high work function causes the electron density of an n -type semiconductor to be much lower than determined by its doping in the bulk, causing a space charge near the electrode. The bias-induced shift and deformation of this space charge determines the corresponding changes in the current. An understanding of this interrelation is the key for deriving the current–voltage characteristics of such a Schottky barrier device. In this chapter, we will analyze the space charge induced by the metal–semiconductor boundary and its deformation by an applied bias, yielding the typical diode characteristics. We analyze the mathematical relations given by the transport and Poisson equations which yield as approximative solutions the diode equation. We will approach this problem by starting from a rather simple model, and will later introduce more realistic modifications that yield results more in tune with experimental observation.

26.1 The Classical Schottky Barrier

When an n -type semiconductor is connected to a metal of a sufficiently high work function, electrons from the semiconductor leak out into the adjacent

metal.¹ The electron density at the interface between the metal electrode and the semiconductor is reduced below its equilibrium bulk value n_{10} , and thereby a positive space-charge region is created within the semiconductor near the metal contact. The corresponding negative charge to render the total device neutral is located at the metal/semiconductor interface.

The space-charge layer in the semiconductor results in a field ramp and a potential step, referred to as the *Schottky barrier*.²

The electron density at the metal/semiconductor interface is given by

$$n_c = n(x=0) = N_c \exp\left(-\frac{e\phi_{MS}}{kT}\right) \quad (26.1)$$

where $\phi_{MS} = \phi_M - \chi_{Sc}$ in the linear model, is the *metal/semiconductor work function* and N_c is the effective level density at the metal-semiconductor interface.³ This interface electron density n_c is initially assumed to be independent of current and applied voltage:

$$n_c = n_j (x=0^+, j \neq 0), \quad (26.2)$$

where n_j is the electron density at the semiconductor side of the interface which will later be allowed to change as a function of the current. The electron density in the bulk is given by the density of the shallow, uncompensated donors

$$n_{10} \approx N_{d1}. \quad (26.3)$$

When n_c is *lower* than the electron density in the bulk, a depletion region results near the electrode that has properties similar to the depletion region in the highly doped half of the nn^+ -junction discussed in Sect. 25.1. It produces a rectifying (*blocking*) contact, which can be substantially more rectifying than in an nn^+ -junction since the ratio n_c/n_{10} is usually much smaller than n_{10}/n_{20} caused by doping gradients.

First, we discuss an example with the same parameters for the highly doped region as in Sect. 25.1, but with a *lower* electron density at the boundary: $n_c = 10^{10} \text{ cm}^{-3}$ (see Table 26.1), resulting in a pronounced Schottky barrier behavior.

¹Even though the electron density *inside* a metal is much higher than in the semiconductor, at its boundary to the semiconductor this density is substantially reduced according to its effective work function. It is this electron density which causes a reduction of n in the semiconductor at the interface.

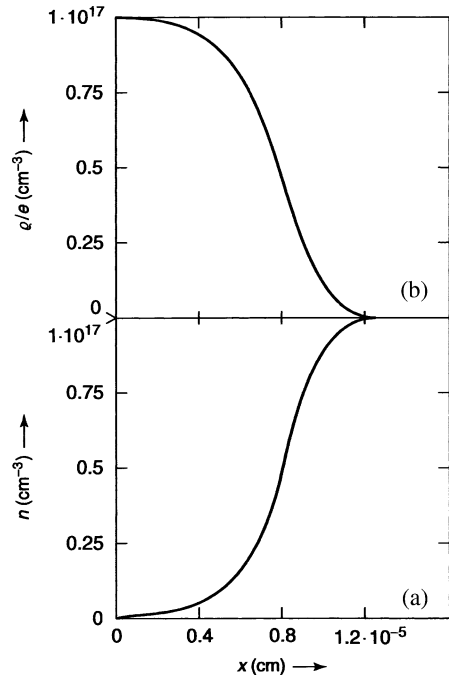
²A similar Schottky barrier appears in p -type semiconductors near a metal electrode with *low* work function, again when the hole density near the electrode is much smaller than in the bulk. Here the space-charge region is negatively charged and the resulting field is positive.

³This is slightly different from N_c within the semiconductor bulk (see Eq. (25.26)) because of a different effective mass at the interface.

Table 26.1 Parameters used for Fig. 26.1

Parameter	μ_n	ε	T	N_{d1}	n_c
Value	100	10	300	10^{17}	10^{10}
Dimensions	$\text{cm}^2/\text{V s}$	—	K	cm^{-3}	cm^{-3}

Fig. 26.1 Typical electron density (a) and space-charge distribution (b) in a Schottky barrier computed from Eqs. (26.5)–(26.7) (parameters are listed in Table 26.1)



26.1.1 Schottky Approximation: Field and Potential Distributions

In Fig. 26.1 the electron distribution is shown, computed from Eqs. (26.5)–(26.7) with parameters listed in Table 26.1 (electrode interface at $x = 0$). Because of the large ratio of the bulk-to-surface carrier densities n_{10} and n_c , the electron density in the space-charge region rapidly decreases to values very small compared to the donor density N_d , thus rendering the space charge

$$\rho(x) = e[p_d - n(x)] \approx e[N_d - n(x)] \approx eN_d \quad \text{for } 0 \leq x < x_D^t \quad (26.4)$$

independent of n in a substantial fraction of this junction-region (with $x_D^t < x_D$ —see below); p_d is the density of positively charged, ionized donors.

In using this constant space charge⁴ within the entire width of the Schottky barrier (i.e., assuming $x_D^t x_D \approx 8 \cdot 10^{-6}$ cm) in this example. The resulting *Schottky approximation* permits a major simplification⁵ of the governing set of equations:⁶

$$\frac{dn}{dx} = \frac{j_n - e\mu_n n F}{\mu_n k T} \quad (26.5)$$

$$\frac{dF}{dx} = \frac{eN_d}{\varepsilon_{st}\varepsilon_0} \quad (26.6)$$

$$\frac{d\psi_n}{dx} = F. \quad (26.7)$$

This allows decoupling of the Poisson equation from the transport equation. Integration of Eq. (26.6) yields

$$F(x) = F_c + \frac{eN_d}{\varepsilon_{st}\varepsilon_0}x; \quad (26.8)$$

that is, the field decrease linearly with increasing distance from the metal/semiconductor interface (see dashed line in Fig. 26.2b), with F_c , the *maximum value of the field* at $x = 0$, used here as the integration constant. From the integration of Eq. (26.7) after insertion of Eq. (26.8), one obtains the electrostatic electron potential

$$\psi_n(x) = \psi_{n,D} + F_c x + \frac{eN_d}{2\varepsilon_{st}\varepsilon_0}x^2, \quad (26.9)$$

which decreases parabolically with increasing x , shown as dashed parabola in Fig. 26.2c. As integration constant we used the *electron diffusion potential* $\psi_{n,D}$ which is appropriate for zero current.

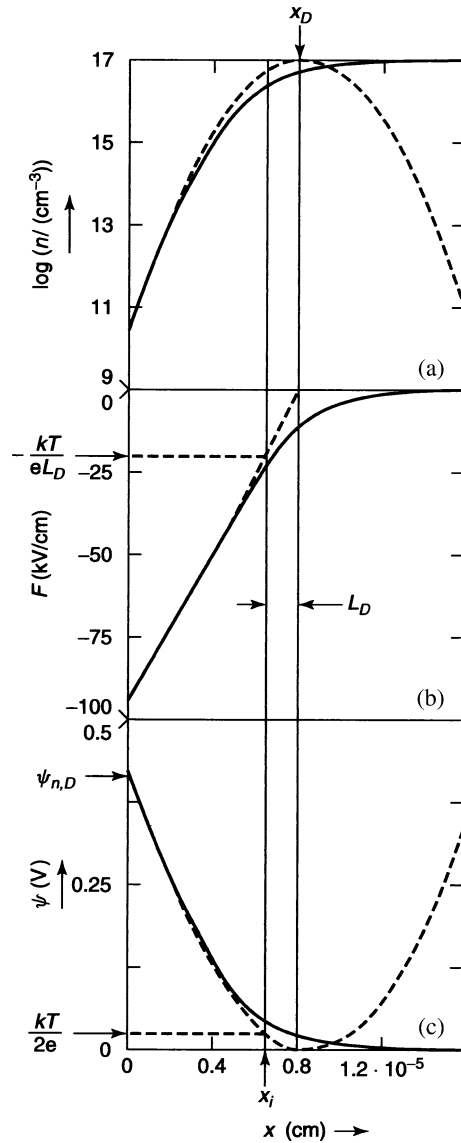
For a finite current, the solutions $F(x)$ and $\psi_n(x)$ have exactly the same form [Eqs. (26.6) and (26.7) don't depend on j_n], however, with integration constants that are current-dependent. This results in a parallel shift of $F(x)$ and $\psi_n(x)$ in x with changing j_n (Fig. 26.5c and d).

⁴The error encountered at the boundary of this range ($8 \cdot 10^{-6}$ cm) seem to be rather large (factor 2) when judging from the plot in linear scale of Fig. 26.1. The accumulative error, when integrating from the metal/semiconductor interface, however, is tolerable, as shown in Fig. 26.2. The substantial simplification in the mathematical analysis justifies this seemingly crude approach.

⁵A comparison with the previously discussed example of majority carrier injection, in which $n \gg N_d$, presents the other alternative for the two cases for which the discussion of this one-carrier space-charge distribution can be drastically simplified.

⁶We have rewritten the first, the transport equation as a function of dn/dx to identify this set as a set of three differential equations that need to be solved.

Fig. 26.2 Electron density (panel (a)), field (panel (b)), and potential panel (c) distributions of a Schottky barrier with parameters given in Table 26.1. The *solid* curves show the exact solutions of Eqs. (26.5)–(26.7); the *dashed* curves show the Schottky approximations, using Eqs. (26.8), (26.9), or (26.14). The part of the approximation shown as continued dashed curve for $x > x_D$ is physically meaningless



For a positive space charge ($+eN_d$), i.e., for an n -type semiconductor, F_c is negative and $\psi_{n,D}$ is positive. When inserting F_c from Eq. (26.18) (see below), the potential distribution can also be written as

$$\psi_n(x) = \frac{1}{\sqrt{2}} \frac{kT}{e} \left[\sqrt{\frac{2e\psi_{n,D}}{kT}} - \frac{x}{L_D} \right]^2, \quad (26.10)$$

an expression that is sometimes helpful. L_D is the *Debye length* [Eq. (26.20)], which is a characteristic length for changing $\psi_n(x)$ and $F(x)$.

Figure 26.2b and 26.2c show a comparison between the Schottky-approximation (dashed) and the exact solutions (solid curves) obtained by numerical integration of Eqs. (26.5)–(26.7) with $\rho(x) = e[N_d - n(x)]$ in the Poisson equation. Near the electrode this approximation is quite satisfactory, and consequently is mostly used.

The Schottky approximation permits the definition of a barrier layer thickness x_D from the linear extrapolation of $F(x)$ with $F(x_D) = 0$, as indicated in Fig. 26.2b. For a computation of x_D , see Sect. 26.2.

26.2 Zero Current Solution of the Electron Distribution

The electron density distribution can be obtained for $j_n = 0$ from the transport equation [Eq. (26.5)]:

$$\frac{dn}{dx} = -\frac{e}{kT} n F(x). \quad (26.11)$$

After replacing $F(x)$ by $d\psi_n/dx$ one obtains by integration the Boltzmann distribution.

$$\boxed{n(x) = n_{10} \exp\left(-\frac{e\psi_n(x)}{kT}\right)}. \quad (26.12)$$

When inserting $F(x)$ from Eq. (26.8) and using as a convenient parameter

$$\frac{1}{L_D^2} = \frac{e}{kT} \cdot \frac{eN_d}{\epsilon_{st}\epsilon_0}, \quad (26.13)$$

with L_D the *Debye length*

$$n(x) = n_{10} \exp\left[-\left(\frac{e\psi_{n,D}}{kT} + \frac{eF_c x}{kT} + \frac{x^2}{2L_D^2}\right)\right], \quad (26.14)$$

which is shown as dashed curve in Fig. 26.2a.

This holds for zero currents or, as a good approximation, as long as the net *current is small compared to both drift and diffusion currents*: $j_n \ll (j_{n,\text{Drift}}, j_{n,\text{Diff}})$. This range is referred to as the *Boltzmann range*.

26.2.1 Diffusion Potential, Junction Field

The solutions [Eqs. (26.8) and (26.9)] contain two integration constants, the electron potential and the electric field at the metal/semiconductor interface.

The electron potential step between bulk and metal/semiconductor interface is obtained from Eq. (26.12) by setting $x = 0$, yielding the “diffusion potential” for zero current with $n(x = 0) = n_c$:

$$\boxed{\psi_{n,D} = \frac{kT}{e} \ln\left(\frac{n_{10}}{n_c}\right)}. \quad (26.15)$$

This *electron diffusion potential* depends only on the ratio of the bulk and interface densities of carriers.

From Fig. 26.2 one sees that the diffusion potential can also be approximated by the product of maximum barrier field and barrier width:

$$\psi_{n,D} = -\frac{F_c x_D}{2}. \quad (26.16)$$

For the barrier field⁷ at $x = x_D$ one obtains from Eq. (26.8):

$$F_c = -\frac{eN_d x_D}{\epsilon_{st}\epsilon_0}. \quad (26.17)$$

After combining Eqs. (26.16) and (26.17) and eliminating x_D , one can express the *barrier field at zero current* as a function of $\psi_{n,D}$:

$$\boxed{F_c = -\sqrt{\frac{2eN_d\psi_{n,D}}{\epsilon_{st}\epsilon_0}}} \quad (26.18)$$

For reasonable values of doping ($N_d > 10^{16}$ [cm⁻³]) and of the electron diffusion potential, F_c is on the order of 40 kV/cm:⁸

$$F_c = -42.3 \sqrt{\frac{N_d}{10^{16}} \frac{\psi_{n,D}}{0.5} \frac{10}{\epsilon_{st}}} \quad (\text{kV/cm}). \quad (26.19)$$

⁷That is, the maximum field which lies in this approximation at the metal/semiconductor boundary (neglecting image forces).

⁸However, at higher doping densities, especially close to the metal interface, tunneling fields may be reached when $N_d > 10^{18}$ cm⁻³. This often is desired to make a contact “ohmic” and such increased defect density can be reached, e.g. by gas discharge treatments (Butler 1980).

26.3 Debye Length and Barrier Width

The Debye length is introduced from Eq. (26.13) as the distance from x_D in which the electron potential has increased by $kT/(2e)$:

$$L_D = \sqrt{\frac{\varepsilon_{st}\varepsilon_0 kT}{e^2 N_d}} \quad (26.20)$$

and typically is on the order of a few hundred or thousand Å:

$$L_D = 381 \sqrt{\frac{\varepsilon_{st}}{10}} \sqrt{\frac{T}{300}} \sqrt{\frac{10^{16}}{N_d}} \text{ (Å)}. \quad (26.21)$$

The *barrier layer thickness* can be expressed in terms of L_D by combining Eqs. (26.16) and (26.17), while eliminating F_c :

$$x_D = L_D \sqrt{\frac{2e\psi_{n,D}}{kT}}, \quad (26.22)$$

which means that x_D is usually a few (typically 3–6) Debye lengths thick, since $\psi_{n,D}$ is typically on the order of $10kT/e$.

The Debye length is also the position (counting from $x = x_D$) at which $n(x)$ for zero current has its *maximum slope*, i.e., the opposing diffusion and drift currents have their maximum value (see Figs. 26.5(f) and (g), curve 1), as one obtains from differentiation of Eq. (26.11)

$$\frac{d^2 n}{dx^2} = -\frac{e}{kT} \left(\frac{ndF}{dx} + \frac{Fdn}{dx} \right) - 0, \quad (26.23)$$

which yields for the inflection point of $n(x)$, located at $x = x_i$

$$F(x_i) = F_c \sqrt{\frac{kT}{2e\psi_D}} = -\sqrt{\frac{kTN_d}{\varepsilon_{st}\varepsilon_0}} = -\frac{kT}{eL_D}, \quad (26.24)$$

which, when compared with the value obtained from the Poisson equation:

$$F(x_i) = \frac{eN_d(x_D - x_i)}{\varepsilon_{st}\varepsilon_0}, \quad (26.25)$$

yields:

$$x_i = x_D - L_D; \quad (26.26)$$

both, x_i and $F(x_i)$ are identified in Fig. 26.2b. This result was already used in Sect. 26.2 without derivation.

Using Eqs. (26.12) and (26.24), the maximum current at the inflection point can be written as

$$j_{n,\text{Drift}}^{\text{max}} = e\mu_n n_{10} \left(\frac{kT}{eL_D} \right) \exp(-0.5) = -j_{n,\text{Diff}}^{\text{max}}. \quad (26.27)$$

With a field $F(x_i) \approx kT/(eL_D)$ which is on the order of 10^4 V/cm, the maximum currents are typically on the order of tens of kA/cm², i.e., very large compared to the net current through Schottky barrier devices.

26.3.1 The Accuracy of the Schottky Approximation

In the part of the junction near $x = x_D$, the Schottky approximation is not satisfactory, since ρ has not yet reached its constant value eN_D (see Figs. 26.1 and 26.2). The error made by computing the maximum field F_c or the barrier width x_D , using the expressions Eq. (26.18) or (26.22), respectively, can be substantial when n_c is not (at least) several orders of magnitude smaller than N_D .

We determine the error by comparing F_c obtained from the computed solutions of Eqs. (26.5)–(26.7) with the approximated value obtained from Eqs. (26.15) and (26.18) for a variety of n_c values. The *computed solutions* of Eqs. (26.5)–(26.7) for $j_n = 0$ are shown in Fig. 26.3 for $n(x)$, $\rho(x)$, $F(x)$, and $\psi(x)$, with n_c as family parameter. Space-charge saturation is achieved for curves 3–5 (subfigure b). The saturation region, however, is much narrower than the total width of the barrier, even for the lowest value of n_c . Nevertheless, the Schottky approximation yields a substantially linear branch of the field distribution near the metal/semiconductor interface as long as n_c/N_d is below $\approx 10^{-2}$ (subfigure c).

The error for the barrier field in the Schottky approximation ($\Delta F_c/F_c$) is plotted in Fig. 26.4 as function of n_c/N_d . It is less than 5 % for $n_c/N_d < 10^{-5}$, but increases rapidly above 10 % when n_c/N_d increases above 10^{-2} .

26.3.2 Non-vanishing Currents

For non vanishing currents, the carrier and field distributions are deformed similar to those of the nn^+ -junction. However, since n at $x = 0$ is kept constant (at n_c), independent of the bias, the $n(x)$ curve is substantially deformed near $x = 0$ (see Fig. 26.5 and discussed below). Other distributions ($F(x)$, $\rho(x)$, and $\psi(x)$) look similar to the highly doped region (i.e., for $x > 0$) of the nn^+ -junction (compare Fig. 26.5 with Fig. 26.9).

Fig. 26.3 Schottky barriers for $j = 0$ with different n_c as family parameter as pointed out by arrows for $x = 0$ in subfigure (a). Curves $n(x)$, $\rho(x)$, $F(x)$, and $\psi(x)$ are obtained by numerical integration of Eqs. (26.5)–(26.7) with other parameters listed in Table 26.1

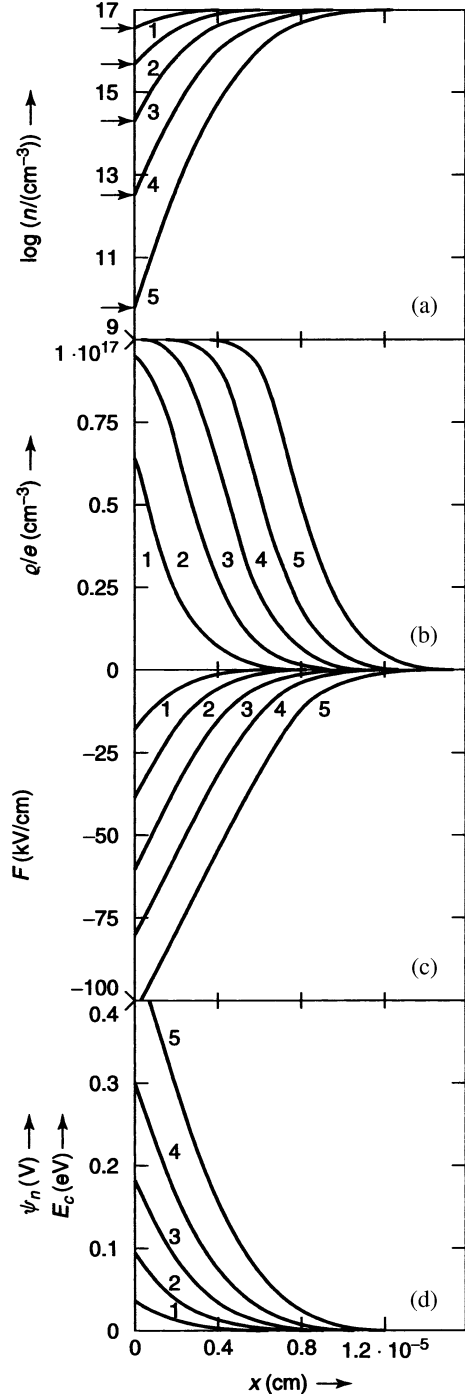
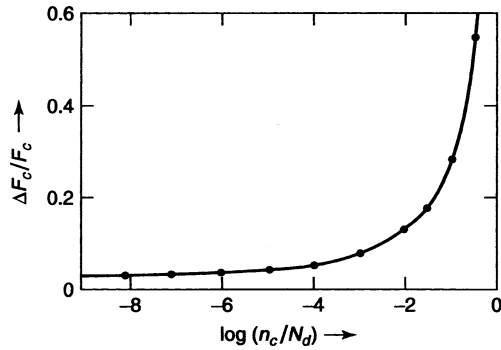


Fig. 26.4 Computed relative error of $F_c = F$ ($x = 0$, $j = 0$) between exact solutions and Schottky approximation as function of n_c/N_d



26.3.3 The Electron Density Distribution

When introducing the Schottky approximation [Eq. (26.8)] for $F(x)$ into the transport equation [Eq. (26.5)], one obtains a linear differential equation for $n(x)$:

$$\frac{dn}{dx} + \frac{e}{kT} \left(F_c + \frac{eN_d}{\varepsilon_{st}\varepsilon_0} x \right) n(x) - \frac{j_n}{\mu_n kT} = 0. \quad (26.28)$$

Integration of Eq. (26.28) yields the general solution⁹

$$n(x') = n_c \exp\left(-\frac{e[\psi_n(x') - \psi_{n,D}]}{kT}\right) + \frac{j_n}{e\mu_n F_e} \cdot 2 \cdot \left[\sqrt{\frac{e\psi_{n,D}}{kT}} D\left(\sqrt{\frac{e\psi_n}{kT}}\right) \right] \quad (26.29)$$

where $D(\xi)$ is Dawson's integral:

$$D(\xi) = \exp(-\xi^2) \int_0^\xi \exp(t^2) dt, \quad (26.30)$$

shown in Fig. 26.6 and tabulated in the *Handbook of Mathematical Functions* (Abramowitz and Stegun 1972). For $\xi > 2$, Dawson's integral can be approximated by

$$D(\xi) = (1/2\xi) \left(1 + 1/2\xi^2 + 3/4\xi^4 + \dots \right), \quad (26.31)$$

the first term of which is sufficiently accurate for $\xi > 4$, as can be judged from Fig. 26.6, yielding

$$D(\xi) \approx \frac{1}{2\xi} \quad \text{for } \xi > 4. \quad (26.32)$$

The solution $n(x)$ given in Eq. (26.29) consists of a Boltzmann term [Eq. (26.12)],¹⁰ and a correction term that is linear in current and has the shape shown in Fig. 26.7.

⁹We have introduced here a shifted coordinate system (x^1, n) . The amount of the shift in x is determined by the boundary condition, as will be discussed later in this section.

¹⁰The first term of Eq. (26.29) is identical with Eq. (25.12) when replacing $\psi_{n,D}$ using Eq. (26.15).

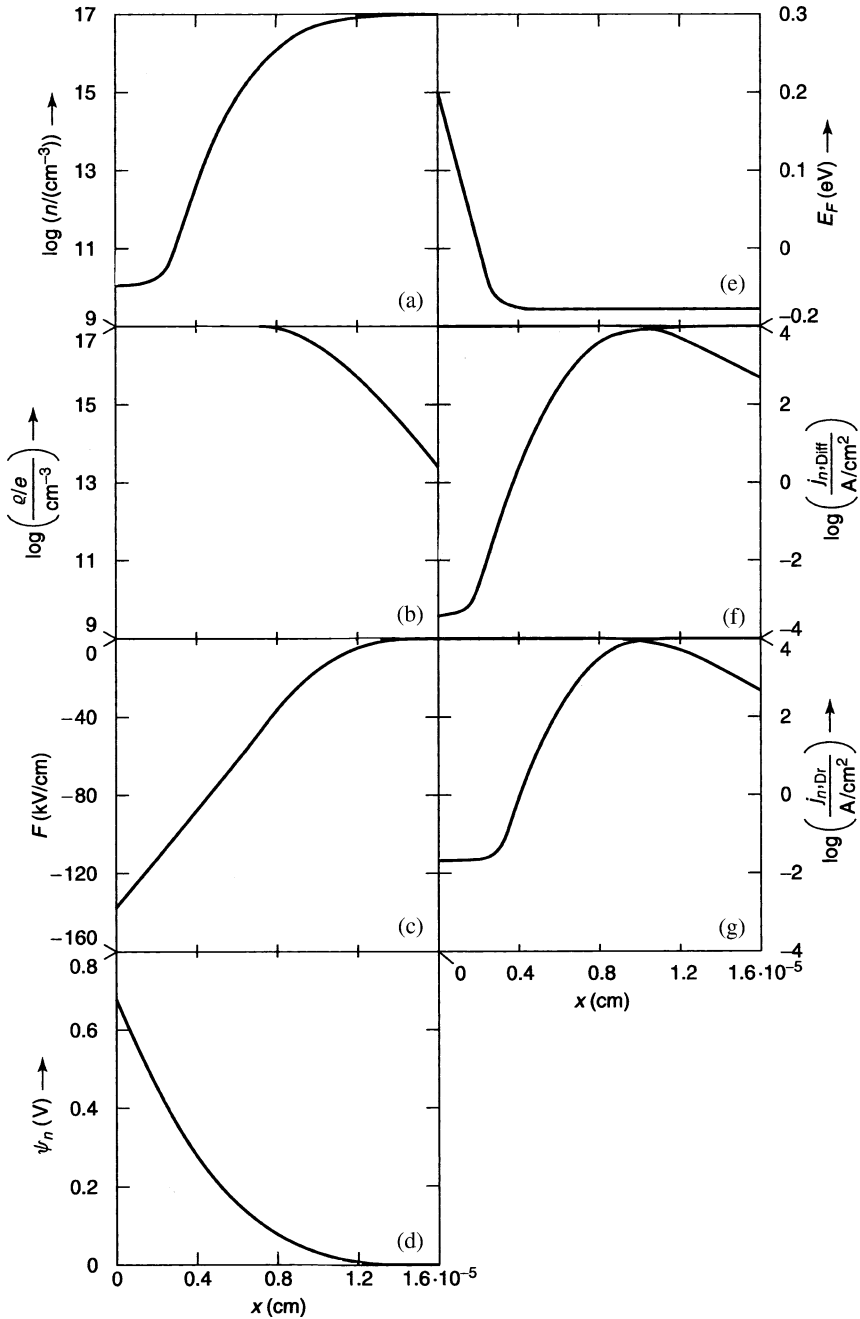


Fig. 26.5 Schottky barrier with $N_d = 10^{17} \text{ cm}^{-3}$, $n_c = 10^{10} \text{ cm}^{-3}$, and $j = -20 \text{ mA/cm}^2$ other parameters are the same as listed in Table 26.1. The exact solution curves of Eqs. (26.5)–(26.7): $n(x)$, $\rho(x)$, $F(x)$, $\psi(x)$, $E_F(x)$, $j_{n,\text{Drift}}(x)$, and $j_{n,\text{Diff}}(x)$ are given in subfigures (a)–(g), respectively, or 0, -10 , and -20 mA/cm^2 , respectively

Fig. 26.6 Dawson's integral ($D(\xi)$) compared with a simple hyperbolic function, indicating excellent agreement for $|\xi| > 4$

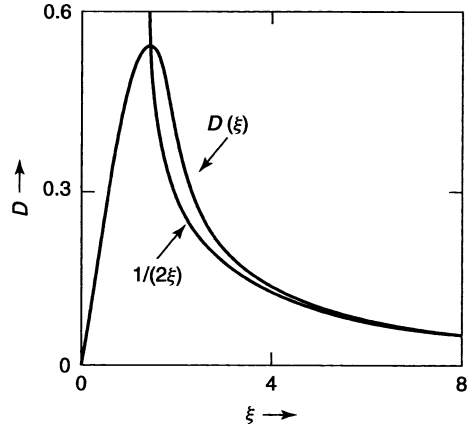
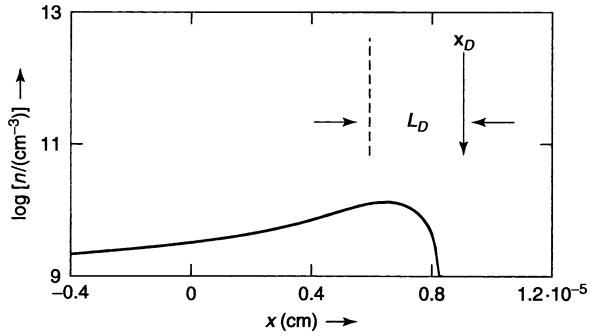


Fig. 26.7 Current term in $n(x)$ [Eq. (26.29)] with $j_n = 5 \text{ mA/cm}^2$. Observe the sign inversion of, and shift in the x -axis by, the width of the Schottky barrier x_D (for $j_n = 0$) compared to Fig. 26.8



This term is zero for $x = x_D$, i.e., at the beginning of the Schottky barrier, goes through its maximum at $x^t \approx x_D - L_D$, and drops hyperbolically for $x^t < x_D - 3L_D$. In reverse bias ($j_n < 0$). The term is added to the zero current solution, causing the electron density distribution to become S-shaped (Fig. 26.8). In forward bias this term is subtracted, which causes the Boltzmann solution (B in Fig. 26.8) to steepen.

Using only the first term of the Dawson's integral approximation, one can reduce Eq. (26.29) to a simple expression:

$$n(x') = n_c \exp \left[\frac{-e\{\psi_n(x') - \psi_{n,D}\}}{kT} \right] + \frac{j_n}{e\mu_n F(x')} \quad (26.33)$$

with $F(x^t)$ obtained similar to Eq. (26.18):

$$F(x') = \sqrt{\frac{2eN_d\psi_n(x')}{\epsilon_{st}\epsilon_0}}. \quad (26.34)$$

One can determine $\psi_n(x)$ from Eq. (26.9) and obtain $\psi_n(x^t)$ after the shift $x - x^t$ is known. This shift is a function of j_n and can be obtained for each curve from the boundary condition $n(x = 0) = n_c$.

Fig. 26.8 Electron density distribution in a Schottky barrier with j_n as the family parameter; the curves are obtained from the Schottky approximation, yielding Eq. (26.33) with x^1 as the abscissa, defined so that the Boltzmann parts of the solutions coincide. Curves 1–3 for $j_n = -20, 0$, and 10 mA/cm^2 , respectively. B identifies the Boltzmann solution for $j_n = 0$

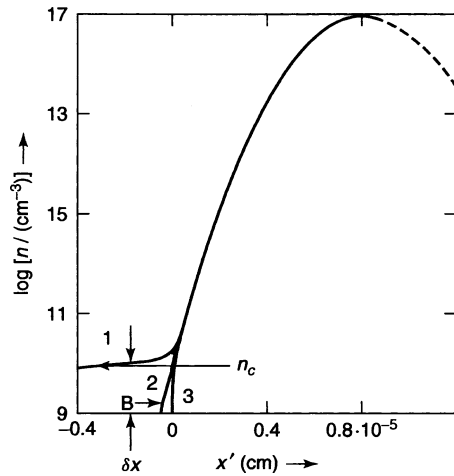
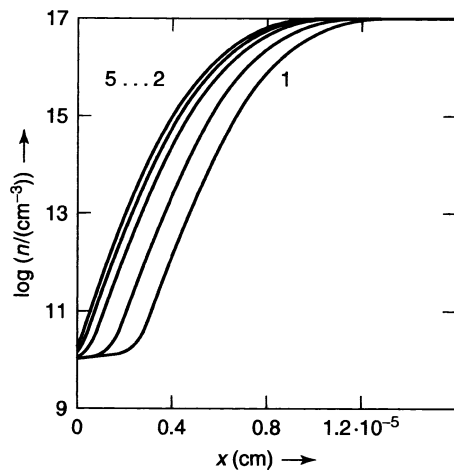


Fig. 26.9 Electron density distribution for Schottky barrier as in Fig. 26.8, however, shifted by $x - x^1$ for each curve to start at $n(x = 0) = n_c$. This set also contains the exact solutions of Eqs. (26.5)–(26.7) and drawn with x as abscissa; j_n is the family parameter: curves 1–5 for $j_n = -20, -15, -10, 0$, and 10 mA/cm^2 , respectively. The exact and Schottky-approximation curves fall within the width of the plotted lines on top of each other



When this is done graphically from Fig. 26.8, one obtains a replotted set $n(x)$ as shown in Fig. 26.9.

This approximation is excellent for $N_d/N_c > 10^3$ and cannot be distinguished within the width of the plotted curves from the exact solutions of Eqs. (26.5)–(26.7), which are also computer-drawn in Fig. 26.9. Therefore, Eq. (26.33) will be used as the key equation in the following discussions describing the behavior of $n(x)$ within the Schottky barrier.

An analysis of this solution exposes an important behavior: The *Boltzmann term* of Eq. (26.33) is independent of j_n and describes the exponential decrease of n in the bulk-adjacent part of the barrier. The second term shown in Fig. 26.7 depends linearly on the current, and, when added to (or subtracted from) the Boltzmann term (B in Fig. 26.8), permits an expansion (or compression) of the barrier with increased reverse (or forward) bias by moving the Boltzmann region away from (or closer to)

the metal/semiconductor interface in order to fulfill the boundary condition $n(x = 0) = n_c$. In the coordinate system used for the integration, $x^t = 0$ is identified in Figs. 26.7 and 26.8 as the position in which the *Boltzmann solution* crosses n_c . In all discussions given in this chapter and the approximation given here, n_c is left unchanged with changing j_n that is used simply as a family parameter.

This means that starting from the bulk and approaching the barrier, the shape of the solution curve $n(x)$ does *not* depend on bias; it is only shifted in x . A noticeable deformations of the shape of $n(x)$, however, occur only closer to the contact interface.

With increasing width of the junction, the value of the field between $x^t = 0$ and $x = 0$ continues to increase linearly [Eq. (26.8)].

The electrostatic potential at the interface, and consequently the voltage drop across the junction, therefore continues to increase parabolic with increasing width as given by Eq. (26.34).

This analysis is important to obtain a better description for the often discussed Schottky barrier and can be compared with the experiment more satisfactory.

26.4 Current–Voltage Characteristics

One obtains an analytical expression of the current–voltage characteristic when solving Eq. (26.33) for j_n and using the boundary condition $n(x = 0) = n_c$. This yields

$$j_n = e\mu_n n_c F_j \left\{ \exp \left[-\frac{e(\psi_{n,j} - \psi_{n,D})}{kT} \right] - 1 \right\} \quad (26.35)$$

with

$$F_j = F(x = 0) = \sqrt{\frac{2eN_d\psi_{n,j}}{\epsilon_{st}\epsilon_0}} \quad (26.36)$$

and

$$\psi_{n,j} = \psi_n(x = 0). \quad (26.37)$$

The index j identifies the value of the variable at the interface for a given current j_n .

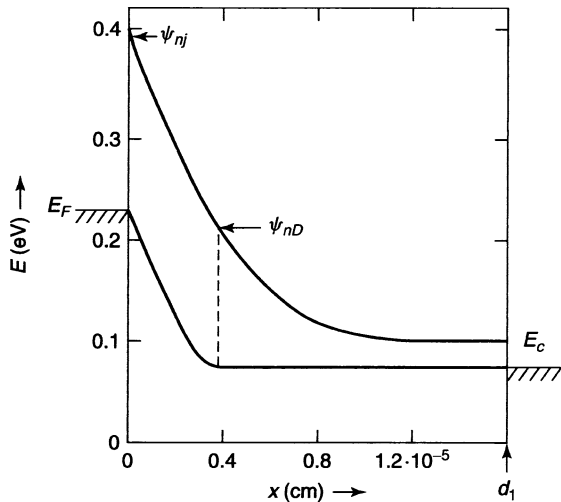
This Eq. (26.35) is the *diode equation* for which the expression $[\exp() - 1]$ is typical. The applied voltage, defined by

$$V = -\frac{1}{e} [E_F(x = 0) - E_F(x = d_1)] \quad (26.38)$$

can be easily obtained in the range where $E_c(x)$ and $E_F(x)$ run parallel to each other (Fig. 26.10) which yields

$$V = \psi_{n,j} - \psi_{n,D}. \quad (26.39)$$

Fig. 26.10 Band-model of a Schottky barrier for reverse bias with conduction band and Fermi-potential distribution computed from Eqs. (26.5)–(26.7) for a bias of $V = (1/e)[E_F(d_1) - E_F(d_2)] = -0.15$ V and the values of the Parameters given in Table 26.1



When introducing Eq. (26.39) into Eq. (26.35) one obtains as an approximation the often used *classical diode equation of drift-current-limited Schottky barriers*.¹¹

$$j_n = e\mu_n n_c F_j \left[\exp\left(\frac{eV}{kT}\right) - 1 \right], \quad (26.40)$$

and with the field at the barrier interface given by

$$F_j = \sqrt{\frac{2eN_d(\psi_{n,D} - V)}{\epsilon_{st}\epsilon_0}} \quad (26.41)$$

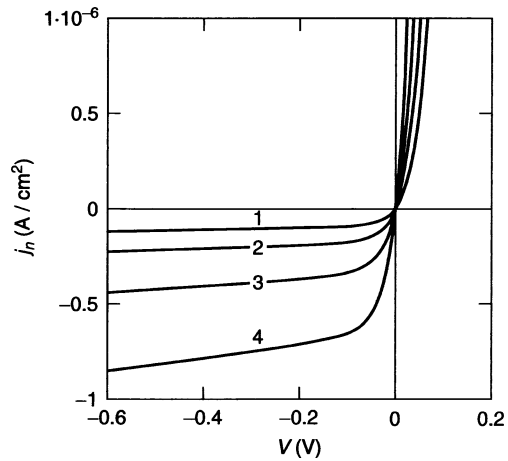
A set of these characteristics with n_c as family parameter is given in Fig. 26.11. These curves show the typical diode behavior but no true current saturation in reverse bias for reason of the bias dependence of the pre-exponential factor, containing F_j . We will return to the behavior of the current in reverse bias in Sect. 26.2.

26.5 Modified Schottky Barrier

The basic approximation and conclusions, derived in Sects. 27.1 and 26.1 for the classical nn^+ -junction and the Schottky barrier, apply for numerous metal/semiconductor barriers and a large number of heterojunctions (see Sect. 26.4). From

¹¹Since its pre-exponential factor is the drift current, which for a large reverse bias (i.e. for a vanishing exponential) is the limiting current.

Fig. 26.11 Drift-limited diode characteristics [Eq. (26.40)] with n_c as family parameter: curves 1–4 for $n_c = 3.2, 6.3, 12.6$, and $25 \cdot 10^4 \text{ cm}^{-3}$, respectively. $N_d = 10^{17} \text{ cm}^{-3}$, $\mu_n = 100 \text{ cm}^2/\text{V s}$, $\varepsilon_{\text{st}} = 10$



here, several modifications relating to boundary conditions, drift velocity limitation, and space charge generation expand the basic model and will be discussed in the following sections.

26.5.1 The Schottky Barrier with Current-Dependent Interface Density

In the previous section we have assumed a constant carrier density at the metal/semiconductor boundary which does not depend on the current through the barrier. We will now modify this condition.

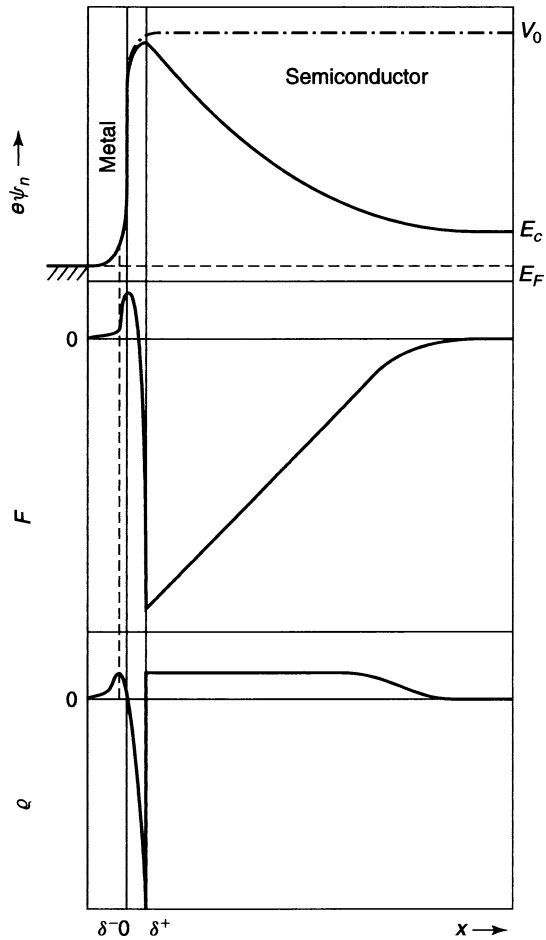
26.5.2 Metal/Semiconductor Boundary Condition

The potential barrier at the metal/semiconductor boundary prevents the leaking-out of metal electrons into the semiconductor.

Figure 26.12 illustrates in a simplified schematic and not-to-scale presentation the space charge, field, and electron potential distributions near the metal/semiconductor interface. The potential barrier keeps the conduction electrons in the metal. This barrier is created by a $(+ -)$ space-charge double layer at the surface, caused by some of these electrons escaping through the metal surface, thereby charging the metal ($x < 0$) positive and the adjacent space ($x > 0$) negative.

With an adjacent semiconductor, this dipole layer merges with a similar one at the semiconductor surface, which prevents its conduction electrons from leaking out. The resulting triple layer $(+ - +)$ at the interface is asymmetric since. It is created by the superposition of two double layers of different magnitude. This can

Fig. 26.12 Classical representation of the electron potential, field, and space-charge distributions near the metal/semiconductor interface, excluding image forces. (Schematic, not to scale)



be seen if the interface is opened and we have to separate surfaces, metal to vacuum and vacuum to semiconductor each one having its own double layer. When these surfaces merge, the triple layer results that can be regarded as a net double layer with an effective $(+-)$ charge given by the difference of the charges in the two double layers. This (effective) double layer “at” the metall/semiconductor “interface” retains most of the conduction electrons in the metal and results in the work function between metal and semiconductor.

We will here forgo the more detailed considerations, and assume a simplified potential distribution shown in Fig. 26.12 with a maximum at $x = \delta^+$; here the field vanishes, and the current is carried by diffusion only. The maximum diffusion current that can be drawn from this metal surface is given by the *Richardson-Dushman emission* (Seitz 1940)

$$j_n = en_c v_n^* \quad (26.42)$$

as the rms velocity of electrons:

$$v_n = \sqrt{\frac{3kT}{m_n}} \quad (26.43)$$

With a bias, the current at $x = \delta^+$ can be described as the difference of two components, one which passes through this interface from left to right (j_n) and one which passes from right to left (j_n):

$$j_n = \overrightarrow{j}_n - \overleftarrow{j}_n. \quad (26.44)$$

When assuming each of these currents to be Richardson-Dushman currents¹² at $x = \delta^+$, with

$$\overrightarrow{j}_n = en_c v_n^* \quad \text{and} \quad \overleftarrow{j}_n = en_j v_n^*, \quad (26.45)$$

one obtains a jump of n from $n(x = \delta^{+-}) = n_c$ at the metal side to $n(x = \delta^{++}) = n_j$ at the semiconductor side of the interface at $x = \delta^+$.

This *jump of the carrier density* at the interface, between the metal and the semiconductor is essential to be recognized for any discussion of such electrical contact. In recognizing this we obtain for the *net current through the interface*

$$j_n = ev^*(n_j - n_c). \quad (26.46)$$

With Eq. (26.46) we have now introduced a *modified boundary condition* for the electron density at the semiconductor side¹³ of this junction, $n_j(j_n)$ that is current-dependent.

26.5.3 Current–Voltage Characteristic in a Modified Schottky Barrier

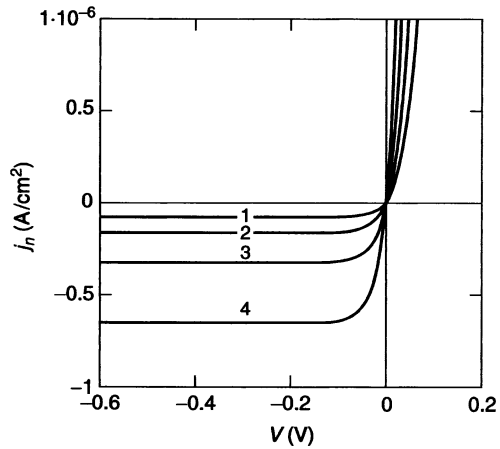
With the modified boundary condition [Eq. (26.46)] we now can calculate the current–voltage characteristics from Eq. (26.33) and, replacing $n(x = \delta^+)$ with n_j from Eq. (26.46); this yields

$$j_n = \frac{ev_n^* n_c \{ \exp[\frac{e(\psi_{n,D} - \psi_{n,j})}{kT}] - 1 \}}{1 - \frac{v_n^*}{\mu_n F_j}}. \quad (26.47)$$

¹²The formalism used here is similar to the one used to develop the expression for the diffusion currents inside a semiconductor with gradually varying carrier density. However, the rather abrupt (in less than a mean free path) change in carrier density at both sides of the surface interlayer justifies the use of the Richardson-Dushman electron emission relation here.

¹³We assume that n_c (at the metal side of the junction) remains constant and is given by Eq. (26.1).

Fig. 26.13 Diffusion-limited diode characteristics [Eq. (26.50)] with n_c as family parameter: curves 1–4 for $n_c = 12.6, 25, 50$, and $100 \cdot 10^4 \text{ cm}^{-3}$, respectively; $v^* = 4 \cdot 10^6 \text{ cm/s}$



The replacement of $\psi_{n,D} - \psi_{n,j}$ follows the same procedure used in Sect. 26.1.1, yielding again Eq. (26.39) which leads to the *modified Schottky diode equation*

$$j_n = \frac{ev_n^* n_c \left\{ \exp\left[\frac{eV}{kT}\right] - 1 \right\}}{1 + \frac{v_n^*}{|\mu_n F_j|}}. \quad (26.48)$$

For low fields ($|\mu_n F_j| \ll v^*$) in forward and low reverse bias, this equation reverts back to the *drift-limited Schottky diode equation*:

$$j_n = en_c \mu_n F_j \left\{ \exp\left[\frac{eV}{kT}\right] - 1 \right\}. \quad (26.49)$$

For high fields¹⁴ ($\mu_n F_j \gg v^*$), i.e., for sufficiently high reverse bias, Eq. (26.48) converts to the *diffusion-limited Schottky diode equation*:

$$j_n = en_c v_n^* \left\{ \exp\left[\frac{eV}{kT}\right] - 1 \right\}. \quad (26.50)$$

A family of such characteristics are given in Fig. 26.13 with n_c as family parameter. They show a simple exponential behavior with forward bias, but now with *perfect current saturation in reverse direction*. Such characteristic is commonly referred to as *ideal characteristics*.

The transition from the drift- to the diffusion-limited diode is determined by the denominator in Eq. (26.48). This denominator is of the form¹⁵ $1 + v/|\mu F|$, which

¹⁴This approach is mathematically correct; however, one should recognize that, even though the drift velocity is limited to approximately the rms velocity in bulk semiconductors (Böer 2002, Chap. 26) resulting in a factor 1/2 in Eq. (26.50), conditions at the thin boundary layer are more complex, and need detailed studies to also become physically appropriate.

¹⁵Here we have used a general velocity v and a general field to indicate the type of relationship rather than the specific one explained in this section.

is typical for the characteristics of Schottky-like barriers with current-dependent boundary conditions (see Sects. 26.2.1–26.4). It determines the shape of the characteristic, and $1/[1 + v/|\mu F|]$ shall therefore be called the *shape factor* (Böer 1985a, 1985b).

26.5.4 The Shape Factor

When introducing the shape factor

$$SF = \frac{1}{1 + \frac{v_n^*}{|\mu_n F_j|}}, \quad (26.51)$$

one can separate the classical diode equation from its modifying factor

$$j_n = j_s \left\{ \exp \left[\frac{eV}{kT} \right] - 1 \right\} SF. \quad (26.52)$$

One can also interpret this as the result of equalizing the current at the left and right sides of the metal/semiconductor interface. The current at the left side is emission-limited and determined by v^* . At the right side it is bias-dependent because of the drift component $\mu_n F_j$. As a result, the current is lowered from the ideal diode current by the shape factor ($SF, 1$).

The shape factor depends on several diode parameters, mostly contained in F_j . It modifies the characteristic from the ideal case, the more so, the smaller μ_n , V , N_d , and T and the larger ε and n_c . The shape factor is shown for N_d and n_c as family parameters in Fig. 26.14. It is of the order of one and approaches unity for large reverse bias.

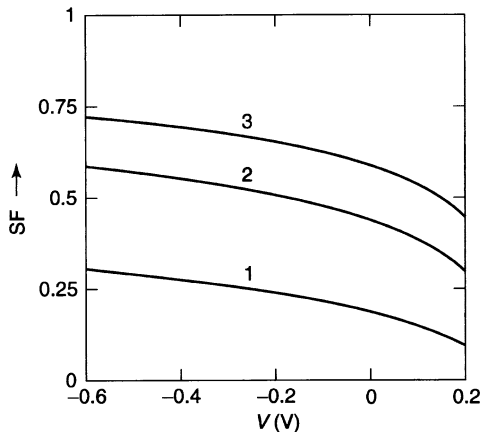
For further discussion, that will be helpful in later discussions of current–voltage characteristics, we will divide the characteristic into two ranges in which different transport mechanisms predominate, the *Boltzmann* and the *DRO range* that will be defined below.

26.5.5 Modified Boltzmann Range

The current within the Schottky barrier is composed of drift and diffusion currents, each of which exhibits a large maximum at one Debye length from the onset of the barrier.

For a sufficiently low bias, the drift and diffusion currents in most of the barrier are very large compared to the net current. In this part of the junction, the current

Fig. 26.14 Shape factor [Eq. (26.51)] as function of bias for N_d as main family parameter: curves 1–3 for $N_d = 10^{15}$ – 10^{16} , and $3 \cdot 10^{16} \text{ cm}^{-3}$; respectively $\mu_n = 100 \text{ cm}^2/\text{V s}$, $\varepsilon = 10$. F_j is computed from Eq. (26.34)



term in Eq. (26.33) can be neglected, and $n(x)$ becomes a simple exponential function of $\psi_n(x)$:

$$n(x) = n_c \exp \left[-\frac{e(\psi_n(x) - \psi_{n,D})}{kT} \right]. \quad (26.53)$$

This approximation is identical to the one applied in Sect. 26.1.1 with $n(x)$ following the *Boltzmann distribution*. This region is therefore called the *Boltzmann region*.

However, when calculating the *current*, the drift current-term in Eq. (26.33) can no longer be neglected near $x = 0$. Replacing $n(x = 0)$ with n_j from Eq. (26.46), as was done for deriving the characteristic [Eq. (26.47)], but here leaving the terms separated to identify their origin, one obtains

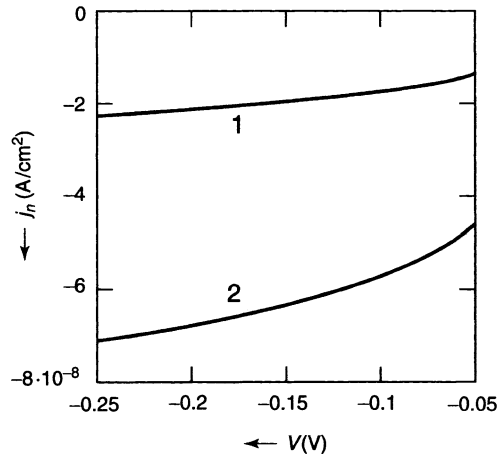
$$\frac{j_n}{ev_n^*} - n_c \left\{ \exp \left[\frac{e(\psi_{n,D} - \psi_{n,j})}{kT} \right] - 1 \right\} - \frac{j_n}{e\mu_n F_j}, \quad (26.54)$$

and recognizes that near $x = 0$ the drift current term on the right hand side [i.e., the current term in $n(x)$] remains important, even for low currents, as long as v^* is of the same order as, or larger than, the drift velocity $\mu_n F_j$. This drift current term in Eq. (26.54) influences the shape of the characteristic near zero bias and in the entire forward bias range, since here F_j is smallest. In order to emphasize this influence, we refer to this bias range as the *modified Boltzmann range*, and the resulting current–voltage characteristic as the *non-ideal characteristic*.

26.5.6 DRO-Range

A major deformation of $n(x)$ appears with *larger reverse bias* near $x = 0$, as shown in Figs. 26.7 and 26.8. When the drift current term on the right side of Eq. (26.54) becomes *dominant*, and carrier diffusion can be neglected. Here the net current is

Fig. 26.15 Square root branch of the characteristic, in a relatively small, limited bias range using Eq. (26.56) for the same parameters as in Fig. 26.14, except $n_c = 2 \cdot 10^6 \text{ cm}^{-3}$. The family parameters N_d for curves 1 and 2 are, 10^{15} , and 10^{17} cm^{-3} respectively



almost exclusively carried by drift in this region. We therefore identify this region in contrast to the Boltzmann region as the *DRO-region*, since it is controlled by DRift Only. When this region determines the current through the barrier, we call the corresponding bias range the *DRO-range*.

When with increased reverse bias ($-V \geq 2kT/e$) the exponential term in Eq. (26.54) can be neglected, and as long as $\mu_n F_j$ is small compared to v^* , the DRO-range determines the current, with

$$j_n = e\mu_n n_c F_j. \quad (26.55)$$

The bias dependence of j_n is obtained explicitly by introducing F_j from Eq. (26.41):

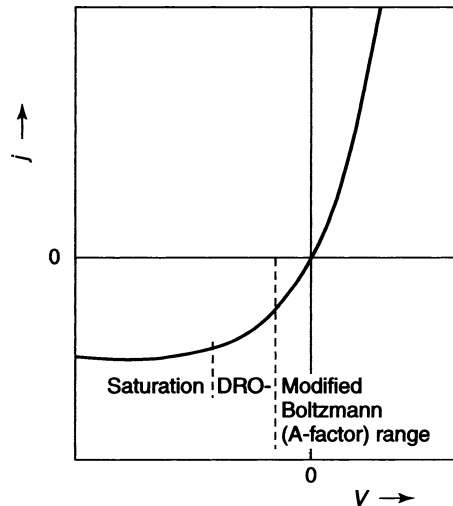
$$j_n = -e\mu_n n_c \sqrt{\frac{2eN_d(\psi_{n,D} - V_{\text{DRO}})}{\epsilon_{\text{st}}\epsilon_0}}, \quad (26.56)$$

yielding the typical *square-root dependence* of the reverse current on bias in this DRO-range.¹⁶ Nearly all of the voltage drop then occurs across in the DRO-region; hence $V \approx V_{\text{DRO}}$. The DRO-range of the current–voltage characteristics is the bias range between the modified Boltzmann range and the saturation range. In Fig. 26.15 the square root behavior in this range is shown with the donor density as family parameter. It shows an increase of the reverse current and an *increase of the slope* with increasing N_d for a given n_c . This is typical for a change in space charge within the DRO-range.

With some caution, this can be used to *determine the density of depleted donors* N_d as long as the other parameters of this Eq. (26.56) (namely ϵ_{st} , μ_n and n_c) are known. Or, inversely if N_d is better estimated from other information, one can use this range to verify n_c and hence obtain more information about the *work function*.

¹⁶Therefore this range is also referred to as the *square root range*.

Fig. 26.16 Typical non-ideal diode characteristic with the characteristic saturation, DRO, and Boltzmann ranges identified (schematically plotted)



This fact should be remembered as a tool for barrier material analysis, rather than simply as an interesting mathematical clarification.

The DRO-region can be identified by carefully viewing the semilogarithmic plot of $n(x)$, since in this region n decreases only hyperbolically¹⁷ with decreasing x (see Figs. 26.5a, 26.7 and 26.8). The identification of the DRO-range in a current–voltage characteristic is more difficult, since the square-root dependence of the DRO-region joins smoothly with current saturation at larger reverse bias when the drift velocity at $x = 0$ approaches v^* ; consequently, the shape factor then approaches unity.

Figure 26.16 summarizes the different ranges of a typical Schottky diode characteristic. It contains in small reverse and in forward bias the modified Boltzmann range, with larger reverse bias the DRO-range, and finally at high reverse bias the saturation range.¹⁸

26.5.7 Electrostatic and Electrochemical Potentials in a Schottky Barrier

The electrostatic electron potential distribution is parabolic, reaches the diffusion potential $\psi_{n,D}$ for vanishing current, and increases (decreases) with reverse (forward) bias according to Eq. (26.14).

¹⁷Since $F(x)$ increases linearly with decreasing x , the product $n(x)F(x)$ must remain constant in the DRO-range; namely $nF = j_n/e\mu_n$ and $j_n = j = \text{const.}$

¹⁸We neglect here pre-breakdown effects which cause a steep increase of the current at still higher reverse bias.

The electrochemical potential, however, is flat for $j_n = 0$ (i.e. in thermodynamic equilibrium) but it becomes tilted¹⁹ with non vanishing currents in the bulk and in the Boltzmann region. With increased reverse bias, the electrochemical potential bends away in the DRO-region from the rather flat range and obtains a nearly constant slope, and remains almost parallel to $E_c(x)$, since here n decreases only hyperbolically with decreasing x , causing comparatively little change in $E_c - E_F$.

The applied voltage $V = \psi_n, D - \psi_n, j$ across a Schottky barrier device drops mostly in the region adjacent to the metal/semiconductor interface (see Fig. 26.5E). With sufficient reverse bias, almost the entire bias drops in the DRO-range (see Fig. 26.10). This becomes important in later discussions when higher bias cases are analysed since most *carrier heating occurs only in the DRO-region*. The description of the potentials will later (Sect. 27.3) be extended when two carriers are considered, and a split of the Fermi level into two quasi-Fermi levels is discussed.

¹⁹This tilting is too small to be visible in Fig. 26.6.

Chapter 27

Minority Carriers in Barriers

Abstract Minority carriers play an important role when generation and recombination is important for steady state $n(x)$, when minority carriers influence space charges with bias; when minor carrier densities and their cross over occur in junctions. Carrier generation and recombination is discussed. Thermal excitation is evaluated. Capture cross sections are defined. Field ionization is introduced, with the Frenkel Poole effect at lowest fields. Impact ionization and tunneling are evaluated at higher fields. Trapping and recombination is distinguished. Electron and hole traps. Recombination centers. Quasi Fermi levels and demarcation lines are introduced. Thermal equilibrium and steady state are distinguished. Zero current solutions in equilibrium. Non-vanishing currents in steady state. It is shown that the minority current limits the recombination. Current continuity is identified. The carrier lifetime is defined. Large generation optical excitation is evaluated.

Minority carriers have a significant influence on the carrier transport through space-charge regions when these carriers are created by light, or are present in sufficient concentration as, e.g., in the neighborhood of inversion layers or within pn -junctions. Minority carrier currents of technical interest are predominantly diffusion currents. These currents are in competition with recombination currents at device surfaces or interfaces. In the discussions of the previous chapters we have neglected the influence of minority carriers. This is justified when throughout the entire device the Fermi level remains well above the midpoint of the band gap (for electrons as majority carriers) and there are no excitation mechanisms active to generate electron-hole pairs with a significant rate, specifically, when there is no optical excitation.

We will now extend this discussion to include examples where minority carriers play an important role. These include

- the influence of generation and recombination on the steady state carrier distribution;
- the influence of minority carriers on the space-charge variation

with an applied bias;

- the additive current of minority carriers in junction devices;

- the continuity condition for minority and majority currents, and their crossover in junctions.

The discussion presented in this chapter will provide the groundwork for the inclusion of minority carriers into a more comprehensive model of the carrier transport through space-charge layers.

We will first briefly summarize carrier generation and recombination and then introduce demarcation lines to distinguish between carrier trapping and recombination, and quasi-Fermi levels to conveniently describe steady state carrier distributions.

We finally will analyze carrier lifetimes and their use in describing steady state relations.

We will then analyze the current contribution of minority carriers, while interacting with majority carriers.

27.1 Carrier Generation and Recombination

Carriers are redistributed over conducting (bands) and nonconducting (levels in the band gap) states via generation and recombination mechanisms. They are also influenced by local currents from the surrounding of each volumen element¹

$$\frac{\partial n}{\partial t} = g - \frac{n}{\tau_{n0}} + \frac{1}{e} \operatorname{div} j_n. \quad (27.1)$$

Carrier generation needs a supply of energy; one consequently distinguishes thermal, optical or field-induced generation. It can originate from localized or non localized states and proceed into localized or non localized states.

*Carrier recombination*² is the opposite transition and occurs mostly with a transition from a non localized state into a localized state; it sets free energy as thermal energy or as luminescence.

Local currents follow the changes in carrier distribution from thermal equilibrium caused by a bias across space-charge regions, or by optical, or field excitation.

In Fig. 27.1 a number of typical transitions are shown between a variety of such states. For consistency in the following description we will only identify electron transitions; hole transitions proceed in the opposite direction. The transition coefficients c_{ik} are unambiguously defined by the first index indicating the originating state and the second index indicating the final state. In order to facilitate comprehension we have identified transition coefficients for ‘excitation transition as e_{ik} to set them apart from recombination or ‘capture transitions as c_{ik} .

¹The following analogy may help to remember the formula: the change in population is given by the birth rate (g) minus death rate (= population over life expectancy) plus the drop-off from travelers through the region (change in current multiplied by $-1/e$).

²We are using here the term recombination somewhat loosely before defining the distinction between trapping and recombination in Sect. 27.1.3.

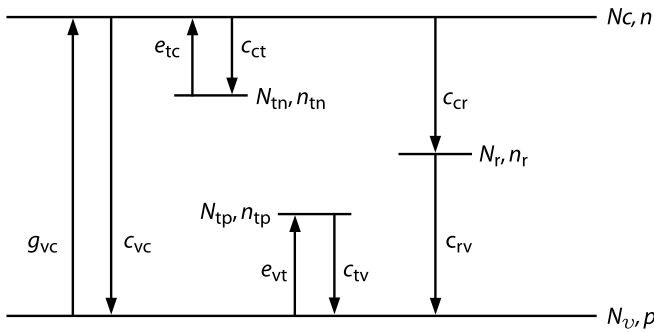


Fig. 27.1 Electron transitions between localized (in band gap) and non localized states (bands)

The transition rate R_{ik} is defined as the product of the electron density in the originating state, the hole density in the final state, and the transition coefficient:

$$R_{12} = c_{12}n_1p_2, \quad (27.2)$$

with the transition rate measured in $\text{cm}^{-3} \text{s}^{-1}$. As an example, the capture of an electron from the conduction band (n —following the convention, we have left off the index c here) into an electron-trap is given by

$$R_{tc} = c_{ct}n(N_t - n_t) \quad (27.3)$$

with N_t and n_t as the densities of electron traps and of captured electrons in these traps, respectively.³

The transition coefficients c_{ik} or e_{ik} have the dimension $\text{cm}^3 \text{s}^{-1}$; the product of such a coefficient with the electron or hole density in the final state, for instance $c_{ik}p_k$, is the transition probability, which has the dimension s^{-1} .

The different excitation mechanisms to populate higher energy states will now be briefly reviewed.

27.1.1 Thermal Excitation

Thermal excitation probabilities can be obtained from thermodynamic arguments. Transition between two levels (or a level and a band) always come in pairs, as a transition into the level and a transition out of this level.

In thermal equilibrium they must be equal to each other. This *detailed balance principle* applied to an electron-trap yields (see Fig. 27.1)

$$e_{tc}n_tp_c = c_{ct}n(N_t - n_t). \quad (27.4)$$

³Capital letters are consistently used to identify the density of states, lower case letters to identify the density of electrons or holes in these states.

This equation can be used to obtain an explicit expression for e_{tc} : in thermal equilibrium the population of these traps is 1/2 when the Fermi level coincides with the energy of the trap level; thus, with $(N_t - n_t)/n_t = 1$, and for the non-degenerate case in which essentially all conduction band states are empty, $p_c \cong N_c$, one obtains

$$e_{tc}N_c = c_{tc}n \quad (27.5)$$

or, when using Eq. (27.4) and $E_F = E_t$:

$$e_{tc}N_c = c_{tc}N_c \exp\left(-\frac{E_c - E_t}{kT}\right), \quad (27.6)$$

yielding for the ratio of emission-to-capture coefficient

$$\frac{e_{tc}}{c_{ct}} = \exp\left(-\frac{E_c - E_t}{kT}\right). \quad (27.7)$$

Even though this condition was obtained for a specific case, namely thermal equilibrium, this ratio holds true in general, since both coefficients are constants and do not change with trap population. One obtains therefore for the *thermal excitation coefficient* (or thermal emission coefficient)

$$\boxed{e_{tc} = s_n v_{rms} \exp\left(-\frac{E_c - E_t}{kT}\right)}, \quad (27.8)$$

using $c_{ct} = s_n v_{rms}$, i.e. the *capture coefficient* as the product of capture cross section and rms velocity of the electron. The thermal excitation is consequently determined by *two parameters*: the *energy* of the level and its *capture cross section*. The *population of this center in thermal equilibrium*, however, is determined by its *energy alone*. The attainment of this equilibrium (i.e., the time it takes to follow changes in excitation), or the change in population to obtain steady state, e.g., after changes of external excitation, is determined also by its kinetic parameters c_{ct} and e_{tc} . These changes may take long times (*frozen-in equilibria*) and need to be carefully considered for deeper centers.

27.1.2 Optical Excitation

We will briefly summarize here only those aspects of the optical excitation which are commonly used to create free electrons and holes, and thereby increase the density of minority carriers and of majority carriers in photoconductors. Such optical excitation typically involves band-to-band transitions. The optical absorption coefficient $\alpha_o(\lambda)$ near the band edge of direct band gap semiconductors⁴ is on the order

⁴In corresponding photon energy ranges of indirect band gap semiconductors, the absorption coefficient is roughly three orders of magnitude smaller.

of 10^5 cm^{-1} ; i.e., light is substantially absorbed in a layer of $1000 \text{ \AA}$ thickness. The flux φ of photons of a certain wavelength λ inside a solid is given by

$$\varphi(\lambda, x) = \varphi_0(\lambda) \exp[-\alpha_o(\lambda)x], \quad (27.9)$$

where $\varphi_0(\lambda)$ is the photon flux per unit wavelength ($\Delta\lambda$) that penetrates through the top layer⁵ of the solid and is given in $\text{cm}^{-2} \text{ s}^{-1} \Delta\lambda^{-1}$.

When polychromatic light is used, the total photon flux as a function of the penetration depth x is obtained by integration:

$$\varphi(x) = \int_{\lambda_1}^{\lambda_2} \varphi_\lambda(\lambda, x) d\lambda, \quad (27.10)$$

with φ in $\text{cm}^{-2} \text{ s}^{-1}$.

The optical generation rate $g_o(x)$ is given by the absorbed light in each slab of infinitesimal thickness; thus

$$g_o(x) = -\frac{d\varphi(x)}{dx}. \quad (27.11)$$

For monochromatic light (λ_0), the optical generation rate depends exponentially on x :

$$g_o(x, \lambda_0) = \alpha_o(\lambda_0) \varphi_0(\lambda_0) \Delta\lambda \exp[-\alpha_o(\lambda_0)x] \quad (27.12)$$

with $\Delta\lambda$ a small wavelength range in which $\alpha_o(\lambda)$ is constant.

For polychromatic excitation, a constant (space-independent) generation rate is often a sufficient approximation: even though φ_λ depends exponentially on the penetration depth, $\varphi(x)$ usually does not, since, with polychromatic light of various absorption coefficients $\alpha_o(\lambda)$, the superposition of a wide variety of such exponential functions causes a substantially lesser-than-exponential dependence of φ on x .

For excitation with sunlight, as used in solar cell application, a wide spectrum of active light is employed and for indirect band gap material one often uses as a reasonable approximation an average generation rate (Böer 1977):

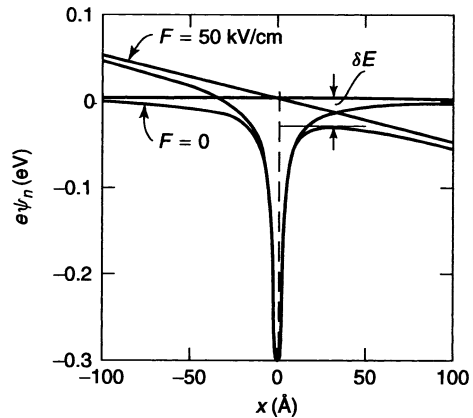
$$g_o = g \text{ cm}^{-3} \text{ s}^{-1}. \quad (27.13)$$

Such average generation rates for AM 1 sunlight⁶ and 1 eV bandgap semiconductors are typically on the order of 10^{21} for indirect band gap materials. For direct band gap materials where the exponential distribution needs to be considered, under certain condition and average generation rate close to the surface of $10^{23} \text{ cm}^{-3} \text{ s}^{-1}$ is often used. For more specific information on sunlight excitation see (Böer 2002).

⁵After reflection is subtracted.

⁶AM 1 stand for air mass 1 and indicates the optical absorption by an air column when the sun stands at the zenith. In total power, this absorption amounts to 26.6 %, namely from 140 mW/cm^2 above the earth's atmosphere to 100 mW/cm^2 at AM 1. With decreased elevation φ the light path through the atmosphere becomes longer as $1/\cos(90^\circ - \varphi)$ which is used as the corresponding air mass value. E.g., for $\varphi = 42^\circ$ one has sunlight of AM 1.5, a value often use as more realistic for solar cell calibration in solar simulators.

Fig. 27.2 Lowering of the electron binding energy of a Coulomb-attractive center by $\delta e \cong 30$ mV with an external electric field of 50 kV/cm and a distance of 35 Å from the funnel center of the barrier maximum over which the electron can leak out in field direction (Frenkel-Poole effect), as computed for $\varepsilon = 10$ and $F = 50$ kV/cm



27.1.3 Field Ionization

The three major field ionization mechanisms—Frenkel-Poole, impact, and tunnel ionizations—all produce free carriers, predominantly by inducing bound-to-free transitions. Band-to-band transitions require substantially higher fields which are not present in normal space charge regions, except for tunneling junctions that are specifically designed for that purpose. Field-ionization is thereby distinguished from optical generation of both types of carriers; it does not generate pairs of mobile carriers as a primary process.

In conjunction with other generation mechanisms, however, field ionization can interfere and thereby shift the population of carriers in defect centers with an applied bias. This, in turn, can influence recombination traffic and space-charge distributions. Field-enhanced deep donor depletion and field quenching (Sect. 26.3.3) are two examples for such important field-induced changes that were already mentioned. We will therefore here briefly summarize the most important relations for field ionization.

As indicated earlier, the *Frenkel-Poole effect* (Frenkel 1938; Poole 1921) needs by far the lowest field⁷ for ionizing Coulomb-attractive centers. Such ionization is achieved by tilting the bands and thereby lowering the energy of such a center at which thermal ionization becomes possible (see Fig. 27.2).

The potential barrier lowering can be described by superimposing the Coulomb potential with an external field:

$$\psi^n(x) = eZ/(4\pi\varepsilon\varepsilon_0) - Fx \quad (27.14)$$

⁷Except for high mobility semiconductors at low temperatures where impact ionization competes favorably.

with Z the charge of the defect. The barrier lowering as shown in Fig. 27.2 can then be expressed as 0

$$\delta E = e \sqrt{\frac{e F Z}{\pi \epsilon \epsilon_0}} = 2.4 \cdot 10^{-4} \sqrt{F \text{ (V/cm)}} \sqrt{\frac{10}{\epsilon}} Z. \quad (27.15)$$

This lowering is equal to kT for a field of

$$F_{kT} = 1.165 \epsilon Z \text{ (kV/cm)} \quad (27.16)$$

which is on the order of 10 kV/cm for typical semiconductors. The Frenkel-Poole effect causes an enhancement of the thermal ionization which may be approximated by an increase of the thermal ionization coefficient

$$e_{tc} = s_n v_{rms} \exp\left(-\frac{E_c - E_t - \delta E}{kT}\right) \text{ (s)}. \quad (27.17)$$

Impact ionization occurs when, between scattering events, the carriers can accumulate sufficient energy from an external field to markedly change their energy distribution, and become “heated”. Fast electrons in this distribution, when colliding with a defect center, may transfer sufficient energy to free a trapped carrier from the center.

The ionization rate per unit path length⁸ due to impact ionization can be approximated as

$$\alpha_i = C \exp\left[-\frac{B(E_c - E_t)}{F^2}\right] \text{ (cm}^{-1}\text{)} \quad (27.18)$$

with C a constant on the order of 1, $B \cong 4\hbar\omega_{LO}/(e^2\lambda_e^2)$, ω_{LO} the longitudinal optical phonon frequency, and λ_e the carrier mean free path (Wolfe 1954).

Tunneling occurs at very high fields, usually across thin insulating layers (typically on the order of 10^6 V/cm) The transmission probability of a one-dimensional rectangular barrier of height V_0 and thickness d (in Å) is given by

$$\begin{aligned} T_t &\simeq 16 \frac{E}{eV_0} \exp\left\{-d \sqrt{\frac{2m_n}{\hbar^2}}(eV_0 - E)\right\} \\ &\simeq 16 \frac{E}{eV_0} \exp\left\{-0.512d \text{ (Å)} \sqrt{(eV_0 - E) \frac{m_n}{m_0}}\right\} \end{aligned} \quad (27.19)$$

where E is the average electron energy, e.g., kT , for thermal electrons.

In an electric field the barrier becomes triangular and the transition probability can be estimated from

$$T_{i\Delta} \simeq \tilde{C} \exp\left\{-\frac{4}{3} \sqrt{\frac{2m}{\hbar^2}} \frac{\Delta E^{3/2}}{eF}\right\} \simeq \tilde{C} \exp\left\{-6.8 \cdot 10^7 \frac{[\Delta E \text{ (V)}]^{3/2}}{F \text{ (V/cm)}}\right\} \quad (27.20)$$

with a pre-exponential C about the same magnitude as in Eq. (27.19). For a review see, e.g., Wolf (1975a).

⁸With increased path length in an electric field more energy is accumulated. The ionization rate per unit path length is measured in cm^{-1} .

Fig. 27.3 Various possible transitions from and to a localized state

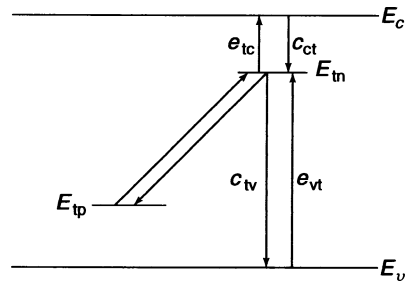
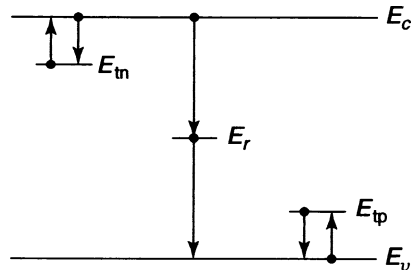


Fig. 27.4 Electron and hole traps at energies E_{tn} and E_{tp} close to the respective bands and recombination centers at an energy E_r closer to the center of the gap



27.2 Trapping and Recombination

In the previous sections we have identified the transitions that require absorption of energy. The inverse transitions that generate energy (e.g., heat or luminescence), shown in Fig. 27.1, are referred to as either trapping or recombination transitions; a differentiation between the two will be discussed in the following section.

27.2.1 Electron and Hole Traps

There are numerous transitions possible between any center and other states. All such transitions can be described by their corresponding rates. These rates are additive and describe the change in population of this center. For example, the change of the electron density in an electron trap can be influenced in four ways: by ionization into, and electron capture from, the conduction band; by recombination with holes from the valence band; and by an electron transfer to another localized state of a nearby defect to which such a transition is sufficiently probable.

For reason of *detailed balance*, in each pair of transitions shown in Fig. 27.3, the excitation transition must be equal to the recombination in thermal equilibrium. Usually their magnitude varies from pair to pair over a wide range; e.g., thermal excitation of an electron from the more distant valence band into the electron trap is much less probable than thermal excitation of a trapped electron into the closer conduction band. Therefore, one can usually neglect all pairs of transitions compared to the pair interacting with the nearest band.

With external excitation, or a shift in the carrier distribution by an applied bias, this is no longer necessary. In *steady state* the total net influx to the center must now equal the net out flux, in order to maintain a constant trap population. Again, with a variation of transition coefficients over many orders of magnitude, one can pick two transitions which are near equal to each other, here, however not necessarily connecting the center to the same band. This identifies different classes of such centers according to the kind of predominant transition.

When the predominant pair of transitions communicates with the same band as, e.g., through e_{tc} and c_{ct} the center is identified as a *trap*. Customarily, traps close to the conduction band are identified as *electron traps* and traps close to the valence band as *hole traps*.

27.2.2 Recombination Centers

When the predominant transitions communicate between two bands as, e.g., through c_{ct} and c_{tv} , the center is called a *recombination center* (Fig. 27.4). Recombination centers usually lie closer to the middle of the band gap and communicate readily with both bands since it is easier for a captured electron to recombine with a hole in the valence band than to be thermally reemitted into the conduction band. It is expected that such recombination centers are only activated when sufficient holes are available, e.g., with optical excitation or in certain regions of a junction with an external bias. We will analyze this relation in the following section.

27.3 Quasi-Fermi Levels, Demarcation Lines

With external means, e.g., light or bias, the electron distribution over levels and bands is changed from the thermodynamic equilibrium distribution. Given sufficient time, the changed distribution becomes stationary, *steady state* is achieved. This new electron distribution near the band edges can again be approximated by a Fermi-type distribution, however, replacing the Fermi level with two *quasi-Fermi levels*, one for electrons E_{Fn} and one for holes E_{Fp} . The measured electron density in the conduction band can now be used to define E_{Fn} via:⁹

$$n \simeq N_c \frac{1}{1 + \exp(\frac{E_c - E_{Fn}}{kT})}; \quad (27.21)$$

the hole density in the valence band defines E_{Fp} via:

$$p \simeq N_v \frac{1}{1 + \exp(\frac{E_{Fp} - E_v}{kT})}. \quad (27.22)$$

⁹The exact relation contains the Fermi integrals $F_{1/2}$ (see Böer 2000). The approximation only holds for the non-degenerate case, i.e., for $E_c - E_{Fn} > kT$.

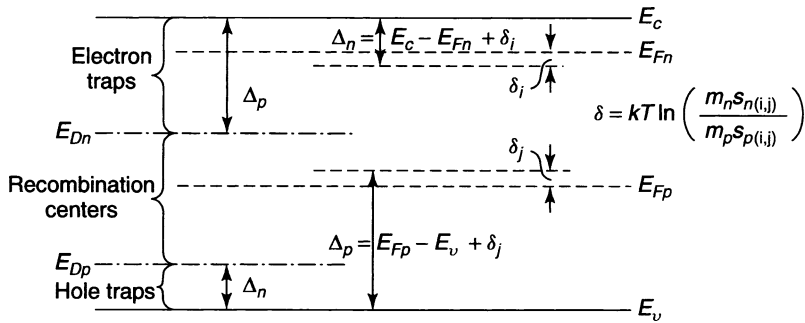


Fig. 27.5 Band-model with quasi-Fermi levels and demarcation lines for one kind of electron traps (with capture cross sections for electrons and holes s_{ni} , s_{pi}) and a corresponding kind of hole traps (with s_{nj} , s_{pj})

With external excitation, n and p will both be larger than the equilibrium densities, hence E_F will be split into E_{Fn} and E_{Fp} with¹⁰

$$E_{Fp} < E_F < E_{Fn}. \quad (27.23)$$

With intrinsic ($h\nu > E_g$) optical excitation, electrons and holes are generated in equal rates. The increase of the steady state carrier densities above the thermal equilibrium densities in typical semiconductors¹¹ is usually only a small fraction for majority carriers, while it is very large for minority carriers. Therefore, most semiconductors show only a slight split of the majority quasi-Fermi level from E_F , while the minority quasi-Fermi level is changed substantially.

We will now analyze the relative strength of the various transitions for a level in the band gap. With external excitation, the changing occupation of the level and bands causes the transition rates to change, making for deeper levels the recombination transitions more probable than the reemission into the adjacent bands. Since that reemission depends exponentially on the energy difference between the level and the nearest band edge, one can now define a *demarcation line* between traps and recombination centers by the condition that the transition rates of electrons from this center to the two bands become equal to each other. For example for electron traps one can compare the excitation rate into the conduction band with the recombination transition into the valence band and require:

$$n_t e_{tc} N_c = n_t c_{tv} p. \quad (27.24)$$

Using Eq. (27.8) for e_{tc} and Eq. (27.22) for p , one obtains the condition that defines the *electron demarcation line* when setting $E_t = E_{Dn}$ for this specific trap level that fulfills Eq. (27.24). This yields

$$E_c - E_{Dn} = E_{Fp} - E_v + \delta_i \quad (27.25)$$

¹⁰The inequality of Eq. (27.23) holds for optical excitation but not for shifted distribution in pn -junctions in reverse bias (see Sect. 31.2).

¹¹In good photoconductors, however, the majority quasi-Fermi level is also substantially changed.

with

$$\delta_i = kT \ln \left[\frac{m_n s_n}{m_p s_p} \right]. \quad (27.26)$$

The demarcation line for electrons defines the energy that separates electron traps above and recombination centers below E_{Dn} . The reference to a *hole* quasi-Fermi level for determining the *electron* demarcation line is understandably confusing at first, but it is based on the fact that the recombination path which competes with thermal ionization depends on the availability of free holes which in turn relates to E_{Fp} . A look at Fig. 27.5 helps to clarify this dependency: the distance of the demarcation line for electrons from the conduction band is the same as the distance of the quasi-Fermi energy for holes from the valence band plus a corrective energy δ_i , which is logarithmically related to the ratio of capture cross sections for electrons and for holes of this center and their effective masses.

A similar relationship holds for the *hole demarcation line*:

$$E_{Dp} - E_v = E_c - E_{Fn} + \delta_j \quad (27.27)$$

(see Fig. 27.5). Neglecting the influence of the correction terms¹² δ_i and δ_j , the anti-symmetric relation of the quasi-Fermi and demarcation lines is obvious: for *n*-type material with a comparatively narrow $E_c - E_{Fn}$ range, there is a wide range of electron traps and a narrow range of hole traps (and vice versa).

27.3.1 Thermal Equilibrium and Steady State

Thermodynamic (thermal) equilibrium is present when a semiconductor is kept at constant temperature without any outside bias or excitation for a sufficient length of time. Deviations from thermal equilibrium can occur because of non thermal excitation by light or electrical field, or by a shift of the carrier distribution in junctions with non vanishing currents. When such deviations occur, and have become stationary, a steady state non equilibrium is reached. We will first discuss the thermal equilibrium condition in more detail.

The shifts δ_i and δ_j in Fig. 27.5 have been chosen accordingly. Other charge characters are possible, such as for Coulomb-repulsive centers, which have capture cross sections of $\approx 10^{-20}$ to 10^{-22} cm². Tightly bound centers usually provide relatively small cross sections (typically 10^{-18} cm² or below for centers with deep relaxation—see Böer 2000). Since the capture cross section may vary from center

¹²For estimating δ_i and δ_j , one needs to know the center's cross section, which may be estimated from the center's charge and bonding character. For example, a center that is neutral without an electron in it has a cross section for an electron on the order of 10^{-16} cm². After it has captured the electron it is negatively charged; thus its capture cross section for a hole has increased to $\approx 10^{-14}$ cm². For this example, $s_n/s_p \cong 10^{-2}$ and $\delta_j \cong -0.12$ eV will be used. For hole traps the charge character may turn from neutral to positive after hole capture, making $s_n/s_p \cong 100$ and $\delta_j \cong +0.12$ eV.

to center from $\approx 10^{-13}$ to $\approx 10^{-22}$ cm², δ_i varies for these different centers by as much as ≈ 0.5 eV; hence the demarcation lines of these centers are spread over a wide range within the band gap. Therefore it is not customary to plot demarcation lines of all possible centers, but, if at all only those demarcation lines are shown that provide the most important transitions in the given device model.

27.3.2 Zero Net-Current, Thermal Equilibrium

In thermal equilibrium, electrons and holes are generated by thermal ionization only. *The same amount of carriers generated in any volume element must recombine in the same volume element.* There is no net transport of carriers, except for statistical fluctuations.

When a space-charge region is introduced, the densities of carriers changes from their bulk value. The balance between generation and recombination, however, is still maintained throughout the bulk and in the entire space-charge region as long as there is no external force, e.g., there is no bias applied. The net¹³ electron and hole currents in each volume element are individually zero; aside from fluctuations, electrons or holes are not brought in or carried away from any volume element. *With vanishing bias, thermal equilibrium is maintained throughout the space-charge region.*

For thermal equilibrium the carrier distribution is given by one Fermi level E_F . Consequently, when using $E_{Fn} = E_{Fp} = E_F$ in Eqs. (27.25) and (27.27) the resulting demarcation lines also coincide: $E_{Dn} = E_{Dp} = E_D$, i.e., causing electron and hole traps to join borders with each other with no recombination center range existing in between.

In thermal equilibrium an important relation between n and p can be derived for non-degenerate semiconductors. From $n = N_c \exp[-(E_c - E_F)/(kT)]$ and $p = N_v \exp[-(E_F - E_v)/(kT)]$, one obtains:¹⁴

$$n_0 p_0 = N_v N_c \exp\left(-\frac{E_c - E_v}{kT}\right) = n_i^2. \quad (27.28)$$

This condition permits the calculation of $p_0(x)$ throughout a device *in thermal equilibrium* if $n_0(x)$ is known, since n_i , the *intrinsic carrier density*, is a constant given by the band gap and temperature alone.

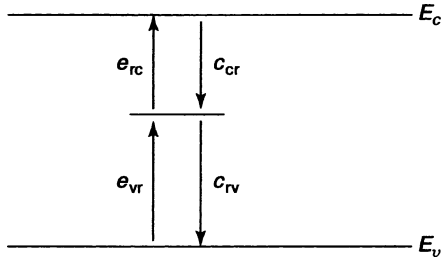
27.3.3 Non-vanishing Current, Steady State

When a bias is applied, the flow of a net current results. The carrier density distribution is deformed from equilibrium; now carriers generated in one volume element

¹³A diffusion current of each carrier is exactly compensated by an opposing drift current.

¹⁴In order to emphasize the equilibrium values of n and p , we have attached a subscript zero.

Fig. 27.6 Shockley-Read-Hall center with all transitions to both bands



are moved to another one by the current before they recombine. In forward bias this results in a carrier surplus, while in reverse bias it results in a carrier depletion within a Schottky barrier.

The balance between the two transitions of a center to its adjacent band is disturbed, and a net generation or recombination through such centers results.

As a consequence the *Fermi level splits into two quasi-Fermi levels* and the two demarcation lines separate; hence some levels which acted as traps before will now act as recombination centers.

When changing the bias, this distribution changes. One, therefore, needs to include all four transitions to the two bands for deeper centers that may become recombination centers (Fig. 27.6).¹⁵ These centers are called Schottky-Read-Hall centers. The net traffic through these centers is conventionally identified as U , given by

$$U = \frac{c_{cr}c_{rv}N_r(np - n_i^2)}{c_{rc}[n + n_i \exp(\frac{E_r - E_i}{kT})] + c_{rv}[p + n_i \exp(\frac{E_i - E_r}{kT})]} \quad (27.29)$$

or

$$U = \frac{c_{cr}c_{rv}N_r(np - n_i^2)}{c_{cr}(n + n_i^+) + c_{rv}(p + n_i^-)} \quad (27.30)$$

with

$$n_i^\pm = \exp\left(\pm \frac{E_r - E_i}{kT}\right) \quad (27.31)$$

and the intrinsic energy level, E_i

$$E_i = \frac{E_c - E_v}{2} + \frac{kT}{2} \ln\left(\frac{N_v}{N_e}\right). \quad (27.32)$$

This equation is representative for the sequential nature of the re-combination through a recombination center: an electron from the conduction band *and* a hole from the valence band must both find their way to the recombination center; the equation for the net recombination traffic [Eq. (27.30)] is therefore of the type $(1/n + 1/p) - 1$.

¹⁵Since these centers are more important when they become recombination centers, they are identified here with the subscript r .

Thus, only when both carrier densities are high, is the recombination traffic large; *the minority carrier limits the recombination*. This will be of importance in *pn*-junctions, where only in the inner part of the junction region both densities are on the same order of magnitude, causing a substantially higher recombination here than in the adjacent bulk regions (see Sect. 27.4 and Fig. 27.9).

From Eq. (27.29) one confirms also that U vanishes for thermal equilibrium; i.e., for $np = n^2$ U represents a *net thermal generation* when, with reverse bias, the np product in the space charge region has decreased below its equilibrium value¹⁶ n^2 . A *net recombination* through the center occurs when with forward bias¹⁷ the np -product exceeds n^2 .

A simplified relation is occasionally used, assuming a center with equal capture coefficients¹⁸ for electrons and holes ($c_{cr} = c_{rv} = c$). Equation (27.29) can then be reduced to

$$U = \frac{cN_r(np - n_i^2)}{n + p + 2n_i \cosh(\frac{E_r - E_i}{kT})}. \quad (27.33)$$

27.3.4 Current Continuity

The difference between generation and recombination is carried as an increment to the current (Fig. 27.7a). For example one obtains for the change of the incremental¹⁹ electron current

$$\frac{d\delta j_n}{dx} = -eU = -e(g - r) \quad (27.34)$$

and consequently for the change of the incremental hole current

$$\frac{d\delta j_p}{dx} = eU = e(g - r); \quad (27.35)$$

with the *total incremental current* to remain constant,

$$\frac{d\delta j}{dx} = \frac{d(\delta j_n + \delta j_p)}{dx} \equiv 0, \quad (27.36)$$

Figure 27.7b shows the contributions of the incremental hole and electron currents, which are complementary to each other, to the total current.

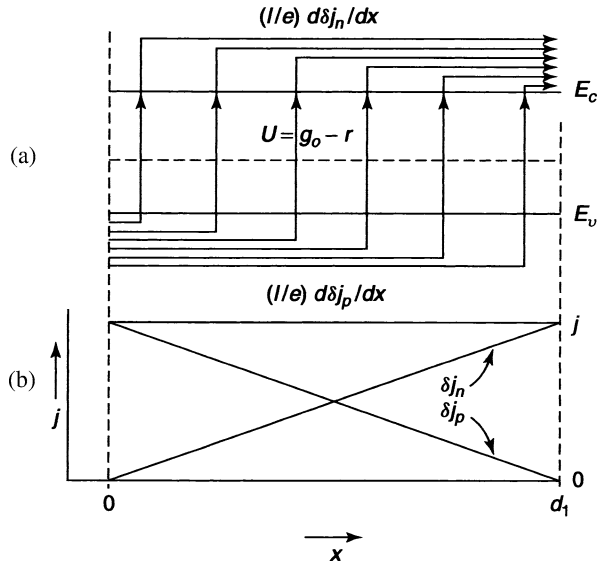
¹⁶Here both $n(x)$ and $p(x)$ have decreased below the equilibrium distribution, while the space charge region has widened.

¹⁷Here both $n(x)$ and $p(x)$ have increased above the equilibrium values.

¹⁸This assumption is not a very realistic one since the charge character of the center changes when capturing a carrier (see Sect. 27.2.2). However, the qualitative behavior deduced from Eq. (27.33) will remain valid.

¹⁹We are using here the notation of an incremental current since in some of the devices only a fraction of the total electron or hole current is influenced, as will be described below.

Fig. 27.7 Current generation with bias in a homogeneous region of $r < g_o$ (g_o = optical excitation is assumed here) with resulting positive electron current increment.
 (a) Band-model;
 (b) incremental current distribution



The figure gives a simple example of a constant, net generation rate U , which can be realized by a uniform optical carrier generation within a homogeneous semiconductor and a sufficient lifetime to render the diffusion length long compared to the width of the device. In the given example the electron current then increases linearly from $x = 0$ to $x = d_1$ while the hole current decreases with the same rate: the incremental current changes from a hole current at the left side to an electron current at the right side of the semiconductor. This crossover and the current continuity is indicated in the band-model of Fig. 27.7a.

In most semiconductors, and at normal optical excitation rates, the majority carrier density is changed only to a small fraction from its equilibrium value. This means that the incremental currents as shown in Fig. 27.7 and given by

$$\delta j = \delta j_n(x_i) + \delta j_p(x_i) \quad \text{at any } 0 < x_i < d_1 \quad (27.37)$$

have to be added to the divergence-free majority carrier current j_{ni} (see Fig. 27.8). In this figure we have also included for completeness a small equilibrium minority carrier current j_{pi} as a divergence-free contribution. The total current is then given by

$$j = j_{ni} + j_{pi} + \delta j = e\mu_n n_0 F + e\mu_p p_0 F + \delta j \quad (27.38)$$

with n_0 and p_0 as the carrier densities in equilibrium in a homogeneous semiconductor.²⁰

The generation/recombination (gr-) contribution which can be dealt with in the fashion given here only for narrow devices [with $d_1 < (L_n, L_p)$], however, becomes

²⁰In an inhomogeneous semiconductor, the determination of the divergence-free electron or hole current is a bit more involved.

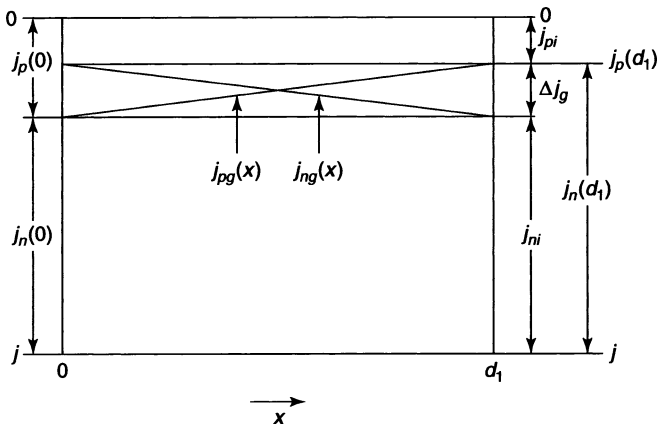


Fig. 27.8 Schematic of current distribution; generation/recombination currents are assumed for a homogeneous optical excitation and therefore are simple linear functions of x . The divergence-free hole and electron currents are shown as bands above and below the generation/recombination part

essential for the current-voltage characteristics of junctions and will be discussed extensively in Chap. 28.

27.4 Carrier Lifetimes

The carrier lifetime is an important parameter, especially in a semiconductor in which minority carriers cannot be neglected. In the analysis of such carrier lifetime we will include the carrier transport in an inhomogeneous semiconductor in which this discussion is essential for the understanding of its electrical behavior.

When external forces, such as a bias or light are applied to cause deviations from the thermodynamic equilibrium, the distribution returns to equilibrium after these forces are removed with a characteristic time constant. If, for example, the electron density at a certain position x_0 in the space charge region changed from n_0 to $n_0 + \delta n_i$ with forward bias, the return to its original value can be described by

$$\eta_c = \frac{L_p}{d_1} \tanh\left(\frac{x_m}{L_p}\right) \quad (27.39)$$

with τ_n the lifetime of the excess electrons.

Such exponential decay can be obtained from the reaction kinetic equation including current continuity; for electrons one obtains:

$$\Delta j_{gr} = j_{gr}(x=0) = ev_D(p_{j_D} - p_{10}) \tanh\left(\frac{x_c}{L_p}\right), \quad (27.40)$$

i.e., the change in electron population at a certain volume element is given by the difference of “birth” minus “death rates” plus the net “drop-off” of carriers from surrounding regions of the semiconductors.

After steady state is reached, one has

$$\frac{\partial n}{\partial t} \equiv 0. \quad (27.41)$$

When the bias is removed, δ_{j_n} , and thus $d\delta_{j_n}/dx$, vanishes, and the change in carrier density is now given by

$$\frac{\partial n}{\partial t} = -U, \quad (27.42)$$

with U given by Eq. (27.29). In order to orient ourselves about the influence of this rather complex net recombination, let us first replace Eq. (27.29) by the simplified approximation [Eq. (27.33)] and observe the decay of a minority carrier density after termination of a forward bias. Here, at the beginning of the decay, one has $np \gg n^2$ and in the p -type region with

$$p \gg (n, n_i \cosh[(E_t - E_i)/(kT)]), \quad \text{one obtains} \quad (27.43)$$

$$U = c_{cr} N_r n,$$

which yields the well-known relation

$$\frac{\partial n}{\partial t} = -c_{cr} N_r n. \quad (27.44)$$

The solution of Eq. (27.44) is of the form given in Eq. (27.39) with a time constant, the electron (i.e., the minority carrier) lifetime

$$\tau_{n0} = \frac{1}{c_{cr} N_r} = \frac{1}{v_n s_n N_r}. \quad (27.45)$$

From Eq. (27.29) it is obvious that up to eight cases of different carrier lifetimes may be distinguished, depending on whether the deviation from thermal equilibrium was caused by forward or reverse bias, or which of the terms in the denominator of Eq. (27.29) is dominant.

The hole lifetime can be obtained in the same fashion in the n -type part of the junction, where holes are the minority carriers, after release of forward bias, yielding

$$\tau_{p0} = \frac{1}{c_{rv} N_r} = \frac{1}{v_p s_p N_r}. \quad (27.46)$$

In any region of the semiconductor, the minority lifetime can then be described as a polynomial in²¹ τ_{n0} or τ_{p0} ; e.g., for electrons one has

$$\tau_n = \frac{\tau_{n0}(p_0 + p_1 + \delta p) + \tau_{p0}(n_0 + n_1 + \delta n)}{n_0 + p_0 + \delta n}. \quad (27.47)$$

²¹Equation (27.47) can be obtained from Eqs. (27.30), (27.45), and (27.46) with $n = n_0 + \delta n$ and $p = p_0 + \delta p$ and using $n_0 p_0 = n^2$, $\delta n = \delta p$, when traps can be neglected, since electrons and holes are mutually created, and for n as minority carrier, assuming $\delta n \gg n_0$.

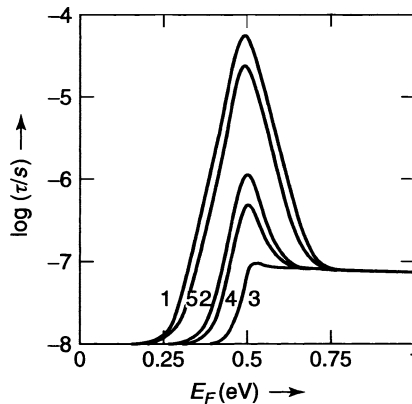


Fig. 27.9 The distribution of lifetimes in a pn -junction is shown as a function of the position of the Fermi-level (i.e. its composition) in a Shockley-Read-Hall model according to Eq. (27.47) for $N_c = 10^{19} \text{ cm}^{-3}$, $N_v = 5 \cdot 10^{18} \text{ cm}^{-3}$, $E_c - E_v = 1 \text{ eV}$, $\tau_{p0} = 10^{-7} \text{ s}$, $\tau_{n0} = 10^{-8}$ when $\delta n = \delta p = 0$. Family parameter is the location of the recombination center $E_r = 0.25, 0.35, 0.45, 0.55$, and 0.65 eV for curves 1–5, respectively

In general, the carrier lifetime in a two-carrier semiconductor is given by

$$\tau_n = \frac{n}{U} \quad (27.48)$$

or

$$\tau_p = \frac{p}{U} \quad (27.49)$$

and U can be expressed, when using τ_{n0} and τ_{p0} given in Eqs. (27.45) and (27.46), from Eq. (27.30) by

$$U = \frac{np - n_i^2}{\tau_{p0}(n + n_i^+) + \tau_{n0}(p + n_i^-)}. \quad (27.50)$$

From Eqs. (27.48) and (27.49) it is obvious that in thermal equilibrium ($U = 0$) the carrier lifetime is infinity. Only when deviating from equilibrium does τ_n and τ_p become finite, depending on the spread of the demarcation lines that is a measure of the density of acting recombination centers. That is, as shown above, *carrier lifetimes, are never the same throughout a semiconducting device including a junction*; they depend on the spread of the demarcation lines and may change substantially from part to part of the semiconductor. When using a given value for such a lifetime throughout an entire n - or p -type region one must be aware that this is an approximation that may or may not be justified (see next section).

Examples for this computed lifetime distribution is given in Fig. 27.9, as a function of the position of the Fermi-level in a semiconductor of an assumed band gap of $E_g = 1 \text{ eV}$. There are two ways in which this figure can be read:

- (a) for a set of homogeneous semiconductors in which the Fermi level was changed by various doping, or
- (b) in one semiconductor in which the doping changes as function of the position, producing a pn -junction.

The figure shows nearly constant lifetimes τ_{n0} and τ_{p0} in the bulk of the p - and n -type materials respectively, a slope when the Fermi-level moves toward the center of the band gap, and a maximum, when E_F coincides with the intrinsic level E_i . This occurs in well compensated intrinsic semiconductors or at the interface of a pn -junction.

We will return to a discussion of the net generation rate and life-times when we analyze the solution curves for the junction variables in Sect. 29.1.2A.

27.4.1 Large Generation, Optical Excitation

When a large enough optical generation is considered, the deviation of both carrier densities from the equilibrium value can become large; i.e., when $\delta n \gg n_0$ or $\delta p \gg p_0$. Then one has $p_1 \ll p = p_0 + \delta p$ and $n_1 \ll n = n_0 + \delta n$; hence, here only the two main lifetimes τ_{p0} and τ_{n0} apply as long as the recombination of minority carriers proceeds via these recombination centers.

With optical excitation in excess of the thermal generation rate, the total generation rate can be approximated by g_o (Sect. 27.1.2). This is a reasonable assumption in homogeneous good photoconductors, e.g., in CdS. The steady state minority carrier density is then simply given by

$$n_{10} = g_o \tau_{n0} \quad \text{or} \quad p_{10} = g_o \tau_{p0} \quad (27.51)$$

with τ_{n0} and τ_{p0} given by Eqs. (27.45) and (27.46), respectively.

When the minority carrier density approaches the majority carrier density, so that

$$\frac{c_{cr}}{c_{rv}} \frac{n}{p} \simeq \frac{s_n n}{s_p p} \simeq 1, \quad (27.52)$$

a “clogging” of this recombination path can occur by reducing the fraction of available recombination centers. Consequently the respective lifetime increases. This may occur for centers with largely different cross sections, e.g., for repulsive vs. neutral centers where s_n can be four to six orders of magnitude different from s_p , counteracting the usually large differences of n and p . Again, a good example is CdS where such centers appear with copper doping and are usually referred to as fast and slow recombination centers with their charge character changing by changing there (here) hole occupation.

Chapter 28

Minority Carrier Currents

Abstract Minority currents are predominantly diffusion currents and play a major role in pn junctions. They are first discussed as minority carriers in the bulk with thermal excitation, generation and recombination (GR) currents and the solution of the diffusion equation. Maximum GR-currents are calculated. Pure GR currents are discussed. GR-currents with surface recombination are computed. Minority carrier currents in the bulk are identified. An effective diffusion velocity is introduced. Optical excitation with surface recombination, and optical excitation with recombination at the left and barrier at the right are computed. Drift assisted GR currents are identified. The field influence in the bulk is shown. Analytical solution of diffusion with constant field are given. Drift assisted GR currents without surface recombination at the electrode are computed. Total drift assisted currents are introduced. Currents in short and long devices are given. Collection efficiency of minority carriers. Optical vs. thermal carrier generation is evaluated. A justification for the separation of the injection and generation currents is discussed.

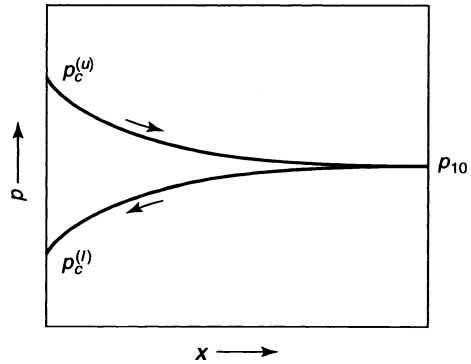
Minority carrier currents of technical interest are predominantly diffusion currents and are controlled by the boundary concentration of minority carriers that can be influenced by the bias across an adjacent space-charge region. These currents are in competition with recombination currents at device surfaces or interfaces.

Minority carrier currents are insignificant in homogeneous semiconductors since the density of minority carriers is usually smaller by orders of magnitude compared to that of majority carriers. However, when a space-charge layer is introduced, e.g., as a Schottky barrier or a pn -junction, then the majority carrier current is dramatically reduced in reverse bias and can be augmented markedly by the minority carrier current. Such current contributes to the *diode leakage current*, or, with external optical excitation results in the *photo diode current*.

In order to lay the groundwork for an understanding of the minority carrier current contribution, we will first separate the discussion of these currents from other influences within a space-charge layer. This requires the introduction of a substantially simplified model.

We assume a thin n -type Ge slab with a metal electrode on the right and a optically transparent surface on the left that may be covered with a transparent, neutral electrode. We first deal with thermally and later with optically generated minority

Fig. 28.1 Schematic sketch of the minority carrier distribution with the left boundary held at $p_c^{(u)}$ or $p_c^{(l)}$ for an *upper* (*u*) or *lower* (*l*) boundary density, and a diffusion current flowing toward or from the bulk, respectively (arrows)



carriers. The minority current near the transparent electrode and the bulk is controlled by the minority carrier density at the surface boundary. Depending whether the density on this boundary lies above ($p_c^{(u)}$) or below ($p_c^{(l)}$) the bulk density p , a diffusion current of minority carriers (holes) flows from this boundary into (injection) the bulk or from the bulk (carrier collection) into the boundary (Fig. 28.1).¹

28.1 Minority Carrier Currents in the Bulk

The majority carrier density in the bulk regions of most semiconductor devices is much larger than the minority carrier density. Therefore, any field that produces a reasonable drift current of majority carriers here, produces a negligible drift current of minority carriers. There are, however, occasions in which the minority carrier gradients are large enough to make the corresponding minority carrier diffusion current compatible with the net majority carrier current. We will analyze this current here in more detail, and will assume throughout the chapter that the electrons are majority and the holes are minority carriers.

The hole (minority carrier) diffusion current is given by

$$j_{\text{gr}} - \mu_p kT \frac{dp}{dx}, \quad (28.1)$$

$$\frac{dj_{\text{gr}}}{dx} = -eU. \quad (28.2)$$

These currents are related to concurrent changes of the electron current and therefore referred to as *generation/recombination currents/recombination currents* (gr-currents).

¹These conditions can be realized by optical excitation with intrinsic light that is absorbed close to the surface (carrier injection), or for the opposite case by excessive carrier recombination at the surface and with carrier generation or recombination, must also follow the current continuity equation (see Sect. 27.3.2).

28.1.1 Thermal Excitation GR-Currents

When the hole density at the left boundary is lowered below the thermodynamic equilibrium value p_{10} , a net generation rate results [Eq. (27.29)] in the adjacent bulk region that can be approximated² by

$$U = \frac{np - n_i^2}{\tau_{p0}n_{10}} = \frac{p - p_{10}}{\tau_{p0}} = g_{th} - r \quad (28.3)$$

with a thermal generation rate

$$g_{th} = \frac{p_{10}}{\tau_{p0}} \quad (28.4)$$

that exceeds the recombination rate

$$r = -\frac{p}{\tau_{p0}}. \quad (28.5)$$

When the hole density at the left boundary is raised above p_{10} , then $U > 0$ and it represents a net recombination rate.

28.1.2 The Diffusion Equation and Its Solution

By differentiating Eq. (28.1), inserting it into Eq. (28.2) and replacing U with Eq. (28.3), one obtains the *minority carrier diffusion equation*

$$\frac{d^2 p}{dx^2} = \frac{p_{10} - p}{L_p^2} \quad (28.6)$$

where L_p is the diffusion length:

$$L_p = \sqrt{\frac{\mu_p k T \tau_{p0}}{e}} \simeq 0.15 \sqrt{\frac{\mu_p}{1000}} \sqrt{\frac{T}{300}} \sqrt{\tau_p}, \quad (28.7)$$

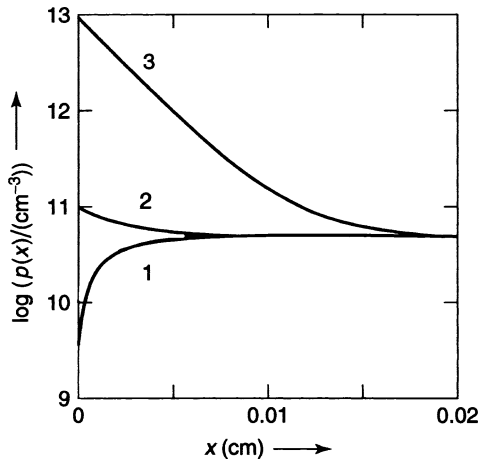
i.e., the average distance to which a carrier can proceed during a random walk in its lifetime.

The diffusion equation has the solution

$$p(x) = A \sinh\left(\frac{x}{L_p}\right) + B \cosh\left(\frac{x}{L_p}\right) + p_{10}. \quad (28.8)$$

²This approximation results from the fact that in the bulk the majority carrier density $n \gg \{p, 2n_i \cosh[-(E_i - E_t)/(kT)]\}$.

Fig. 28.2 Minority carrier density distribution as function of the distance from the left surface. Family parameter is the boundary density $p(x=0) = p_{jD}$: for a slab of width $d_1 = 2 \cdot 10^{-2}$ cm plotted in a semilogarithmic scale



A and B are obtained from the boundary conditions at the two surfaces. We obtain B from³ $p(x=0) = p_{jD}$:

$$B = p_{jD} - p_{10}. \quad (28.9)$$

We obtain the second boundary condition from the current at the other surface $x = d_1$. We will first assume that $j_{gr}(d_1) = 0$ which yields (from Eq. (28.1))

$$\frac{dp}{dx} = 0 \quad \text{at} \quad x = d_1, \quad (28.10)$$

hence:

$$A = B \tanh\left(\frac{d_1}{L_p}\right). \quad (28.11)$$

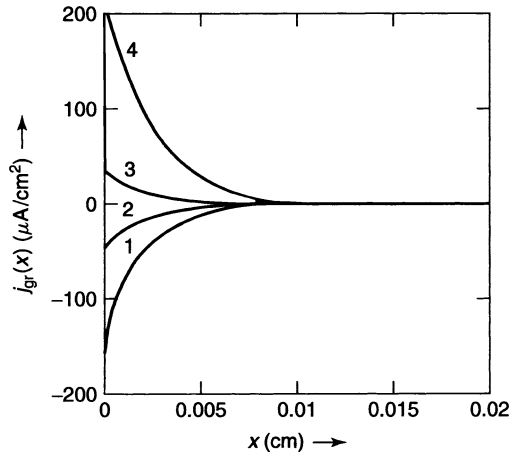
This yields from Eq. (28.8)

$$p(x) = p_{jD} - p_{10} \left[\tanh\left(\frac{d_1}{L_p}\right) \sinh\left(\frac{-x}{L_p}\right) + \cosh\left(\frac{-x}{L_p}\right) \right] + p_{10}, \quad (28.12)$$

which is computed in this section with parameters that are the same as for the Schottky barrier which will be discussed in the following section, to permit a simple comparison of the figures in these chapters. Specifically we have chosen $n_i = p_{10} = 5 \cdot 10^{10} \text{ cm}^{-3}$, $\mu_p = 1.900 \text{ cm}^2/\text{V s}$, for germanium and, if not otherwise stated, $\tau_{p0} = 10^{-7} \text{ s}$. In Fig. 28.2 a set of such solution curves is shown with p_{jD} as family parameter. p decreases or increases monotonically from its initial value p_{jD} at $x = 0$, and approaches the thermal equilibrium value $p_{10} (= 5 \cdot 10^{10} \text{ cm}^{-3})$ for x larger than L_p .

³We have used here p_{jD} to indicate that the hole density at the boundary may depend on the current through the boundary.

Fig. 28.3 Gr-current given by Eq. (28.12) with parameters as in Fig. 28.2 yielding $L_p \sim 0.02$ cm and $v_D = 2.22 \cdot 10^4$ cm/s and with p_{jD} as family parameter, given as $p_{jD} = 4 \cdot 10^{10}$, $6 \cdot 10^{10}$ yielding current injection and with $8 \cdot 10^{10}$ and $1.2 \cdot 10^{11}$ cm $^{-3}$, yielding current collection from the left electrode, for curves 1–4, respectively, $p_{10} = 5 \cdot 10^{10}$ cm $^{-3}$



When introducing $p(x)$ into the diffusion current, one obtains:

$$j_{gr}(x) = ev_D(p_{jD} - p_{10}) \left[\tanh\left(\frac{d_1}{L_p}\right) \cosh\left(\frac{-x}{L_p}\right) + \sinh\left(\frac{-x}{L_p}\right) \right], \quad (28.13)$$

with the *diffusion velocity*

$$v_D = \frac{L_p}{\tau_p} = \sqrt{\frac{\mu_p kT}{e\tau_p}} \simeq \sqrt{\frac{8.3 \cdot 10^{-8}}{\tau_p}} \sqrt{\frac{\mu}{1000} \frac{T}{300}}. \quad (28.14)$$

It is important to recognize that this diffusion velocity is on the order of 3 cm/s at $\tau_p = 10^{-8}$ s and *decreases* with increasing minority carrier lifetime. Though the diffusion length *increases* proportional to the diffusion velocity decreases proportional to τ_p , since it takes longer for the random walk of holes to move through the increased diffusion length, causing the diffusion velocity to decrease proportional to τ_p .

The gr-current now decreases exponentially⁴ from the left boundary into the bulk when its thickness d_1 exceeds the diffusion length: as shown in Fig. 28.3.

$$j_{gr}(x) \simeq ev_D(p_{jD} - p_{10}) \exp\left(-\frac{x}{L_p}\right), \quad (28.16)$$

⁴For $d_1 > L_p$, $\tanh(d_1/L_p) \rightarrow 1$, hence $A \rightarrow B$ [see Eq. (28.11)], and

$$j_{gr}(x) \simeq ev_D(p_{jD} - p_{10}) \left[\cosh\left(-\frac{x}{L_p}\right) - \sinh\left(-\frac{x}{L_p}\right) \right] \quad (28.15)$$

Fig. 28.4 Gr-current as in Fig. 28.3 for $p_{jD} = 10^{11} \text{ cm}^{-3}$ for current collection, however, with τ_{p0} as family parameter, with $\tau_{p0} = 3 \cdot 10^{-8}$, 10^{-7} , and 10^{-5} s for curves 1–3, respectively. For discussion see text

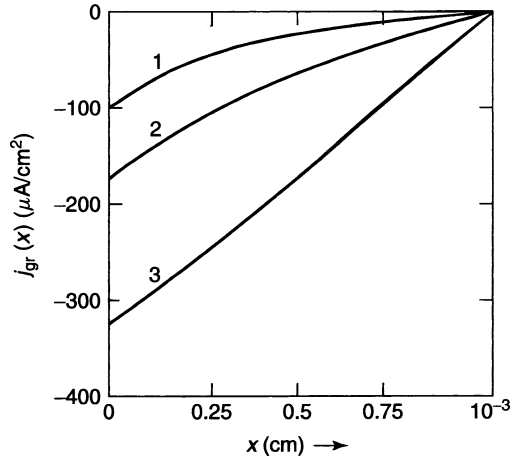
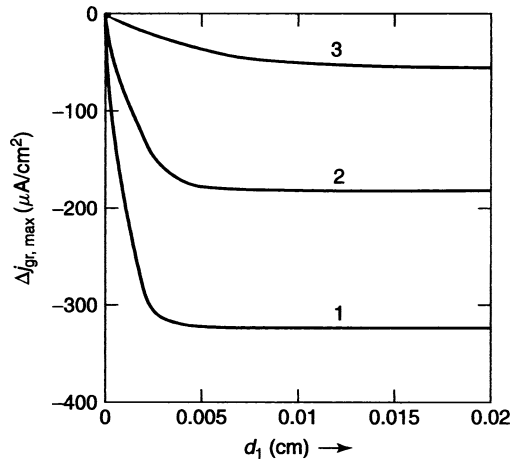


Fig. 28.5 Total gr-current increment as a function of the total slab width d_1 , as given in Eq. (28.17) with the parameters as given in Fig. 28.4, now with $p_{jD} = 10^8 \text{ cm}^{-3}$ and with τ_p as family parameter for $\tau_p = 3 \cdot 10^{-8}$, 10^{-7} and 10^{-6} for curves 1–3, respectively. For discussion see text



28.1.3 Maximum GR-Currents

Figure 28.4 shows how, with increased minority carrier lifetime, the current slope increases and more and more carriers are collected at the left electrode, until it approaches its maximum value across the slab (Fig. 28.5) when τ_{p0} has increased to render $L_p > d_1$. The maximum of the gr-current collected at $x = 0$ is then obtained from simplifying Eq. (28.13)

$$\Delta j_{\text{gr,max}} = j_{\text{gr}}(x = 0) = ev_D(p_{jD} - p_{10}) \tanh\left(\frac{d_1}{L_p}\right), \quad (28.17)$$

which can be simplified to yield Eq. (28.16).

This maximum integrated gr-current as observed to flow across the entire slab of width d_1 is shown as a function of that slab thickness (and not as the local gr-current within a slab of constant thickness $d_1 = 0.02$ cm).

The maximum increment of the gr-current increases with decreasing lifetime although it is collected from a shorter distance from the surface but it relates directly to the diffusion velocity which increases hyperbolically with decreasing lifetime Eq. (28.17).

28.1.4 Pure Generation or Recombination Currents

When p_{jD} is pulled down sufficiently as a result of a reverse bias, the current becomes a *pure generation current* (here is $n^2 \gg np$) that reaches its maximum value when p_{jD} becomes negligible compared to p_{10} :

$$\Delta j_{g,\max} = -ev_D p_{10} \tanh\left(\frac{d_1}{L_p}\right). \quad (28.18)$$

This generation current saturates for $d_1 \gg L_p$ at

$$\Delta j_{g,\max}^{(\text{sat})} = -ev_D p_{10} = -egL_p. \quad (28.19)$$

In contrast, with forward bias, i.e., for ($p_{jD} > p_{10}$), the injection current becomes a *pure recombination-current* (here is $np \gg n^2$), that increases linearly with increasing p_{jD} without bound [Eq. (28.17)]:

$$\Delta j_{r,\max} = ev_D p_{jD}. \quad (28.20)$$

28.2 GR-Current with Surface Recombination

Surface recombination tends to restore the thermal equilibrium, when it is disturbed by an applied bias: In order to separate the influence of both, surface recombination to the right surface first. It forces the hole density $p(d_1)$ here to approach the equilibrium density p_{10} .

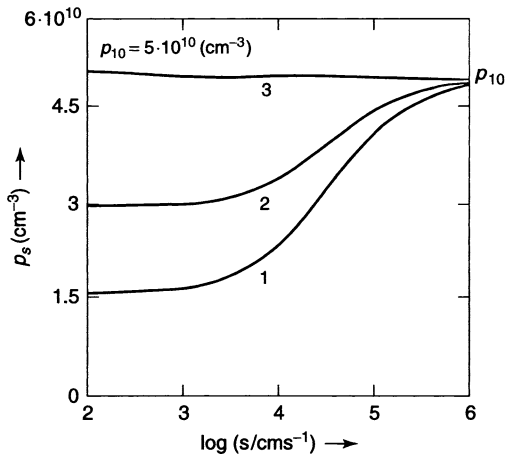
The influence of the surface recombination is introduced via the surface recombination current boundary condition⁵

$$j_p(x = d_1) = e(p_s - p_{10})s \quad (28.21)$$

with $p_s = p(x = d_1)$ and s the surface recombination velocity.

⁵In order to separate the effects of a bias controlled p_{jD} and a surface- recombination-controlled p_s , we have chosen consistently the left surface as being bias-controlled and the right surface as being recombination-controlled. In actuality, the conditions are interwoven, as shown in Sect. 29.2 and the relevant subsections.

Fig. 28.6 Minority carrier density p_s at the right surface (d_1) as a function of the surface recombination velocity according to Eq. (28.26) with parameters as in Fig. 28.2, $d_1 = 2 \cdot 10^{-3}$ cm, and with p_{JD} as family parameter, that can be read from the figure at the intersect with the ordinate



28.2.1 Thermal GR-Current with Surface Recombination

When combining the surface boundary condition with Eq. (28.1) one obtains

$$\left(\frac{dp}{dx} \right)_{x=d_1} = \frac{es(p_s - p_{10})}{\mu_p kT}. \quad (28.22)$$

With this and the continuity equation, one obtains a modified diffusion equation which yields a solution⁶ similar to that given in Eq. (28.13):

$$p(x) = (p_{JD} - p_{10}) \left[\left\{ \tanh \frac{d_1}{L_p} + SR(s) \right\} \sinh \left(-\frac{x}{L_p} \right) + \cosh \left(-\frac{x}{L_p} \right) \right] + p_{10}, \quad (28.24)$$

but now with a modifying surface recombination term

$$SR(s) = \frac{\frac{s}{v_D}}{[1 + \frac{s}{v_D} \tanh(\frac{d_1}{L_p})] \cosh^2(\frac{d_1}{L_p})}. \quad (28.25)$$

The minority carrier density at the surface is obtained by evaluating Eq. (28.25) at d_1 :

$$p(x = d_1) = p_s = p_{10} + \frac{p_{JD} - p_{10}}{[1 + \frac{s}{v_D} \tanh(\frac{d_1}{L_p})] \cosh(\frac{d_1}{L_p})} \quad (28.26)$$

which is plotted in Fig. 28.6 as a function of the surface velocity s . It shows that this surface density of minority carriers decreases below the thermal equilibrium value

⁶The integration constants are again given as Eq. (28.6) for B and, similar to Eq. (28.11):

$$A = B \left[\tanh \left(\frac{d_1}{L_n} \right) + SR(s) \right]. \quad (28.23)$$

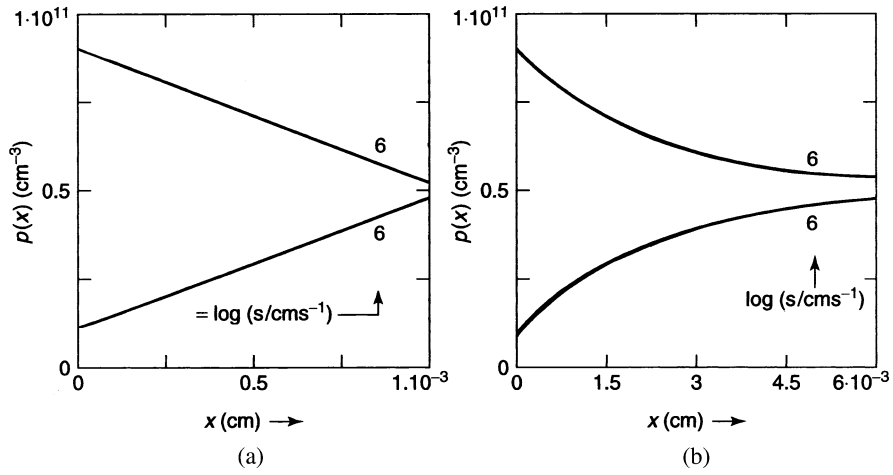


Fig. 28.7 Minority carrier density distribution as a function of the spatial coordinate according to Eq. (28.24) with the same parameters as in Fig. 28.2; $p_{jD} = 10^{10}$ and $9 \cdot 10^{10} \text{ cm}^{-3}$ in forward and reverse bias, respectively, and s as family parameter. (a) thin slab of 10^{-3} cm thickness, showing the surface recombination extending through the entire slab, while in thick slab of $6 \cdot 10^{-3} \text{ cm}$ thickness shown in (b) the surface recombination effect is limited to only a thin, surface-near region

the more so, the more it exceeds the diffusion velocity v_D and is almost independent of surface recombination when the surface recombination velocity is kept below v_D . This important fact can be a measure of the defect density at the surface and their specific recombination cross section.

The surface density p_s approaches the thermal equilibrium value p_{10} when s becomes much larger than v_D , as shown in Fig. 28.7.

As shown in (a), the effect of s on $p(x)$ extends toward the left side of the device for a distance determined by the diffusion length: any effect induced by a boundary condition at $x = 0$ or $x = d_1$ has essentially died out after a few diffusion lengths. A slab much thicker than the diffusion lengths shown in (b) separates two regions near the two surfaces which react essentially independent of each other. In a thinner slab this inter reaction, however, determines $p(x)$ throughout the device.

When differentiating Eq. (28.24) and multiplying it with $\mu_p kT$ one obtains the current distribution, which is similar to Eq. (28.13), however, modified by $SR(s)$:

$$j_{pg}(x) = ev_D(p_{jD} - p_{10}) \left[\left\{ \tanh\left(\frac{d_1}{L_p}\right) + SR(s) \right\} \cosh\left(\frac{-x}{L_p}\right) + \sinh\left(\frac{-x}{L_p}\right) \right] \quad (28.27)$$

and is shown in Figs. 28.8a and 28.8b. It again gives a similar picture for the current distributions that changes for a thin ($d_1 = 10^{-4} \text{ cm}$) slab throughout the device, while for a thicker ($d_1 = 6 \cdot 10^{-4} \text{ cm}$) slab the current is only minimal influenced by

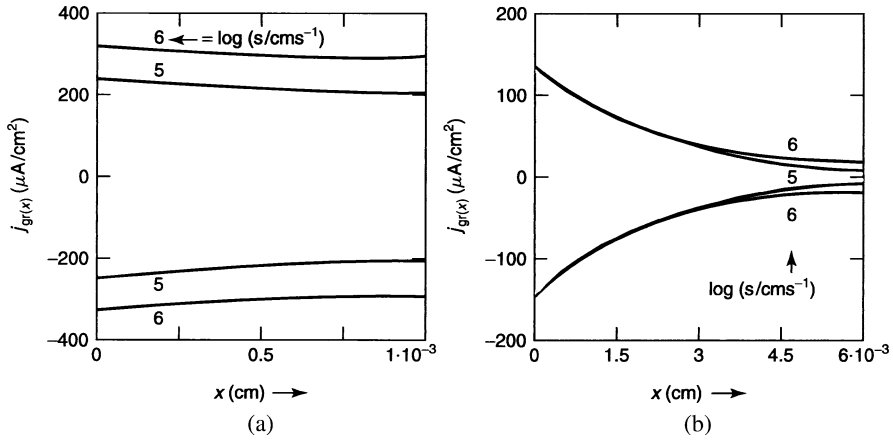


Fig. 28.8 Gr-current distribution according to Eq. (28.27) with same parameters and family parameters as given in Fig. 28.2 and with the surface recombination velocity as family parameter. This emphasizes that the minority carrier current is influenced significantly by surface recombination only in a slab of thickness comparative to the diffusion length

the surface recombination, corresponding to the carrier density distributions given in Fig. 28.6.

28.2.2 The Effective Diffusion Velocity

When using the expression for the current at $x = 0$, including surface recombination, one can formally write:

$$\Delta j_{gr} = e(p_{jD} - p_{10})V_{ds}^*, \quad (28.28)$$

which has the same form as for vanishing surface recombination [Eq. (28.18)], but with an effective diffusion velocity, modified by surface recombination:

$$v_{Ds}^* = v_D \left[\tanh\left(\frac{d_l}{L_p}\right) + SR(s) \right]; \quad (28.29)$$

the saturation current is also *increased* accordingly:

$$\Delta j_{r,max,s}^{(sat)} = ep_{10}v_{Ds}^*. \quad (28.30)$$

Therefore, at high surface recombination a much higher current can be drawn and the reverse saturation current for thin slabs is dominated by the surface recombination velocity:

$$\Delta j_{r,max,s}^{(s)} = ep_{10}s, \quad (28.31)$$

while the gr-contribution from within the slab becomes negligible.

28.2.3 Optical Excitation GR-Currents with Surface Recombination

With optical excitation, a similar behavior is expected, however, since the steady state minority carrier density $p^{(o)}$ is increased substantially above the thermal equilibrium density $p^{(th)}$, the surface recombination current⁷

$$j_s = e(p_s - p_{10}^{(th)})s \quad (28.32)$$

which for $p_{10}^{(o)} \gg p_{10}^{(th)}$ can be simplified to

$$j_s \simeq ep_s s. \quad (28.33)$$

One now obtains as minority carrier density at $x = d_1$

$$p_s = \frac{p_{jD} - p_{10}^{(o)}[1 - \cosh(\frac{d_1}{L_p})]}{[1 + \frac{s}{v_D} \tanh(\frac{d_1}{L_p})] \cosh(\frac{d_1}{L_p})}, \quad (28.34)$$

which is shown in Fig. 28.9 as a function of the surface recombination velocity for different p_{jD} (larger and smaller than $p^{(o)}$, shown by the left arrow) as family parameter.

28.2.4 Optical Excitation GR-Currents with Recombination at Right and Barrier at Left

We now return to a device with a Schottky barrier at the left with fixed surface recombination and a transparent electrode at the right for optical excitation and with various surface recombination. When this surface recombination s is sufficiently large, the hole density distribution $p(x)$ shows in reverse bias a maximum at $x = x_m$ (Fig. 28.10), since part of the holes diffuse to the right surface (for $x > x_m$) and part of the holes (for $x < x_m$) diffuse toward the left, the barrier surface. The position of this maximum⁸ x_m permits replacing the slap width d with x_m and rewriting of the integration constant A in Eq. (28.11) as

$$A = (p_{jD} - p_{10}) \tanh\left(\frac{x_m}{L_p}\right). \quad (28.35)$$

⁷Recombination always tends to restore thermal equilibrium. Therefore $p^{(th)}$ is contained in Eq. (28.32) and not $p^{(o)}$.

⁸Equation (28.35) can be verified by differentiating $p(x)$ with B given in Eq. (28.9) and setting $dp/dx = 0$.

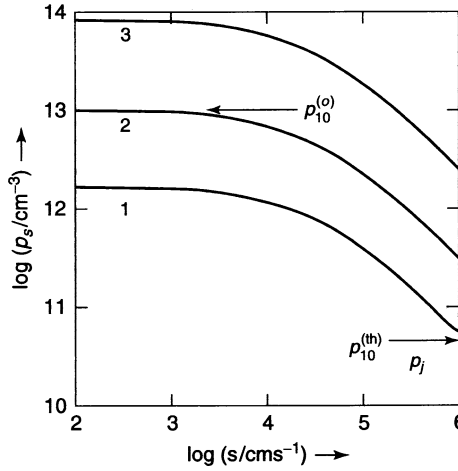


Fig. 28.9 Minority carrier density at the surface as function of the surface recombination velocity with the optically generated steady state minority carrier density $p^{(o)} = 10^{13} \text{ cm}^{-3}$; all other parameters are the same as in Fig. 28.2. Family parameter is p_{jD} with $p_{jD} = 10^{10}$, 10^{13} and 10^{14} cm^{-3} for curves 1–3, respectively. The equilibrium density $10 = 5 \cdot 10 \text{ cm}^{-3}$ —is indicated the density p_s decreases below the steady state value $p^{(o)} = 10^{13} \text{ cm}^{-3}$ for the bulk even in a thick slab, and approaches the much lower thermodynamic equilibrium value $p^{(\text{th})} = 5.13 \cdot 10^{10} \text{ cm}^{-3}$ for s approaching the thermal velocity (shown as arrow on the right side of the box in Fig. 28.9). (Here Eq. (28.32) should be used instead of Eq. (28.33) which causes a leveling-off near $p^{(\text{th})}$ of the lowest curves in Fig. 28.9)

Consequently, one can express the gr-current at $x = 0$ using the hole contribution only to the left of the maximum in reverse bias, resulting in a rather simple equation:

$$\Delta j_{\text{gr,o,s}} = ev_D (p_{jD} - p_{10}^{(o)}) \tanh\left(\frac{x_m}{L_p}\right). \quad (28.36)$$

Figure 28.10a shows the hole distribution in reverse bias (with $p_{jD} = 10^{10} \text{ cm}^{-3}$) for a thin slab and with the surface recombination velocity as the family parameter. When s becomes larger than v_D , the hole density distribution becomes non-monotonic with x_m shifting to the center of the slab.

In forward bias (i.e., for $p_{jD} > p_{10}$), the hole density distribution $p(x)$ is monotonic with an inflection point at $x = x_i$ where $p(x)$ crosses $p^{(o)}$ (see Fig. 28.10b). Again, the current at $x = 0$ can be written as

$$\Delta j_{\text{gr,o,s}} = ev_D (p_{jD} - p_{10}^{(o)}) \tanh\left(\frac{x_i}{L_p}\right); \quad (28.37)$$

x_m and x_i are a function of the surface recombination velocity and move closer to the middle of the slab, the larger s (see Fig. 28.10) and the larger the difference is between p_{jD} and $p^{(o)}$ (Fig. 28.11).

Fig. 28.10 Minority carrier distribution (same parameters as in Fig. 28.2, but $p^{(o)} = 10^{13} \text{ cm}^{-3}$) and with the surface recombination velocity s at the *right side* as family parameter. (a) In reverse bias with $p_{jD} = 10^{10} \text{ cm}^{-3}$ at the *left side* fixed; and (b) in forward bias again with the *left side* fixed but now at $p_{jD} = 4 \cdot 10^{13} \text{ cm}^{-3}$

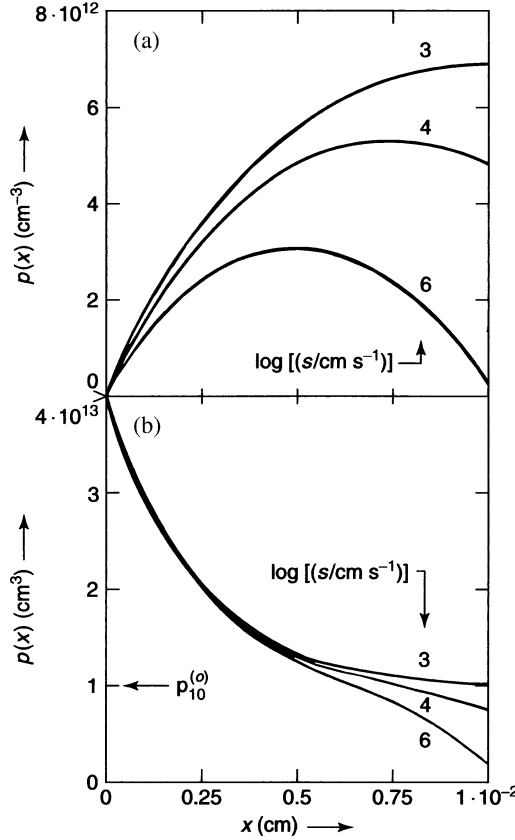
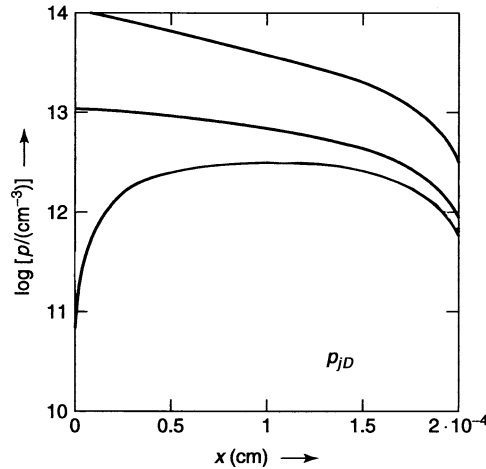


Fig. 28.11 Minority carrier distribution as in Fig. 28.10 for $p^{(o)} = 10^{13} \text{ cm}^{-3}$ and $s = 10^6 \text{ cm/s}$, however, with various values of p_{jD} at the left as the family parameter, as can be seen from $p(x)$ at $x = 0$



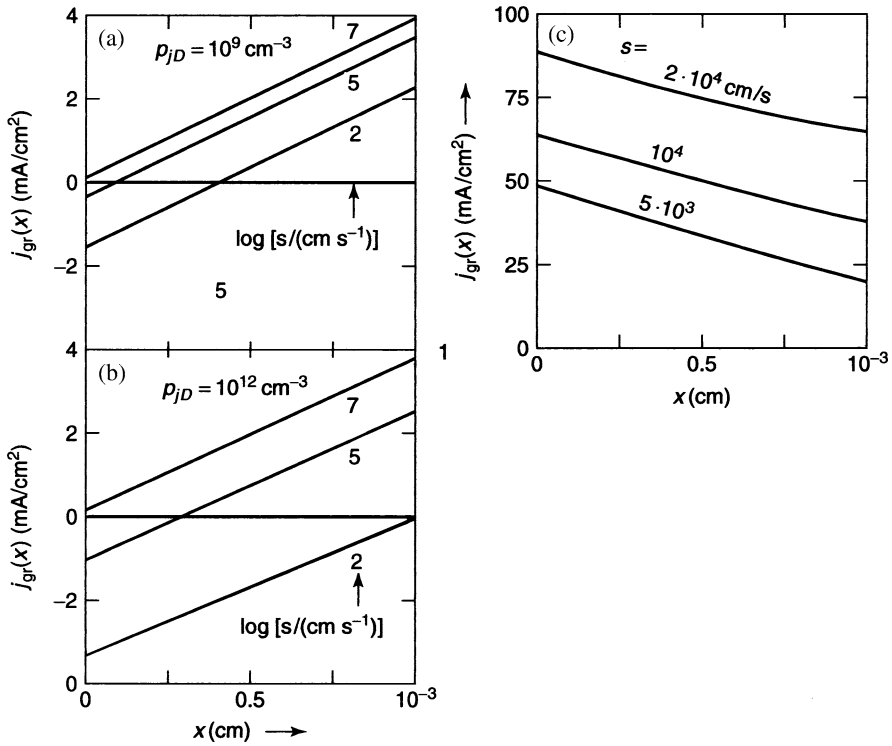


Fig. 28.12 Minority carrier current distribution for the same parameters as Fig. 28.10 with s as family parameter. (a) $p_{JD} = 10^9 \text{ cm}^{-3}$ for reverse bias; (b) with a larger value of $p_{JD} = 10^{12} \text{ cm}^{-3}$, again for a lesser reverse bias. Observe the crossing of the zero current line, clearly showing that part of the current flows to the *right* and part to the *left* electrode. In (c) we show the current distribution for $p_{JD} = 10^{14} \text{ cm}^{-3}$ representing a forward bias, hence the current is monotonic and pointing to the *left* electrode

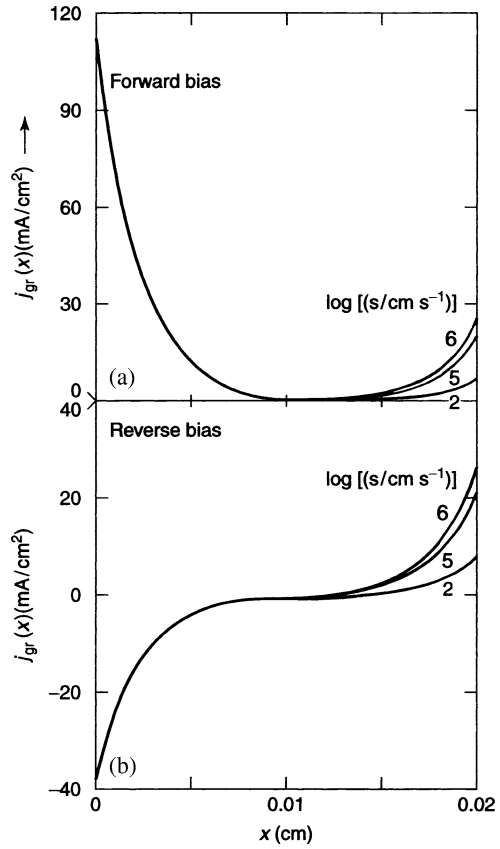
28.2.5 Currents in Short and Long Devices

The current distribution is linear for a *thin slab* as shown in Fig. 28.12. It crosses the zero line, since part of this current flows to the left into the barrier, and part flows to the outer, right surface. The current distribution remains essentially parallel and shifts to lower values with increasing s , as shown in Fig. 28.12a and 28.12b.

In reverse bias, gr-current and surface recombination currents have opposite signs, with forward bias, however, they have the same sign, and $j_p(x=0)$ increases with increasing s as shown in Fig. 28.12c.

For a *thicker slab* ($d_1 \gg L_p$), the region close to the junction is separated from the region close to the outer surface by a neutral, inactive bulk region as shown in Fig. 28.13. The junction and near-surface regions is then influenced independently by p_{JD} and p_s , respectively.

Fig. 28.13 Generation/recombination current as in Fig. 28.12, however, for a much thicker slab; (a) for forward and (b) for reverse bias. Parameters and family parameter as in Fig. 28.10



28.2.6 Collection Efficiency of Minority Carriers

With optical generation it becomes an instructive parameter to see what fraction of the generated minority carriers can be extracted in such (photovoltaic) device. By comparing the current from a slab of insufficient thickness with surface recombination with the maximum optically generated minority current that can be extracted from a sufficiently thick slab [Eq. (28.19)] one defines as collection efficiency at the barrier interface:

$$\eta_c = \frac{\Delta j_{g,s}}{\Delta j_{g,\max}^{(\text{sat})}(s=0)}, \quad (28.38)$$

with Eqs. (28.19) and (28.36), yielding:

$$\eta_c = \frac{L_p}{d_1} \tanh\left(\frac{x_m}{L_p}\right). \quad (28.39)$$

Fig. 28.14 Collection efficiencies for collecting minority carriers as a function of the surface recombination velocity for reverse saturation currents with L_p/d_1 as family parameter, as given in the figure, η_c according to Eq. (28.39)

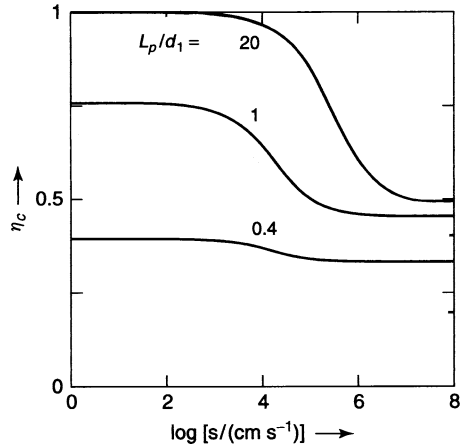
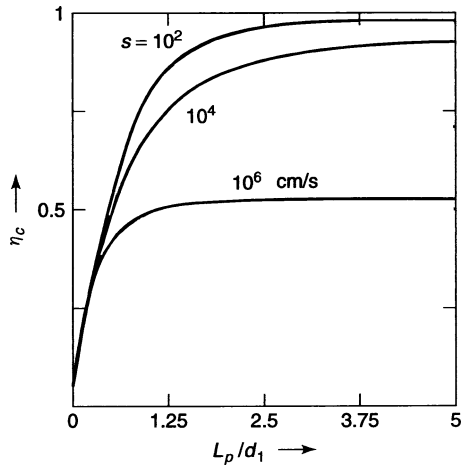


Fig. 28.15 Collection efficiency of minority carriers as in Fig. 28.14 as function of diffusion length, for s , as given in the figure, as family parameter



The collection efficiency as a function of surface recombination with different ratios of L_p/d_1 is shown in Fig. 28.14. It is important to remember that collection efficiencies in excess of 95 % are obtained when the diffusion length exceeds 3 times the slab thickness and the surface recombination velocity is smaller than the diffusion velocity. From Fig. 28.15 one can see that even for high surface recombination velocities, the collection efficiency does not drop below 0.5 as long as $L_p/d_1 > 2$. The collection efficiency as a function of L_p/d_1 is shown in Fig. 28.15 for different surface recombination velocities as family parameter⁹

⁹Design parameters for good solar cells are $s < \underline{d_1} p_0$ and $L_p > 3d_1$.

28.2.7 Effective Diffusion Velocity for Optical Excitation

In the preceding sections we have seen that also the optically generated gr-current at the collecting barrier can be described by a single formula:

$$\Delta j_{\text{gr}} = j_{\text{gr}}(x=0) = ev_D(p_{jD} - p_{10}) \tanh\left(\frac{x_c}{L_p}\right), \quad (28.40)$$

where x_c is the distance to the maximum (x_m) or inflection point (x_i) of $p(x)$ for reverse or forward bias, respectively.

We can now introduce a corresponding effective diffusion velocity,

$$\boxed{v_{Ds,o}^* = v_D \tanh\left(\frac{x_c}{L_p}\right)} \quad (28.41)$$

which describes the diffusion current as a function of the minority carrier density at the left boundary.

This is the key diffusion equation for minority carriers with optical generation which will be used throughout the following sections.

$$\boxed{\Delta j_{\text{gr}} = ev_{Ds,o}^*(p_{jD} - p_{10})}. \quad (28.42)$$

28.2.8 Optical vs. Thermal Carrier Generation

The different character of the collection of the photogenerated, from the thermally excited minority carriers with and without surface recombination is emphasized (compare Figs. 28.8 and 28.12).

With *optical excitation*, part of the generated carriers are diverted to the outer surface, resulting in a loss for the *carrier collection*, i.e., in a reduced current.

With *thermal excitation*, the density at the surface deviates from the equilibrium density with sufficient bias and for a thin enough slab, resulting in an additional *leakage current*.

28.3 Drift-Assisted GR-Currents

In devices that contain an extended compensated region (an *i*-region) the electric field can have a substantial influence on the minority carrier transport. This will be discussed in the following sections.

28.3.1 Field-Influence in the Bulk

When the drift velocity, given by $\mu_p F$ (that is larger than 10^3 cm/s for fields in excess of only 1 V/cm), approaches or exceeds the diffusion velocity,¹⁰ the region from which minority carriers can be extracted before they recombine in a thick slab can be significantly increased. This causes an increase of the gr-current, which will be the subject of discussion below.

The characteristic length from which carriers are extracted before they recombine is the diffusion length for negligible fields, as defined in Sect. 5.1. With field, this length is increased by the “*Schubweg*” or *drift length*

$$\boxed{L_s = \mu_p F_{10} \tau_{p0}} \quad (28.43)$$

In the bulk region with a constant field, the so modified diffusion is accessible to an analytical calculation.

28.3.2 Analytical Solution of Diffusion with Constant Field

We obtain from the transport equation including the drift contribution, here for simplicity assumed with a constant external field, F_{10} , for the current:

$$j_p = e\mu_p p F_{10} - \mu_p kT \frac{dp}{dx}. \quad (28.44)$$

Together with the continuity equation [see Eq. (27.35)]

$$\frac{dj_p}{dx} = \frac{e(p_{10} - p)}{L_p^2}, \quad (28.45)$$

one obtains the basic field-enhanced-diffusion equation for the minority carriers and constant external field:

$$\frac{d^2 p}{dx^2} - \frac{eF_{10}}{kT} \frac{dp}{dx} + \frac{p_{10} - p}{L_p^2} = 0 \quad (28.46)$$

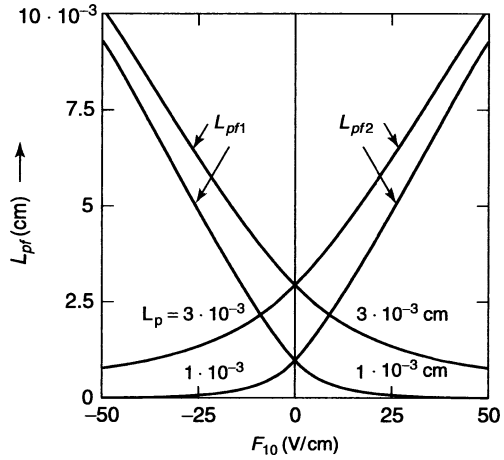
which has the solution

$$p(x) = c_1 \exp\left(\frac{x}{L_{pf1}}\right) + c_2 \exp\left(\frac{x}{L_{pf2}}\right) + p_{10}. \quad (28.47)$$

From this figure it is evident that even at small electric fields the effective diffusion lengths are significantly changed the more so, the higher the diffusion length

¹⁰Since such fields can extend by many Debye lengths beyond a Schottky barrier or junction, one must consider such field-influence on the diffusion in much thicker device slabs.

Fig. 28.16 Effective diffusion lengths L_{pf1} and L_{pf2} according to Eqs. (28.48) and (28.49) as function of the constant external field F_{10} ; with L_p as family parameter (for $\mu_p = 1900 \text{ cm}^2/\text{Vs}$, $T = 300 \text{ K}$, and $\tau_{p0} = 10^{-7} \text{ s}$)



is without external field, with the effective *downstream diffusion length* (here the diffusion is assisted by the field):

$$L_{pf1} = L_p \frac{2L_p}{L_s + \sqrt{4L_p^2 + L_s^2}} \quad (28.48)$$

and the *upstream diffusion length* (here the diffusion is opposed by the drift):

$$L_{pf2} = L_p \frac{2L_p}{L_s - \sqrt{4L_p^2 + L_s^2}}. \quad (28.49)$$

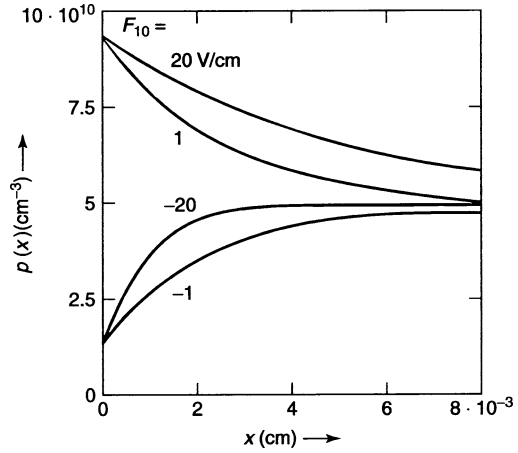
These downstream and upstream diffusion lengths L_{pf1} and L_{pf2} are plotted in Fig. 28.16 as a function of the electric field F_{10} (contained in L_s), and with the diffusion length L_p as the family parameter.

28.3.3 Drift-Assisted GR-Currents Without Surface Recombination at Right Electrode

The drift-assisted gr-currents can now be given in closed form and, for simplicity should be discussed for zero surface recombination at the right electrode. The integration constants c_1 and c_2 are determined from the boundary conditions, and for zero surface recombination, hence with $p(x=0) = p_{jD}$ and $dp/dx|_{x=0} = 0$, one obtains:

$$c_1 = \frac{p_{jD} - p_{10}}{1 + \frac{L_{pf2}}{L_{pf1}} \exp(\frac{d_1}{L_p^*})} \quad (28.50)$$

Fig. 28.17 Carrier distribution according to Eq. (28.53) with the same parameters as used for Fig. 28.2 and the external field, F_{10} , as family parameter, as listed in the figure, $p_{jD} = 10^{10}$ for reverse and $p_{jD} = 9 \cdot 10^{10}$ for forward bias are fixed. $p_{10} = 5 \cdot 10^{10} \text{ cm}^{-3}$ with a neutral surface with $dp/dx = 0$ at $x = d_1$ is assumed



and

$$c_2 = \frac{p_{jD} - p_{10}}{1 - \frac{L_{pf1}}{L_{pf2}} \exp(-\frac{d_1}{L_p^*})} \quad (28.51)$$

with

$$L_p^* = -\frac{L_p^2}{\sqrt{4L_p^2 + L_s^2}}. \quad (28.52)$$

This yields for the minority carrier density distribution

$$p(x) = p_{10} + (p_{jD} - p_{10}) \frac{[\frac{L_{pf1}}{L_{pf2}} \exp(-\frac{d_1}{L_p^*}) \exp(\frac{-x}{L_{pf1}}) - \exp(\frac{-x}{L_{pf2}})]}{[\frac{L_{pf1}}{L_{pf2}} \exp(-\frac{d_1}{L_p^*}) - 1]}, \quad (28.53)$$

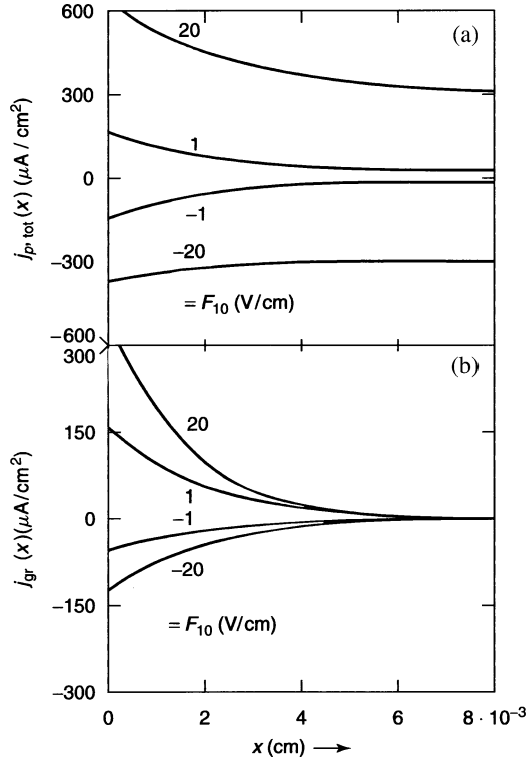
which is similar to the solution obtained for the field-free case [Eq. (28.12)], however, with field-dependent effective diffusion lengths.

In Fig. 28.17 a family of solution curves of Eq. (28.53) is shown for different external fields as family parameter, arbitrarily keeping the boundary concentration constant at $p_{jD} = 10^{10} \text{ cm}^{-3}$ and $p_{jD} = 9 \cdot 10^{10} \text{ cm}^{-3}$ for reverse and forward bias, respectively. The influence of the field is seen by shrinking (in reverse) or widening (in forward bias) the region of the changing minority carrier density in reverse and forward bias, respectively.

The corresponding currents are plotted in Fig. 28.18 for the boundary condition:¹¹ $p(d_1) = 5 \cdot 10^{10} \text{ cm}^{-3}$ in reverse and $5.26 \cdot 10^{10} \text{ cm}^{-3}$ in forward bias with $p_{10} = 5.13 \cdot 10^{10} \text{ cm}^{-3}$.

¹¹ $p(d_1)$ is kept constant in forward and in reverse bias in order to simplify the following discussion.

Fig. 28.18 Current distribution corresponding to Fig. 28.17 except $p_{10} = 5.13 \cdot 10^{10}$, $p(d_1)_{\text{forw}} = 5.26 \cdot 10^{10}$, and $p(d_1)_{\text{rev}} = 5 \cdot 10^{10} \text{ cm}^{-3}$. **(a)** Total hole currents $[j_{p,\text{tot}}(x)]$; **(b)** gr-currents $[j_{\text{gr}}(x)]$; both Figures with the external field as family parameter



28.3.4 Total Drift Assisted Minority Carrier Current

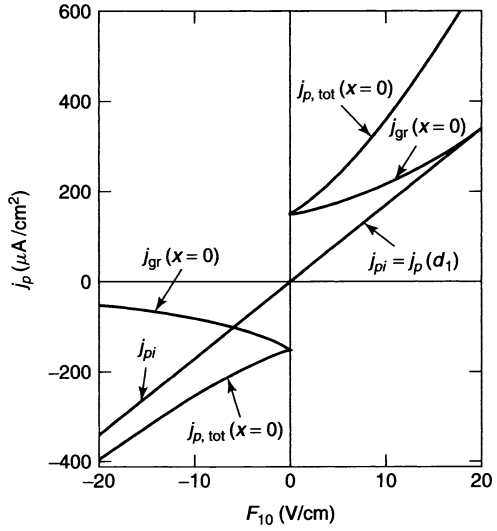
When evaluating the hole current obtained from Eq. (28.53) at $x = 0$, one obtains the *total hole current*; it has the same form as Eq. (28.45) except for the tanh factor times the diffusion length that is now replaced by the downstream diffusion length L_{pf1} :

$$j_{p,\text{tot}}(x=0) = e \frac{L_{pf1}}{\tau_{p0}} (p_{jD} - p_{10}). \quad (28.54)$$

Figure 28.19 shows the currents as functions of the external field F_{10} . The *generation/recombination* (part of the) *current* is obtained by using the upstream diffusion length L_{pf2} as the effective diffusion length:

$$j_{\text{gr}}(x=0) = \Delta j_{\text{gr}} = e \frac{L_{pf2}}{\tau_{p0}} (p_{jD} - p_{10}). \quad (28.55)$$

Fig. 28.19 Hole currents with the same parameters as in Fig. 28.16 as obtained for $p_{jD} = 10^{10} \text{ cm}^{-3}$ in reverse, and for $9 \cdot 10^{10} \text{ cm}^{-3}$ in forward and for $p_{(d1)} = 5 \cdot 10^{10} \text{ cm}^{-3}$ in reverse and $5.26 \cdot 10^{10} \text{ cm}^{-3}$ in forward bias as function of a constant external field, F_{10} . The figure shows as three branches the generation-recombination branch j_{gr} , the divergence-free drift branch j_{pi} and the sum of both j_p , tot all evaluated at $x = 0$ in reverse (left side) and in forward bias (right side of the figure)



The *divergence-free* (part of the) *current*, as defined by $j_{p,tot}(x=0) - j_{gr}(x=0) = j_{pi}$, is given by

$$j_{pi} = e \frac{L_{pf1} - L_{pf2}}{\tau_{p0}} (p_{jD} - p_{10}). \quad (28.56)$$

From Eqs. (28.48) and (28.49) one has for sufficiently high fields, when $L_s \gg L_p$:

$$L_{pf1} - L_{pf2} = L_s; \quad (28.57)$$

hence

$$j_{pi} = e\mu_p F_{10} (p_{jD} - p_{10}), \quad (28.58)$$

which is in agreement with Eq. (28.44) for $p_{jD} \ll p_{10}$.

A homogeneous external field, therefore, causes an increase in the minority carrier current which, with increasing field, becomes more and more a simple drift current.

In *forward bias*, the gr-current increases linearly with the field for $L_s \gg L_p$:

$$L_{pf2}^{\text{forw}} (L_s \gg L_p) \rightarrow L_s. \quad (28.59)$$

For high fields the gr-current approaches the drift current

$$j_{gr}^{\text{forw}} \rightarrow e\mu_p F_{10} (p_{jD} - p_{10}). \quad (28.60)$$

In addition one has the divergence-free current

$$j_{pi} = e\mu_p F_{10} (p_{jD} - p_{10}); \quad (28.61)$$

hence the total minority current with sufficient forward bias equals twice the drift current for a thick devices. When the field is further increased, the effective diffusion length increases and will finally surpass the device thickness. The device then becomes a thin device, reducing the additional contribution of the gr-current; the total hole current then becomes the *simple drift current*:

$$j_p(x=0, L_s > d_1) \rightarrow j_{pi} = e\mu_p(p_{jD} - p_{10})F_{10}, \quad (28.62)$$

an equation which now holds for sufficiently large forward bias in the homogeneous part of the device. In *reverse bias*, L_s is negative and L_{pf2} decreases hyperbolically with the field

$$L_{pf2}^{\text{rev}}(-L_s \gg L_p) \rightarrow \frac{L_p^2}{L_s}. \quad (28.63)$$

This means that in reverse bias $L_{pf1} - L_s$ goes asymptotically to zero. At large enough reverse bias, again Eq. (28.62), i.e. the simple drift current holds.

The *influence of the device thickness* can be included explicitly by introducing the above neglected tanh factor, i.e., by using v^* [Eq. (28.41)] for optical minority carrier generation, but with L_{pf2} instead of L_p in its argument

$$j_{\text{gr}} \simeq e(p_{pD} - p_{10}) \frac{L_{pf2}}{\tau_{p0}} \tanh\left(\frac{x_m}{L_{pf2}}\right), \quad (28.64)$$

with x_m depending on the surface boundary condition as described in Sect. 28.2.5.

28.3.5 Justification for the Separation of Injection and Generation Currents

In principle, we could use field-assisted diffusion with L_{pf1} and L_{pf2} as effective diffusion lengths using only Eq. (28.53) and its spatial derivative for all further discussion.

This leaves the gr- and drift-part entangled. We have chosen to separate these two currents from the beginning, since they represent different transport mechanisms. Such separation is possible since the divergence-free current j_{pi} remains constant throughout the device ($L_{pf1} - L_{pf2}$ is independent of x). The drift-part is divergence-free and uniquely determined by the hole-density and the field¹² at d_1 .

On the other hand, only the gr-current contributes to the interchange between minority and majority carriers. Only to the extent that j_{gr} for holes changes in x will j_{gr} for electrons also change, causing a corresponding changeover between electron

¹²The selection of d_1 here is due to the specific example in which we assumed a neutral electrode at d_1 with a flat-band (no space charge) connection to the semiconductor/metal interface. When a space-charge layer is also present at d_1 , the identification of j_{pi} is more involved (see Sect. 29.2.2).

and hole currents as discussed in Sect. 27.3.2. If Δj_{gr} is small compared to the total current, j_n will be essentially divergence-free. This aspect will be helpful in the distinction between the behavior of Schottky barriers and pn -junctions. Only in the latter, a nearly complete changeover occurs between predominant hole current in the p -type material to a predominant electron current in the n -type part and only here the divergence-free part becomes negligible. In many Schottky barriers, the divergence-free current remains significant and often provides most of the reverse saturation current.

Our approach permits a cleaner separation of different current contributions as they relate to device operation.

Chapter 29

Schottky Barrier in Two-Carrier Model

Abstract Electron and hole currents in barriers are analyzed. Divergence free electron and hole currents are introduced. GR currents in Schottky barrier devices are computed. GR currents in the space charge region are evaluated. The field influence in the barrier region is shown. A definition of the carrier density at the splitting boundary is given. Minority carrier density at the metal/semiconductor surface is given. A Schottky barrier with two carriers is analyzed. The governing set of equations including the continuity equation is introduced. Example set of parameters for Ge device is given. Boundary conditions are introduced. Example solutions for a thin device are given. The carrier distribution is computed. The Boltzmann region for minority carriers is identified. Demarcation lines are identified and the Shockley-Frank-Read recombination centers are introduced. Currents in the Schottky barrier are calculated. The Quasi Fermi levels and demarcation lines are given. The electron and hole density crossing is analyzed. A carrier inversion layer with consequences on space charge is discussed. Schottky barrier devices are analyzed. Medium width devices, boundary conditions, and general solution behavior is discussed. The Schottky barrier in wider devices and a violation of the van Roosbroek approximation is pointed out. The relative contribution of the divergence free and GR currents in barrier devices are discussed.

In Schottky barriers one needs to consider the influence of minority carriers when the barrier is sufficiently large. Here carrier generation and recombination become important.

We will now extend the analysis of the transport properties of a two-carrier model to a Schottky barrier. One of the main differences between a one-carrier Schottky barrier discussed earlier and the two-carrier Schottky barrier is the electron-hole inter-relation to its currents that was discussed for a homogeneous semiconductor in the previous chapter. We will again assume here an n -type Schottky barrier.

29.1 Electron and Hole Currents in Barriers

The majority carrier current (j_n) is controlled by the properties of the barrier, as discussed in Chap. 26. The minority carrier current (j_p), though also controlled by

Table 29.1 Parameters of germanium-barrier

Parameters	N_d	N_r	N_c	N_v	n_{10}
Values	10^{16}	10^{16}	10^{19}	$6 \cdot 10^{18}$	10^{16}
Dimensions	cm^{-3}	cm^{-3}	cm^{-3}	cm^{-3}	cm^{-3}
Parameters	E_g	$E_i - E_r$	$\psi_{\text{MS},n}$	$\psi_{\text{MS},p}$	p_{10}
Values	0.66	0.10	0.319	0.341	$5.13 \cdot 10^{10}$
Dimensions	eV	eV	V	V	cm^{-3}
Parameters	c_{cv}	μ_n	μ_p	n_c	p_c
Values	10^{-9}	3900	1900	$4.48 \cdot 10^{13}$	$1.15 \cdot 10^{13}$
Dimensions	$\text{cm}^{-3} \text{ s}^{-1}$	$\text{cm}^2/\text{V s}$	$\text{cm}^2/\text{V s}$	cm^{-3}	cm^{-3}
Parameters	v_n^*	ε	T	n_i^*	n_i
Values	$5.7 \cdot 10^6$	16	300	$1.077 \cdot 10^{15}$	$2.265 \cdot 10^{13}$
Dimensions	cm/s	—	K	cm^{-3}	cm^{-3}

the barrier, is mostly generated in the bulk region near the barrier, as described in the preceding chapter. Both regions have a different thickness, the barrier relating to the Debye length L_D , and the active part of the bulk relating to the minority carrier diffusion length L_p .

In most devices L_p is much larger than L_D . In the Schottky barrier discussed here as an example (see Table 29.1) $L_D = 480 \text{ \AA}$ and $L_p = 22 \text{ }\mu\text{m}$, with a ratio L_p/L_D of ~ 500 , so that the different properties in these regions can be well separated for transparency of the following discussion. In order to identify the different contributions to the current j , we have subdivided¹ the current into several contributions, even though there are inter reactions between several of them.

We distinguish four contributions to the total currents:

- the $n(x=0) = n_j$ -controlled, divergence-free majority-current, j_{ni} ;
- the $p(x=d_1) = p_j$ -controlled, divergence-free minority-current, j_{pi} ; and
- the gr-current for minority-carriers $j^{(p)}(x)$, and
- the complementary gr-current for majority-carriers $j^{(n)}(x)$.

In a device containing a space charge region, each of these currents has, in part of the device, drift and diffusion contributions.

29.1.1 Divergence-Free Electron and Hole Currents

The divergence-free current is the part of the current that does not interact via generation or recombination with the opposite carrier. Its separation provides an imme-

¹For justification of this unconventional approach see Sect. 29.3.

diate check on the influence of minority carriers. In a one-carrier model only the divergence-free majority carrier current j_{ni} exists. In the bulk it is carried by drift, in the barrier by the difference between drift and diffusion. $j_{ni} = j_n$ is used as an input parameter for numerical integration of the system of governing differential equations, e.g., in Eqs. (27.5)–(27.7) as described in Chap. 28 and Sect. 27.1. It will be used later in a similar fashion in Eqs. (29.12)–(29.17) for the two-carrier model (Sect. 29.2).

In the two-carrier model there are two divergence-free current contributions j_{ni} and j_{pi} . These currents can be determined at any convenient position of the device in which the gr-current contribution can be neglected. Without surface recombination, this could be at the cathode for j_{ni} and at the anode for j_{pi} since $j^{(n)}(x=0) = j^{(p)}(x=d) = 0$. When including surface recombination, the task of current separation is more involved, as will be shown in Sect. 29.1.3.

29.1.2 GR-Currents in Schottky Barrier Devices

The gr-current contribution can be subdivided into four parts,

- gr-currents from the bulk region (as discussed in Chap. 30);
- gr-currents from the space charge region;
- gr-currents from metal/semiconductor interfaces; and
- gr-currents from other surfaces.

We separate the contribution of the gr-currents in the space-charge region and in the bulk region in this discussion, and present some typical device examples later in this chapter. The interface recombination will be discussed in different Sections, emphasizing their contributions to the diode leakage.

29.1.3 GR-Currents in the Space-Charge Regions

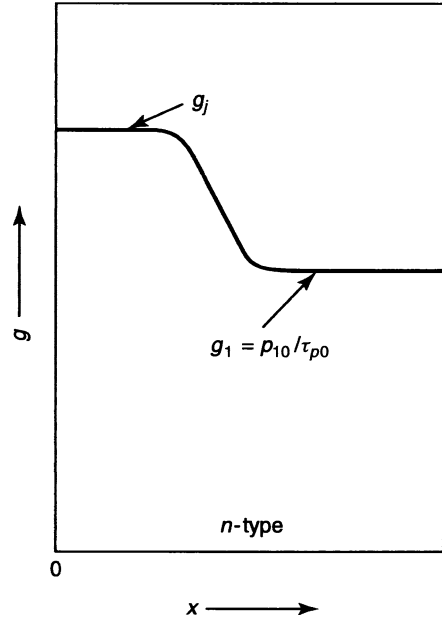
In the space-charge region, the net gr-rate U changes as a function of x . In order to show the main features, we separate generation and recombination. We first approximate the generation rate $g(x)$ for thermal excitation by [see Eq. (27.33)]

$$g(x) = \frac{c_{cv} N_r n_i^2}{n(x) + p(x) + 2n_i \cosh\left(\frac{E_r - E_i}{kT}\right)} \quad (29.1)$$

$$g(x) = \frac{1}{\tau_{p0}} \frac{n_i^2}{n(x) + p(x) + n_i^*}. \quad (29.2)$$

In the Schottky barrier region, $n(x)$ decreases below $n^{(\text{th})} = N_d$ to approach n_c at the metal/semiconductor interface. Consequently the generation rate increases, until

Fig. 29.1 Generation rate that show a step-like behavior between bulk and barrier (schematic)



$n(x)$ crosses $p(x)$ or n^* in the denominator of Eq. (29.2), depending on which of these terms predominates.

One therefore distinguishes two regions, the n -type bulk with the generation rate

$$g_1(x) = g_n = \frac{n_i^2}{\tau_{p0}n_{10}} = \frac{p_{10}}{\tau_{p0}}, \quad (29.3)$$

and the barrier where n becomes comparable to p , with $g_1(x)$ increasing. For $E_r - E_i \neq 0$ the third term in the denominator finally becomes the largest, and one obtains a flat maximum of the generation rate with

$$g_2(x) = g_j = \frac{n_i^2}{\tau_{p0}n_i^*} \quad (29.4)$$

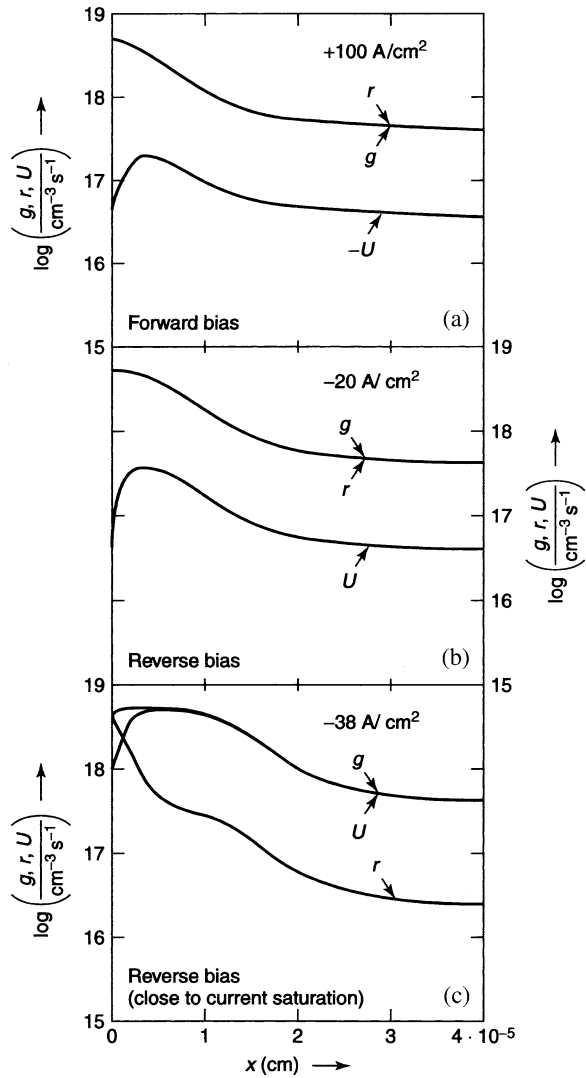
typical generation rate distribution is shown in Fig. 29.1 with these two ranges depicted.

The recombination rates, corresponding to the above mentioned generation rates are given by

$$r(x) = \frac{1}{\tau_{p0}} \frac{np}{n(x) + p(x) + n_i^*} \quad (29.5)$$

and changes within the barrier region in a similar manner. For zero bias (i.e. in thermodynamic equilibrium) the recombination rate is the same as the generation rate distribution (since $np = n^2$). It shows the same step like behavior.

Fig. 29.2 Generation, recombination and net gr-rates in a Schottky barrier, as computed from Eqs. (29.12)–(29.17) with parameters given in Table 29.1; for forward bias: (a) with $j = 100 \text{ (A/cm}^2\text{)}$; and for reverse bias in (b) with $j = -20 \text{ (A/cm}^2\text{)}$; or in (c) with $j = -38 \text{ (A/cm}^2\text{)}$



With *reverse bias* both $n(x)$ and $p(x)$ decrease below the equilibrium distribution, thus causing $r(x)$ to become smaller than $g(x)$, and resulting in a positive *net* gr-rate U of similar shape. The opposite relation appears with *forward bias*: $n(x)$ and $p(x)$ becomes larger than the equilibrium distribution; hence the recombination dominates: $r(x) > g(x)$ and $U(x)$ becomes negative. Figure 29.2 shows an example of such a distribution for $g(x)$, $r(x)$ and $U(x)$ as computed for an actual Schottky barrier with parameters listed in Table 29.1 (observe the changing sequence of g , r and U in panels a, b and c) observe that in Fig. 29.2 the absolute values of $r(x)$ and

$U(x)$ are plotted in order to permit an easy comparison of the shape of these two curves. The change in sign for U in forward bias is indicated by $-U$ in Fig. 29.2a and by $+U$ in reverse bias in Figs. 29.2b and c.

The net gr-rate U can also be approximated by two (nearly) constant space-independent values, joining each other in a step like fashion,² in the bulk by U_{10} :

$$U_{10} \simeq \frac{p_{jD} - p_{10}}{\tau_{p0}}; \quad (29.6)$$

and in the barrier,³ by U_j :

$$p_{jD}^* = p_{jD} \frac{n_j}{n_i^*} \quad \text{and} \quad p_{10}^* = p_{10} \frac{n_{10}}{n_i^*}; \quad (29.7)$$

with

$$\Delta j_{\text{gr}} = e \int_0^{d_1} U(x) dx \quad (29.8)$$

for n^* see Eqs. (29.1) and (29.2). The variation of the bias influences the boundary density p_{jD} (or p^*), hence the net gr-rate. This causes a change in the step-height; by influencing the changeover from p_{jD} to p^* , it makes the step in the barrier region wider or narrower in reverse or forward bias, respectively.

The step like behavior permits the use of the same diffusion equation as discussed in Sect. 29.1.1 within the horizontal range of each step. Δj_{gr} to be approximated by line segments as shown in Fig. 29.3:

$$\Delta j_{\text{gr}} = e \int_0^{d_1} U(x) dx \simeq -e [U_j x_D + U_{10}(d_1 - x_D)]. \quad (29.9)$$

For wider slabs, $U(x)$ in the bulk starts to vanish for $x > L_p$, as discussed in Sect. 28.1.1.

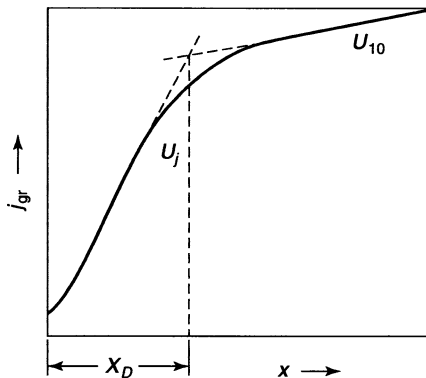
29.1.4 Field Influence in the Barrier Region

In the space-charge region the field is much larger than in the bulk and thus its influence on the minority carrier current needs to be considered. The changes of the effective diffusion length due to the *Schubweg* are mostly negligible, since the

²Even though Eq. (29.6) should contain the space-dependent minority carrier densities, we have replaced these by the constant p_{jD} and later in Eq. (29.7) by n_j ; this is justified to an improved approximation with reverse bias as can be seen from the computed result of a step like $U(x)$.

³For simplicity of the mathematical description we have chosen modified carrier densities p^* and p^* rather than the modified minority carrier lifetime τ_p [given in Eq. (28.49)], which would result in a somewhat longer expression.

Fig. 29.3 Schematics of gr-current with bias in the barrier of width x_D and in the bulk with barrier and bulk net-generation rates U_j and U_{10} , respectively shown



length in which the field acts, the Debye length, is usually much smaller than the minority carrier diffusion length in which most of the minority carrier collection occurs.

A significant influence of the field, however, on $p(x)$ requires a large minority carrier gradient near the interface to the electrode, in order to compensate the ensuing drift current. We will discuss this balance in the following section.

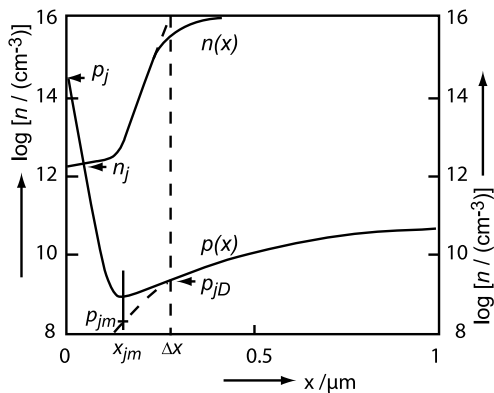
29.1.5 The Definition of the Carrier Density at the Splicing Boundary

The minority carrier distribution in the bulk as a function of the density p_{jD} at the barrier-to-bulk interface is discussed in Chap. 28. The connection of this density with the computed $p(x)$ distribution in the barrier region was indicated in Fig. 28.1, and was mentioned as a means of the bias to control the minority carrier current through the bulk. We need now to refine the discussion of the boundary condition p_{jD} .

The steep increase of the minority carrier density toward the density p_j at the metal boundary is shown in Fig. 29.4 (see also Sect. 29.2.2). Such increase is required for obtaining a balancing diffusion current toward the bulk to counteract the drift current toward the metal boundary. Depending on the bias, the field-ramp and therefore the minority carrier density slope changes in the barrier region, in order to maintain almost exact cancellation of drift and diffusion. This results in a shift of the density p_{jD} at the end of the barrier where the barrier field vanishes and the minority current becomes almost exclusively diffusion-controlled.

In reverse bias this transition is clearly visible in Fig. 29.4, as $p(x)$ goes through a minimum with the diffusion current changing sign at x_{jm} . Between x_{jm} and Δx a small and decreasing drift field maintains current continuity. or computational reasons, we treat the Schottky barrier region and the bulk region separately in the approximation given earlier, and splice the solution curves at the boundary Δx .

Fig. 29.4 Minority carrier and majority carrier distribution in the junction as given by the computed solution of Eqs. (29.12)–(29.17) with parameters given in Table 29.1, and for $j_{ni} = -39 \text{ A/cm}^2$. The solution curves for $p(x)$ with $x > \Delta x$ are also shown as obtained from the approximation of Eq. (29.9) for $p_{10} = 5.13 \cdot 10^{10} \text{ cm}^{-3}$



Such splicing is shown in reverse bias in Fig. 29.4: One can define a density p_{jm} on the extrapolated diffusion curve at the position x_{jm} of the minimum of the exact $p(x)$ distribution in reverse bias. For the diffusion analysis in the bulk, given in the previous chapter, we would have obtained exactly the same answer if we started at x_{jm} with p_{jm} rather than at Δx with p_{jD} as we did.

Whenever $p_{\min}$ is easier to determine than $p(\Delta x) = p_{jD}$ we may indeed do so. For most devices, however, $\Delta x - x_{jm}$ is very small compared to L_p and to the device thickness, so that the error introduced by omitting Δx altogether is small.

29.1.6 Minority Carrier Density at the Metal/Semiconductor Interface

The metal/semiconductor interface acts as a perfect recombination surface which forces the *two quasi-Fermi levels* (see Sect. 29.2.2) to *collapse* and connect to the Fermi level of the metal. The product of the of minority and majority carrier densities at the interface is therefore given by n^2 . With zero bias this means

$$p_c = \frac{n_i^2}{n_c}. \quad (29.10)$$

n_c with bias, the majority carrier density slides near this boundary according to Eq. (28.30). When assuming that the interface recombination also determines the shifted boundary densities, one has as a condition for the holes

$$p_j = \frac{n_i^2}{n_j} \quad (29.11)$$

which we will use consistently in the following sections. This condition holds as long as $j_p(x=0) \ll j_n(x=0)$, that means that the electron current controls the minority carrier relation at the metal/semiconductor interface.

29.2 Schottky Barrier with Two Carriers

The interaction between the two carriers in a Schottky-barrier device now becomes transparent. Its discussion will guide further understanding about the minority carrier contribution in *pn*-junction devices, where this interaction becomes essential for controlling the total current.

29.2.1 The Governing Set of Equations

The entire behavior of the space charge region is analytically described by one set of six first order differential equations: This governing set of differential equations includes the transport equations for both carriers (given here in a form to emphasize the set of governing differential equations):

$$\frac{dn}{dx} = \frac{j_n - e\mu_n n F}{\mu_n k T} \quad (29.12)$$

and

$$\frac{dp}{dx} = \frac{-j_p + e\mu_p p F}{\mu_p k T}; \quad (29.13)$$

continuity equations⁴

$$\frac{dj_n}{dx} = -eU \quad (29.14)$$

and

$$\frac{dj_p}{dx} = eU, \quad (29.15)$$

and the Poisson equation, which now includes electrons and holes (assuming only minor compensation: $N_a \ll N_d$):

$$\frac{dF}{dx} = \frac{e(N_d - n + p)}{\epsilon \epsilon_0} \quad (29.16)$$

with

$$\frac{d\psi_n}{dx} = F. \quad (29.17)$$

⁴One of the continuity equations can be replaced by the total current equation $j = j_n + j_p$.

Fig. 29.5 Band-model of the Schottky barrier used in this section

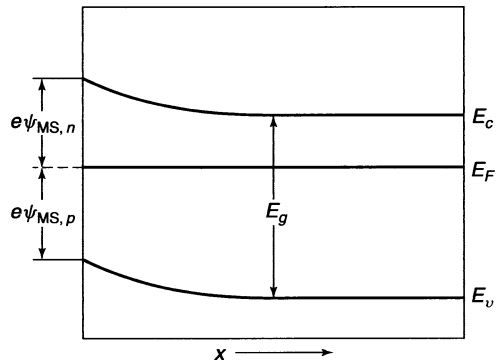
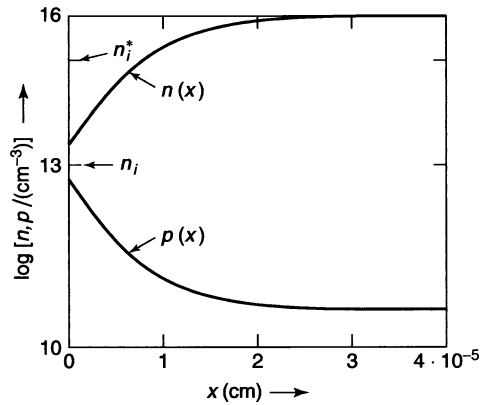


Fig. 29.6 Electron and hole distributions for thermal equilibrium as computed from Eqs. (29.12)–(29.17) with parameters given in Table 29.1, with n_i and n^* indicated in the figure



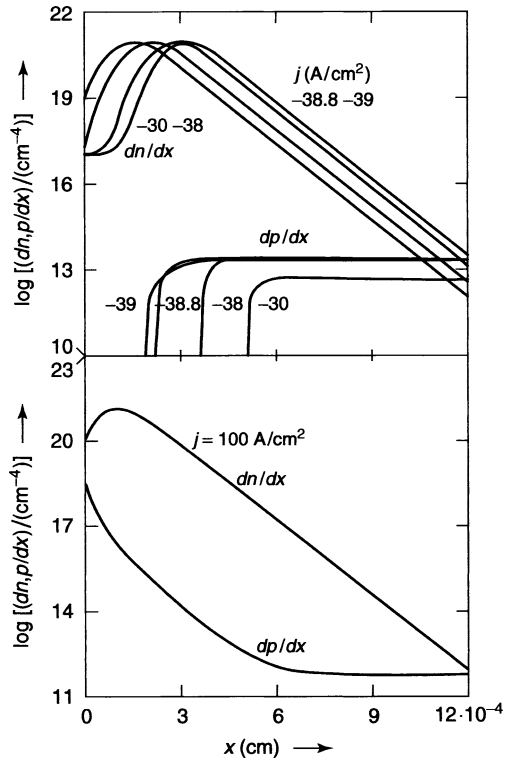
29.2.2 Example Set of Parameters

In order to make minority carrier contributions more important, we have chosen as the first example a small band-gap material (Germanium) with $E_g = 0.66$ eV in which the majority and minority carrier densities can be kept in closer proximity to each other (Figs. 29.5 and 29.6).

For reasons of initial simplicity, the metal/semiconductor work function was chosen so that the electron density at the metal/semiconductor interface in equilibrium at $T = 300$ K, is only slightly larger than the corresponding hole density (see Fig. 29.6).

A shallow, totally ionized donor is assumed to produce n -type semiconductivity. The complete set of parameters used in the computation is summarized in Table 29.1.

Fig. 29.7 Slopes of n and p as obtained from numerical integration of Eqs. (29.12)–(29.17) and parameters of Table 29.1 with the total current as family parameter. (a) For reverse bias with $j = -30, -38, -38.8$, and -39 A/cm^2 for curves 1–4, respectively; (b) for forward bias with $j = 100 \text{ A/cm}^2$



29.2.3 Boundary Conditions

One distinguishes several cases depending on the excitation (whether it is thermal only, or predominant optical), the width of the device d_1 (short or long compared to the minority carrier diffusion length), and the surface condition (negligible or predominant surface recombination). Accordingly, different approximations may be employed.

With six first order differential equations describing the problem, we need six boundary conditions, n_b , F_b , ψ_b , p_b , j_{nb} , and j_{pb} , which would conventionally be given for one side of the device, i.e., either at $x = 0$ or at $x = d_1$. Unfortunately, some of these boundary conditions are sufficiently known only at one side, others at the other side. This requires a mixed condition approach, necessitating iteration.⁵

The boundary conditions for the thin device are first chosen for a neutral right surface with $s(d_1) = 0$, $n(d_1) = N_d - \delta n$ (δn obtained by iteration to assure an exponential decrease of dn/dx with increasing x , as shown in Fig. 29.7 beyond

⁵For educational purposes it is advantageous to use a forward numerical integration of the governing set of differential equation rather than a more conventional finite element method (Snowden 1985). Straightforward integration permits one to study the interaction of different variables and the cause-and-effect relation of changing boundary conditions.

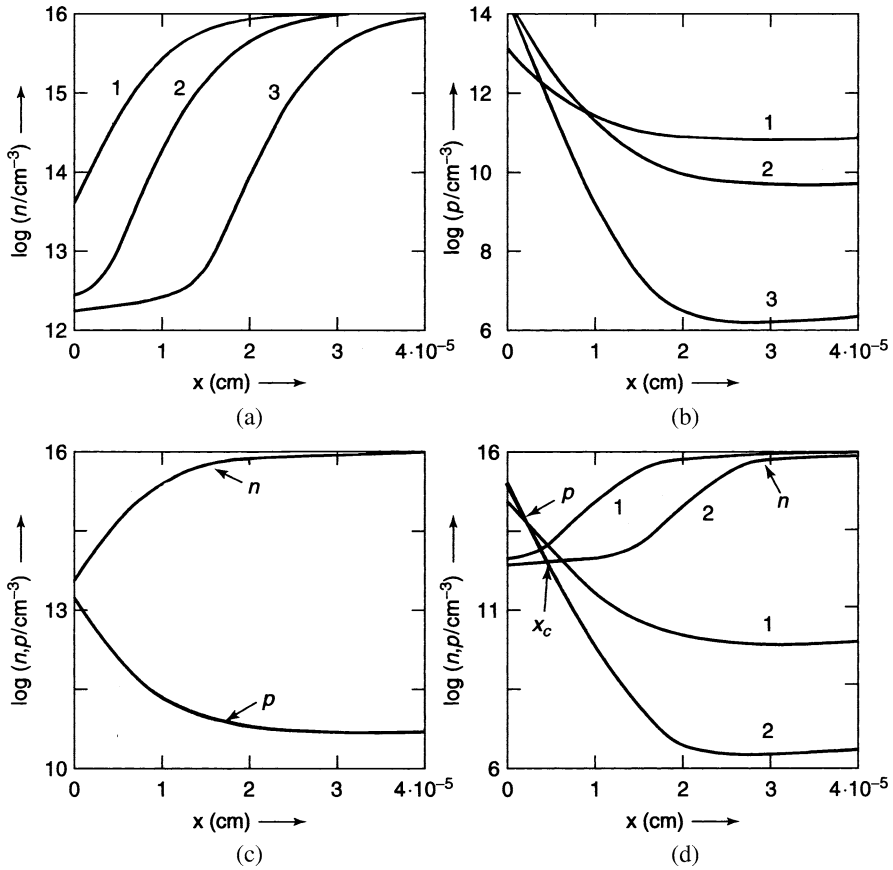


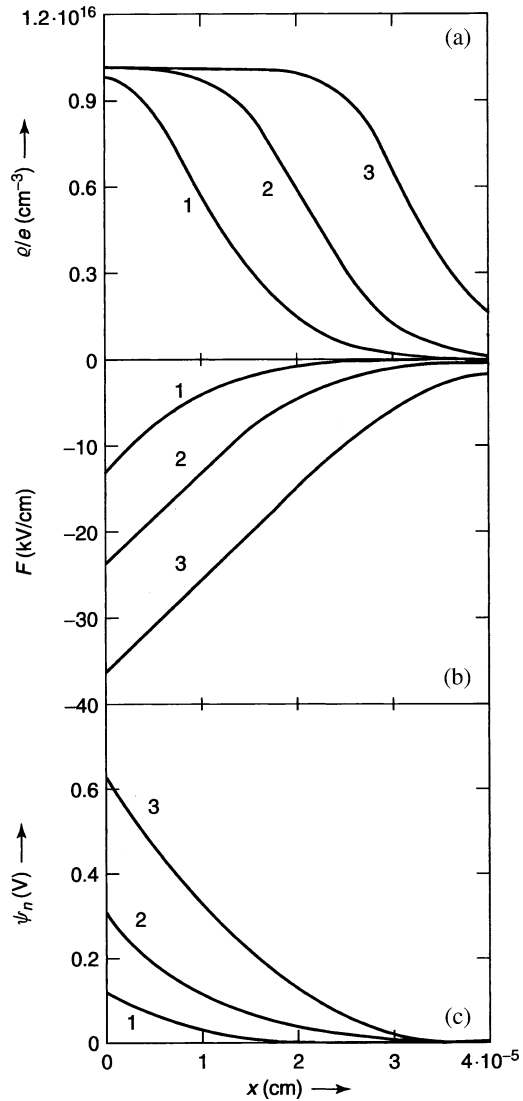
Fig. 29.8 Carrier density distribution curves obtained as solutions of Eqs. (29.12)–(29.17), with parameters given in Table 29.1 for the total current as family parameter. Curves 1, 3, 4, and 6 for $j = 100, 0, -38$, and -39 A/cm², respectively. (a) Electron density distribution; (b) hole density distribution; (c) electron and hole distributions for curves 1 and 3 only; and (d) electron and hole distributions for larger reverse currents (curves 4 and 6 only). (c) and (d) are plotted to demonstrate the relation between $p(x)$ and $n(x)$ with a cross-over near $x = 0$ at higher reverse bias

the maximum—for more see Sect. 29.2.3), $F(d_1) = j_{ni}/[e\mu_n n(d_1)]$, $\psi_n(d_1) = 0$, $j_{pi} = e\mu_p p(d_1)F(d_1)$ and $j_{ni}(d_1)$ as input parameter. The remaining $p(d_1)$ is first guessed and then iterated so that $p(0) = p_j = n^2/n_j$, assuring perfect recombination at $x = 0$.

29.2.4 Example Solutions for a Thin Device

In Figs. 29.8 and 29.9 we present a family of example solutions for the Schottky barrier within a thin slab of the n -type Germanium, as described above.

Fig. 29.9 Space-charge, field, and electrostatic electron potential distributions as solutions of Eqs. (29.12)–(29.17) with parameters given in Table 29.1; the total current as family parameter for curves 1, 3, 4, and 6 as listed in Fig. 29.8



These solution curves show a similar behavior for $n(x)$, $\rho(x)$, $F(x)$, and $\psi_n(x)$, as given in Fig. 26.9 for the single carrier model. $p(x)$ is essentially flat within the bulk with a barely visible slope toward the barrier in reverse, and away from the barrier in forward bias. Most remarkable is the steep increase of $p(x)$ in the barrier with a cross-over of $n(x)$ at higher reverse bias. However, the influence of p on other variables is negligible well within the width of the drawn curves except for ρ at the highest reverse bias and close to $x = 0$ when $p(x)$ has risen above N_d (not shown in Fig. 29.8).

29.2.5 Carrier Distributions

The steeply changing carrier distribution is caused by the increasing field and thereby increasing drift that needs to be almost exactly compensated by an increasing diffusion current in the opposite direction to keep the total current essentially⁶ constant throughout the device. This problem is not unlike the one discussed in Sect. 28.3 and governed by Eqs. (28.44) and (28.45) but here with an impressed (fixed) field distribution $F(x)$ as given by the majority carrier distribution, yielding an inhomogeneous differential equation for the minority carriers

$$\frac{d^2 p}{dx^2} - 2 \left[\frac{1}{L_D} \frac{2e(\psi_{n,D} - V)}{kT} + \frac{x}{L_D^2} \right] \frac{dp}{dx} - \left[\frac{1}{L_p^2} + \frac{1}{L_D^2} \right] p + \frac{p_{10}}{L_p^2} = 0 \quad (29.18)$$

with L_D the Debye length—see Eq. (26.20) and $\psi_{n,D}$ the diffusion electron potential—see Eq. (26.15). The solution of Eq. (29.18) now contains a mixture of bulk- (hole-related— L_p) and junction- (electron-related— L_D) characteristic lengths.

29.2.6 Boltzmann Region for Minority Carriers

A substantially simpler approximation can be obtained within the barrier region where the net current j_p is small compared to the drift and diffusion of holes; here one obtains from the transport equation, by neglecting j_p ,

$$\frac{dp}{dx} = \frac{epF}{kT}. \quad (29.19)$$

From the balance between drift and diffusion currents for holes in the entire barrier region, namely $ep\mu_p F = \mu_p kT dp/dx$ one can obtain the Boltzmann solution for holes, that is very similar to the Boltzmann solution for electrons:

$$p(x) = p_j \exp \left[- \left[\frac{e\psi_{n,j}}{kT} + \frac{eF_j x}{kT} + \frac{x^2}{2L_D^2} \right] \right], \quad (29.20)$$

with all parameters $\psi_{n,j}$, F_j and L_D , however, controlled by the electron-distribution. One can then substitute $\psi_{n,j} = (kT/e) \ln(n_{10}/n_j)$, using $n_{10}p_{10} = n^2$ and introducing F_j from Eq. (26.40), to obtain for the *Boltzmann distribution of minority carriers*

$$p(x) = \frac{n_i^2}{n_j} \exp \left[- \frac{x}{L_D} \sqrt{2e \frac{\psi_{n,D} - V}{kT}} + \frac{x^2}{2L_D^2} \right], \quad (29.21)$$

⁶The gr-current is a very small fraction of the currents.

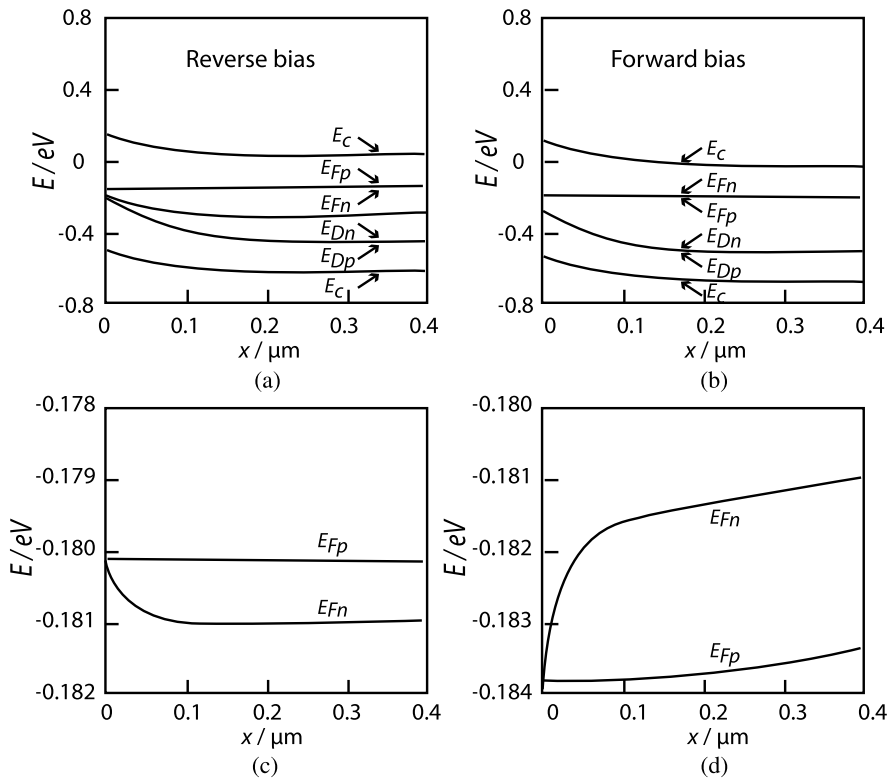


Fig. 29.10 Band-model with quasi-Fermi and demarcation lines computed from Eqs. (29.12)–(29.17) and parameters listed in Table 29.1 for the Ge-Schottky barrier for different reverse bias conditions with $j = -38.8$ and -39 A/cm² for panels (a) and (b), respectively. In panel (a) the quasi-Fermi level for holes is flat throughout, the Boltzmann, or DRO region, while at higher reverse bias in panel (b) a bending down of E_{Fp} , following essentially parallel to E_c is observed, identified as DO region for diffusion only. Observe that the demarcation lines have dropped below both quasi-Fermi levels and are even extending into the valence bands

which describes the exponentially decreasing branch of $p(x)$ within the Schottky barrier. Since this distribution is Boltzmann-like⁷ and, consequently, the hole quasi-

⁷The crossing of $p(x)$ for different bias within the barrier region is a direct result of the control of the boundary concentration p_j by the electron density n_j via $n_j p_j = n^2$ required by perfect recombination at the interface. n_j , however, is controlled by the dominant majority carrier current which forces a decrease of n_j with increased reverse bias, and, in turn, causes an increased p_j . This, together with an increased slope of $p(x)$ due to the increased barrier field, results in the crossing of the different $p(x)$ curves in the family of curves of Fig. 29.8. In contrast, $n(x)$ is the dominant variable with an increasing fraction of drift current as the bias is reduced, causing the $n(x)$ profile to widen, the $n(x)$ slope thereby to reduce hence avoiding an $n(x)$ -crossover (the solution curves of the dominant variables must be unique—Fig. 29.8A).

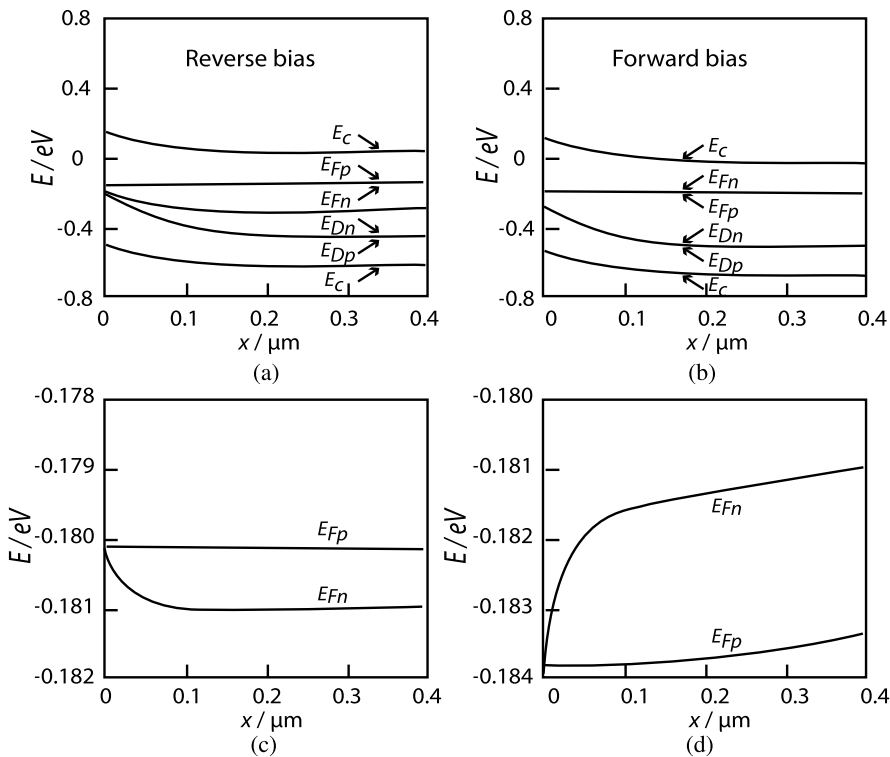


Fig. 29.11 The quasi-Fermi levels, computed for the Ge-Schottky barrier device as in Fig. 6.10, but with enlarged energy resolution, here for reverse bias in panel (a) with $j = -10 \text{ A/cm}^2$ and in forward bias with $j_{ni} = 100 \text{ A/cm}^2$ in panel (b). Observe the marked sloping up of both quasi-Fermi levels in forward bias

Fermi level is flat⁸ in reverse bias in the entire barrier region, as can be seen in Figs. 29.10 and 29.11a.

In Fig. 29.10b the DRO range is identified close to the left electrode where the drift dominates, and toward the bulk the DO range (for (D)iffusion (O)nly) is identified where diffusion dominates. In between these two regions is at high reverse bias the relatively small Boltzmann region where drift and diffusion compensate each other.

In Fig. 29.11b the two quasi-Fermi levels are given that show a distinct parallel sloping toward the right electrode.

⁸The quasi-Fermi level remains flat wherever drift and diffusion currents are large compared to the net current, i.e., for holes almost in the entire barrier region until $x = x_D$ is approached.

29.2.7 Demarcation Lines and Shockley-Franck-Read Recombination Centers

Figure 29.10 also include the two demarcation lines E_{Dn} and E_{Dp} . They lie well below the two quasi-Fermi levels and spread over a relatively wide energy range. Centers within the energy range of the demarcation lines are considered recombination centers and consequently discussed in the Shockley-Frank-Read accounting. But for this, one needs to know the specific energy level and its capture cross sections. It is probable that in such a wide energy range is also a significant distribution of energy levels with a variety of capture cross sections. Under limited circumstances one may approximate all of them with one effective recombination center and one set of capture cross sections. But, as seen from Fig. 29.11 this energy range shifts in respect to the band edges as one moves from the electrode boundary into the bulk of the semiconductor. This makes even that approximation more problematic.

This may be remembered as a warning, that, whenever one resorts to the Shockley-Frank-Read approximation to compute the behavior in barriers or junctions, a much better understanding of the recombination traffic is necessary, in order to avoid misleading result. There is no consolation from the fact that such demarcation lines are usually not shown, because they are at best confusing for different sets of centers. But since recombination becomes an important factor in determining the efficiency of solar cells, it must be emphasized to pay sufficient attention to independently determine their position within the material, their energy spectrum and recombination cross sections.

29.2.8 Currents in the Schottky Barrier

The main current in the Schottky barrier⁹ is the *divergence-free electron current* j_{ni} ,

$$j_{ni} = ev^*(n_j - n_c); \quad (29.22)$$

with $n_c = 4.48 \cdot 10^{13} \text{ cm}^{-3}$ and $v^* = 5.7 \cdot 10^6 \text{ cm/s}$, one obtains a rather large saturation current in reverse bias of $j^{(s)} = -40.6 \text{ A/cm}^2$. To support such a current through the bulk,

$$j_{ni} = en_{10}\mu_n F_{10}, \quad (29.23)$$

a reverse saturation field of $F_{10} = 6.55 \text{ V/cm}$ must be maintained in the bulk with an electron drift velocity of $\mu_n F_{10} = 2.55 \cdot 10^4 \text{ cm/s}$.

The divergence-free hole current in the bulk is given by

$$j_{pi} = ep(d_1)\mu_p F_{10}. \quad (29.24)$$

⁹The chosen example of a Ge-diode with a relatively high barrier density results in an unfavorable diode characteristic with high reverse saturation current. A much improved Schottky barrier can be obtained with a substantially lower n_c .

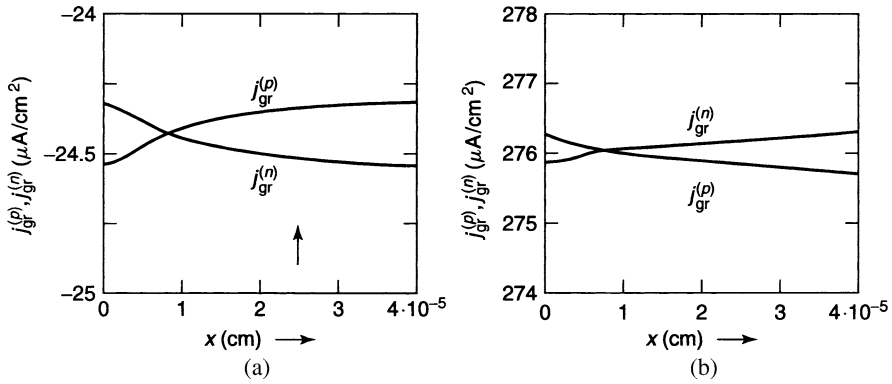


Fig. 29.12 Electron and hole gr-current distribution for different total current: $j = -38$, and $+100$ A/cm² with reverse and forward bias for panels (a) and (b), respectively. Observe that the ordinate scale is shifted by j_{pi} on top of which $j^{(p)}$ and starts at $x = d$

Because of the much lower minority carrier density in the bulk it is more than five orders of magnitude smaller than j_{ni} . The *gr-current* obtained by numerical integration is shown in Fig. 29.12 for four bias conditions. Near electron reverse saturation, we obtain the maximum contribution of $\Delta j_{gr} \cong 20$ μA/cm². This current is also more than six orders of magnitude smaller than the divergence-free electron current since, in spite of the larger net gr-rate it develops only in a thin slab of only $4 \cdot 10^{-5}$ cm width (Fig. 29.12), the electron gr-current is complementary to the hole gr-current. The sum of both add up to the same Δj_{gr} at any position of the slab, as shown in Fig. 29.12.

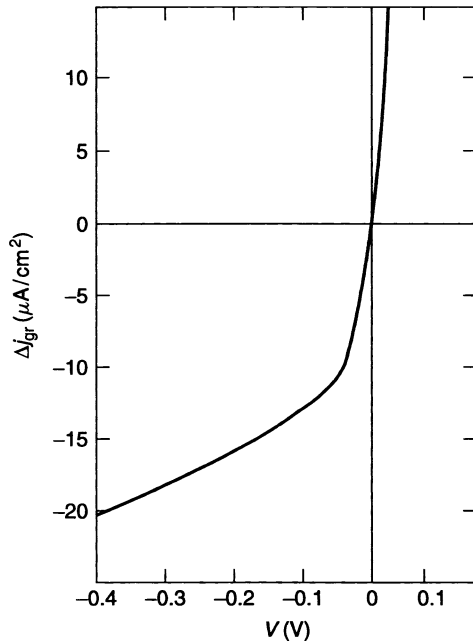
The total gr-contribution does not saturate but increases with reverse bias as shown in Fig. 29.13, since U increases with increasing width of the barrier region.

29.2.9 Quasi-Fermi Levels and Demarcation Lines

With the information given in this chapter it is important to review some of the detail of the most important quasi-Fermi levels in the understanding of the barrier behavior that can easily be expanded to junctions, as we will see in the next chapter.

It also gives another opportunity to reflect on the change of the behavior of defect centers from being carrier traps to becoming recombination centers, and the possibility of the wide range of energy in which such changes can take place, but also warn again to be careful in using a simple Shockley-Read-Hall model for computing the barrier or junction behavior since the energy range in which new recombination centers become activated, that is the range between the demarcation lines usually changes significantly throughout such space charge layers. This means that in different regions of the device the recombination traffic takes place through different centers that may have quite different recombination parameters.

Fig. 29.13 Total gr-current Δj_g as function of the applied voltage, obtained by integrating Eqs. (29.12)–(29.17) with parameters listed in Table 29.1



Let us first review again the quasi-Fermi levels. As $n(x)$ and $p(x)$ deviate from their equilibrium distribution for non vanishing currents, the Fermi levels splits into two quasi-Fermi levels E_{Fn} and E_{Fp} , and two demarcation lines E_{Dn} and E_{Dp} separate to identify the recombination centers in between, as computed for four reverse currents and plotted in Fig. 29.10.

At the metal/semiconductor interface the *quasi-Fermi levels collapse* because of the complete recombination at the metal surface. In reverse bias the quasi-Fermi level for electrons, E_{Fn} drops *below* the Fermi level E_{Fp} that remains essentially constant.

When near the electrode the quasi Fermi level for majority carrier E_{Fn} changes parallel to the band edge $E_c(x)$, a DRO-range for majority carriers appears. Where the quasi-Fermi level remains independent of x , the Boltzmann range appears. At higher reverse bias (subfigure b) E_{Fp} also starts to slope downward. Here the hole current is exclusively carried by diffusion only,¹⁰ indicating a DO-range for minority carriers. These DO and DRO ranges are identified in Fig. 29.10b.

The main portion of the voltage drop¹¹ occurs in the barrier near the metal/semiconductor interface, where the majority quasi-Fermi level $E_{Fn}(x)$ shows a similar sloping as the Fermi level for the single carrier model (compare with Fig. 26.5): al-

¹⁰We have introduced the DO-range, which is similar to the DRO-range: i.e., the total carrier current is given by one of the contributing currents only.

¹¹The total voltage drop across the entire device is equal to the drop of the majority quasi-Fermi potential: $V = [E_{Fn}(x=0) - E_{Fn}(d_1)]/e$.

most all of the voltage drop occurs in the DRO-range. The sloping becomes marked for a larger reverse currents and can be clearly identified in sub Figs. 29.10a and b.

In reverse bias the quasi-Fermi level for holes lies *above* the one for electrons, indicating *minority carrier depletion*, i.e., in this region are substantially less minority carriers than in equilibrium. In forward bias (shown in Fig. 29.11b), the majority carrier quasi-Fermi level E_{Fn} lies above E_{Fp} as expected when additional majority carriers are pulled from the bulk into the barrier (*carrier accumulation*).

With large enough reverse bias the hole density in the bulk is sufficiently reduced so that the minority quasi-Fermi level enters the majority carrier (conduction) band. This strong depletion has no other significance¹² attached to it.

The *demarcation lines* given in Figs. 29.10 and 29.11 lie close to the valence band, and for the given example (with the assumed $c_{ct} = c_{tv}$) are almost a mirror-image of the quasi-Fermi levels.

It is striking that at higher reverse bias (Fig. 29.10b) there are *no hole traps* as the hole demarcation line approaches and enters the valence band. Here, near the bulk, the preferred recombination can extend into the valence band (intrinsic recombination, band-to-band recombination). This is understandable when referring to the very low hole density in this region in high reverse bias (Fig. 29.8d).

Near the metal/semiconductor interface the sets of quasi-Fermi levels and demarcation lines cross each other, indicating the rapidly changing role of different levels¹³ in the gap in the first part of the barrier. This again emphasizes the need for precaution to use a too simplified recombination model for an entire device.

29.2.10 Electron and Hole Density Crossings

We have chosen in the preceding sections an example in which ending near a Schottky barrier a cross-over of electron and hole densities may occur under certain bias condition. It is important to point out that such a cross-over per se does not mean the existence of pn-junction that will be discussed in the following chapter and is caused by a change in doping, but most importantly is identified by a change in the sign of the space charge causing a change in the sign of the slope of the field.

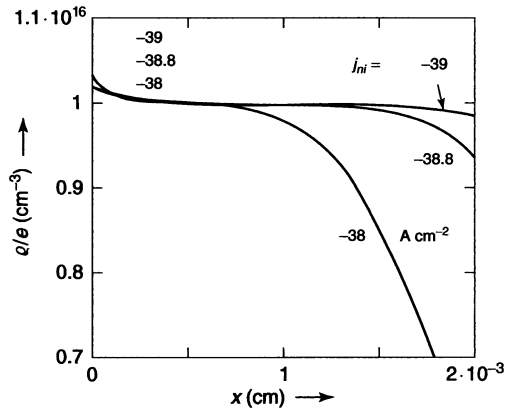
One must remember that the space charge is determined by the *sum of free and trapped charges*. Though the carrier density may change the entire distribution, it does not signify a parallel change over of the sign of the sum of all charges.

We have shown that close to the metal/semiconductor interface, $n(x)$ and $p(x)$ cross each other at higher reverse bias at a bias-dependent position x_c (Fig. 29.8b).

¹²In contrast to the entry of the majority carrier Fermi-level into its band, that signifies degeneracy.

¹³In this example only two kinds of levels were assumed: very shallow electron donors and deep recombination centers. In actual practice a larger variety of levels exist, making such an analysis more important.

Fig. 29.14 Space-charge distribution in the Ge-Schottky barrier computed as for Figs. 29.8 and 29.9; shown in an enlarged scale with high reverse currents as family parameter indicating the increase of space charge above eN_d near $x = 0$ due to the contribution of free holes



The transport properties remain unchanged for $x < x_c$ where p becomes larger than n : j_n remains more than five orders of magnitude larger than j_p . An inspection of the solution curves shown in Figs. 29.8 and 29.9 does not reveal significant changes of any of these curves¹⁴ at x_c .

We therefore ignore such a crossing of n and p , and describe the entire Schottky barrier as an n -type barrier, independent of whether $n > p$, or a *carrier inversion* to $p > n$ occurs close to the interface.

29.2.11 Carrier Inversion Layer with Consequences on the Space Charge

When in strongly blocking electrodes at sufficient reverse bias minority carrier injection becomes large enough to compensate the donor density, one speaks of a true *inversion layer* neat the contact. In the given example of an n -type Ge, the hole density at sufficient reverse bias becomes comparable to the donor density N_d , and consequently the space charge increases beyond the donor density, that otherwise determines the positive space charge when depleted close to the metal/semiconductor interface. This is shown close at the left in (Fig. 29.14). As a consequence the field slope increases and n decreases to keep j_n constant in the DRO-region:

$$n(x) = \frac{j_n}{e\mu_n F(x)}. \quad (29.25)$$

This inversion layer has only a slight effect on the barrier as it reduces the increment in barrier width with further increasing reverse bias; i.e., the solution will not expand as readily as it would without such a carrier inversion. The influence on the voltage

¹⁴The only expected change would be in U from being n -controlled to becoming p -controlled; however, this changeover is hidden near n_c by n^* in the denominator of $U(x)$.

drop, however, can become noticeable since the DRO-region shrinks, even though the change of $F(x)$ is minute.

29.3 Schottky Barrier Device

Any real Schottky barrier device has two metal electrodes. Earlier, we have neglected such a contact at d_1 . We will now introduce perfect recombination also at d_1 , however, still assuming a neutral contact with a flat band connection at d_2 . Such influence of the second electrode is usually negligible in long devices with a width substantially exceeding the Debye length and the diffusion length. However under certain circumstances, e.g. in solar cells with indirect band gaps, having a nearly homogeneous optical excitation throughout the cell, the second electrode may also exert its influence because of the carrier recombination there. To analyse the effects of the second electrode we will analyse a few examples below.

29.3.1 Medium Width Device, Boundary Conditions

We first assume a thin device of 10^{-4} cm thickness with the set of parameters given in Table 29.1, with a neutral metal contact at $x = d_1$ and a surface recombination velocity of $s(d_1) = 2 \cdot 10^7$ cm/s to provide perfect recombination at that surface, and leaving $n(d_1) = n_{10}$ and $F(d_1) = F_{10}$, but forcing $p(d_1) = n^2/n_{10}$, hence forcing both quasi-Fermi levels also at the right surface to collapse.

29.3.2 General Solution Behavior

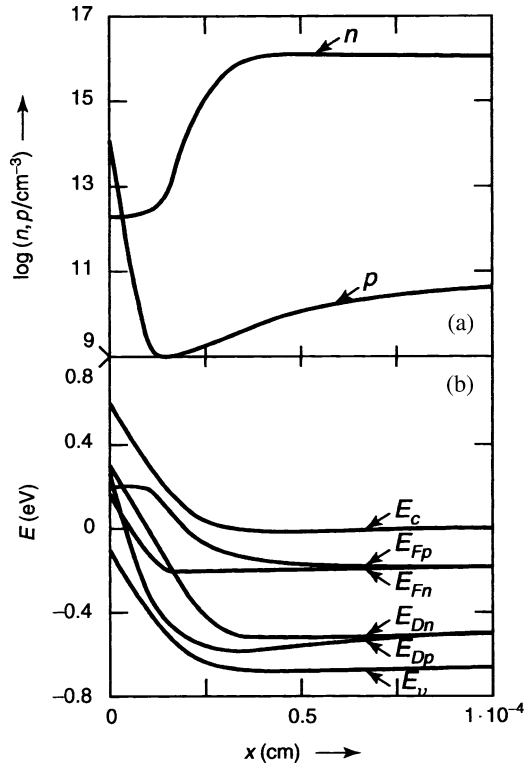
Figure 29.15 shows the influence of this increased surface recombination the right electrode (at d_1).

The hole density is increased in the bulk; the minimum is shifted further into the bulk and is not as deep compared to Fig. 29.15. This can be understood by the increased diffusion current toward the right surface, which brings $p(d_1)$ closer to p_{10} . The electron density distribution, however, is essentially unchanged since $n \gg p$. The quasi-Fermi levels collapse now at $x = 0$ and at $x = d_1$.

Close to the neutral contact, E_{Fn} remains constant (as n does) while $E_{Fp}(x)$ decreases in reverse bias until it joins E_{Fn} at $x = d_1$.

In summary, strong surface recombination influences minority carriers throughout the thin device: $p(x)$, $E_{Fp}(x)$, and therefore also $j_p(x)$ are substantially changed. The majority carrier properties, however, are essentially unchanged, except for a comparatively small reduction of the DRO-range width when the minority carrier density exceeds the majority dopant density. This causes a slight steepening of the characteristics before attaining saturation.

Fig. 29.15 Solution curves of Eqs. (29.12)–(29.17) with parameters given in Table 29.1 and surface recombination at $d_1 = 10^{-4}$ cm with $s = 2 \cdot 10^7$ cm/s that shows relatively little influence on $n(x)$ but an increase of $p(x)$ toward the right electrode (panel (a)). The quasi-Fermi levels shown in panel (b) collapse at both metal surfaces



29.3.3 Schottky Barrier in Wider Device and Violation of the Roosbroek Approximation

Earlier, we analyzed a device that extended only little beyond the barrier width. The integration much beyond the barrier width the analysis can be simplified substantially by assuming $n(x) = n_{10}$ and $F(x) = F_{10}$ as soon as both variables have approached the constant values within sufficient accuracy.

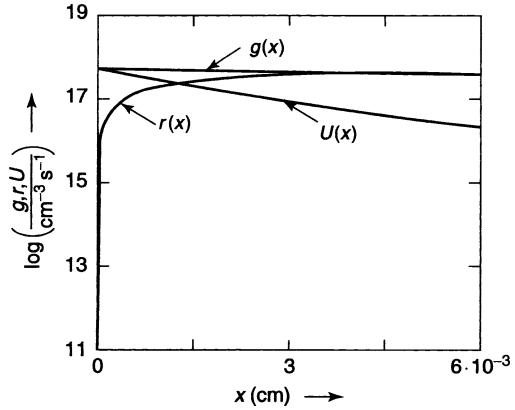
How close $n(x)$ has approached the constant n_{10} can be estimated from the transport and Poisson equations for electrons (after differentiation of the first and substituting the second):

$$\frac{d^2 n}{dx^2} \simeq \frac{n}{L_D^2} \frac{N_d - n}{N_d}, \quad (29.26)$$

yielding the approximate solution

$$\frac{dn}{dx} \simeq \frac{N_d - n(x=0)}{L_D} \exp\left(-\frac{x}{L_D}\right), \quad (29.27)$$

Fig. 29.16 $g(x)$, $r(x)$, and $U(x)$ for a total current of -38 A/cm^2 plotted for comparison in an unbroken linear scale



and decreases exponentially. After a second integration one obtains for

$$\delta n = n_{10} - n(x), \quad \delta n = N_d - n(x) = N_d \exp\left(-\frac{x}{L_D}\right), \quad (29.28)$$

with $n_{10} = N_d$. Equation (29.27) agrees well for $x \gg L_D$ with the exponential slopes obtained from the “exact” computation in Fig. 29.7.

In contrast, the slope dp/dx changes comparatively little (see below) for $x > x_D$ as it is necessary to support the continuous gr-current. In our example, dp/dx is on the order of 10^{12} cm^{-4} , as shown in Fig. 29.3.

In the bulk region the slope of minority carriers decreases linearly as can be estimated from

$$\frac{dp}{dx} = \frac{e}{\mu_p kT} \int_x^{d_1} U(x) dx \simeq \frac{e}{\mu_p kT} \frac{p_{10}}{\tau_{p0}} (d_1 - x). \quad (29.29)$$

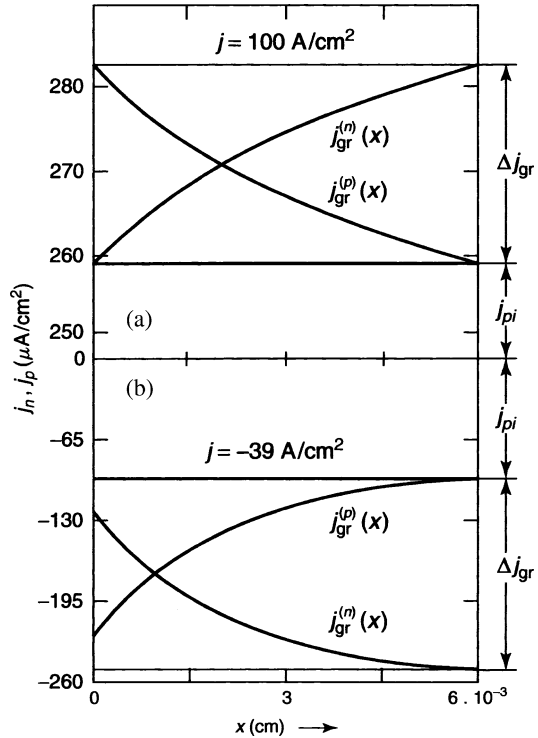
The large difference of dn/dx and dp/dx in regions extending beyond the diffusion lengths precludes the use of the approximation of *ambipolar diffusion*. Only when the condition $dn/dx \cong dp/dx$ is fulfilled (the well-known van Roosbroek assumption, can one use as a reasonable approximation an *ambipolar transport equation* with the corresponding *ambipolar diffusion coefficient* $D^* = (n + p) D_n D_p / [n D_n + p D_p]$ and an *ambipolar mobility* $\mu^* = (n - p) \mu_n \mu_p / [n \mu_n + p \mu_p]$, in a very small parts of such devices.

In order to avoid misleading conclusion we have therefore refrained from using the ambipolar approximation.

29.3.4 The Relative Contribution of Divergence-Free and GR-Currents in Schottky Barrier Devices

At the end of the chapter of Schottky barrier devices we should emphasize the enormous difference between the magnitude of the usually minute generation-

Fig. 29.17 Gr-currents for -39 and 100 A/cm^2 in (a) and (b), respectively. Observe the ordinate break at $250 \mu\text{A/cm}^2$ in (a)



recombination current to the divergence-free current that is constant throughout the crystal. We have shown the solution curves for the generation and recombination rate as well as for the sum of both $U(x)$ in Fig. 29.16 for the same parameters as before used in this chapter but for a wider device.

Even for such wider devices the g-r currents amount only to about $\pm 20 \mu\text{A/cm}^2$ at reasonable forward or reverse bias (see Fig. 29.17) while the divergence-free currents are $=100$ or -39 A/cm^2 respectively. Consequently, in the total current is negligible except for large optical excitation that will be discussed in later chapters.

For a more detailed analysis of Schottky structures see e.g., Racko et al. (1992); for effects of surface space charge on the shape of the potential barrier see Feng (1999), for bipolar injection see Swistacz (1995).

Chapter 30

pn-Homojunctions

Abstract Starting with a simplified *pn*-junction model, its basic features are related to a step function change in doping from *n* only to *p* only. The solutions of the set of transport and Poisson equations of the simplified model is given and discussed, first in steady state. Junction capacitance, that is often used to infer on space charge densities, is analyzed. Current voltage characteristics are calculated. A diode quality factor is introduced. The relevance to actual *pn* junctions is discussed. The abrupt *pn* junction in Ge is computed with example parameters listed and the governing set of equations given. The solution curves are first given for the devices. The position of the *pn* junction. Junction field and potential distribution is computed. Quasi Fermi level and current distribution in a *pn* junction are given. Identifying the Boltzmann, DO and DRO ranges with a very instructive graph of $j_n(x)j_p(x)$, $E_c(x)$, $E_v(x)$, $E_{Fn}(x)$, $E_{Fp}(x)$, $j_n(x)$ and $j_p(x)$. Carrier heating in a *pn* junction. GR and divergence free currents are discussed. The current voltage characteristics are computed. Thick *pn* junction devices in Ge are analyzed. The changes in current contribution with device thickness is discussed. The quasi Fermi levels of thicker devices are given. The Si homojunction is analyzed. Current voltage characteristics are computed. More complex homojunctions are introduced and analyzed. Linearly doped devices are discussed. High minority carrier injection is discussed. Series resistance limitation is identified. Position dependent parameters are given.

pn-Junctions are the single most important part of almost all semiconductor devices. They are highly efficient in controlling the current as a function of the bias and yield excellent diode characteristics.

The *pn*-homojunction is produced by a doping transition from an acceptor-doped *p*-type region to a donor-doped *n*-type region of the same semiconductor. This doping transition creates a space charge double layer with a built-in field and a potential barrier to separate the majority carriers from one to the other part of the device.

We will first orient ourselves along the classical depletion layer approximation in steady state which yields analytical solutions and has guided generations of researchers and engineers in the field.

We will then briefly compare this model with two Schottky barriers, one *p*-type and one *n*-type, which are connected back-to-back with each other, except for a

thin metal inter layer. Such an analysis will help us to indicate similarities and to emphasize the main differences between the Schottky barrier and the *pn*-junction.

We will then analyze computer solutions of an *abrupt pn-homo-junction* as an example, i.e., a junction in which the doping changes abruptly from *p*- to *n*-type. Here we can follow some of the characteristic junction properties in more detail.

Finally, we will briefly discuss the properties of more complex *pn*-junctions.

30.1 Simplified *pn*-Junction Model

We first present a simple depletion-type model for analyzing the main features of a *pn*-junction. This model permits a general overview of the *pn*-junction which will assist us later in discriminating more detail of the actual device behavior.

30.1.1 Basic Features of the Simplified Model

We assume a semiconductor with two adjacent regions of homogeneous doping, one with shallow donors and the other one with shallow acceptors that are joining each other with an abrupt transition as shown in Fig. 30.1a and b:

$$N_a(x) = \begin{cases} N_a & \text{for } x < 0 \\ 0 & \text{for } x \geq 0 \end{cases} \quad N_d(x) = \begin{cases} 0 & \text{for } x < 0 \\ N_d & \text{for } x \geq 0. \end{cases} \quad (30.1)$$

In the process of joining these two parts, electrons diffuse from the *n*-type region into the adjacent *p*-type region, producing a positively charged region in the depleted part of the *n*-type region. In a similar manner, the holes diffuse from the *p*-type into the *n*-type region, producing a negatively charged depletion region as indicated in Fig. 30.1b.

We now assume a rather abrupt and complete depletion so that both adjacent depletion regions have a box-like space charge profile as shown in Fig. 30.1c:

$$\varrho(x) = \begin{cases} -\varrho_p = -eN_a & \text{for } l_p \leq x < 0 \\ \varrho_n = eN_d & \text{for } 0 \leq x \leq l_n. \end{cases} \quad (30.2)$$

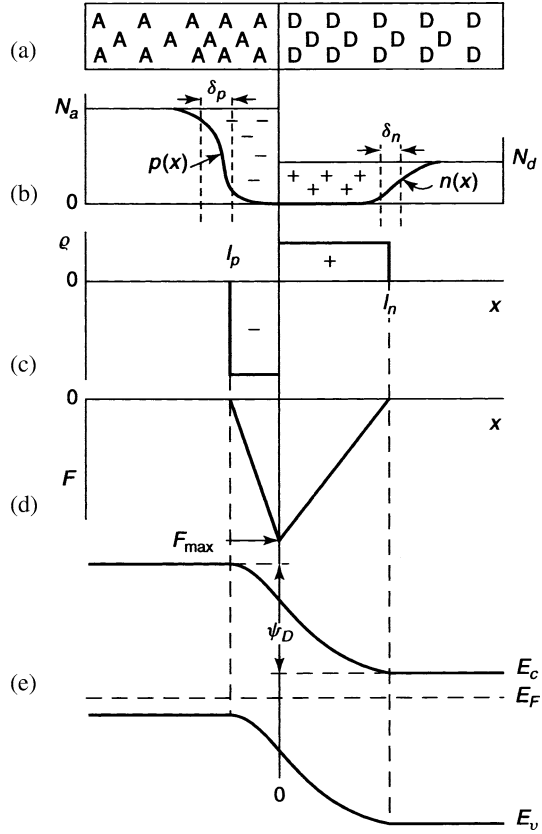
For reason of total neutrality in equilibrium one requires in an asymmetric junction (here $N_a > N_d$) symmetric junction

$$N_d l_n = N_a l_p \quad (30.3)$$

with l_p and l_n the widths of the depletion regions in the *p*- and *n*-type parts of the junction (here $l_n > l_p$). In each of these space charge regions we obtain the field distribution from the Poisson equation

$$F(x) = \frac{e}{\varepsilon \varepsilon_0} \varrho(x) x. \quad (30.4)$$

Fig. 30.1 Schematics of a simplified model of a pn -junction in thermal equilibrium. (a) Doping distribution; (b) doping and carrier distribution with δ_n and δ_p the widths of the transition regions to achieve complete carrier depletion; (c) space-charge distribution in the two depletion regions of width l_p and l_n in the p - and n -type material, respectively; (d) triangular field distribution; and (e) potential distribution (band model) with the diffusion potential ψ_D identified. δ_n and δ_p are neglected in panels (c) and (d). A more careful inspection of panels (d) and (e) shows that the higher doped, thinner p -type region has a steeper field slope but has a lower fraction of the diffusion potential than the lower doped, wider n -type region



This field distribution is triangular (Fig. 30.1d) and is familiar to us in each half of the junction from the Schottky barrier: with two back-to-back depletion layers, it yields two joining triangles with the same height

$$|F_{\max}| = \frac{e}{\epsilon\epsilon_0} N_a l_p = \frac{e}{\epsilon\epsilon_0} N_d l_n. \quad (30.5)$$

The electron potential distribution can be obtained by integrating once more the Poisson equation, yielding

$$\psi_n(x) = \begin{cases} \psi_n(-\infty) & \text{for } x < l_p \\ \psi_n(-\infty) + \frac{e}{\epsilon\epsilon_0} N_a (x + l_p)^2 & \text{for } l_p < x \leq 0 \\ \psi_n(+\infty) - \frac{e}{\epsilon\epsilon_0} N_d (x - l_n)^2 & \text{for } 0 < x \leq l_n \\ \psi_n(+\infty) & \text{for } x > l_n. \end{cases} \quad (30.6)$$

Continuity of the electrostatic potential at $x = 0$ yields the diffusion electron potential across the p - and n -type region of the junction (Fig. 30.1E):

$$\psi_{n,D} = \psi_n(\infty) - \psi_n(-\infty) = \frac{e}{\varepsilon\varepsilon_0} (N_d l_n^2 + N_a l_p^2); \quad (30.7)$$

the sum of the diffusion potentials can also be expressed as

$$\boxed{\psi_{n,D} = \frac{kT}{e} \ln \left[\frac{N_d}{n(x=0)} \right] + \frac{kT}{e} \ln \left[\frac{N_a}{p(x=0)} \right] = \frac{kT}{e} \ln \left[\frac{N_d N_a}{n_i^2} \right]} \quad (30.8)$$

since in thermal equilibrium at any position of the junction $n(x)p(x) = n_i^2$. The width of the depletion regions in equilibrium, as obtained from Eqs. (30.3) and (30.7), yields

$$l_{n,p} = \sqrt{\frac{\varepsilon\varepsilon_0 \psi_{n,D}}{e(N_a + N_d)} \left(\frac{N_a}{N_d} \right)^{\pm 1}} \quad (30.9)$$

for l_n and l_p with the upper and lower sign in the exponent, respectively.

30.1.2 Simplified Junction Model in Steady State

With reverse bias, both depletion layers expand (Fig. 30.2), and with forward bias¹ they shrink according to (see Sect. 32.2.2)

$$\boxed{l_{n,p} = \sqrt{\frac{\varepsilon\varepsilon_0 (\psi_{n,D} - V)}{e(N_a + N_d)} \left(\frac{N_a}{N_d} \right)^{\pm 1}}} \quad (30.10)$$

The maximum field varies as

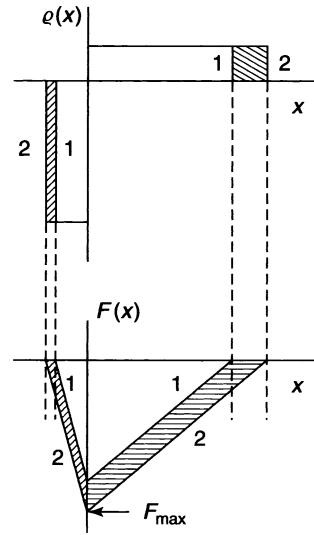
$$\boxed{F_{\max} = \sqrt{\frac{e N_d N_a}{\varepsilon\varepsilon_0 (N_a + N_d)} (\psi_{n,D} - V)}} \quad (30.11)$$

in this simple model the entire applied bias drops across the barrier with

$$\psi_n(\infty) - \psi_n(-\infty) = \psi_{n,D} - V. \quad (30.12)$$

¹However, the depletion layer approximation becomes inadequate for larger forward bias.

Fig. 30.2 Schematics of the changes of space charge and field distribution in the simplified pn -junction model. Thermal equilibrium (curves 1) and reverse bias applied (curves 2)



30.1.3 Junction Capacitance

With the junction depletion layer embedded between two highly conducting layers, namely the p - and n -type bulk semiconductor, this depletion layer acts as the dielectrics of a capacitor, which, per unit area has the capacitance of²

$$C = \left| \frac{dQ}{dV} \right| = \left| \frac{d(e[N_d l_n + N_a l_p])}{d(\psi_{n,D} - V)} \right| \quad (30.13)$$

$$C = \frac{\varepsilon \varepsilon_0}{l_n + l_p} = \sqrt{\frac{\varepsilon \varepsilon_0 e N_a N_d}{(N_a + N_d)(\psi_{n,D} - V)}}. \quad (30.14)$$

This provides for an often used method to determine the diffusion voltage by plotting $1/C^2$ versus bias voltage, as can be seen by reordering Eq. (30.14):

$$\boxed{\psi_{n,D} - V = e \varepsilon \varepsilon_0 \frac{N_a N_d}{N_a + N_d} \cdot \frac{1}{C^2}}. \quad (30.15)$$

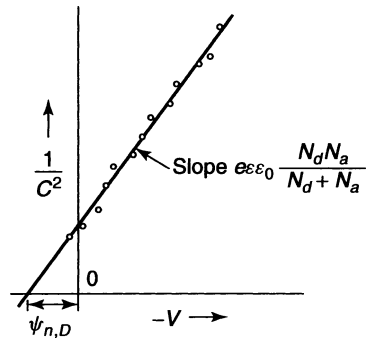
In an asymmetric junctions with $N_a \gg N_d$, one obtains also from the slope of $\psi_{n,D} - V$ versus $1/C^2$:

$$\psi_{n,D} - V = e \varepsilon \varepsilon_0 N_d \cdot \frac{1}{C^2} \quad (30.16)$$

the *lower* of the two doping densities (see Fig. 30.3 as an example for some measurements of an actual abrupt pn -junction Si device).

²Equation (30.14) is identical to the result of the more general expression.

Fig. 30.3 Example of a capacitance measurement of an abrupt *pn* junction in a Si device as function of the applied bias from which the diffusion voltage and the lesser space charge in a highly asymmetric *pn*-junction can be determined



30.1.4 The Current–Voltage Characteristic of the Simplified Junction

The current through such a junction device is the sum of electron and hole current

$$j = j_n + j_p. \quad (30.17)$$

Each one of these currents is composed of a *generation current* caused by minority carriers that are generated close enough to the junction so that they can diffuse to the junction where they can be swept by the junction field to the other side, and a *recombination current* caused by majority carriers that have enough energy to surmount the barrier and then recombine with the oppositely charged majority carrier on the other side of the junction. In addition, generation and recombination within the junction can make a significant contribution under certain circumstances.

In the simplified model (essentially representing two back-to-back connected simplified Schottky barriers), described in the previous section, we can obtain an analytical description by separating three regions of the device, the *n*-type and the *p*-type bulk, and the junction region (see, e.g., Sze 1985).

Since the *bulk regions* are essentially field-free, the current of the minority carriers is a diffusion current, as given in Sect. 28.1.1. In the *p*-type region one has as electron current—see Eq. (28.15)). With the boundary condition

$$j_n(x) = -\mu_n kT \frac{dn}{dx} = ev_D(n_{jD} - n_{p0}) \exp\left(-\frac{x}{L_n}\right) \quad (30.18)$$

$$n_{jD} - n_{p0} = n_{p0} \left[\exp\left(\frac{eV}{kT}\right) - 1 \right] \quad (30.19)$$

one obtains for the electron current

$$j_n = \frac{\mu_p kT n_{p0}}{L_n} \left[\exp\left(\frac{eV}{kT}\right) - 1 \right] \quad (30.20)$$

with $n_{p0} = n_p(x = \infty)$ assuming here a “long device” with $d_2 \gg L_n$. The majority current is complementary to $j_n(x)$ rendering

$$j_n(x) + j_p(x) = j = \text{const}$$

A similar hole current is contributed from the n -type bulk

$$j_p(x) = \frac{\mu_p k T p_{n0}}{L_p} \left[\exp\left(\frac{eV}{kT}\right) - 1 \right]. \quad (30.21)$$

As long as the contribution of the junction region is negligible,³ the current–voltage characteristic of such a device is consequently given by:

$$j = j_s \left[\exp\left(\frac{eV}{kT}\right) - 1 \right] \quad \text{with} \quad j_s = \left(\frac{\mu_n p_{n0}}{L_n} + \frac{\mu_p p_{n0}}{L_p} \right) kT, \quad (30.22)$$

where we introduced the saturation current j_s that is the sum of the two saturation diffusion currents from each bulk region.

This is the *diode current-voltage characteristic* which has the typical form $j \propto [\exp(eV/kT) - 1]$ with a pre-exponential factor that is subject to further modification dependent on the type of approximation that is used and other contributions that need to be considered.

30.1.5 Contribution of the GR-Currents

The contribution within the *junction region* is a generation/recombination current which can be approximated by

$$j_n = j_p = eUW \quad \text{with} \quad U = \frac{np - n_i^2}{\tau(n + p + n_i^\pm)} \quad (30.23)$$

In *reverse bias* with $W = l_n + l_p$ both n and p are reduced so that $np \ll n^2$ and the junction current becomes a generation current:

$$j_g = \frac{en_i^2 W}{\tau n_i^\pm} \quad (30.24)$$

with

$$n_i^\pm = 2n_i \exp\left(\pm \frac{E_i - E_r}{kT}\right)$$

³This can indeed occur for long devices with narrow band gap.

the maximum contribution to the generation rate is obtained for recombination centers close to the middle of the band gap, thereby, with $E_r \cong E_i$, yielding approximately

$$j_g \simeq \frac{en_i W}{\tau} \quad (30.25)$$

In *forward bias* with $np \gg n^2$ the current in the junction is described by recombination:

$$j_r = e \frac{npW}{n+p} \quad (30.26)$$

with

$$np = n_i^2 \exp\left(\frac{eV}{2kT}\right); \quad (30.27)$$

this results in a recombination current of

$$j_r \simeq \frac{n_i W}{2\tau} \exp\left(\frac{eV}{2kT}\right); \quad (30.28)$$

The *total current-voltage characteristic* consists of the three contributions and is given by

$$j = j_s \left[\exp\left(\frac{eV}{kT}\right) - 1 \right] + \frac{en_i W}{\tau} \left[1 + \exp\left(\frac{eV}{2kT}\right) \right] \quad (30.29)$$

$$j = en_i \left(\frac{L_n n_i}{\tau_n N_a} + \frac{L_p n_i}{\tau_p N_d} \right) \left[\exp\left(\frac{eV}{kT}\right) - 1 \right] + \frac{W}{\tau} \left[\exp\left(\frac{eV}{2kT}\right) + 1 \right]. \quad (30.30)$$

With sufficiently small band gap (larger n_i) and large diffusion lengths, the *bulk contribution* dominates. When the generation/recombination term in the junction region prevails, the generation term dominates in reverse and the recombination term dominates in forward bias.

30.1.6 The Diode Quality Factor

This leads to a characteristic that can be approximated in forward bias by

$$j \propto \exp\left(\frac{eV}{AkT}\right) \quad (30.31)$$

with a *quality factor* $A \cong 2$; its origin is associated with the second term in Eq. (7.30), i.e. with junction recombination.

In summary, when in a *pn*-junction the bulk region dominates, the quality factor $A \cong 1$, however with the junction dominating $A \rightarrow 2$.

We will return to this often used diode factor in the following sections.

Table 30.1 Parameters Used for the Abrupt Ge pn -Junction

Parameters	N_d	N_d	N_{r1}	N_{r2}	N_c	N_v
Values	10^{17}	10^{16}	10^{17}	10^{16}	$1.04 \cdot 10^{19}$	$5.76 \cdot 10^{28}$
Dimensions	cm^{-3}	cm^{-3}	–	cm^{-3}	cm^{-3}	cm^{-3}
Parameters	n_{10}	p_{10}	n_{20}	p_{20}	μ_{n0}	μ_{p0}
Values	$5.138 \cdot 10^9$	10^{17}	10^{16}	$5.138 \cdot 10^{10}$	3900	1900
Dimensions	cm^{-3}	cm^{-3}	cm^{-3}	cm^{-3}	$\text{cm}^2/\text{V s}$	$\text{cm}^2/\text{V s}$
Parameters	E_g	$E_l - E_r$	$C = C_{cr} = C_{cv}$	$v_n^* = v_p^*$	ε	T
Values	0.66	0.1	10^{-9}	$5.7 \cdot 10^6$	16	300
Dimensions	eV	eV	$\text{cm}^3 \text{ s}^{-1}$	$\text{cm}^3 \text{ s}^{-1}$	–	K

30.1.7 Relevance to Actual pn -Junctions

The simplified pn -junction model with two box-like space charge layers joining each other back-to-back, describes reasonably well the general features of a pn -junction device. The relations given in the preceding sections are therefore often used to obtain first estimates about junction fields, barrier heights, capacitance and current-voltage characteristics and some indication of the importance of junction recombination.

However, a quantitative agreement cannot be expected with an actual pn -junction device. This is especially important when attempting to obtain information on the space charge distribution from capacity measurements or a critical evaluation of reverse saturation currents or of curve shapes from the diode characteristics. For such an analysis a more sophisticated model needs to be referenced which will be discussed in Sect. 30.2; however, we will remain on the topic of a rather simplified pn -junction throughout the following three sections.

30.2 Abrupt pn -Junction in Ge

In this study we present computer generated solution curves for a specific Ge device that show more directly the interrelations between the different junction variables.

30.2.1 Governing Set of Equations and Example Parameters

For convenience, we have collected and rewritten here all time-invariant equations for the pn -junction, assuming Boltzmann gas statistics for carriers within the bands, and tabulated all of the parameters used for an abrupt Ge pn -junction in Table 30.1.

$$\frac{dn}{dx} = \frac{j_n - e\mu_n n F}{\mu_n k T} \quad (30.32)$$

$$\frac{dp}{dx} = \frac{-j_p + e\mu_p p F}{\mu_p k T} \quad (30.33)$$

$$\frac{dj_n}{dx} = -eU; \quad \frac{dj_p}{dx} = eU \quad (30.34)$$

$$U = U_1 = \frac{np - n_i^2}{\tau_{p0}^{(1)}(n + n_i^+) + \tau_{n0}^{(1)}(p + n_i^-)} \quad \text{for } d_1 \leq x < 0 \quad (30.35)$$

$$U = U_2 = \frac{np - n_i^2}{\tau_{p0}^{(2)}(n + n_i^+) + \tau_{n0}^{(2)}(p + n_i^-)} \quad \text{for } 0 \leq x \leq d_2. \quad (30.36)$$

$$\frac{dF}{dx} = \frac{e(p - N_a)}{\varepsilon \varepsilon_0} \quad \text{for } d_1 \leq x < 0 \quad (30.37)$$

$$\frac{dF}{dx} = \frac{e(N_d + p - n)}{\varepsilon \varepsilon_0} \quad \text{for } 0 \leq x \leq d_2 \quad (30.38)$$

$$\frac{d\psi_n}{dx} = F \quad (30.39)$$

$$n_i^\pm = n_i \exp\left(\pm \frac{E_i - E_r}{kT}\right) \quad (30.40)$$

$$n_i^2 = np \quad \text{in equilibrium} \quad (30.41)$$

$$\tau_{n0}^{(1,2)} = \frac{1}{c_{cr} N_r(1,2)}; \quad \tau_{p0}^{(1,2)} = \frac{1}{c_{rv} N_r(1,2)}. \quad (30.42)$$

30.2.2 Solution Curves for Thin Germanium *pn*-Junction

We analyze first a thin device with $(d_1, d_2) \ll (L_n, L_p)$, which emphasizes the contributions of the junction and the two electrodes while deemphasizing the bulk. Figure 30.4 shows the solution curves for such a thin⁴ Ge *pn*-junction device, $n(x)$, $p(x)$, $\rho(x)$, $F(x)$, and $\psi_n(x)$ with the total current j as a family parameter, as obtained by numerical integration of Eqs. (30.32)–(30.42) with the parameters listed in Table 30.1 and the boundary conditions given by surface recombination at d_2 or d_1 with $s(d_1) = s(d_2) = 5 \cdot 10^6$ cm/s, and a flat-band outer electrode connection.⁵

This behavior of the solution curves is typical for *pn*-junction devices with a sharp peak of the field at the junction interface and a cross-over of the carrier density extending substantially beyond this interface into the lower doped region.

⁴The device extends only slightly beyond the junction region.

⁵Such a flat band electrode connection requires a metal/semiconductor work function $\psi_{MS} = E_0 - E_c - E_d$ for the *n*-type side and $\psi_{MS} = E_0 - E_v + E_a$ for the *p*-type side (E_0 is the vacuum level).

30.2.3 The Position of the pn -Junction

The carrier densities $p(x)$ and $n(x)$ show a crossover, i.e., a change between the respective majority carriers that lies within the lower doped part of the device.

The boundary between the p - and n -type regions, however, is precisely at the doping boundary. To emphasize: The metallurgical interface is the locus of the pn -junction boundary and the cross-over between $p(x)$ and $n(x)$, as will be explained below.

The space charge shape in an asymmetrically doped junction is itself asymmetric and is in the higher doped region no longer block-shaped. The carriers diffusing out from this region produce here a triangular space charge layer, as shown in Fig. 30.4b. In addition, the hole density in the n -type bulk increases above the donor density in this lower doped region, thereby causing a spike of the positive space charge near the junction interface (see Fig. 30.4b).

This modifies the Schottky-type solution: in the higher doped region, the field distribution is non-linear, and it shows a gradual field slope in the lower doped region up to a spike exactly at the doping boundary, as shown in Fig. 30.4c. Consequently, the field distribution is best estimated from the lowly doped side of the junction.

The width of the lower doped space charge region is approximately given by the Schottky relation

$$l_n = \Delta x_2 = L_{Dn} \sqrt{2e \frac{\psi_{n,Dn} - V}{kT}}, \quad (30.43)$$

while the width of the higher doped space charge region is comparatively small. For the diffusion potential $\psi_{n,Dn}$ see Eq. (30.45).

30.2.4 Junction Field and Potential Distribution

The field distribution in the junction is triangular shaped with a curved branch in the higher doped side and a mostly linear branch in the lower doped side, except for a small spike (barely visible in panel c) close to the interface, caused by the overshoot of the space charge here (Fig. 30.4c).

The maximum field, except for this spike, is given by

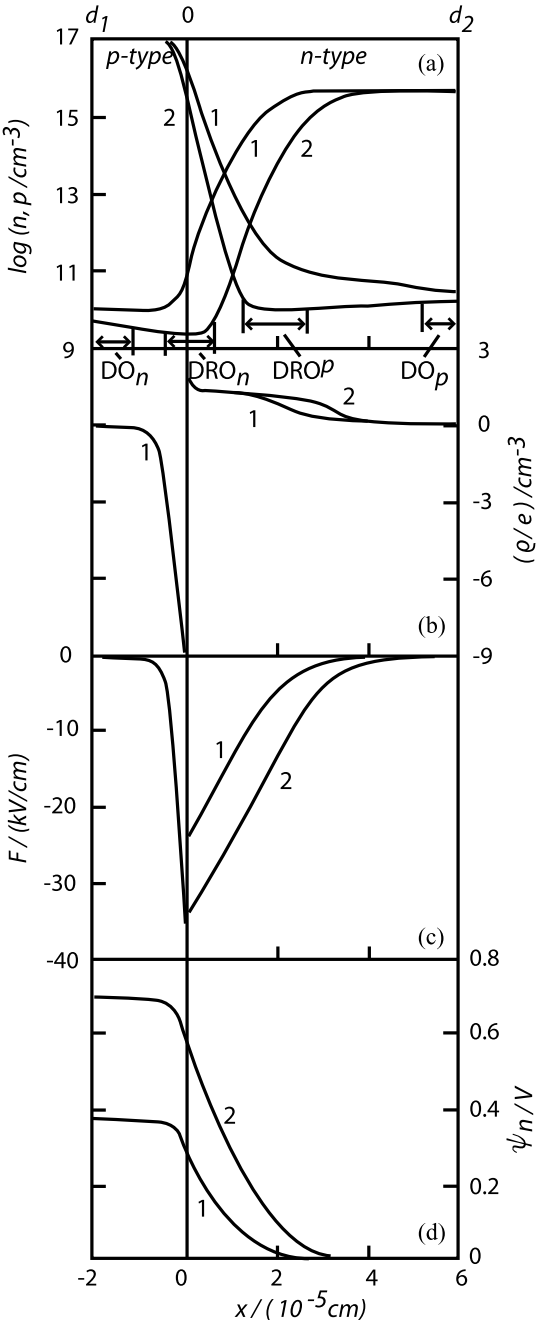
$$F_{\max} \simeq \sqrt{\frac{2eN_d(\psi_{n,Dn} - V)}{\epsilon\epsilon_0}} \quad (30.44)$$

with

$$\psi_{n,Dn} = \frac{kT}{e} \ln\left(\frac{N_d}{n_i}\right), \quad (30.45)$$

using the lower doped side for the estimate.

Fig. 30.4 Solution curves for a Germanium thin *pn*-junction device obtained by computation from Eqs. (30.32) to (30.40). Parameters given in Table 30.1; $j = 6$, and -9.84 mA/cm^2 for curves 1 and 2, respectively. For curve 2 the extent of the DO- and DRO-regions for holes and electrons are identified in panel (a) (see Sect. 30.2.1 for further explanation)



The electrostatic potential distribution is obtained by integrating $F(x)$ and is shown in Fig. 30.4d. It has the typical potential step shape which increases or decreases with applied bias, but with most of the changes in barrier width and step height occurring in the lower doped region.

The total diffusion potential is given by

$$\psi_{n,D} = \psi_{n,Dn} + \psi_{n,Dp} = \frac{kT}{e} \ln \left(\frac{N_a N_d}{n_i^2} \right) \quad (30.46)$$

or, using Eq. (27.28),

$$\psi_{n,D} = \frac{E_g}{e} - \frac{kT}{e} \ln \left[\frac{N_v N_c}{N_a N_d} \right]. \quad (30.47)$$

The diffusion potential is 0.38 V in the given example.

With bias, the electrostatic electron potential distribution is deformed, resulting in a bias-dependent step size according to

$$\psi_n(d_1) - \psi_n(d_2) = \psi_{n,D} - V, \quad (30.48)$$

again with most of the changes occurring in the lower doped n -type region.

30.2.5 Quasi-Fermi Level and Current Distributions in the pn -Junction

At each of the Ge/metal interfaces, the two quasi-Fermi levels collapse at the majority quasi-Fermi level, which coincides with the Fermi level of the adjacent metal. Thus, the applied voltage can be expressed by

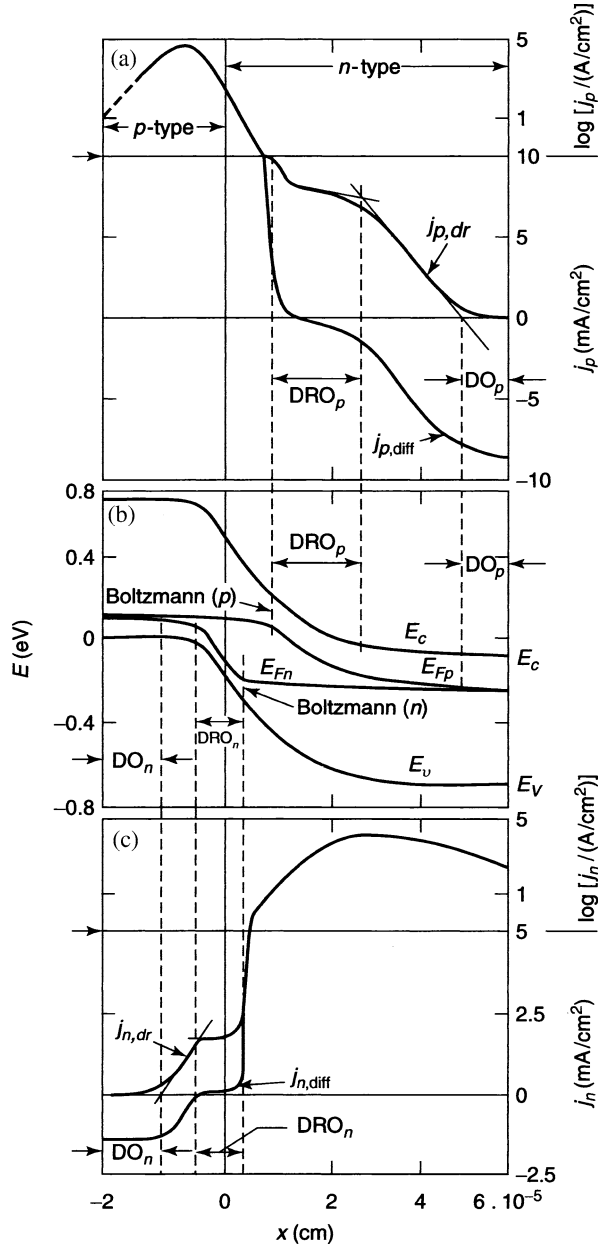
$$V = \frac{1}{e} \{ E_F(d_1^-) - E_F(d_2^+) \} \simeq \frac{1}{e} \{ E_{F_p}(d_1) - E_{F_n}(d_2) \}, \quad (30.49)$$

with d_- and d_+ indicating the position inside the metal.

Instructive information about the operation of a pn -junction device can be obtained by analyzing the different current ranges within the junction. These can best be identified in conjunction with the band-model, shown in reverse bias in the composite drawing of Fig. 30.5 as computed from Eqs. (30.32)–(30.42) with parameters listed in Table 30.1. This figure deserves full attention since it explains clearly the operation of the pn -junction. It includes in its top and bottom panel the current distributions and in its central panel the band edges and quasi-Fermi levels. The example shown is computed for sufficient reverse bias to show well-developed DRO-(drift only) and DO-(diffusion only) regions. The forward current distributions are relatively benign and will be mentioned briefly later.

Fig. 30.5 Current distributions and band-model in a Ge *pn*-junction with quasi-Fermi level distribution for reverse bias near current saturation:

$j = -9.5 \text{ mA/cm}^2$. (a) Hole current distribution showing the split between drift and diffusion current, also indicating DRO- and DO-regions for holes where these are the minority carriers. (b) Band-edge and quasi-Fermi level distributions showing their split near the junction, but mainly in the lower conducting *n*-side, and their collapse close to each electrode. (c) Electron current distribution showing the split between drift and diffusion, again starting in the junction and being most pronounced where electrons are minority carriers, again indicating DRO- and DO-regions for electrons. Observe the break of the ordinate at the top of each current graph to show the full extent of the current



30.2.6 Boltzmann-, DRO-, and DO-Ranges

In the upper (a) and lower (c) panel of Fig. 30.5 the current distributions are given for holes and for electrons, respectively. The current scales in panels a and c are

broken at 10 mA/cm^2 and 5 mA/cm^2 , respectively, to present the Boltzmann range in the upper part in a logarithmic scale and to demonstrate the split between drift and diffusion currents in the lower parts of these panels in a linear scale.

These show the typical step like behavior of the currents with sufficient reverse bias: they drop from the high-current Boltzmann range, where drift and diffusion current almost completely compensate each other to a distinct DRO-range, where the drift current predominates and then near the outer contact in another step to the DO-range, where the diffusion current predominates. This rather complex figure needs more elaboration.

In panel (b) the split of the quasi-Fermi levels is shown: the majority quasi-Fermi levels⁶ in reverse bias remain flat in the Boltzmann regions. The extent of these regions differ in the *p*- and *n*-type parts of the junction; their ranges are slightly overlapping for electrons and holes.

The major drop of the quasi-Fermi levels occurs in the DRO-regions of holes and electrons, identified as DRO_p and DRO_n where they change parallel with the respective band edges. In these regions the corresponding carriers become *minority carriers*.

The DRO-regions for electrons and holes are well separated from each other and start near the crossover point of *n* and *p* (compare with curves 5 of Fig. 30.4a), i.e., where the carriers have become minority carriers (and not at $x = 0$).

In the bulk-related DO-regions, one also observes a sloping of the quasi-Fermi levels, however, a much reduced one. The DO-range is caused by the predominant diffusion of minority carriers in the bulk and near the electrodes.

30.2.7 Carrier Heating in *pn*-Junctions

As can be seen from Fig. 30.5, major gradients of the quasi-Fermi levels occur only where the carriers have become minority carriers; only here in a well-developed DRO-region does major carrier heating occur due to the action of the external field; this then becomes strictly a minority carrier heating. Majority carrier heating in *pn*-junctions, however, is negligible as long as series resistance can be neglected (Böer 1985a, 1985b).

Figure 30.5 shows the separation of the Boltzmann regions for electrons and for holes; in these regions both drift and diffusion currents are very large compared to the net current as shown in panels a and c. The overlap of these Boltzmann regions decreases⁷ with increasing reverse bias (see Fig. 30.11).

In contrast to the Schottky barrier, where a DRO-region only appears for majority carriers at currents close to reverse current saturation, the DRO-region in the

⁶There are two majority quasi-Fermi levels in a *pn*-junction, E_{Fp} in the *p*-type region and E_{Fn} in the *n*-type region.

⁷For vanishing current both Boltzmann regions fill the entire device width with $s = 5 \cdot 10^6 \text{ cm/s}$, for a total reverse current contribution of 9.8 mA/cm^2 .

pn -junction surrounds the minimum of the minority carrier density where the diffusion current vanishes (see Sect. 30.3 for more details). In this DRO-range, minority carriers are heated.

In forward bias there is no DRO-range for n or p . Both electron and hole currents maintain the same sign throughout the entire bulk and junction. Near the end of the junction, in the adjacent bulk, the minority carrier current becomes a DO-current. However, the electrochemical fields are usually too small here to cause any significant carrier heating.

The spread of the drift and diffusion currents for electrons at d_1 is smaller in the higher doped p -side than the spread for hole currents at d_2 in the n -side of the junction.

30.2.8 GR-Currents and Divergence-Free Currents

In a thin device, the minority carrier density in reverse bias is substantially lower than the equilibrium density throughout each bulk and up to the surface. This causes substantial *surface recombination currents*:

$$j_s(d_1) = e[n_{10} - n(d_1)]s(d_1) \simeq 1.58 \text{ mA/cm}^2 \quad (30.50)$$

and

$$j_s(d_2) = e[p_{20} - p(d_2)]s(d_2) \simeq 8.20 \text{ mA/cm}^2 \quad (30.51)$$

The *gr-current* in bulk and junction region is much smaller than the recombination currents at the electrode interfaces in thin devices which contribute by far the largest part of the current.

The *gr-rates* in the main part of the device show steps between bulk and junction similar to the ones for Schottky barriers. Three steps⁸ are clearly identified. The jump at the metallurgical interface is caused by the step in the density of recombination centers at this interface. The surface recombination causes a slanting of the net *gr-rates* toward the outer surfaces.

The *gr-currents*, shown in Fig. 30.7 are composed in each part of the device of the two slopes in bulk and junction, with dominant contribution in the lower doped material. Near reverse saturation, the total contribution of the *gr-current* is approximately $20 \text{ } \mu\text{A/cm}^2$; with its largest contribution of almost $15 \text{ } \mu\text{A/cm}^2$ generated in the n -part of the junction.

In comparison, the divergence-free currents in pn -junctions are negligible. They are determined by the *divergence-free minority carrier currents* $j(p)$ and $j(n)$, presenting the bottleneck, and can be estimated from the fields in the bulk near the outer surfaces: $F(d_1) \cong j_s/[e\mu_p p(d_1)] \cong 10^{-3} \text{ V/cm}$ and $F(d_2) \cong j_s/[e\mu_n n(d_2)] \cong$

⁸A fourth step in the highly doped region is not fully developed because of the triangular steep decline of $p(x)$.

Fig. 30.6 Generation-, recombination-, and net gr -rates plotted for the reverse saturation current $j = -9.84 \text{ mA/cm}^2$

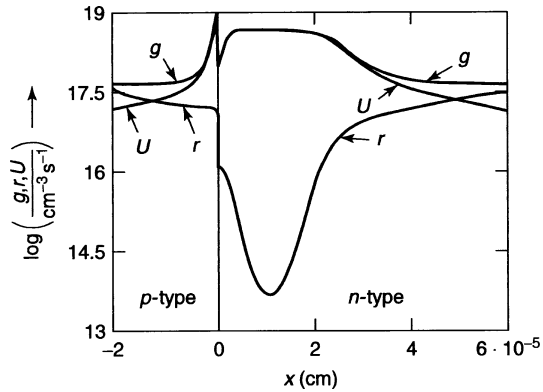
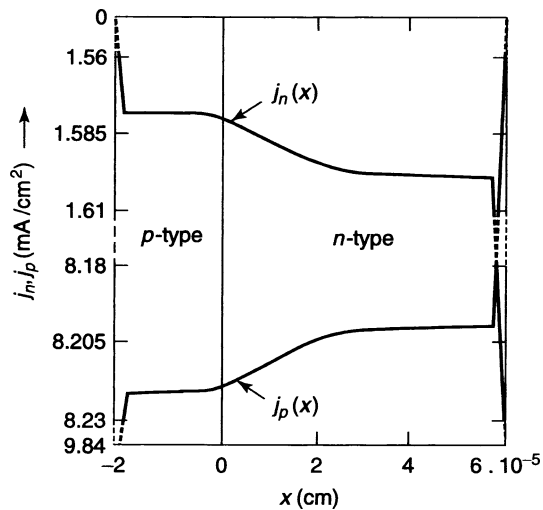


Fig. 30.7 Current distribution in the thin Ge pn -junction device, including recombination currents at $x = d_1$ and d_2 for a total of $= -9.84 \text{ mA/cm}^2$. Observe the broken ordinate scale at the upper, lower and middle part of the figure, to show the behavior of the gr -current within the device. Near the metal boundaries the surface recombination parts are indicated. Also observe the cross over of the currents at the right electrode



10^{-2} V/cm and the minority carrier densities of $n(d_2) \cong 5 \cdot 10^9$ and $p(d_1) \cong 5 \cdot 10^{10} \text{ cm}^{-3}$ yielding

$$j_{ni}^{(p)} = e\mu_n n_{10} F(d_1) \simeq 3 \cdot 10^{-9} \text{ A/cm}^2 \quad (30.52)$$

and

$$j_{pi}^{(n)} = e\mu_p p_{20} F(d_2) \simeq 1.5 \cdot 10^{-7} \text{ A/cm}^2. \quad (30.53)$$

The total current distribution in this device is shown in Fig. 30.7 in a broken ordinate scale. It demonstrates the vast dominance of the surface recombination current that is of the order of 10 mA/cm^2 at the metal interfaces (Eqs. (30.50) and (30.51)). Inside the device only a very small (0.2 %) fraction of the gr -current is generated ($\Delta j_{gr} \simeq 20 \text{ } \mu\text{A/cm}^2$). This is typical for small devices.

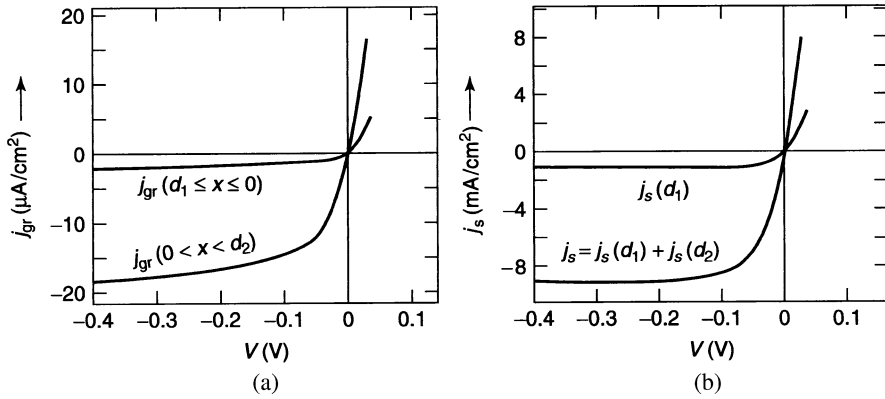


Fig. 30.8 Current-voltage characteristic for the same thin Ge *pn*-junction as in Figs. 30.4–30.7 with parameters as given in Table 30.1. (a) *Gr*-current increments for *p*-type part and for *n*-type parts of the device. (b) Surface recombination currents at d_1 and sum of these at d_1 and d_2 ; the total $j(V)$ is essentially equal to $j_s(d_1) + j_s(d_2)$ because of the vast differences of the currents in panel (a) and panel (b)

30.2.9 The Current-Voltage Characteristic

In Fig. 30.8 four current-voltage characteristics are plotted, as computed from the solutions of Eqs. (30.32)–(30.42). We have here separated the *different contributions* to the characteristic because of their vastly different magnitude. The *gr*-currents in bulk and junction are shown in panel (a). The increment in the higher doped *p*-type part is smaller because of the lower generation rate and the smaller width of the bulk region. The current shows good saturation as can be traced to the sufficient reduction of $r(x)$ below $g(x)$, shown in Fig. 32.6. The *gr*-current in the *n*-type region is not yet saturated: with increasing reverse bias, the width of the barrier region in which the generation rate is larger, slowly increases until it fills the entire width of the *n*-type region; this results in a maximum *gr*-current (current saturation) in the *n*-type region of $\Delta j^{(n)} \cong 40 \mu\text{A}/\text{cm}^2$ which is reached only at still higher reverse bias.

The contributions of the surface recombination to the current-voltage characteristics are shown in panel b of Fig. 30.8. They are approximately 500 times larger than the *gr*-currents, but show a surprisingly similar diode-like shape (compare panels (a) and (b)). The total current-voltage characteristic for a thin *pn*-junction device is in good approximation given by the sum of the two surface recombination currents, i.e., they are essentially the leakage currents from the semiconductor/metal interfaces, control reaches each metal surface by diffusion from the junction, and thereby causes a similar diode-type shape.⁹

⁹The difference between the minority carrier density at the outer surface and the equilibrium density [Eqs. (30.56) and (30.57)] that controls the surface recombination current is proportional to the difference at the bulk/junction interface (at l_n or l_p) that controls the diode current [Eq. (30.18)].

This remarkable interrelation totally escapes the simple junction analysis presented in Sect. 30.1. It amplifies the importance of a detailed check of the complete set of solution curves to identify the reasons for a behavior that could otherwise be attributed to completely different causes, as it is easily mistaken for its similar diode type shape to Eq. (30.30). Again, this is typical only for thin devices, where surface recombination dominates.

30.3 Thick pn -Junction Device (Ge)

We now increase the width of the device on both sides of the junction interface (to $d_1 = 2 \cdot 10^{-3}$ and $d_2 = 6 \cdot 10^{-3}$ cm) to make each side thicker by a factor of 2 or 2.7 respectively than the minority carrier diffusion length ($L_n = 10^{-3}$ and $L_p = 2.2 \cdot 10^{-3}$ cm).

30.3.1 Changes in Current Contributions with Device Thickness

With increasing width of the device the surface recombination currents decrease, as $n(d_1)$ and $p(d_2)$ approach the equilibrium densities. This is a sensitive measure that relates to the thickness to diffusion length ratio. On the other hand, the gr -currents increase to approach their limit value for reverse bias, that is in the n -type region

$$\Delta j_{gr,\max}^{(p)} = egL_p \simeq 175 \mu\text{A}/\text{cm}^2 \quad (30.54)$$

and in the p -type region

$$\Delta j_{gr,\max}^{(n)} = egL_n \simeq 80 \mu\text{A}/\text{cm}^2. \quad (30.55)$$

The computed $n(x)$ and $p(x)$, show the same typical behavior as shown for the thin device except now the carrier densities near the device surface $n(d_1)$ and $p(d_2)$ have increased to within less than 1 % of the equilibrium densities, rendering (at -0.3 V bias) the recombination current small but not yet negligible:

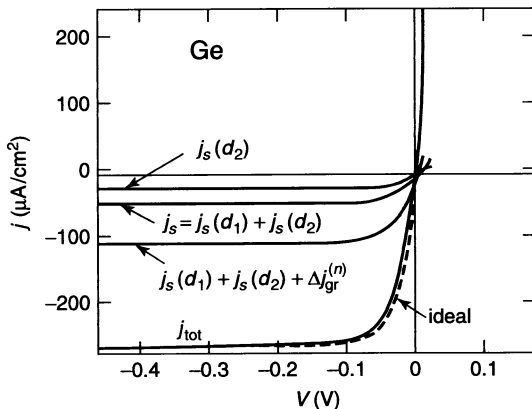
$$j_s(d_1) = e(n(d_1) - n_{10})s \simeq 22 \mu\text{A}/\text{cm}^2 \quad (30.56)$$

and

$$j_s(d_2) = e(p(d_2) - p_{20})s \simeq 26 \mu\text{A}/\text{cm}^2. \quad (30.57)$$

Therefore, the total current, which was dominated by the large recombination current at the outer electrodes of the thin device, is now reduced by two orders of magnitude and the sum of all four of the above listed currents can now be drawn at

Fig. 30.9 Current-voltage characteristic computed from Eqs. (30.32)–(30.40), here for a thick Ge-diode. Here surface recombination and bulk gr -currents can be drawn within the same figure. For more see text



the same ordinate scale:¹⁰

$$j_{\text{tot}} = j_s(d_1) \mid j_s(d_2) \mid \Delta j_{gr}^{(n)} \mid \Delta j_{gr}^{(p)}. \quad (30.58)$$

in Fig. 30.9. Here the bulk gr -current of holes $\Delta j_{gr,\text{max}}^{(p)}$ gives the largest contribution to the total current j_{tot} , because of the larger diffusion length of holes in the n -type region.

The device width no longer enters the gr -current behavior, as both bulk currents are now saturated and the junction currents have become comparatively small. However, even for a device with dimensions two times larger than the minority carrier diffusion length, the interface recombination at the electrodes is not yet negligible and contributes about 15% to the total current.

The shape of the current-voltage characteristic composed of these four different contributions is surprisingly close to an ideal diode characteristic

$$j = j_0 \left[\exp\left(\frac{eV}{kT}\right) - 1 \right], \quad (30.59)$$

which is shown as a dashed curve in Fig. 30.9.

The spatial distribution of these currents is shown for a forward current in the upper panel, and for a reverse current in the lower panel of Fig. 30.10. These curves identify the additive contribution from electrode recombination and gr -currents in the p -type and n -type parts of the device. The surface recombination is emphasized by plotting it within a small band of the surface layer (sl) symbolizing the metal/semiconductor interface, and extending beyond the central part of the figure on each side. In order to identify the contribution of the junction region and the two bulk regions, this and the following figures in this section are plotted with two

¹⁰The divergence-free current is now reduced to below 10^{-8} A/cm², i.e., to completely negligible values in reverse bias.

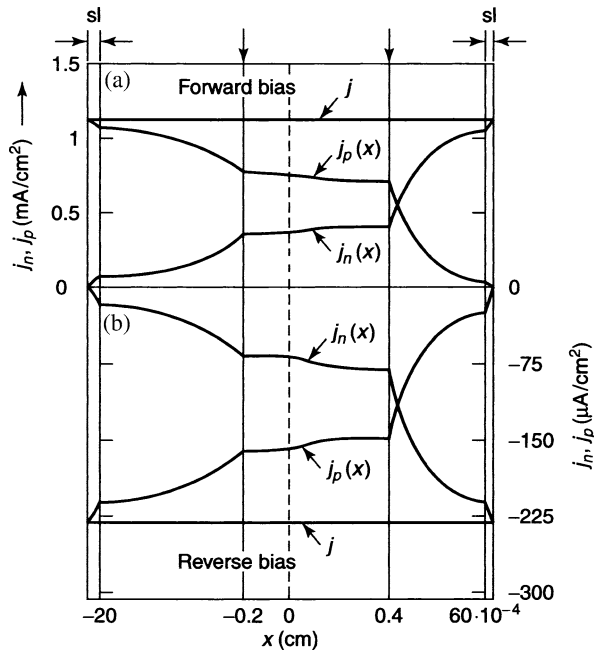


Fig. 30.10 Electron and hole current distribution in a thick Ge-diode computed from Eqs. (30.32)–(30.40) with parameters listed in Table 7.1; $d_1 = 2 \cdot 10^{-3}$ cm, $d_2 = 6 \cdot 10^{-3}$ cm, and $s(d_1) = s(d_2) = 5 \cdot 10^6$ cm/s. (a) Forward bias with $j = 1.14$ mA/cm²; (b) reverse bias near saturation with $j = -230$ μA/cm². Observe the asymmetric abscissa scale break at $-2 \cdot 10^{-5}$ and $+4 \cdot 10^{-5}$ cm that is chosen to show clearly the entire behavior in one figure. The cross over of the currents are now clearly visible within the figure in the *n*-type region. The thin slabs at both electrodes marked sl indicate the region of surface recombination

breaks of the abscissa at $-0.2 \cdot 10^{-4}$ and at $+0.4 \cdot 10^{-4}$ cm.¹¹ The junction interface is located at $x = 0$.

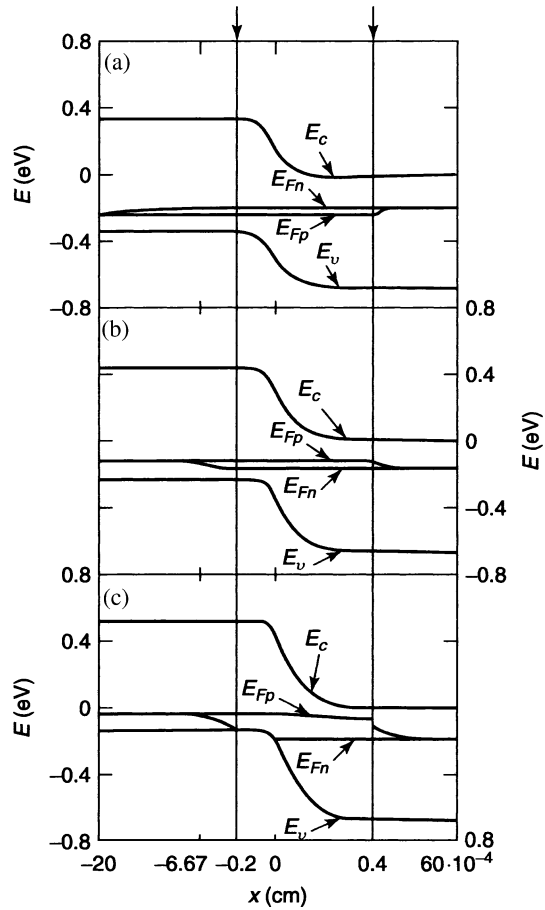
30.3.2 The Quasi-Fermi Levels of the Thicker Device

The quasi-Fermi levels remain spread much beyond the junction region (Fig. 30.11) and join each other more gradually as the electrodes are approached. The distinction between the rapid changes in the DRO-region, where quasi-Fermi levels and band edges slope parallel to each other, and the more gradual changes¹² of the quasi-Fermi levels in the DO-region, where the band edges remain essentially horizontal, are visible at higher reverse bias in panel C of Fig. 30.11.

¹¹Such a scale break results in a break of slopes at the break point. The actual curves, however, have continuous slopes.

¹²Consider the scale break of the figure in your comparison between the DRO and DO ranges.

Fig. 30.11 Band and quasi-Fermi level distributions in the bulk and junction regions of the thick Ge-diode computed as in Fig. 30.10. (a) Forward bias with $j = 1.14 \text{ mA/cm}^2$; (b) reverse bias with $j = -230 \text{ } \mu\text{A/cm}^2$; and (c) reverse bias with $j = -262 \text{ } \mu\text{A/cm}^2$. The spread of the quasi-Fermi levels represent the distribution of the solution curves $n(x)$ and $p(x)$ that show the typical junction behavior, but here, for the thicker device, the bulk and surface regions are more clearly separated, as indicated by the spread and the collapse of the quasi-Fermi levels before the boundary is reached



The generation and recombination rates in the central part of the device are similar to the curves of the thin device shown in Fig. 30.6 except that the recombination rates drop more readily and thereby permit the net gr -rate $U(x)$ to attain the shape of $g(x)$ at lower reverse bias.

In summary, the recombination currents at the outer surfaces of a thicker device are greatly reduced as soon as the widths of both bulk regions substantially exceed the diffusion lengths of the minority carriers; the surface recombination current can be neglected when the bulk width exceeds ≈ 4 diffusion lengths. The total current is then given by the sum of the two gr -currents as discussed for the ideal junction model in Sects. 28.1 and 28.2. These currents increase with bias as $r(x)$ is shifted away from $g(x)$. In reverse bias the net gr -rate $U(x)$ approaches readily $g(x)$ and the current saturates as the maximum of the minority carriers diffusion is reached. This current is many orders of magnitude smaller than the saturation current of a Schottky barrier device of the same material.

Thus, a *pn*-diode (with thermal carrier generation) is a much better rectifying device than a simple Schottky diode, since the recombination leakage current at the metal/semiconductor interface can be shifted to a region far away from the junction where it vanishes when the carrier densities approach their thermal equilibrium value. This is not possible for an electrode that is part of the current-controlling barrier in the Schottky diode.

30.4 The Si-Homojunction

In the previous chapters and sections we have described a narrow band-gap semiconductor in order to identify the intricate relationship of the different contributions to the current-voltage characteristics which influence their shape in an actual device, and to avoid the complications caused by a frozen-in carrier distribution, which appear in wider band gap semiconductors and often hinders a general discussion using a simple quasi-Fermi level model. We also have avoided the discussion of a highly asymmetric *pn*-junction with only a very thin highly doped one side of the junction.

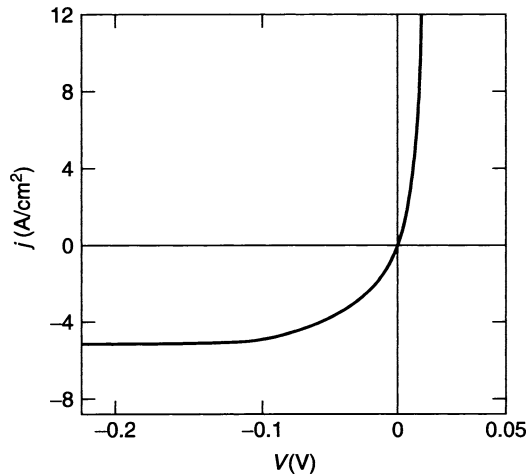
The Si-homojunction device is a borderline example for such devices since it has a wider band gap of 1.16 eV that could put a quasi-Fermi level in reverse bias away from the corresponding band edge by more than 1 eV. This is the critical energy distance for which frozen-in equilibria need to be considered. We will do this in following chapters and here will only refer to cautions when low reverse currents are to be discussed that depend on the minority carrier density and this density is limited by the position of the quasi-Fermi level. This means that it is usually higher than expected when a quasi-Fermi level approach is used, disrespecting frozen-in equilibria. As a first approximation one may use the above mentioned 1 eV limit for such frozen-in distribution resulting in a minimum minority carrier density on the order of 10^2 cm^{-3} .

Another limitation stems from the fact that a very thin highly doped layer tends to put one side of the junction in too close proximity to the metal contact to permit the recombination current on current there to be neglected in reverse bias. Since this has in principle been discussed with thin devices already, we do not need to go into more detail here, except to mention that in some conventional Si devices the front *p*-type layer is only 500 Å thick with 10^{18} cm^{-3} shallow acceptors. Here the minority carrier density is about 200 cm^{-3} close to the froze-in equilibrium, and about acceptable for room temperature experiments, while the thickness of the highly doped layer is not large enough to neglect surface recombination for reverse bias.

And finally, if one side of the *pn*-junction is much larger than the diffusion length, then the additional contribution to the *gr*-current from the field enhanced diffusion needs to be considered in reverse bias that shifts the onset of the reverse current saturation to higher bias.

All these contributions have been discussed in separate examples before, and even though the solution curves of the set of transport equations that determine the

Fig. 30.12 Computed current-voltage characteristics of a Si-diode as described in the text with $j_s(d_1)$ and $^{(p)}\Delta j_{gr}$ shown; $j_s(d_2)$ and $^{(n)}\Delta j_{gr}$ are negligible. The marked contribution of the surface recombination is shown separately



junction behavior are quite similar to the set of solution curves discussed before, except for quantitative differences, we will here skip the Figures showing such examples, but include the current voltage characteristic for such a device that summarizes the effects mentioned above for the example of the specific Si diode.

30.4.1 The Current-Voltage Characteristics

The current-voltage characteristic is determined mainly by the *gr*-current in the junction. However, because of the comparatively thin *p*-type layer, a non-negligible recombination contribution of $\sim -5 \cdot 10^{-11}$ A/cm² from the surface of the *p*-type side must be added in reverse saturation (see Fig. 30.12).

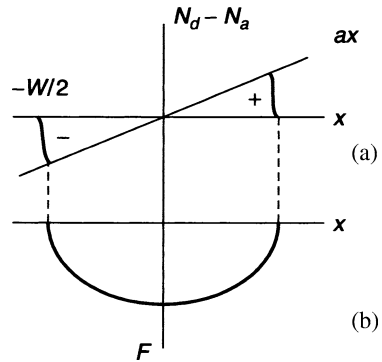
Any additional contributions can be neglected: the current caused by the surface recombination at d_2 is $<10^{-12}$ A/cm², the *gr*-current in the *p*-type region is $<10^{-14}$ A/cm² and the divergence-free current is $<10^{-16}$ A/cm².

The lack of current saturation for the total current shown in Fig. 30.12 is caused by the *gr*-current generated in the junction that expands with increasing bias, as described in the previous section. The current will therefore continue to increase until the junction fills the entire bulk of the *n*-type region, or other high-field effects not considered in this section, terminate the validity range of the discussed model.

This example indicates once more the relationship of the different contributions to the current-voltage characteristics which influence their shape in an actual device. This includes the influence of the recombination current at the front contact of an asymmetrically doped devices, and the bias influence of the widening junction, that is responsible for the lack of an ideal current saturation.

We have intentionally selected her a device in which a variety of contributions determine the current-voltage characteristics, to demonstrate the intricate interrelationship of the different junction variables, but not necessarily to exemplify the more typical devices.

Fig. 30.13 (a) Doping profile of a pn -junction with a linear doping gradient. Depletion region and sign of space charge indicated; (b) corresponding built-in field distribution



30.5 More Complex Homojunctions

In the preceding sections we analyzed steady state effects of rather simple homojunctions with homogeneous and moderate doping profiles. Effects that influence the properties and operation of a pn -junction include

- doping gradients
- inhomogeneous distribution of recombination centers
- series resistance contribution, and
- high injection effects.

In addition one needs to consider modifications of the governing set of equations when material parameters become position-dependent, caused by inhomogeneous heavy-doping, graded composition or substantial surface treatments. The position-dependent material parameters can be

- the relative position of the conduction and valence band edges $E_c(x)$ and $E_v(x)$ with respect to each other, and thereby the band edge distribution $E_g(x)$;
- the density-of-state distribution within the bands $g_c(x)$ and $g_v(x)$;
- the carrier mobility $\mu_n(x)$ and $\mu_p(x)$, and
- the optical constants $\varepsilon(x)$, $\kappa(x)$ and $n_k(x)$.

These extensions present opportunities for designing new devices. The first set requires a study of more involved device properties. With limited space, we will only give a few selected examples here. The second set of extensions requires a more generalized set of equations which we will briefly introduce; (see also Neudeck 1983; Gray 1967).

30.5.1 Linearly Doped Junction

In the previous sections, we have assumed a constant doping within the n - and the p -type region. In most devices at least one of the regions has a substantial doping

gradient. As an example, we discuss here a linear grading of the doping profile¹³ as shown in Fig. 30.13a.

With carrier depletion, one obtains from the corresponding Poisson equation

$$\frac{dF}{dx} = \frac{e a x}{\varepsilon \varepsilon_0} \quad (30.60)$$

and after integration, the field distribution:

$$F(x) = -\frac{ea}{\varepsilon \varepsilon_0} \cdot \frac{(W/2)^2 - x^2}{2}, \quad (30.61)$$

as shown in Fig. 30.13B, with a *rounded* maximum value of the field

$$|F_{\max}| = \frac{eaW^2}{8\varepsilon \varepsilon_0}. \quad (30.62)$$

the barrier width W can be expressed as

$$W = \sqrt[3]{\frac{12\varepsilon \varepsilon_0 V_D}{ea}} \quad (30.63)$$

with V_D the diffusion potential, given by

$$V_D = \frac{eaW^3}{12\varepsilon \varepsilon_0} = \frac{2kT}{e} \ln\left(\frac{aW}{2n_i}\right), \quad (30.64)$$

The diffusion potential increases logarithmically with the doping gradient. The width of the depletion layer varies according to the third root of $V_D - V$. The qualitative behavior of the electronic properties of the linearly doped junction, however, remains similar to the abrupt junction discussed before.

30.5.2 High Minority Carrier Injection

With sufficiently large forward bias, the minority carrier density near the start of the junction (at l_n) can become comparable to the majority carrier density:

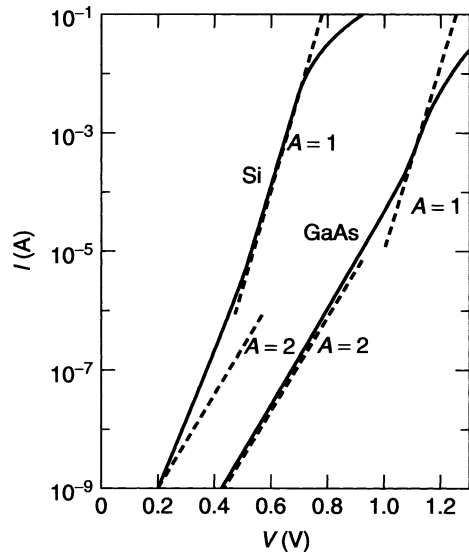
$$p_n(l_n) \simeq n_n = N_d \quad (30.65)$$

This permits an approximation of the current-controlling minority carrier density as

$$p_n(l_n) \simeq n_i \exp\left(\frac{eV}{2kT}\right) \quad (30.66)$$

¹³Such profile can (rarely) be achieved by cross diffusion of dopands for compensation; even though this is usually not symmetric, we will assume such symmetric compensation here.

Fig. 30.14 Current-voltage characteristics of a typical Si- and GaAs- *pn*-junction-diode in forward bias. At small bias, the junction recombination predominates with quality factors close to $A \approx 2$; at higher bias, the diffusion current predominates with $A \approx 1$; at still higher bias, minority injection and finally series resistance limitation reduces the slope significantly



and consequently

$$j \propto \exp\left(\frac{eV}{2kT}\right), \quad (30.67)$$

i.e., a reduction of the slope of the characteristics with a quality factor of ≈ 2 .

30.5.3 Series Resistance Limitation

In high forward bias, the current becomes large enough to induce a voltage drop across the space charge-free part of the device that can no longer be neglected. The voltage drop across the lower doped bulk region needs to be considered in the current-voltage characteristic:

$$j = j_s \exp\left[\frac{e(V - IR)}{kT}\right] \quad (30.68)$$

and causes a significant reduction in the slope, as indicated for some non typical Si and GaAs diodes in Fig. 30.14.

30.5.4 Position-Dependent Material Parameters

When material parameters are position-dependent, one needs to use a set of appropriately extended transport equations that are capable of dealing with such inhomogeneities.

Chapter 31

The Photovoltaic Effect

Abstract Carrier generation and recombination with light within a *pn* junction device is analyzed. Photoconductors are identified. Photocurrent and photo emf are computed. A table of recent solar cell efficiencies is given. Quasi equilibrium approximation is used first. Reaction kinetic balance is given. A simple model of the photodiode is introduced. Derived photodiode parameters are given. A resistive network influencing the diode characteristics is discussed. A device cooling is pointed out when electric energy is extracted. A detailed energy balance is performed.

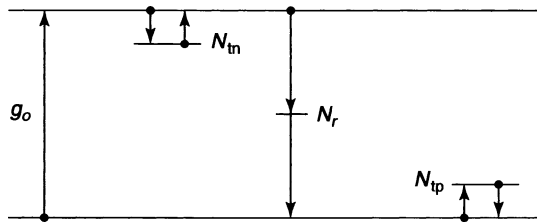
When a semiconductor is exposed to greater than band gap optical excitation, minority and majority carriers are produced which can be separated within the built-in field of a junction or barrier, thereby producing a photo-emf and/or generating a photocurrent in an external circuit. This is a sensitive device to detect light and an efficient means to convert light into electric power. We will discuss in this chapter optical excitation after stationarity is reached. The influence of optical excitation is discussed on the behavior of a variety of typical semiconductor devices. We will first introduce light with an energy in excess of the band gap that generates with equal rates majority and minority carriers.¹ Without an external bias applied, both types of carriers diffuse and when reaching the built-in field region, they can be separated before they recombine. This causes a relative charging of both sides of the junction with respect to each other, or, when an external pathway is provided it results in a photo-generated current.

The efficiency of this *photovoltaic effect* depends on the balance between generation, recombination and carrier transport to the built-in field region, as well as the ability of this space charge region to separate both types of carriers effectively.

We will devote this chapter to a general overview of the photovoltaic effect with a basic reaction kinetic discussion relating to the lifetime of the photogenerated minority carriers and its related diffusion, and discuss this first in a simplified pho-

¹Since we disregard in this first section the inhomogeneity of the optical absorption constant, this approach is justified only for thin platelets of a thickness of less than the optical absorption constant at the excitation energy. However, for indirect bandgap materials, such as Si this absorption constant is on the order of a typical thickness of such devices (a few hundred μm) this approach is justified.

Fig. 31.1 Band and defect level model with optical carrier generation, recombination and trapping



todiode model. This model connects the bulk diffusion with the junction-controlled minority carrier density, resulting in the basic photodiode equation.

31.1 Carrier Generation and Recombination with Light

When light is introduced in addition to the thermal excitation, both majority and minority carrier densities will rise until the generation rate equals the recombination. The increased carrier densities can be obtained from the basic set of *reaction kinetic equations*:²

$$\frac{dn}{dt} = g - r - \frac{1}{e} \frac{dj_n}{dx} \quad (31.1)$$

and

$$\frac{dp}{dt} = g - r + \frac{1}{e} \frac{dj_p}{dx}, \quad (31.2)$$

with g , the sum of optical and thermal generation rate, given by

$$g = g_o + \frac{n_i^2}{\tau_{p0}(n + n_i^+) + \tau_{n0}(p + n_i^-)} \quad (31.3)$$

for a simple model with a one-level recombination center (see Sect. 27.3 and Fig. 27.6). The recombination rate follows the same formula as for thermal excitation alone, however, now with increased carrier concentration:

$$r = \frac{np}{\tau_{p0}(n + n_i^+) + \tau_{n0}(p + n_i^-)}. \quad (31.4)$$

The additional recombination traffic into regions of increased recombination needs to be considered in inhomogeneous semiconductors containing junctions or recombination surfaces and is represented by the dj/dx -term.

In Fig. 31.1 a typical reaction kinetic model for optical carrier generation in an n -type semiconductor is shown.

²Also referred to as *continuity equations*, that contains generation and recombination, and traffic out of each volume element into junction or interfaces for additional recombination.

The balance between the different transitions depends on the optical generation rate in addition to the transition parameters, and on the boundary conditions in inhomogeneous semiconductors. This in turn will influence the changes of space charges and the development of currents in such semiconductors.

We will first describe the redistribution of carriers over the different levels as the result of optical generation in a *homogeneous semiconductor*. In this case there are no net carrier currents involved, except for fluctuations; hence, one has

$$\frac{dj_n}{dx} = \frac{dj_p}{dx} \equiv 0. \quad (31.5)$$

We refer to semiconductors that change their conductivity significantly with light as *photoconductors*.

31.1.1 Photoconductors

Optical generation increases the density of both minority and majority carriers. Depending upon doping and recombination, two types of materials may be distinguished: *semiconductors* and *photoconductors*.

In typical semiconductors the density of thermally created *majority carriers* is so high that the optical generation causes only an insignificant increase of their density. The major changes are observed in a large increase of the density of *minority carriers*, resulting in a split of the quasi-Fermi levels by shifting the minority Fermi level only,³ with negligible shift of the majority quasi-Fermi level.

In typical *photoconductors* the density of thermally created majority carriers is usually low: in the dark the material acts as an insulator. CdS is an example which, when properly doped, may have a dark resistivity in excess of $10^{10} \Omega \text{ cm}$; it is *n*-type with $n < 10^7 \text{ cm}^{-3}$. Even with low light intensity the *majority carrier* density increases significantly. In a photoconductor the band gap is wider than in typical semiconductors, the distance of the donor from the conduction band is larger, and most of the donors are depleted because of a large degree of compensation. With light the compensation is partially lifted, donors and acceptors are partially filled with electrons and holes respectively and both quasi-Fermi levels are shifted significantly. In addition, good photoconductors are *sensitized*, i.e., they are doped with minority carrier traps, which have a very small cross section to capture majority carriers, and consequently result in a *very low recombination rate* (e.g., Cu-doping in CdS), increased carrier lifetime and cause a high photosensitivity.

³This state is often referred to as *low injection* state. With sufficient optical generation, e.g., for solar cells with concentrator, *high injection* can be reached, in which both carrier densities increase significantly above the equilibrium concentration.

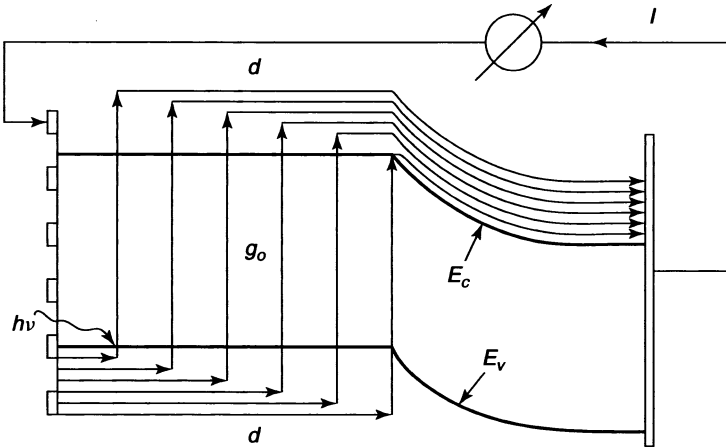


Fig. 31.2 Schematic of a photovoltaic device, indicating optical generation (g); separation of minority and majority carriers in the built-in field via minority carrier diffusion (d); and consequent recombination current (r) in the external circuit. The *arrows* represent electron paths (holes in the valence band move in the opposite direction)

31.1.2 Photo-emf and Photocurrents

In principle, either photoconductors or semiconductors produce a *photo-emf* when a space charge region is incorporated within the device. The built-in field of the space charge region separates some of the optically generated minority and majority carriers from each other, causing a relative charging of the two sides of the space charge region, or causing a *photocurrent* with carrier recombination within the external circuit when a path through an external circuit is provided (Fig. 31.2).

The *photovoltaic devices* have gained substantial commercial interest when using sunlight for carrier generation. They are called *solar cells* and convert solar energy into electrical energy with a respectable conversion efficiency.⁴

Highly efficient solar cells need a lower band gap in the 1.0–1.5 eV range to convert a large fraction of the solar light, and therefore are more typical *semiconductors*. Examples are Si, Cu_2S , CuInSe_2 , CdTe, and GaAs as the material in which most of the sunlight is absorbed and the desired minority carriers are generated. (Histogram of most solar cells is shown in Fig 31.3.)

⁴Better solar cells (Si and GaAs) have presently achieved in excess of 24 % conversion efficiencies (Zhao et al. 1990), and, with more sophisticated technology (tandem cells); such In-GaP/GaAs tandem cells exceeded 30 %; with sunlight concentration solar cells have exceeded 40 % (Geisz et al. 2008 and King et al. 2007), and recently, as GaInP₂/GaAs/Ge triple junction cells reached 40 %.

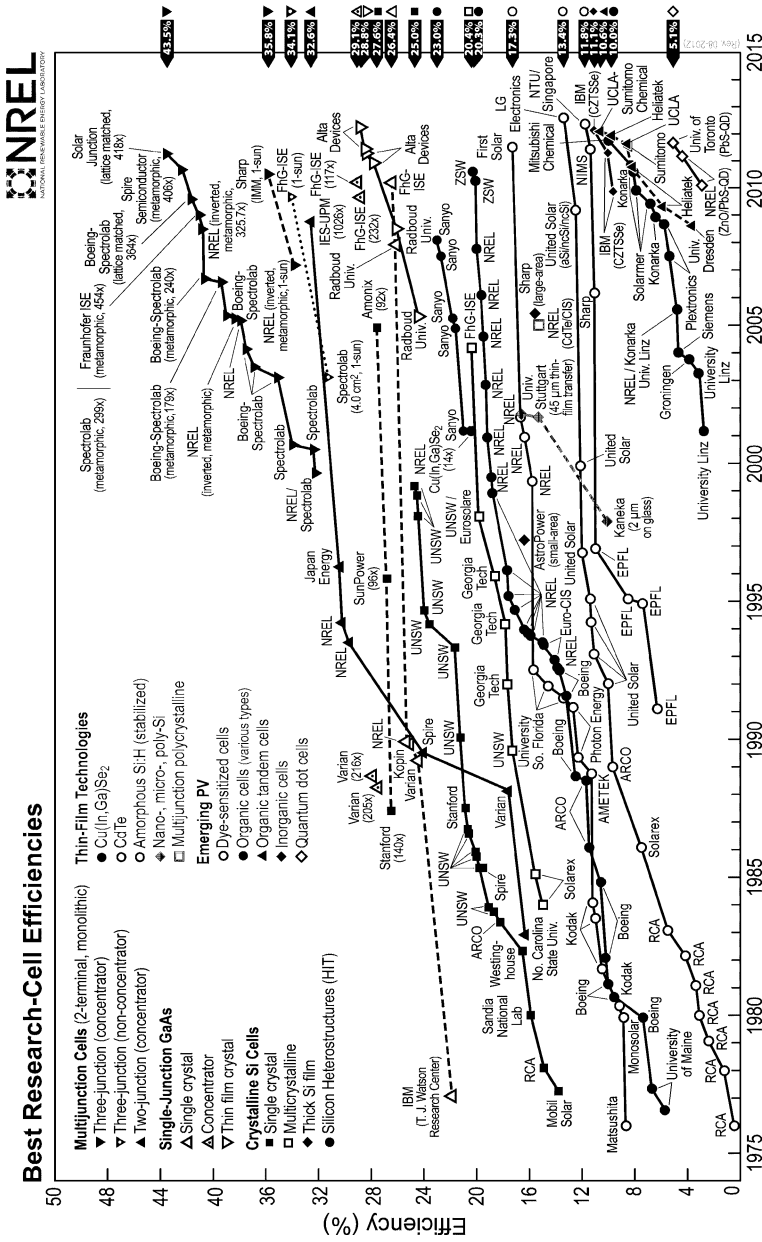


Fig. 31.3 History of developing highest efficiencies of various solar cells from 1975 to 2009 (cortsey of Lawrence Kazmerski, NREL, 2009, for specific quotation see Green et al. 2009b)

31.1.3 Quasi-equilibrium Approximation

At the high generation rate associated with sunlight absorption,⁵ the density of optically generated minority carriers

$$p = g_o \tau_p, \quad (31.6)$$

varies between 10^{10} for low lifetime (10^{-11} s) direct gap material to in excess of 10^{16} for high lifetime ($>10^{-6}$ s) indirect band gap material.

This minority carrier density is proportional to the light intensity as long as the lifetime is independent of the generation rate; then the split of the quasi-Fermi levels is proportional to the logarithm of the light intensity

$$E_{Fn} - E_{Fp} = E_g - kT \ln \left(\frac{N_c N_v}{N_d g_o \tau_p} \right), \quad (31.7)$$

assuming that the majority quasi-Fermi level remains essentially unchanged and is given by the density of shallow donors.

A constant lifetime is observed when the density of available recombination centers is constant; that is, when the capture of electrons (in this example) into recombination centers is more rapid than that of minority carriers (holes). A constant density $n_r \cong N_r$ of available centers is then provided. This can be achieved when the product of carrier density and capture cross section fulfills the condition

$$n s_{rn} \gg p s_{rp}. \quad (31.8)$$

It also requires that most of the generated minority carriers remain in the valence band rather than being trapped in hole traps. If substantial hole trapping needs to be considered, a pinning of the quasi-Fermi level for holes may occur with increasing optical generation rate until these hole traps are filled.

31.2 Reaction Kinetic, Balance

Whenever the recombination path for recombining holes becomes saturated ($n_r \ll N_r$) (e.g., at higher light intensities) or a major fraction of the optically generated holes is trapped at hole traps, the minority carrier lifetime becomes a function of the generation rate. A balance evaluation permits the determination of the minority carrier lifetime $\tau_p(g_o)$. The balance is determined by the difference between generation and recombination for each center, and is influenced by the carrier

⁵The photon flux impinging on a semiconductor is on the order of $10^{17} \text{ cm}^{-2} \text{ s}^{-1}$ in the active part of the solar spectrum at AM 1. Indirect gap semiconductors with an absorption coefficient (weighted average) of $\sim 10^4 \text{ cm}^{-1}$ thus have an effective generation rate (averaged) of $10^{21} \text{ cm}^{-3} \text{ s}^{-1}$ and (thin) direct band gap semiconductors with an absorption efficient of $3 \cdot 10^5 \text{ cm}^{-1}$ have an average generation rate of $3 \cdot 10^{22} \text{ cm}^{-3} \text{ s}^{-1}$.

distribution over other centers via the neutrality condition, making more generated electrons available⁶ for recombination than free holes (most of them are trapped). The change in minority carrier density with generation rate can be estimated from the formalism developed in Sect. 27.4 (see also Böer 2002).

In general, all competing transitions need to be considered. This yields for steady state a set of balance equations⁷

$$g_o - [c_{cd}np_d - e_{dc}N_c n_d] - [c_{cr}np_r - (e_{rc}N_c n_r)] = \frac{dn}{dt} \equiv 0 \quad (31.9)$$

$$c_{cd}np_d - e_{dc}N_c n_d = \frac{dn_d}{dt} \equiv 0 \quad (31.10)$$

$$[c_{cr}np_r - (e_{rc}N_c n_r)] - [c_{rv}n_r p - (e_{vr}N_v p_r)] = \frac{dn_r}{dt} \equiv 0 \quad (31.11)$$

$$[c_{cr}np_r - (e_{rc}N_c n_r)] - [c_{rv}n_r p - (e_{vr}N_v p_r)] = \frac{dn_r}{dt} \equiv 0 \quad (31.12)$$

$$g_o - [c_{av}n_d p - e_{va}N_v p_a] - [c_{rv}n_r p - (e_{vr}N_v p_r)] = \frac{dp}{dt} \equiv 0. \quad (31.13)$$

The terms in parenthesis are usually negligible because of insufficient thermal excitation from the deep levels.

In addition to Eqs. (31.9)–(31.13) one has the neutrality condition

$$n + n_a + n_r = p + p_d, \quad (31.14)$$

with

$$\begin{aligned} N_d - p_d &= n_d \\ N_r - p_r &= n_r \\ N_a - n_a &= p_a; \end{aligned} \quad (31.15)$$

we have here assumed an acceptor-like charging of the recombination centers.

One obtains from the balance of electrons in the conduction band, using Eqs. (31.9) and (31.10) by neglecting the term in parenthesis:

$$g_o = c_{cr}n(N_r - n_r). \quad (31.16)$$

In a similar fashion one obtains from the balance of holes, using Eqs. (31.13) and (31.12), and neglecting the term in parenthesis:

$$g_o = c_{rv}n_r p. \quad (31.17)$$

⁶This effect becomes active only at high enough light intensities, when the majority carrier density increases markedly.

⁷The capture and emission coefficients are identified by c and e respectively with subscripts identifying origin and target level (see Sect. 27.2).

Equations (31.16) or (31.17) can be used under certain conditions to estimate the carrier density generated by light. For instance, the minority carrier density for $n_r \simeq N_r$ is then simply given by

$$\boxed{p = \frac{g_o}{c_{rv}N_r}} \quad (31.18)$$

which is identical to the well-known relation Eq. (31.6), with the hole life time

$$\tau_{p0} = \frac{1}{c_{rv}N_r}. \quad (31.19)$$

In case n_r is no longer $\approx N_r$ a better analysis of the system of Eqs. (31.9)–(31.13) is required. When substituting the unknown densities of the trapped carriers

$$\begin{aligned} p_d &= \frac{e_{dc}N_cN_d}{c_{cd}n - e_{dc}N_c}, \\ n_r &= \frac{c_{cr}nN_r}{c_{rv}p - c_{cr}n}, \\ n_a &= \frac{e_{va}N_vN_a}{c_{av}p - e_{va}N_v}, \end{aligned} \quad (31.20)$$

and using total neutrality, one obtains

$$\frac{g_o}{c_{cr}(N_r - n_r)} + \frac{e_{va}N_vN_a}{c_{cv}p - e_{va}N_r} + \frac{c_{cr}nN_r}{c_{rv}p - c_{cr}n} = \frac{g_o}{c_{rv}n_r} + \frac{e_{dc}N_cN_d}{c_{cd}n - e_{dc}N_c}. \quad (31.21)$$

This equation can be converted into an implicit polynomial expression for computing the carrier densities n or p as function of the optical generation rate g_o by using Eqs. (31.16) and (31.17). For certain cases Eq. (31.21) can be simplified as explicit polynomials:

$$n = n(g_o) \quad \text{or} \quad p = p(g_o). \quad (31.22)$$

For instance, at very high generation rates, where $n \cong p$ one obtains from the first terms on each side of Eq. (31.21):

$$n_r = N_r \frac{c_{cr}}{c_{cr} + c_{rv}} \quad \text{or} \quad N_r - n_r = N_r \frac{c_{rv}}{c_{cr} + c_{rv}}. \quad (31.23)$$

From this condition one obtains an often used relation

$$\boxed{n = p = \frac{g_o}{N_r} \left[\frac{1}{c_{cr}} + \frac{1}{c_{rv}} \right]} \quad (31.24)$$

for the density of mutually created carriers, neglecting trapping. This is a typical bottleneck equation which determines the carrier density from the smaller of the two capture coefficients c_{cr} and c_{rv} .

The discussion given here is given merely to indicate the general trend and is by no means exhaustive. In a broader discussion, a larger variety of defect levels need to be included as and their spatial distribution needs to be considered as well as other transitions and recombination mechanisms, including field dependent excitation and Auger recombination (see Böer 2002).

31.2.1 Trap-Controlled Carrier Densities

Traps may act as storage reservoirs to take part of the optically generated carriers out of circulation. Shallow traps usually are in quasi-thermal equilibrium with the corresponding band, with their degree of filling determined by the position of the quasi-Fermi level, ranging from $n \cong N_t$ for $E_{Fn} < E_t$ to $n_t \ll N_t$ for $E_{Fn} > E_t$ for an electron trap. But with changing optical excitation the position of the quasi-Fermi level can be shifted, and hence the degree of occupation of these traps.

In order to illustrate the involved principle, let us assume a simple n -type photoconductor with electron traps and recombination centers as the only important defect center. The corresponding reaction kinetic equations are

$$g_o - [c_{ct}n(N_t - n_t) - e_{tc}n_tN_c] - c_{cr}n(N_r - n_r) = \frac{dn}{dt} \equiv 0 \quad (31.25)$$

$$c_{ct}n(N_t - n_t) - e_{tc}n_tN_c = \frac{dn_t}{dt} \equiv 0 \quad (31.26)$$

$$g_o - e_{vr}pn_r = \frac{dp_r}{dt} \equiv 0 \quad (31.27)$$

with the corresponding neutrality equation

$$n + n_t + n_r = p. \quad (31.28)$$

When assuming predominant carrier trapping, one can simplify Eq. (31.28) to

$$n + n_t = p \quad (31.29)$$

and obtains from Eqs. (31.25) and (31.26) the simple relation

$$g_o = c_{cr}n(N_r - n_r). \quad (31.30)$$

After replacing n_r from Eq. (31.27) and p from Eq. (31.29) one obtains a modified equation between carrier density and optical generation rate

$$n(n + n_t) - \frac{g_o}{N_r} \left[\frac{n + n_t}{c_{cr}} + \frac{n}{c_{rv}} \right] \quad (31.31)$$

which is non linear in n and shows a modified bottleneck relation in square brackets. For higher generation, $n \gg n_t$, Eq. (31.31) reverts back to Eq. (31.24) and shows

that n rises proportional to g_o . For lower generation, $n_t \simeq N_t \gg n$, one obtains from Eq. (31.31):

$$n = \frac{g_o}{N_r} \left[\frac{c_{rv}}{c_{cr}} \cdot \frac{N_r N_t}{c_{rv} N_r N_t - g_o} \right] \quad (31.32)$$

which shows a sublinear rise of n with g_o .⁸

A similar relation can be developed for minority carriers.

We will now discuss in a simplified model how the photogenerated minority carriers produce the photodiode current in a photo diode.

31.3 Simple Model of the Photodiode

A simplified model for the photodiode can be derived from the diode model discussed in Sect. 30.1, which yields the basic diode equation [Eq. (30.59)]. In addition to the diffusion current of thermally generated minority carriers that provided the saturation current in reverse bias, we have now to add the photo-generated carriers.

We will take here a modified formalism from the one used in earlier sections (Sects. 28.1, 6.1, and 31.1). This approach permits direct comparison between the thermal ionization (dark current) and the optical excitation (photovoltaic current).

The controlling equation for the minority carriers in the bulk is the current continuity equation (in steady state)

$$\frac{dj_p}{dx} = e(U + g_o) \quad (31.33)$$

with g_o the optical generation rate of electrons and holes, and

$$U = \frac{np - n_i^2}{\tau_{p0}(n + n_i^+) + \tau_{n0}(p + n_i^-)} \quad (31.34)$$

the net gr -rate, which, for $n \gg p$ becomes

$$U \simeq \frac{p - \frac{n_i^2}{n}}{\tau_{p0}} = \frac{p - p_0}{\tau_{p0}} \quad (31.35)$$

as long as the majority carrier density n remains close to its thermal equilibrium value n_0 , which permits the use of $p_0 = n^2/n_0$.

In the space charge-free region, the minority carrier current is exclusively given by diffusion:

$$j_p = -\mu_p kT \frac{dp}{dx}; \quad (31.36)$$

⁸However, when optical generation at longer wavelength is applied, a superlinear branch can be observed, when optical *excitation* from filled traps increases.

with Eqs. (31.33) and (31.35) one obtains the diffusion equation for minority carriers, including thermal and optical excitation

$$\frac{\mu_p kT}{e} \frac{d^2 p}{dx^2} = \frac{p - p_0}{\tau_{p0}} - g_o, \quad (31.37)$$

which has the general solution:

$$p(x) = p_0 + g_o + A \exp\left(\frac{x}{L_p}\right) + B \exp\left(-\frac{x}{L_p}\right) \quad (31.38)$$

with the diffusion length

$$L_p = \sqrt{\frac{\mu_p kT}{e} \tau_{p0}}. \quad (31.39)$$

By providing two boundary conditions, the particular solution curve can be picked from this set of general solutions. In a long device we require

$$p(x \rightarrow \infty) = \text{finite} \quad (31.40)$$

which renders $A = 0$.

At the other side of the device, we are now connecting the minority carrier density to the density at the boundary of the barrier which is obtained from integrating the transport equation

$$j_p = e\mu_p p \frac{dV}{dx} - \mu_p kT \frac{dp}{dx} \quad (31.41)$$

for small net currents,⁹ resulting in

$$p(x_B) = p_0 \exp\left(\frac{eV}{kT}\right), \quad (31.42)$$

where $p_0 = p_0(x_B)$ is the equilibrium density at the barrier boundary x_B and V is the applied voltage (neglecting series resistances). Neglecting also the thickness of the barrier¹⁰ for current generation, i.e., setting $x_B = 0$, one obtains for the particular solution after inserting Eq. (31.42) into Eq. (31.38)

$$p(x) = p_0 + g_o \tau_{p0} + \left[p_0 \left(\exp\left\{\frac{eV}{kT}\right\} - 1 \right) - g_o \tau_{p0} \right] \exp\left(-\frac{x}{L_p}\right). \quad (31.43)$$

⁹ Assuming $j_p \ll (e\mu_p p F, \mu_p kT dn/dx)$.

¹⁰ The connection of $p(x_B)$ as $p(x=0)$ with Eq. (31.38) to determine the second boundary condition B, is not clear cut for a simple barrier. A more transparent connection of bulk and barrier is discussed in Sect. 33.1.3 for the d-type high-low heterojunction.

When using this hole distribution in Eq. (31.36) one obtains for the minority carrier current:

$$j_p(x) = \frac{\mu_p kT}{L_p} p_0 \left[\exp\left(\frac{eV}{kT}\right) - 1 \right] \exp\left(-\frac{x}{L_p}\right) - e g_o L_p \exp\left(-\frac{x}{L_p}\right). \quad (31.44)$$

A complimentary solution can be obtained for the majority carrier current $j_n(x)$ with the total current given by $j_n + j_p = j = \text{const}$ for steady state.

The total *photocurrent* is then easily determined at any convenient position, e.g., at $x = 0$, where $j_p(x)$ has its maximum value [here $j_n(x) = 0$], yielding

$$j(V) = \frac{\mu_p kT}{L_p} p_0 \left[\exp\left(\frac{eV}{kT}\right) - 1 \right] - e g_o L_p \quad (31.45)$$

the photo diode equation in this simplified model as the sum of the photo current and the *dark current*, as obtained from the simple Schottky diode equation

$$j(V) = \frac{\mu_p kT}{L_p} p_0 \left[\exp\left(\frac{eV}{kT}\right) - 1 \right] \quad (31.46)$$

which is identical with Eq. (30.59) by setting the reverse dark saturation current

$$\boxed{j_0 = p_0 \frac{\mu_p kT}{L_p} = e p_0 v_{Dp}} \quad \text{with} \quad \boxed{v_{Dp} = \frac{L_p}{\tau_{p0}}}. \quad (31.47)$$

The photo current, that is the maximum current of photogenerated minority carriers (photocurrent)

$$\boxed{j_L = e g_o L_p} \quad (31.48)$$

Hence one obtains a simple shift of the dark current by j_L for the *ideal photovoltaic current-voltage characteristic*

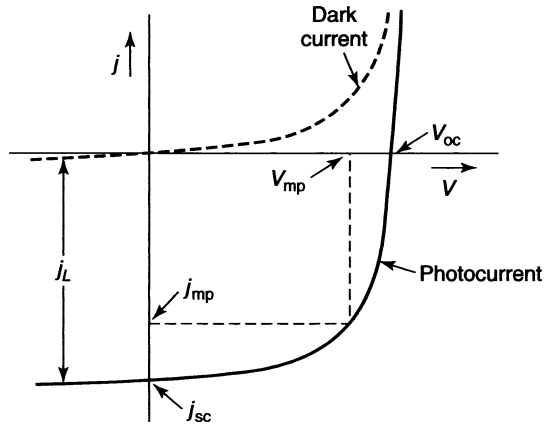
$$\boxed{j = j_0 \left[\exp\left(\frac{eV}{kT}\right) - 1 \right] - j_L}, \quad (31.49)$$

as shown in Fig. 31.4.¹¹

It should be emphasized here that such a shifted diode equation which is often used to approximate the characteristics of photo diodes contains numerous approximations, that renders such discussion of limited value. Especially the often experimentally found cross-over of photo diode and dark characteristics should be judged as an important sign that the analysis of that particular device needs to be studied in a much more detailed model. Nevertheless, the obtained shift by the photo diode current (Eq. (31.48)) is a valuable tool to determine the diffusion length of the minority carrier.

¹¹In actuality such simple shift is rarely observed, as often the dark- and photo-diode characteristics cross-over in forward bias.

Fig. 31.4 Dark- and photodiode characteristic with the photocurrent shifted from the dark current by the saturation current $j_{sc} = j_L$. Maximum obtainable power rectangle with v_{mp} and j_{mp} shown.



31.3.1 Derived Photodiode Parameters

In contrast to passive devices which have current-voltage characteristics lying exclusively in the first and third quadrant, the photodiodes (solar cells) have a major segment in the second quadrant, where electric power can be extracted directly from the device. For technical purposes this part of the characteristic is conventionally described by three parameters:

- (1) the short circuit current, i.e., the maximum current that can be extracted from the device by connecting both electrodes to an ammeter with negligible internal resistance;
- (2) the open circuit voltage, i.e., the maximum voltage generated by the device that can be measured between both electrodes while drawing a negligible current; and
- (3) the maximum power point, i.e., the point in the characteristic from which the maximum electric power can be extracted.

From the photodiode characteristic [Eq. (31.49)] one obtains as short circuit current (for $V = 0$)

$$j_{sc} = j_0 + j_L \simeq j_L \quad (31.50)$$

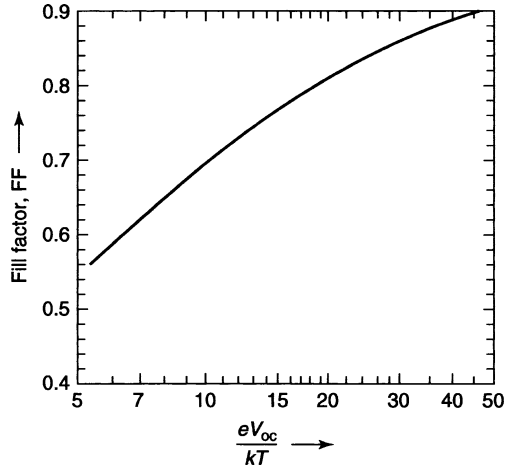
and as open circuit voltage (for $j = 0$)

$$V_{oc} = \frac{kT}{e} \ln\left(\frac{j_L}{j_0} + 1\right) \simeq \frac{kT}{e} \ln\left(\frac{j_L}{j_0}\right). \quad (31.51)$$

Using the maximum possible open circuit voltage derived from the difference of the quasi-Fermi levels ($V_{oc} = E_{Fn} - E_{Fp})/e$, one can rewrite Eq. (31.51) to the usefull approximation for the maximum achievable open circuit Voltage as

$$V_{oc}^{\max} = E_g/e - (kT/e) \ln[(n_L - n_0)/N_c N_v] \quad (31.52)$$

Fig. 31.5 Fill factor of an ideal photodiode as a function of the open circuit voltage according to Eq. (31.55). It lies between 55 and 80 % for typical photo diodes. (It is reported at 81.20 % for the best CdS based multi layer solar cells (Repins et al. 2008))



that is, the open circuit voltage decreases with increasing temperature, and its maximum achievable value approaches the band gap at $T = 0$ K.

With Eq. (30.51) one can eliminate j_0 and thereby rewrite the simple model photodiode equation [Eq. (31.49)] in a form containing only experimentally accessible parameters:

$$j = j_{sc} \left[\exp \left\{ \frac{e(V_{oc} - V)}{kT} \right\} - 1 \right]. \quad (31.53)$$

The maximum power point is determined by the maximum rectangle that can be inscribed in the fourth quadrant of the characteristic (Fig. 31.4) and can be obtained from the point at which the slope of the characteristic equals minus one:

$$\frac{V_{mp}}{j_{mp}} \frac{dj(j_{mp}, V_{mp})}{dV} = -1. \quad (31.54)$$

In solar cell technology another parameter is often used, the *fill factor*, which is given by

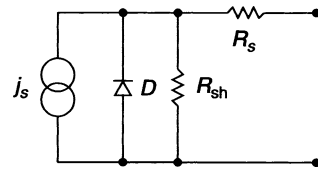
$$FF = \frac{V_{mp} j_{mp}}{V_{oc} j_{sc}}, \quad (31.55)$$

which can be derived from Eqs. (31.49) and (31.53) and can be *approximated* by (Green 1982):

$$FF \simeq \frac{\frac{eV_{oc}}{kT} - \ln\left(\frac{eV_{oc}}{kT} + 0.72\right)}{\frac{eV_{oc}}{kT} + 1}. \quad (31.56)$$

The fill factor is a measure of the “squareness” of the characteristics in the fourth quadrant and is shown in Fig. 31.5 for the (simple model) “ideal” photo-diode characteristic as a function of the normalized open circuit voltage.

Fig. 31.6 Simple equivalent circuit of a solar cell diode D with series and shunt resistances identified



The *power conversion efficiency* η can be derived from the above given parameters. It is the most important parameter of solar cells. This *efficiency* η is defined by the ratio of electrically generated power over the total power of light P_{in} impinging on the solar cell per unit area

$$\eta = \frac{V_{mp} j_{mp}}{P_{in}} = \frac{V_{oc} j_{sc} F F}{P_{in}} \quad (31.57)$$

31.3.2 Resistive Network Influence on the Diode Characteristics

In actual practice, photodiodes do not obey the (simple model) ideal diode equation [Eq. (31.49)], even though some of the better diodes come relatively close to it. One often uses a network of series and parallel resistors to model the experimentally observed characteristics (Fig. 31.6).

However, there are many reasons for such deteriorating deviations, most of them related to junction or surface recombination, or to the influence of traps on transport and space-charges, as discussed in previous chapters, and this is the subject of a more detailed analysis in the following chapter.

An empirical means to deal with some of the reduced diode performance is the introduction of an empirical exponential correction factor, as used in diodes, the *diode quality factor*, A which is larger than 1:

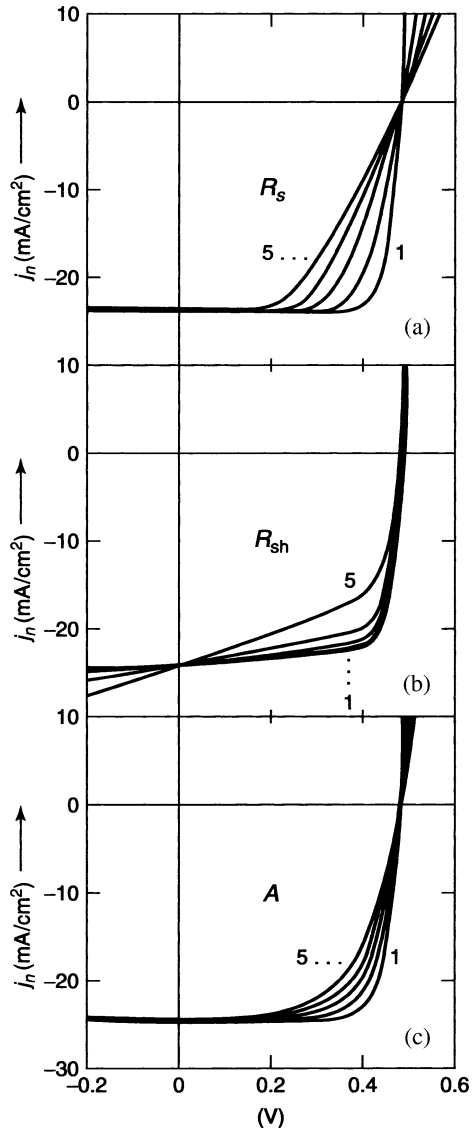
$$j = j_0 \exp\left(\frac{eV}{AkT}\right) - j_L. \quad (31.58)$$

The influence of the quality factor on the shape of the diode characteristics is indicated in Fig. 31.7c; it causes a reduction in the fill factor with little changes at and beyond j_{sc} and at V_{oc} .

In addition, for some of the polycrystalline devices, rather simple series or shunt resistances¹² as shown in Fig. 31.6 can interfere with the device performance. Even though of limited and often misleading use we will show such influence here, more

¹²Such resistances may actually exist in polycrystalline devices as paths between the electrodes through grain boundaries or as interlayers between grains and the electrodes. But their assumed existence is often overstated and can result in expensive searches for the wrong causes of such deviations from diode curve idealities in solar cell development.

Fig. 31.7 Diode characteristics of a 1 cm^2 solar cell, modified (a) by a series resistance of 0, 2, 4, 6 and 8 Ohms for curves 1–5, respectively, (b) by a shunt resistance of 250, 200, 150, 100 and 50 Ohms for curves 1–5, respectively, and (c) by various diode A factors of 1 (ideal), 1.5, 2, 2.5 and 3 for curves 1–5, respectively (j_0 is adjusted to keep $V_{oc} = \text{const.}$)



as a warning that with introduction of a number of parameters (justified or not) one can approximate experimental curves easily.¹³

A series resistance R_s may result from insufficiently conducting electrodes, or excessive bulk material of insufficient doping. The effect of such series resistance is

¹³Often the equivalent circuit is extended by other elements, such as another diode and more resistances, providing even more adjustable parameters to produce “better” (and more misleading) agreements with the experiment.

the tilting of the characteristic along the ascending branch and around V_{oc} , as shown in Fig. 31.7a.

A *shunt resistance* R_{sh} can be the result of a crystal fault or other electric pathways across the junction, possibly near surfaces or internal crystal boundaries. R_{sh} influences the slope of the characteristics near j_{sc} and simulates incomplete saturation as shown in Fig. 31.7b.

The so modified diode characteristic is given by

$$j = j_0 \left[\exp \left\{ \frac{e(V - jR_s)}{AkT} \right\} - 1 \right] - j_s + \frac{V - jR_s}{R_{sh}}. \quad (31.59)$$

When using these empirical correction factors, many actual characteristics can be closely approximated. This, however, may lead to erroneous conclusions about the possible presence of a network of parasitic resistors, while the actual reasons for a shape deviation from the ideal characteristic lies much deeper in the diode performance, as will be discussed in the following chapters.

31.4 Device Cooling when Electric Energy is Extracted from Solar Cells Exited with Light

With the open circuit voltage decreasing with temperature it is expected that the solar cell efficiency can be increased by cooling the cell. Since that such solar cells can be used to directly extract heat that is directly related to the absorption of sunlight, a cooling can be achieved by extracting the heat for comfort conditioning, that is, using a solar panel as a hybrid solar collector to convert sunlight directly into electric power and into useful heat. Both conversions are related via entropy production. When one part of the energy is extracted, e.g., the electrical energy, then the other part, the heat, must change: the solar cell must lower its temperature. Inversely, when the temperature of a solar cell is lowered, e.g., by cooling it, the solar cell electrical efficiency must increase.

We will explain this below in more detail and will give an experimental example when measuring the temperature on a solar panel before and after extracting electrical energy from it (Böer 2001).

31.4.1 Detailed Energy Balance

In order to obtain an insight into the intricate relationship we must provide a detailed energy balance between the different parts of energies as shown in Fig. 31.8 and expressed by

$$E_{in} = E_{opt} + E_{th} = E_{refl} + E_{PV} + \varepsilon \sigma T^4 + h_1(T - T_s) + h_2(T - T_{extr}), \quad (31.60)$$

with E_{opt} the optical excitation energy (for solar cells exposed to sunlight of the described as *insolation*), $E_{\text{th}} = \sigma T^4$ the thermal energy from the surroundings at a temperature of $T = T_s$ and the coefficients h_1 and h_2 describing the thermal heat transfer to the surrounding and a heat extracting (cooling) medium at the other surface. ε is the emissivity from the cell. $E_{\text{refl}} = \kappa E_{\text{opt}}$ with κ the optical reflectivity, and $E_{PV} = \eta E_{\text{opt}}$ with η the photo voltaic efficiency of the cell. σ is the Stephan-Boltzmann constant $5.67 \times 10^{-8} \text{ W/m}^2 \text{ K}^4$. Without extraction of electrical energy open switch S in Fig. 31.9 we obtain for the cell temperature T_1 the implicit equation

$$E_{\text{opt}}(1 - \kappa) + \sigma T_{\text{extr}}^4 = (\varepsilon_1 + \varepsilon_2)\sigma T_1^4 + h_1(T_1 - T_s) + h_2(T_1 - T_{\text{extr}}), \quad (31.61)$$

with ε_1 and ε_2 the emissivity from the front and the back surface of the cell, respectively.

When closing the switch S and extracting electrical power from the cell at maximum power point, we obtain a similar equation, except for now including the extracted electrical energy, and specifically using the efficiency η that has now to be evaluated at the lower cell temperature T_2

$$E_{\text{opt}}(1 - \kappa - \eta) + \sigma T_{\text{ext}}^4 = (\varepsilon_1 + \varepsilon_2)\sigma T^4 + h_1(T_2 - T_s) + h_2(T_2 - T_{\text{extr}}). \quad (31.62)$$

Since most of these parameters are known to a reasonable degree, Eqs. (31.61) and (31.62) can be used to obtain the reduction of the cell temperature when electric energy is extracted.

In a simple first approximation the temperature difference can be obtained from subtracting Eq. (31.61) from Eq. (31.62) and developing the Stephan-Boltzmann part with the approximation

$$(T_1^4 - T_2^4) = (T_1 - T_2)(T_1 + T_2)(T_1^2 + T_2^2) \cong 4T_{\text{op}}(T_1 - T_2)$$

with the average operational Temperature

$$T_{\text{op}} \cong (T_1 + T_2)/2.$$

This yields for the cooling of the cell with electrical power extraction

$$\frac{\Delta T = T_1 - T_2 = \eta E_{\text{opt}}}{4\varepsilon T_{\text{op}}^3 + h_1 + h_2}. \quad (31.63)$$

The estimated temperature differences are given for solar panels as estimated from Eq. (31.63) in Fig. 31.8 for typical parameter values as given in the figure and for an insolation of 1000 W/cm^2 as a function of the cell efficiency and lie between 4 and 20°C .

In an actual setting of a hybrid solar roof on the Guest house of Solar Knoll in Kennett Square, PA, (Böer 2001) the rise and fall of the temperature of the solar

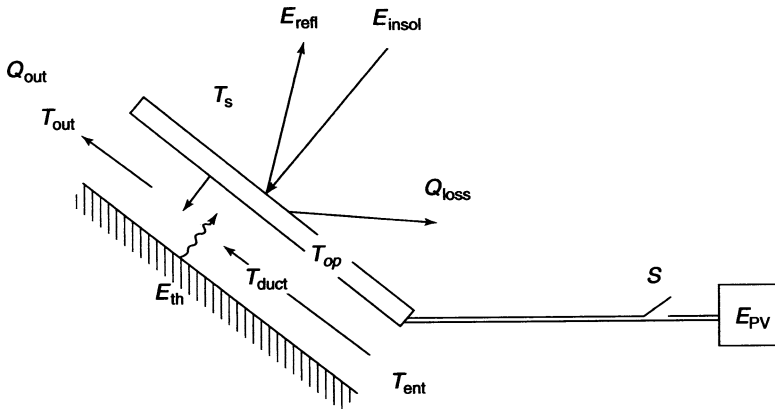
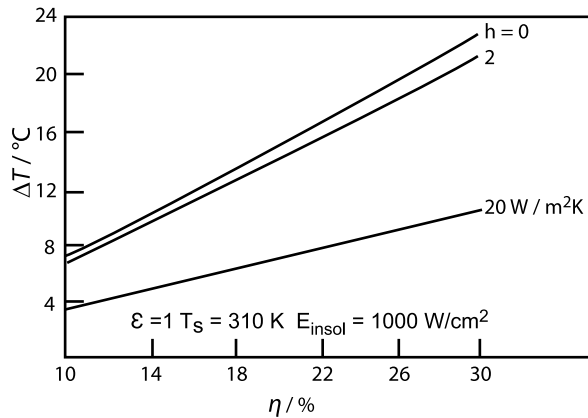


Fig. 31.8 Energy balance of a solar cell within a hybrid collector. The energy input is given by the insolation E_{opt} and the thermal radiation composed of the thermal radiation from the surrounding front and the back. The useful energy is divided between the electrical energy E_{PV} and the heat out Q that is the sum of the radiated heat out from the front Q_{loss} and the extracted heat Q_{extr} , here assumed to be from air in an air duct below the cells at a temperature T_{duct} (averaged), heating the air from the inlet at T_{ent} to the temperature at the outlet T_{out} . During the operation the temperature of the cell is increased to T_{op} , that is more precisely distinguished in the text between T_1 and T_2 without and with extraction of electrical power

Fig. 31.9 Cooling temperature difference of a solar cell when exposed to sunlight at 1000 W/cm^2 with an electric load at maximum power point as a function of the cell efficiency. Other parameters are given in the figure



cells in the panels on the roof was measured with thermo couples and registered after switching off and switching on respectively of the electric load tuned close to the maximum power point. With 14 % conversion efficiency of the panel and on a hazy day with 880 to 900 W/m^2 upper curves in Fig. 31.9. The cooling or heating takes about 10 min to become stationary as shown in the lower curves of Fig. 31.9.

The values of the heat transfer coefficients can be estimated from the family of curves for different heat transfer coefficients in Fig. 31.10 that shows the calculated cooling temperature ΔT as a function of the outside temperature T_s and an estimated $\varepsilon = 0.8$ at an insolation of 880 W/cm^2 . From the measured values of ΔT of

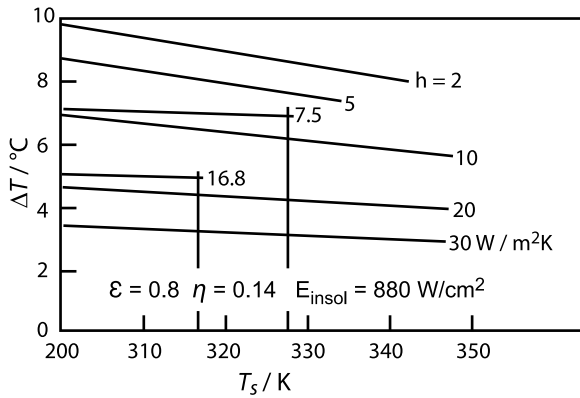


Fig. 31.10 Temperature difference from cooling when electric power is extracted from a solar panel calculated from Eq. (31.63) after stationarity is reached at an insolation of 880 W/m^2 as a function of the outside temperature. The average heat transfer coefficient h is family parameter. The values 7.5 and 16.8 are indicated corresponding to the measured cooling temperatures at calm and 10 m/s wind velocity

7° one obtains a heat transfer coefficient of about 7.5, and a few minutes later when the wind velocity has picked up from calm to 10 m/s of about $10.8 \text{ W/cm}^2 \text{ K}$.

Even though these temperature differences are relatively small in normal solar panel operation and are not reported, they can be substantial when solar concentration is used and cell efficiencies are higher. They are estimated to exceed $100 \text{ }^\circ\text{C}$ with cells of 20 % efficiency when exposed to a sunlight concentration of 1000 (Böer 2001).

Chapter 32

The *pn*-Junction with Light

Abstract Open circuit conditions are discussed first. A thin symmetric Si diode with abrupt junction is used first. The current distribution in a symmetric *pn* junction is computed. Solution curves for symmetric *pn* junctions are given. A recombination overshoot is identified that influences V_{oc} . The influence of device thickness, of recombination center density, of generation rate, energy of the recombination centers and of doping density is discussed. The parameter dependence of V_{oc} for insufficient minority carrier supply is discussed. Thin asymmetric Si diodes with abrupt junctions are then analyzed. The recombination through charged recombination centers is discussed. Inhomogeneous optical excitation is discussed. Optical excitation only in a thin front layer of the device is computed as example. A thin asymmetric junction design is introduced. Asymmetric bulk thickness, asymmetric recombination rate, and asymmetric generation is discussed. A thick asymmetric Si solar cell is introduced. Non-vanishing bias is discussed. Thin symmetric *pn* junction devices with bias are analyzed. A Si solar cell with bias is analyzed.

The *pn*-junction is a highly efficient means to convert optical into electrical energy. Because of the importance of such junction devices we will spend extensive attention to their performance, using the tools we have developed in the previous chapters. In the course of these discussions we will distinguish between a variety of such *pn*-junctions with different degrees of asymmetry in doping and material composition (heterojunctions). All of these *pn*-junction have three important advantages compared to a Schottky barrier:

- it permits changing from one to the other majority quasi-Fermi level, thereby permitting a large increase in open circuit voltage;
- it removes the surface of major recombination from the barrier (junction region), minimizing its impact on the performance of the diode; and
- it eliminates the divergence-free current term of the majority carriers, which causes major current leakage in the Schottky diode.

We will discuss each of these advantages in more detail below for the example of a Si *pn*-junction, and will first analyze the behavior at zero currents, i.e., open circuit condition.

Table 32.1 Main parameters used in the computation of a thin symmetric Si-diode with an Abrupt junction

Parameters	$N_a = N_d$	$N_{r1} = N_{r2}$	$E_i - E_r$	n^*
Values	10^{16}	10^{17}	0.10	$7.03 \cdot 10^{10}$
Dimensions	cm^{-3}	cm^{-3}	eV	cm^{-3}

32.1 Open Circuit Conditions

All of the following discussions are based on the solutions of the complete set of transport equations given in previous chapters. The interesting part of the pn -photo diode extends by a few Debye lengths for the space charge and by a few diffusion lengths for minority carrier collection to either side of the doping interface of the junction. In order to separate this inner part of the device from electrode effects, we first assume neutral outer boundary conditions.

Zero surface recombination at both outer surfaces (of $x = d_1$ and $x = d_2$) requires at open circuit condition that

$$j_n(d_1) = j_p(d_1) = j_n(d_2) = j_p(d_2) = 0. \quad (32.1)$$

For thermodynamic equilibrium, one has in addition

$$j_n(x) = j_p(x) \equiv 0 \quad (32.2)$$

throughout the device.

32.1.1 Thin, Symmetric Si-Diode with Abrupt Junction

We assume first a symmetrical thin device of double the thickness of the thin Schottky-barrier device.

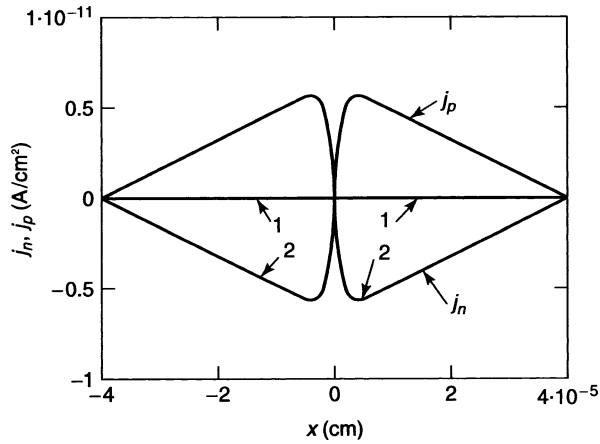
We have kept the p -type side on the right side of the device. The same set of governing equations and parameters are used as for the Si Schottky-barrier device, with the few changes listed in Table 32.1

32.1.2 Current Distribution in a Symmetric pn -Junction

In steady state, i.e., with optical generation $g_o > 0$, a net gr-current flows from both bulk regions toward the junction. For reasons of anti-symmetry both j_n and j_p must vanish in the center of this symmetric junction. This typical behavior is shown in Fig. 32.1, as computed for $g_o = 10^{12} \text{ cm}^{-3} \text{ s}^{-1}$ for curves 2. The figure also contains the zero current line (curve 1) for thermal equilibrium ($g_o = 0$).

The slope of the current curves depends on the net generation rate, which shows a behavior similar to that of the Schottky device in the bulk. However, near the

Fig. 32.1 Typical electron and hole current distributions in a thin symmetrical Si pn -junction device with negligible surface recombination; computed from Eqs. (31.32)–(31.40) with parameters given in Table 32.1 and with $g_o = 0$ and $1 \cdot 10^{12} \text{ cm}^{-3} \text{ s}^{-1}$ for curves 1 and 2, respectively



center of the junction one observes a larger difference. The current density goes here through a maximum, returns to zero at the center plane of the junction and continues after changing sign to an antisymmetric behavior at the other side of the junction. This behavior is caused by an overshoot of the recombination over the generation rate which is typical for pn -junctions near the center plane, where the minority carriers move close to each other and have the greatest chance to recombine. The result is shown by comparison of corresponding curves in Fig. 32.2a and b.¹ In Fig. 32.2a family of low generation rates is shown with g_o as family parameter. The constant optical excitation is superimposed on the bell-shaped thermal excitation:

$$g(x) \simeq \frac{1}{\tau_0} \frac{n_i^2}{n(x) + p(x) + n_i^*} + g_o, \quad (32.3)$$

with energy of the recombination center level. The maximum of the thermal excitation (for $n = p = n_i$) is given by

$$g_{\text{th,max}} = \frac{1}{\tau_0} \cdot \frac{n_i}{2\{\cosh(\frac{E_i - E_f}{kT}) + 1\}} \simeq 1.4 \cdot 10^{16} \text{ cm}^{-3} \text{ s}^{-1}. \quad (32.4)$$

The thermal generation in the center of the junction can be neglected when the optical generation rates exceed $g_{\text{th,max}}$ (the limit of *low optical generation*—here about $10^{17} \text{ cm}^{-3} \text{ s}^{-1}$). The recombination rate in the p -type region

$$r = \frac{1}{\tau_0} \cdot \frac{np}{n + p + n_i^*} \simeq \begin{cases} \frac{p}{\tau_0} & \text{in the } n\text{-type region} \\ \frac{n}{\tau_0} & \text{in the } p\text{-type region} \end{cases} \quad (32.5)$$

lies below the optical generation rate in the bulk, since minority carriers are drawn into the junction for enhanced recombination here. The recombination rate lies

¹This comparison is easiest seen for curve pair 7.

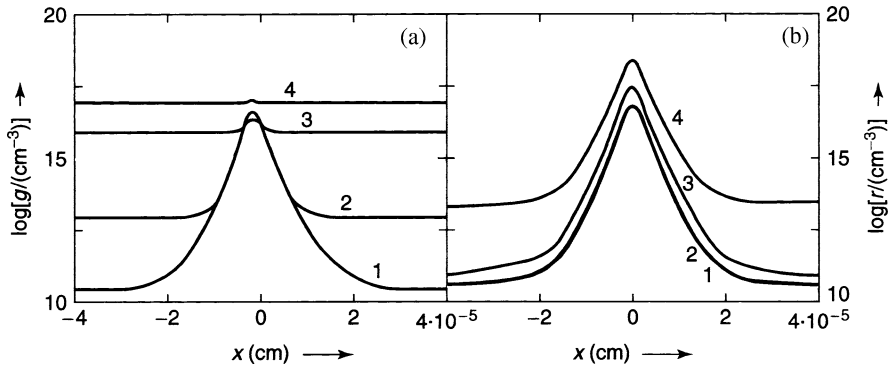


Fig. 32.2 Generation (a) and recombination rates (b) for a thin symmetrical Si pn -junction device computed as in Fig. 32.1 with the optical generation rate as family parameter: $g_o = 0, 10^{13}, 10^{16}$ and $10^{17} \text{ cm}^{-3} \text{ s}^{-1}$ for curves 1–4, respectively. The recombination rates of curves 1 and 2 lie on top of each other within the drawing error

above the optical generation rate at and near the center of the junction, since more minority carriers are now available here, supplied from the bulk. The increased² minority carrier density is caused by the continuity of $n(x)$ and $p(x)$ through the junction, as shown in Fig. 32.3. The enhanced recombination is localized within the central junction region of a width $\approx 10^{-5} \text{ cm}$ (Figs. 32.1 and 32.2). This recombination, however, is rather benign compared to perfect recombination at the semiconductor/metal interface in a Schottky barrier.

Near the region where $n(x) = p(x)$, the recombination in steady state and open circuit conditions exceeds the generation rate, a condition which is referred to as the *recombination overshoot*.

The junction net recombination compensates the bulk net generation. This general behavior should not be confused with additional junction recombination which may occur when, because of compensation of all panels of this figure and to understand their discussion is most important for the understanding of the operation of a typical solar cell.

With compensation in a gradient-doped homojunction, additional recombination centers (donor-acceptor pairs) are created within the region of cross-doping, an effect which further enhances the recombination over-shoot, and is detrimental to the photo-diode performance; this is neglected in this section.

We will now analyze the entire set of solution curves for this Si pn -junction. In order to give an instructive picture of the behavior of the solution curves we have chosen an unusually large family of curves that show a rather transparent development from small to large optical excitation rates.

²It is important for the understanding of this critical relation of a net junction recombination and the depletion of minority carriers from the adjacent bulk regions, to focus on current continuity that forces the transport of minority carriers to the recombination sink near the center of the junction, and results in a lemniscate shape of $j_n(x)$ and $j_p(x)$, as shown in Fig. 32.1.

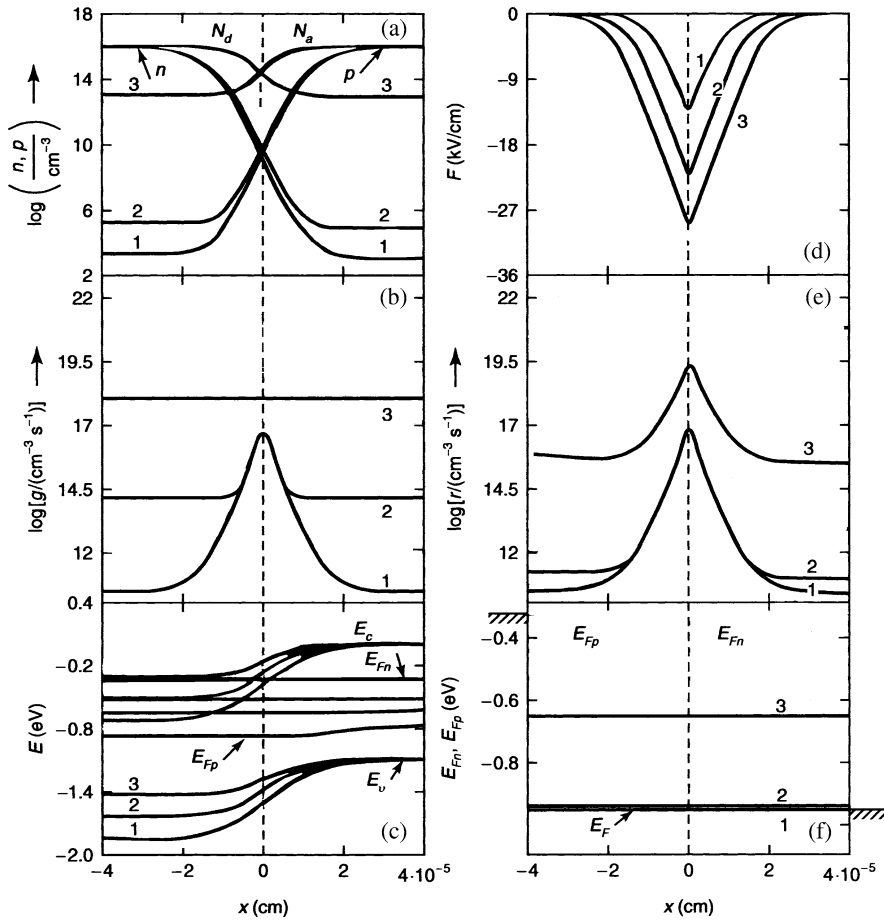


Fig. 32.3 Solution curves for a symmetrical thin Si pn -junction device computed as described for Fig. 32.1 with g_o as family parameter; for $N_r = 10^{11} \text{ cm}^{-3}$ and $g_o = 0, 10^{15}$, and $10^{21} \text{ cm}^{-3} \text{ s}^{-1}$ for curves 1–3, respectively. (a) Carrier density distribution; (b) generation rates; (c) band edges and quasi-Fermi levels; (d) field distribution; (e) recombination rates; (f) quasi-Fermi level distribution in expanded scale; connecting metal Fermi levels are shown for curve pair 3 adjacent to panel (f)

32.1.3 Solution Curves for Symmetric pn -Junction

The solution curves computed for this symmetric pn -junction in open circuit condition and for neutral surfaces are shown in Fig. 32.3 with g_o as family parameter. They show the typical pn -junction behavior of carrier density (panel a), field (panel d), and potential (band) distribution (panel c), including the expected spread of the quasi-Fermi levels (panel c and, in an enlarged scale, panel f).

Specifically, one observes a raise of the minority carrier densities with increasing g_o , concurring with a *decrease* in junction width, junction field, and barrier height.³ This typical and remarkable effect of a diminishing barrier height with increasing illumination is characteristic for any photovoltaic device and should be remembered. We will discuss its impact on the conversion efficiency later.

For vanishing bias, the barrier height is given by the diffusion voltage which decreases with increasing optical excitation, as the minority carrier densities increase, and consequently the ratio between majority and minority carrier densities ($n_{10} \cong N_d/p_{10}$ or $(p_{20} \cong N_a)/n_{20}$) is reduced:

$$V_D = V_{Dn} + V_{Dp} = \frac{kT}{2e} \ln \left(\frac{N_d}{p_{10}} \frac{N_a}{n_{20}} \right) \quad (32.6)$$

with p_{10} and n_{20} the minority carrier densities in the space charge-free *n*- or *p*-type bulk of the device, respectively.

32.1.4 Quasi-Fermi Levels and V_{oc}

The quantitative analysis reveals some interesting details. In contrast to the Schottky barrier, the split quasi-Fermi levels are flat (except for very high optical excitation) throughout the junction and the bulk (see Fig. 32.3c and f). Consequently, the spread of quasi-Fermi levels within the device directly yields the open circuit voltage

$$V_{oc} = \frac{1}{e} \{ E_{Fn}(d_1) - E_{Fp}(d_2) \}, \quad (32.7)$$

since the metal Fermi level connects directly to the *majority* quasi-Fermi level,⁴ to which both quasi-Fermi levels collapse at any metal boundary, but is not shown in this figure.

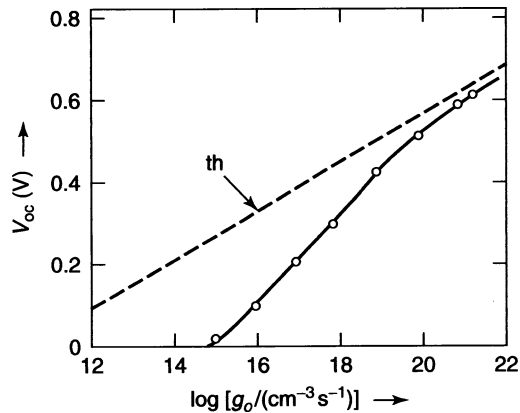
The changes over in a *pn*-junction device from E_{Fn} in the *n*-type to E_{Fp} in the *p*-type part of the junction, while connecting horizontally to the corresponding minority quasi-Fermi levels in the opposite part of the junction can be seen in Fig. 32.3c and f.

The Recombination Overshoot Influence on V_{oc} can be seen from the fact that the minority carrier density in the bulk of this thin device is lower than expected

³The figure shows the tendency to completely eliminate the junction barrier for a flat band connection at sufficiently high optical generation rates. Such flat band connection can be achieved at even lower optical generation rates in devices with lower doping densities and higher minority carrier life times.

⁴In contrast to the jumps of the quasi-Fermi levels at the metal interface of a Schottky barrier, the jumps for the majority quasi-Fermi levels are negligible in the *pn*-junction device when contact is made at each side with an appropriate, neutral (or injecting) contact metal.

Fig. 32.4 Open circuit voltage as a function of the optical generation rate; obtained from the computation shown in Fig. 32.3 (open circles), dashed line given by Eq. (32.8)



from the $g_o \tau_0$ product because of the minority carrier drain into the junction for the enhanced recombination, that becomes visible in Fig. 10.2 from the overshoot of the recombination in the center of the junction. With the reduction of the minority carrier density in the bulk the spread of the quasi-Fermi levels is also reduced from the maximum open circuit voltage that would be attained for vanishing recombination overshoot (here given for a symmetrical junction with $N_a = N_d$):

$$V_{oc,max} = \frac{1}{e} \left[E_g - kT \ln \left(\frac{N_c N_v}{N_a g_o \tau_0} \right) \right] = \frac{kT}{e} \ln \left(\frac{g_o \tau_0}{n_{th}} \right), \quad (32.8)$$

with n_{th} calculated from $n_{th} = n^2 / N_a$. $V_{oc,max}$ is shown as a function of g_o in Fig. 32.4 as the dashed line. In contrast, at low optical excitation the computed spread is negligible and lies below $g_o = 10^{15} \text{ cm}^{-3} \text{ s}^{-1}$; here almost all of the excess minority carriers are used up by recombination in the overshoot region; at higher optical generation rates V_{oc} starts to approach the maximum theoretical level $V_{oc,max}$ but is still lower by about 130 mV at 10^{18} and by 45 mV at $10^{21} \text{ cm}^{-3} \text{ s}^{-1}$. The actual open circuit voltage in thin symmetric devices is given by

$$V_{oc} \simeq \frac{1}{e} \left[E_g - kT \ln \left(\frac{N_c N_v}{N_a n_{10}} \right) \right] = \frac{1}{e} \left[E_g - kT \ln \left(\frac{N_c N_v}{N_d p_{20}} \right) \right] \quad (32.9)$$

when using the computed bulk values for the minority carrier densities (from Fig. 32.3). These are shown as circles in Fig. 32.4 as taken from the $E_{Fn} - E_F$ spread shown in Fig. 32.3f.

It is therefore essential to obtain the actual value of the minority carrier density in the bulk which, as indicated above, is determined by the balance between generation and recombination in the bulk minus the recombination current which transports part of the minority carriers into the junction or to the surfaces (here neglected) for additional recombination.

We will now discuss in the following sections the influence of changes in the recombination, including surface recombination changes in generation and doping of this symmetrical Si *pn*-photo-diode.

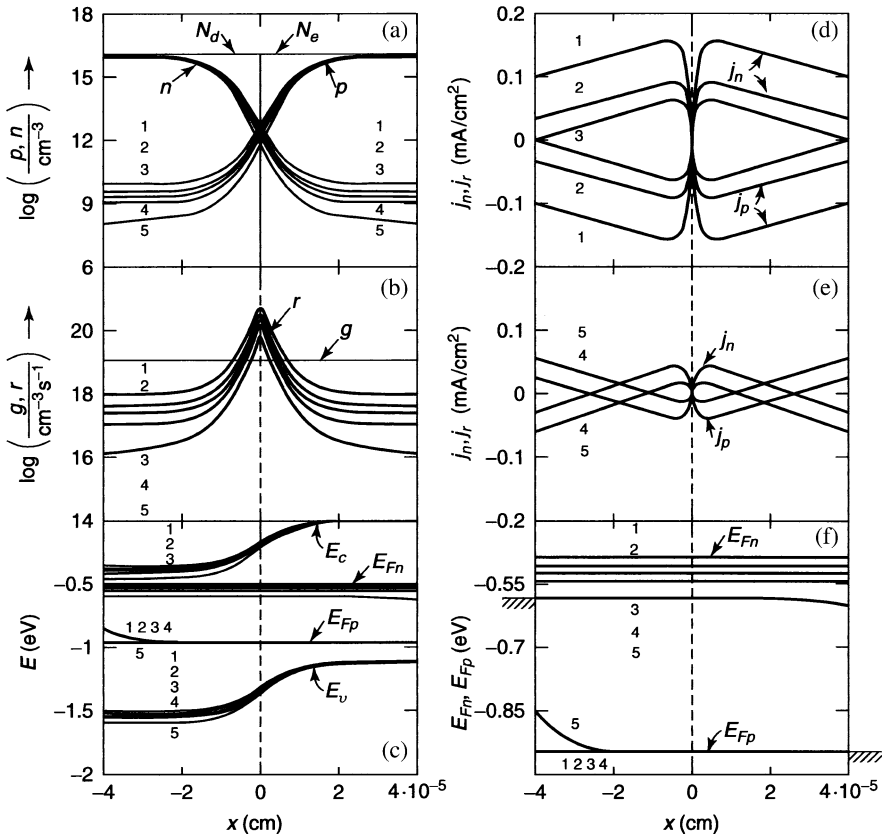


Fig. 32.5 Solution curves for a symmetric thin Si pn -junction device as in Fig. 32.3 for $N_r = 10^{17} \text{ cm}^{-3}$ and the same optical generation rate $g_o = 10^{19} \text{ cm}^{-3} \text{ s}^{-1}$, however, for various surface boundary conditions as indicated by the different currents at the surfaces in (d) for an increased bulk width and (e) for inclusion of surface recombination (see text for more explanation)

32.1.5 Influence of Device Thickness

One can represent a thicker device by simply raising the value of the electron and hole currents at the outer surfaces of the central part of the device. These minority carrier currents are given at these boundaries by the diffusion equation, neglecting any drift contribution. This neglect is justified, for $|x| > 4 \cdot 10^{-5} \text{ cm}$ in the given example, as can be seen from Fig. 32.3d, which indicates negligible fields in this region.

In two examples of Fig. 32.5, the current was raised to 0.03 and 0.1 mA/cm^2 at $x = \pm 4 \cdot 10^{-5} \text{ cm}$ for curves 2 and 3, respectively. The effective device thickness

can be estimated by extrapolating $j_n(x)$ (or $j_p(x)$) linearly⁵ to the x -value where both currents must vanish.

This yields $-d_1 = d_2 = 6 \cdot 10^{-5}$ cm for the second and $1 \cdot 10^{-4}$ cm for the third device.

Concurrently with the increased device thickness, the minority carrier density and quasi-Fermi level spread increases (Fig. 32.5a, c and f), and correspondingly the recombination overshoot heightens (Fig. 32.5b). The effect of a widened bulk region is in some aspects similar to an increase of the optical generation rate. This can be easily understood since more minority carriers are generated in the device that can be collected at the junction. Widening of the bulk also narrows the junction region, decreases the junction field and reduces the barrier height (Fig. 32.5c). This is similar to an increase of the optical excitation at a thinner device.

32.1.6 Influence of Surface Recombination

When surface recombination is introduced, it forces a sign change in these currents near the surfaces as minority carriers are now also drawn toward the surface where they recombine. In shorter devices with strong surface recombination a crossover of $j_n(x)$ and $j_p(x)$ in the bulk can be seen in curves 4 and 5 in Fig. 32.5e. Curve 5 represents the shorter device, or the one with higher surface recombination. As expected, surface recombination has the opposite effect to the widening of the device bulk: it causes a reduction of the minority carrier density and the spread of quasi-Fermi levels decreases, i.e., it causes a decrease of the open circuit voltage V_{oc} . This is most dramatically seen in curve 5 of Fig. 32.5f.

Surface recombination (when within a few diffusion lengths) also widens the junction and increases the barrier height (Fig. 32.5c).

The quasi-Fermi levels remain essentially horizontal in spite of substantial changes in bulk width or surface recombination (except for curve set 5 for the minority carrier quasi-Fermi level). Their spread in the horizontal part, except for curves 5, determines again the open circuit voltage (again we have here omitted the collapse of both quasi-Fermi levels to the majority quasi-Fermi level at each of the device to metal interfaces).

32.1.7 Influence of Recombination Center Density

In order to separate the surface influence from the important junction region, we increase the thickness of both, the p -type bulk region to more than $3L_n$ and an n -type bulk region to more than $3L_p$. We also continue to supply families of curves

⁵This no longer holds when d_1 or d_2 become comparable to L_p and L_n .

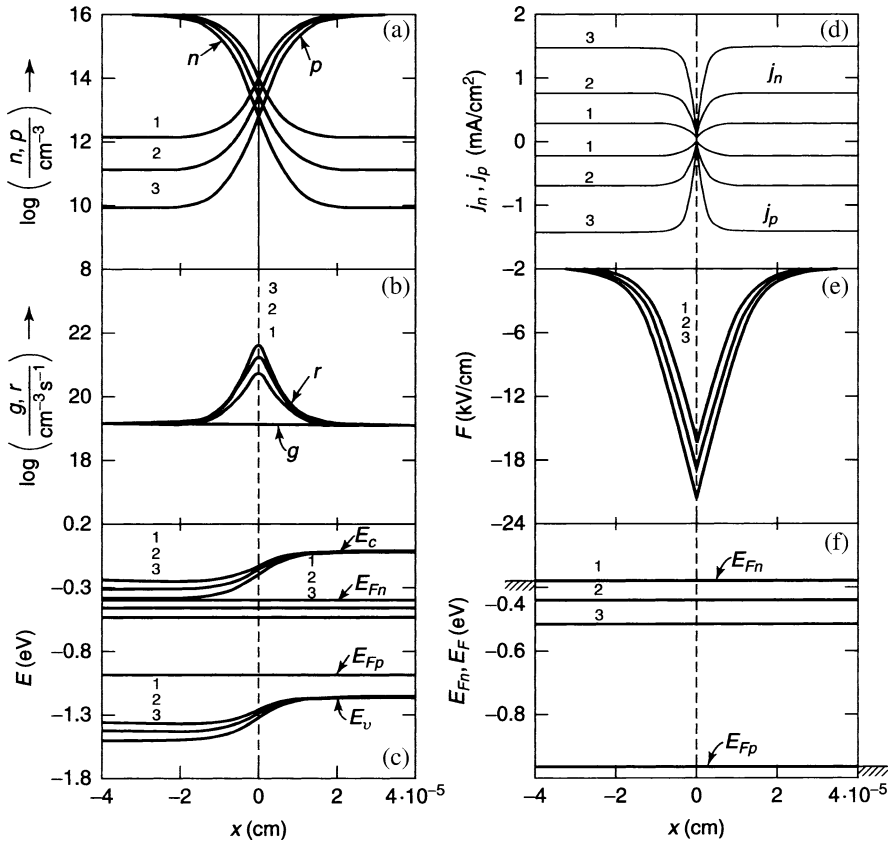


Fig. 32.6 Solution curves for a symmetric long Si pn -junction device computed for $g_o = 10^{19} \text{ cm}^{-3} \text{ s}^{-1}$ and with all other parameters as in Fig. 32.3. The recombination center density is the family parameter: $N_r = 10^{16}, 10^{17}$, and 10^{18} cm^{-3} for curves 1–3, respectively. The subfigures are ordered in the same fashion as in the previous figures

to show the essentially parallel shift and symmetry that is typical for symmetric junctions. The current distribution shows a barely visible slope in the bulk parts of the device, depicted in Figs. 32.6, 32.7 and 32.8; it has only the overshoot visible while the compensating region with $r(x) < g_o$ is located further in the bulk and is not displayed here in the shorter segment shown in the figures.

In Fig. 32.6 the influence of the recombination center density is depicted. With increasing $N_r = 10^{16}, 10^{17}$, and 10^{18} cm^{-3} for curves 1–3, respectively, the minority carrier density and the spread of quasi-Fermi levels decrease (Fig. 32.6a, c and f) causing a corresponding decrease in V_{oc} . One also observes an increase in barrier width, field and diffusion potential with increasing N_r .

As an important result, one notices that the open circuit voltage now approaches closely the maximum theoretical value with decreasing recombination center density (compare Fig. 32.6f with the dashed line in Fig. 32.9).

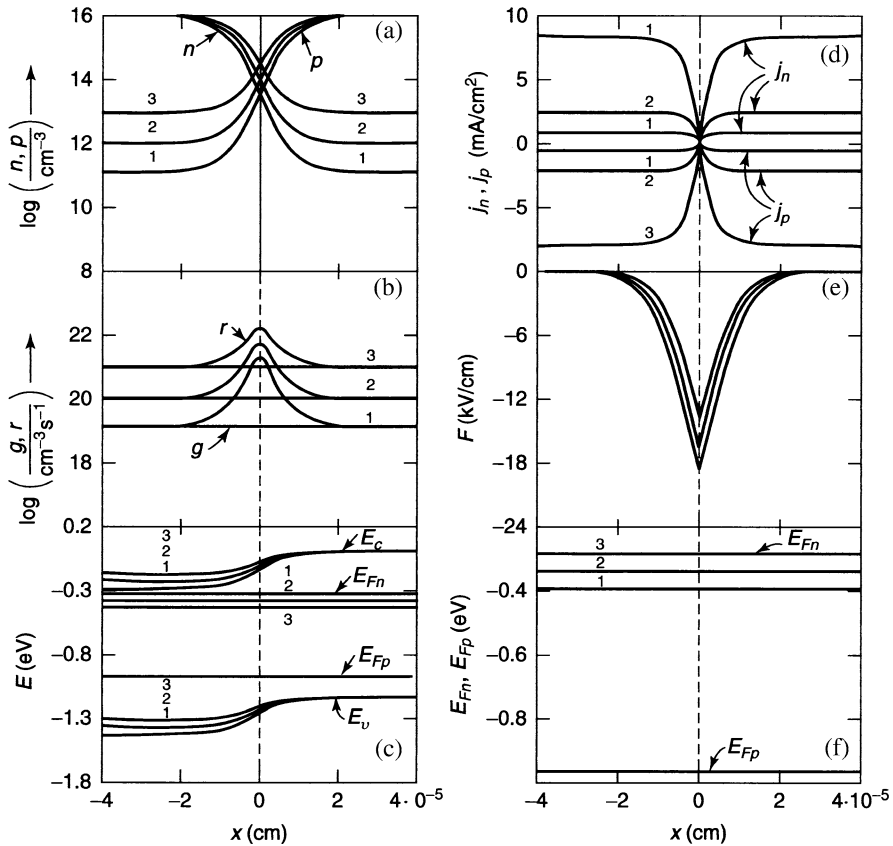


Fig. 32.7 Solution curves for a symmetric long Si pn -junction device computed for $N_r = 10^{17} \text{ cm}^{-3}$ and all other parameters as in the entire set of figures

32.1.8 Influence of the Generation Rate

The dependence on the optical generation rate on a device with thick bulk regions is shown in Fig. 32.7. This figure presents the increase in minority carrier density and open circuit voltage, again closely matching the theoretical maximum values. It also shows the decrease in diffusion potential and field with increasing generation rate $g_o = 10^{19}$, 10^{20} , and $10^{21} \text{ cm}^{-3} \text{ s}^{-1}$ for curves 3–1, respectively. Figure 32.7b shows that the relative overshoot (r_{max}/g_o) decreases with increasing optical generation rate g_o . The maximum gr-current (Fig. 32.7d) increases in the bulk near the junction, however, sub-linearly with g_o . We have repeated the dependence on the optical generation rate from the first figure with a much larger family of curves in order to facilitate the comparison with the somewhat similar influences of the parameters shown in the entire set of figures, however, leaving to the observer to understand the distinct differences.

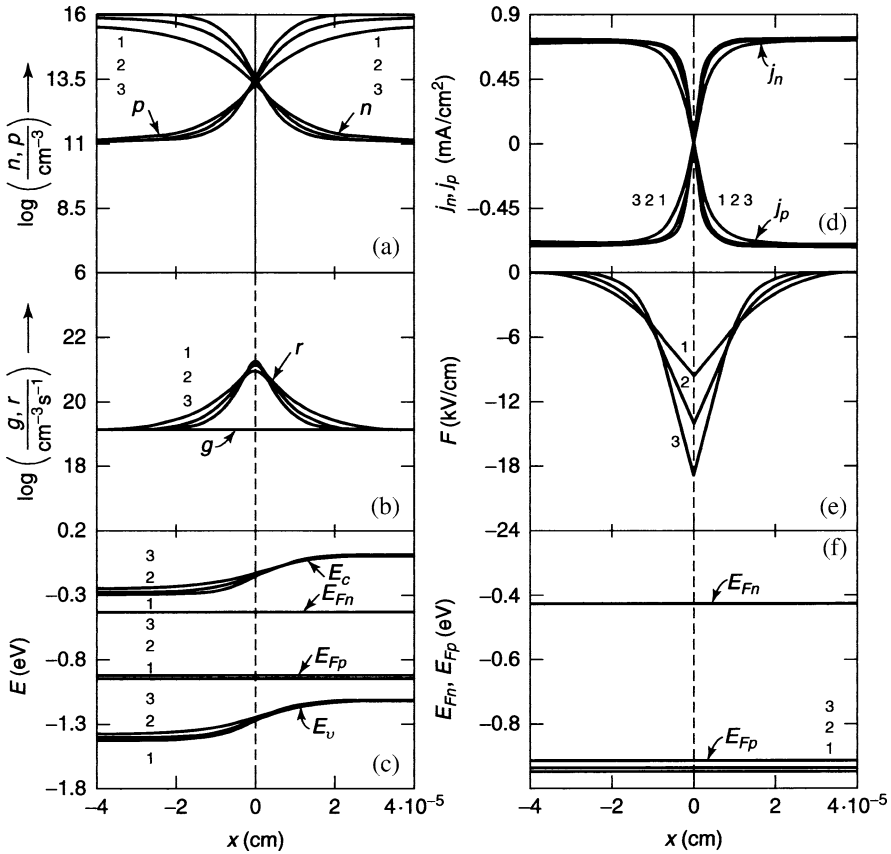


Fig. 32.8 Solution curves for a symmetric thick Si pn -junction device, computed as in Fig. 32.3 for $g_o = 10^{19} \text{ cm}^{-3} \text{ s}^{-1}$ and $N_r = 10^{17} \text{ cm}^{-3}$. Now we have changed the doping densities as family parameter: $N_a = N_d = 3 \cdot 10^{15}$, $6 \cdot 10^{15}$, and 10^{16} cm^{-3} for curves 3–1, respectively. And again with the same order of the subfigures

For more on high generation rate (solar concentration) of Si solar cells see e.g., Gray et al. (1982) and a short review by Schultz (1982).

32.1.9 Influence of the Doping Density

We will now discuss the influence of the doping density first for the symmetrical junction, in which the doping density is changed by equal amounts in both sides of the junction. Figure 32.8 shows the expected changes in majority carrier densities and majority quasi-Fermi level. The junction widens with decreasing doping densities: $N_a = N_d = 10^{16}$, $6 \cdot 10^{15}$, and $3 \cdot 10^{15} \text{ cm}^{-3}$ for curves 1–3, respectively in accord with an increased Debye length. This widening of the junction is also observed

in $r(x)$, $j_n(x)$, and $j_p(x)$ (Fig. 32.8b and d). A small decrease in the overshoot of $r(x)$ with decreasing doping follows from a decrease in the crossover densities of n and p shown in Fig. 32.8a.

The entire change is restricted to a shift of the majority quasi-Fermi level⁶ while the minority quasi-Fermi level is not affected. Observe that the open circuit voltage is influenced by the doping level while all other parameters that have a more pronounced influence on V_{oc} are kept constant.

For more on transport equations in heavily doped devices see e.g. Lundstrom et al. (1981).

32.1.10 Parameter Dependence of V_{oc} for Insufficient Minority Carrier Supply

We will now specifically concentrate our discussion on the influence of certain parameters on the open circuit voltage. this influence shows a significant deviation from the simple diode model that was discussed in the previous chapter and can be deduced from the supply of minority carriers to the junction. When the supply of minority carriers is insufficient to compensate for the junction recombination in a thin device, or in a device with much increased recombination, the open circuit voltage is reduced, often significantly below the theoretical maximum value.

Figure 32.9 shows a summary of these changes in open circuit voltage with the device width or with surface recombination indicated by the reduced current at d_1 and d_2 , as shown in Fig. 32.5d and e, or as a function of the *density of recombination centers*, as a function of *doping density* with $N_a = N_d$, and as a function of the *optical generation rate* shown in Figs. 32.9a–c, respectively. Generation and recombination rates have a larger than kT proportionality in the semilogarithmic plot; the proportionality factor can be equated to the diode ideality factor A :

$$V_{oc} = \frac{1}{e} \left\{ E_g - AkT \ln \left(\frac{N_c N_v}{N_a g_o \tau_{n0}} \right) \right\}. \quad (32.10)$$

The relation (32.10) can be obtained from a simple diode equation shifted by the saturation current, using, however, the diode quality factor.

This results in $A \cong 2$ in this example for the variation of donor densities with N_r , in $A \cong 1.5$ for the variation with g_o , and in $A \cong 1$ for the variation with $N_a = N_d$, as shown in Figs. 32.9a, c, and b, respectively.

⁶The selection of E_{Fp} here as the shifted level is due to the chosen boundary condition of keeping $E_c(x = d_2) = 0$.

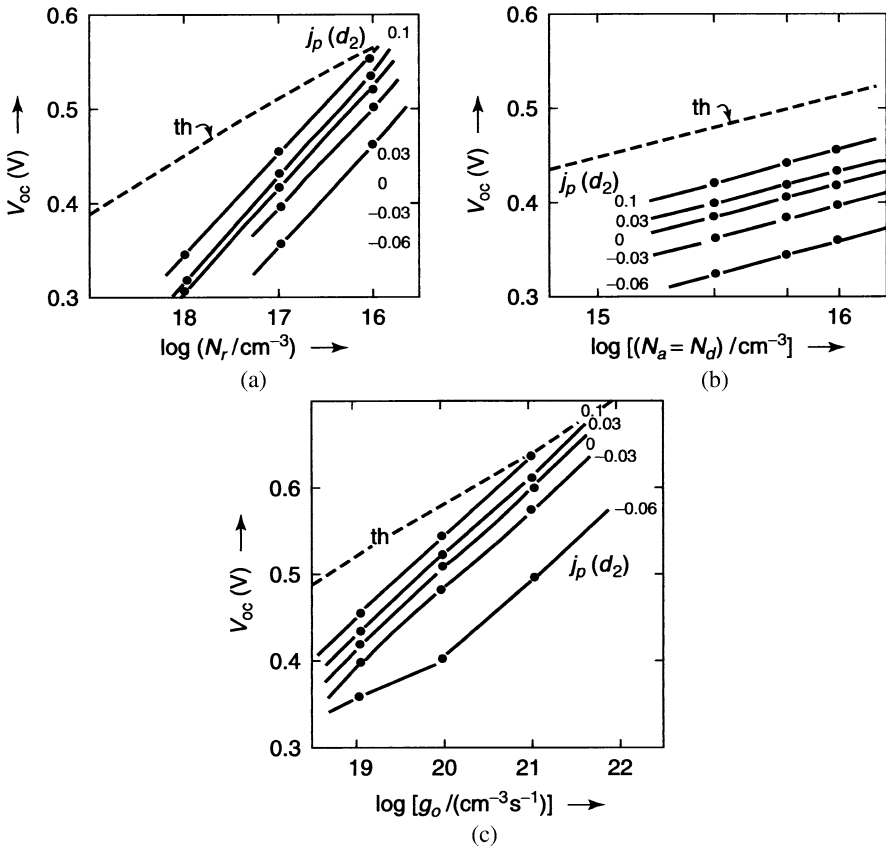


Fig. 32.9 Open circuit voltage as function of N_r , $N_a = N_d$, and g_o in subfigures (a), (b), and (c), respectively. Family parameter is the hole current at $x = d_1$ and $x = d_2$ in mA/cm^2 , representing, with increasing current, a thicker device, or, with increased negative currents, a device with a more effective surface recombination. The *dashed line* represents the maximum theoretical V_{oc} according to Eq. (32.8)

It is important to reflect that the deviation from $A = 1$ resides in the junction, and is caused by a more or less active recombination overshoot.

32.1.11 Influence of the Energy of the Recombination Center

We finally have to add a detail to the recombination traffic that can be influenced by changing the energy E_r of the recombination center, thereby changing:

$$n_i^* = 2n_i \cosh\left(\frac{E_i - E_r}{kT}\right) \quad (32.11)$$

[see Eq. (26.33)].

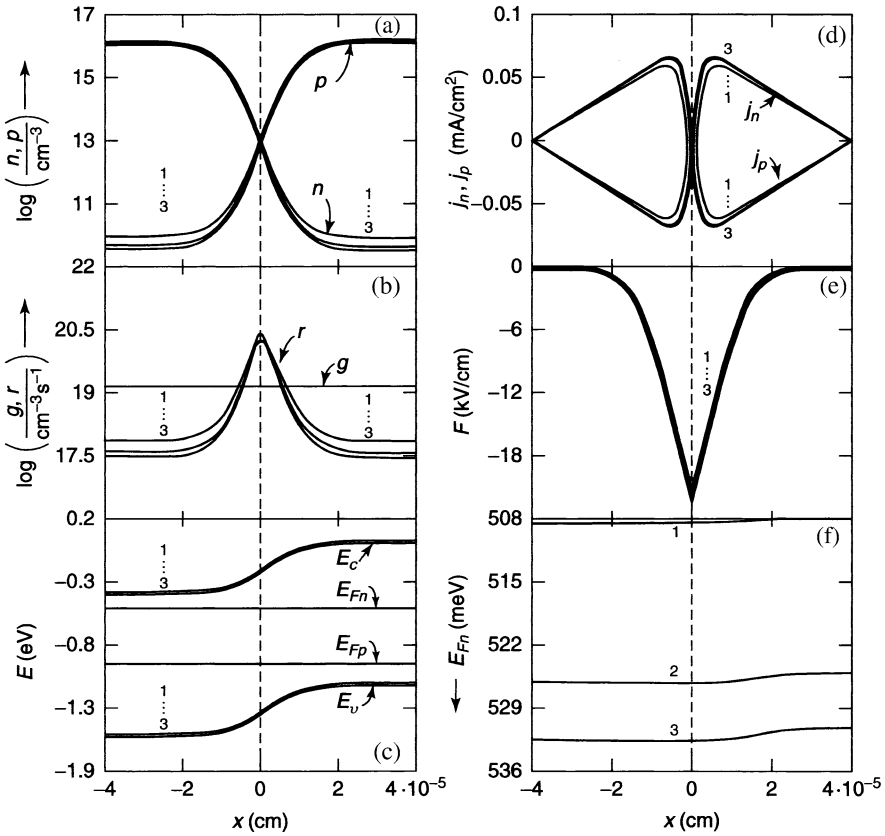


Fig. 32.10 Solution curves for a symmetric thin Si *pn*-junction as in Fig. 32.3 with $N_r = 10^{17} \text{ cm}^{-3}$; the family parameter now is the energy of the recombination center: $|E_i - E_r| = 0.25, 0.2$, and 0.15 eV for curves 1–3, respectively. Again same arrangement of the panels for ease of comparison with the preceding figures

Such an influence is negligible as long as the recombination center resides close to the center of the band gap ($E_r \cong E_i$). When, in the given example, the recombination center lies more than 0.1 eV from the center of the gap, the recombination⁷ and therefore the overshoot is reduced (Fig. 32.10), consequently reducing the gr-current and improving the open circuit voltage in devices with insufficient supply of minority carriers (Fig. 32.10f).

⁷The reduction of the recombination of a center lying at a greater distance from the center of the gap is due to the more trap-like behavior by partial carrier emission into the nearest band rather than recombination.

32.2 Thin Asymmetric Si Diodes with Abrupt Junction

We now enter a more realistic description of devices that are mostly asymmetric. Again we will start with a simple example and point out the similarities but now with a shift in the solution curves. After we identified the recombination overshoot in the junction as a major factor for degrading the open circuit voltage of a symmetrical photo diode, we now extend this analysis to an asymmetrical device and systematically change one parameter at a time between the *n*- and *p*-side of the diode.

32.2.1 Recombination Through Charged Recombination Centers

The first asymmetry in the device can be introduced by simply assuming a different recombination, while the doping is left symmetrical. The recombination through centers is sensitive to their charge character. We have previously assumed that the center has the same capture cross section for electrons or holes with $s_n \cong s_p = 10^{-16} \text{ cm}^2$, and with $c \cong c_{cr} \cong c_{rv} = s_n v_n = s_p v_p = 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. We now lift this restriction and permit $c_{cr} \neq c_{rv}$ with [see Eq. (26.30)].

$$r = \frac{c_{cr} c_{rv} N_r n p}{c_{cr} (n + n_i^+) + c_{rv} (p + n_i^-)} = \frac{np}{\tau_{0p} (n + n_i^+) + \tau_{0n} (p + n_i^-)}. \quad (32.12)$$

We assume that the recombination center is neutral when empty, with a recombination cross section of $s_n \approx 10^{-16} \text{ cm}^2$ for electrons. After an electron is captured, the center becomes negatively charged, and a hole consequently experiences a much larger cross section, say, of $s_p \approx 10^{-14} \text{ cm}^2$. A second electron, however, experiences a repulsive center with a substantially reduced cross section, typically of $s'_n \approx 10^{-18} \text{ cm}^2$ or less. Such changing of cross sections can be taken into consideration by changing the capture coefficient, e.g., from 10^{-9} to 10^{-11} or $10^{-7} \text{ cm}^3 \text{ s}^{-1}$ for repulsive or attractive centers, respectively.

In Fig. 32.11 a family of solution curves is shown for a variety of recombination centers with different capture coefficients for holes and electrons, as given in Table 32.2.

From a change of the capture coefficients alone, the recombination distribution becomes asymmetric as shown in Fig. 32.11b, while the minority carrier density on *both sides* of the *pn*-junction still changes symmetrically. The overshoot peak is *shifted* from the junction interface into the region with increased minority carrier recombination; correspondingly, the crossover of $j_n(x)$ and $j_p(x)$ is shifted to the shifted position.

The quasi-Fermi-level split decreases (or increases) with increasing (or decreasing) recombination, reducing V_{oc} by

$$\Delta V_{oc} \simeq kT \ln \left(\frac{c_{cr}}{c_{rv}} \right). \quad (32.13)$$

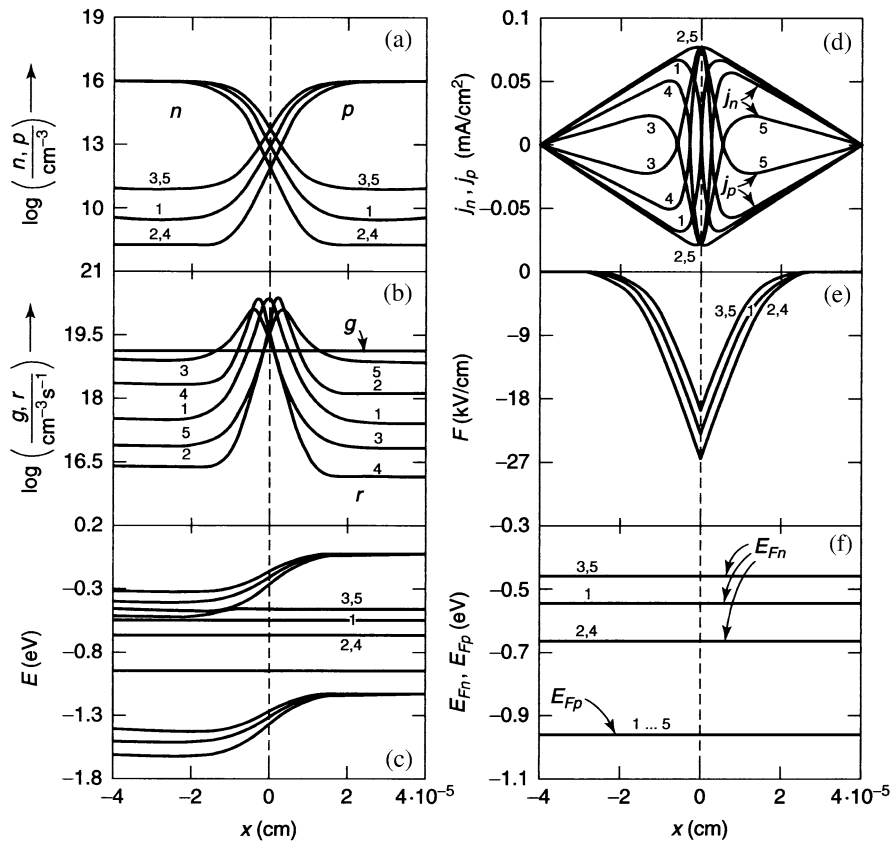


Fig. 32.11 Solution curves computed for a symmetric thin Si *pn*-junction with parameters as in Fig. 32.3, however, for different recombination coefficients for electrons and holes, as listed in Table 32.2 for curves 1–5

Table 32.2 Capture coefficients used in Fig. 32.11

	Curve No.					Dimensions
	1	2	3	4	5	
c_{cr}	10^{-9}	10^{-7}	10^{-11}	10^{-9}	10^{-9}	$\text{cm}^3 \text{ s}^{-1}$
c_{rv}	10^{-9}	10^{-9}	10^{-9}	10^{-7}	10^{-11}	$\text{cm}^3 \text{ s}^{-1}$

However, when the recombination rate is reduced by a factor of 100 in half of the device, the benefit to V_{oc} is smaller than that given by Eq. (32.13), as seen in Fig. 32.11f with a $\Delta V_{oc} = 85 \text{ mV}$ for curve set 3 and 5 vs. the deterioration by 120 mV for the curve set 2 and 4. This enhanced nonlinear behavior becomes significant whenever r approaches g_o in the left or right side of the bulk, as shown in Fig. 32.11b for curve set 3 and 5.

32.2.2 Inhomogeneous Optical Excitation

A more severe change is the introduction of an inhomogeneous optical excitation in an otherwise still homogeneous device. The nonlinearity of $U(x)$ with changing parameters that determine the generation or recombination are modifying factors for the nonlinearity of the minority carrier density with g_o . The involved spatial (and bias) dependence makes a general analytical approximation complex; this is one of the reasons why an estimation of the actual diode A -factor is difficult.⁸ We will return to such analysis in a later section.

In all practical cases, the optical generation is inhomogeneous. It is stronger near the entrance surface of light and weaker near its exit surface: the more light is absorbed at the beginning of its path, the stronger is the decrease of $g_o(x)$ with increasing x . Rather than taking a continuous, say exponential decay of $g(x)$, we introduce here a *stepwise* generation function that results in slope-breaks of the currents $j_n(x)$ and $j_p(x)$, and thereby provides some additional clues for an analysis.

Curve 2 of Fig. 32.12b *simulates an exponential decay* of $g_o(x)$. As more drastic changes we assume a high excitation only in a thin near-surface region, which is followed by a constant and much lower excitation rate in the remainder of the device, thus simulating a direct band gap solar cell exposed to sunlight (curves 3–5) in Fig. 32.12b; also see Böer (1981a). All generation distributions are chosen so that the integrated generation rate is the same as the average homogeneous generation rate of $7.5 \cdot 10^{20} \text{ cm}^{-3} \text{ s}^{-1}$, that is shown as curve 1.

The results of the different step like changes of the generation rate are seen in the abrupt changes in the slopes of $j_n(x)$ and $j_p(x)$ at the left side of panel d of Fig. 32.12 with highly asymmetrical current distributions.

In contrast, the recombination distribution is not influenced (also contained in panel b as bell-shaped curve); the overshoot remains unchanged. The carrier distribution consequently stays *unchanged*.

32.2.3 Optical Excitation Only in a Thin Front Layer of the Device

It should be emphasized that even in the extreme case shown as curve 5 of Fig. 32.12, where all optical excitation occurs in the front half of the n -type region while the rest of the device is kept in the dark. The carrier and field distribution does not recognize such inhomogeneous optical excitation and remains totally symmetric. Figure 32.13a shows the generation and recombination distributions for this example on an extended scale. It indicates the near-perfect symmetry of the recombination rate distribution in spite of the extreme asymmetry of the optical excitation near the front surface, plus a minuscule thermal excitation in the bulk.

⁸Only in a very general approximation one observes the tendency of $A \rightarrow 2$ with excessive recombination in the space charge region, and of $A \rightarrow 1$ with dominant recombination in the space charge-free bulk.

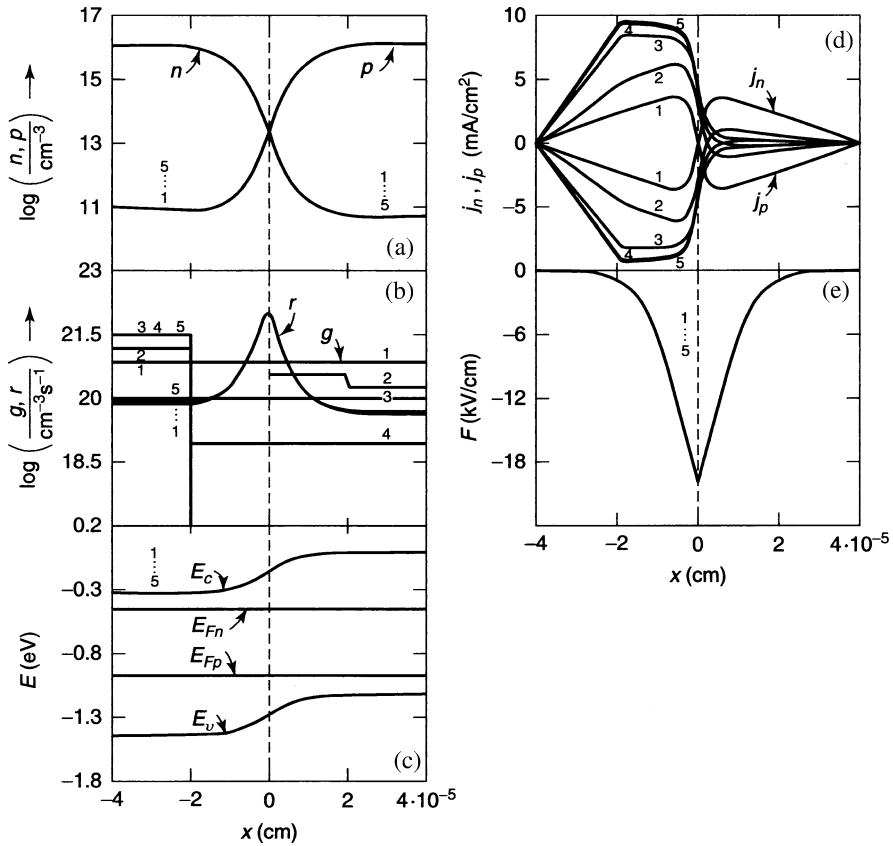


Fig. 32.12 Solution curves for a symmetric thin Si pn -junction as in Fig. 32.3, however, for inhomogeneous optical generation rates shown in subfigure (b), which are normalized to the same average generation rate of $g_o = 7.5 \cdot 10^{-3} \text{ s}^{-1}$ as shown in curve 1

This is an excellent example to demonstrate the dominant effect of the gr-current to communicate between the two parts of the pn -junction, thereby effectively equalizing the carrier distribution on both sides of a symmetrical junction, as long as the device thickness is smaller than the diffusion length. The symmetry will only be disturbed when the device thickness becomes comparable to the diffusion length (see Sect. 32.3.1).

With the carrier distribution unchanged, also the spread of the quasi-Fermi levels remain the same independent of the generation rate distribution. The spread is determined only by the total averaged generation rate. One can now revise the expression for the open circuit voltage to introduce averaged values of generation and recombination:

$$V_{\text{oc}, \text{max}} = \frac{1}{e} \left\{ E_g - kT \ln \frac{N_c N_v}{N_{\text{eff}} \bar{g}_o \bar{\tau}} \right\} \quad (32.14)$$

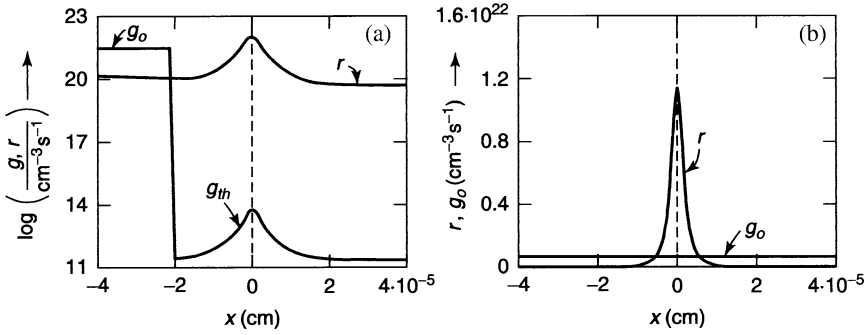


Fig. 32.13 Generation and recombination rate distributions as in Fig. 32.12 (a) for optical excitation in the front layer only; (b) for homogeneous illumination, redrawn in linear scale (same conditions as for curves 5 and 1 in Fig. 32.12, respectively)

with

$$\bar{g}_o = \frac{1}{d_2 - d_1} \int_{d_1}^{d_2} g_o(x) dx \quad (32.15)$$

and

$$\bar{\tau}^{-1} = \frac{1}{d_1} \int_{d_1}^0 \frac{1}{\tau_p} dx + \frac{1}{d_2} \int_0^{d_2} \frac{1}{\tau_n} dx \quad (32.16)$$

and with an effective donor or acceptor density

$$N_{\text{eff}} = (N_a, N_d)_{\text{min}}. \quad (32.17)$$

In the example for homogeneous excitation, $g_o(x)$ and $r(x)$ are replotted in a linear scale in Fig. 32.13b. The recombination rate at the maximum is higher by a factor of 16 than the optical generation rate, corresponding to an effective carrier lifetime⁹ of $1/8$ of the bulk lifetime. Consequently, one estimates from Eqs. (32.15) and (32.16) product of $\approx 10^{11} \text{ cm}^{-3}$, which is in reasonable agreement with the computed minority carrier density in each of the bulk regions shown in Fig. 32.12a. The open circuit voltage estimated from Eq. (32.14) is $V_{\text{oc}} = 498 \text{ mV}$ and is in agreement with the computed value of 497 mV (Fig. 32.12f and g). This value is reduced by 19 mV from the value of 516 mV estimated from the simple V_{oc} equation [Eq. (32.8)].

32.2.4 Thin Asymmetric Junction Design

Most pn -junctions are substantially asymmetric. Such asymmetry can be caused by

⁹Relating to a symmetric carrier flow from both sides of the junction.

- asymmetric thickness ($d_1 \neq d_2$),
- asymmetric doping densities ($N_a \neq N_d$),
- asymmetric recombination center densities ($N_{r1} \neq N_{r2}$),
- asymmetric types of recombination centers (influencing c_{ik}), and
- different electrodes (influencing ψ_{MS}).

Some of the resulting effects can be estimated from the information supplied in the previous section. Quantitative answers, however, can only be obtained from actual computation, since the overshoot is determined in a nonlinear fashion from the various contributions.

32.2.5 Asymmetric Bulk Thickness

When the thickness of a *thin* device is increased, more material is available to absorb light, hence an increase of the number of available minority carriers will result. When increasing the thickness of only one side (here d_2 by a factor of 1.75), the resulting solution curves (Fig. 32.14a) show a symmetric increase of *both* minority carrier densities on either side of the junction. Even though the number of absorbed photons increases by a factor of 1.375 (as the increase in total device thickness) the computed minority carrier densities increase by a slightly lesser factor of ~ 1.3 (Fig. 32.14a). This is caused by an increased recombination, due to the increased recombination rate plus the increased recombination overshoot (Fig. 32.14b).

The quasi-Fermi level for electrons is raised throughout the entire device by 7.5 meV according to the increase of the minority carriers; the open circuit voltage is increased by the same amount.

32.2.6 Asymmetric Recombination

When *surface recombination* is introduced at *one* side of this thin device (here at the right side by forming a crossover of j_n and j_p , as shown in Fig. 32.15) the minority carrier densities on both sides of the junction decrease *symmetrically* (Fig. 32.15a).

Accordingly also the bulk recombination rate on both sides and the recombination overshoot decrease. Consequently the electron quasi-Fermi level decreases within the entire device by 10 meV, and the open circuit voltage decreases by the same amount (subfigures e and f). The junction field increases slightly (by 500 V/cm) since the junction widens by a small amount.

When asymmetric recombination is caused by a stepwise increase of the density of recombination centers from 10^{17} cm^{-3} in the *n*-type region to 10^{18} cm^{-3} in the *p*-type region a super linear decrease¹⁰ by a factor of 17 of the minority carrier density in both sides of the junction (again a symmetrical decrease) is observed (Fig. 32.16).

¹⁰Even though the average increase of the recombination center density is only by a factor of 5.5.

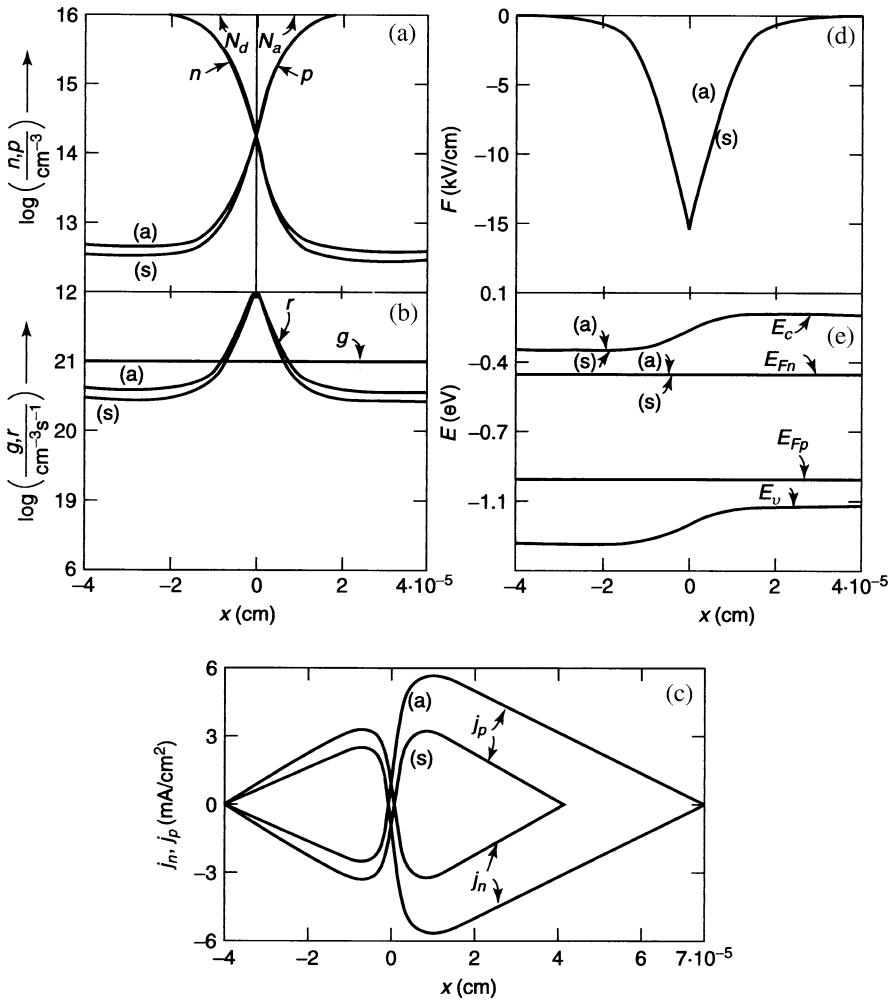


Fig. 32.14 Solution curves for a symmetric (s) (with $d_1 = d_2$) and an asymmetric (a) (with $d_2 \cong 1.75d_1$) thin Si pn -junction device as indicated by the current distribution in (c). The new surface is at the position where $j_n(d_2) = j_p(d_2) = 0$ with $d_2 \cong 7 \cdot 10^{-5}$ cm (this change in abscissa scale is not shown in the other panels of this figure)

The open circuit voltage decreases by 68 mV. This indicates the difficulty of using simple approximations to estimate V_{oc} with sufficient accuracy in such a device.

32.2.7 Asymmetric Generation

When the generation rate is reduced by a factor of 10 in the p -type region (but the total generation rate is not normalized to the same value as assumed before), the

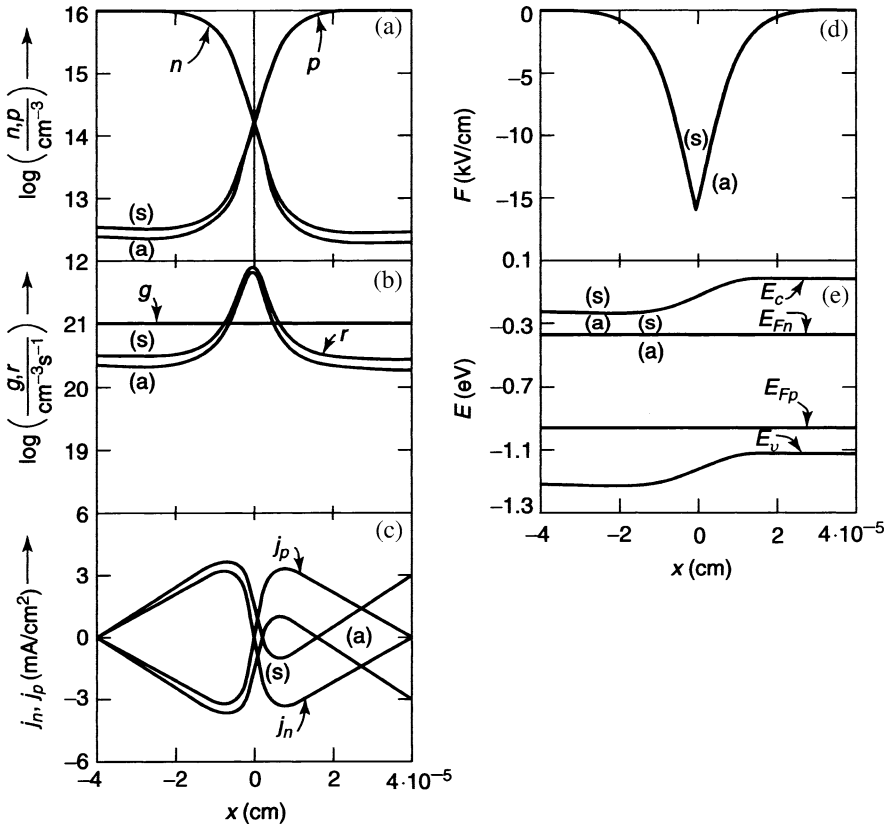


Fig. 32.15 Solution curves as in Fig. 32.14 with asymmetric solution (a) caused by a strong surface recombination current at the right surface (panel (e)) and (s) symmetric solution for comparison.

minority carrier density decreases in both regions by a factor of 0.4, i.e., again super linearly compared to the expected decrease of 0.55 for an averaged lowering of the optical generation.

The recombination rate distribution again decreases symmetrically by the same ratio (Fig. 32.17b).¹¹ The junction field is slightly increased with asymmetric decreased generation due to the widening of the junction (Fig. 32.17d). The open circuit voltage is reduced by 23 mV. When compared to a decrease of 15 mV, expected for the reduction of absorbed photons in the entire device, the increased reduction can be interpreted by an A-factor of 1.7, with $\Delta V_{oc} = (AkT/e) \ln(\bar{g}/g_o)$.

¹¹This information is complementary to the one given in Sect. 32.2.2; indicating that the solution curves for n and p and the potentials are independent of the distribution of $g_o(x)$ in thin devices, provided that the total number of absorbed photons remains the same.

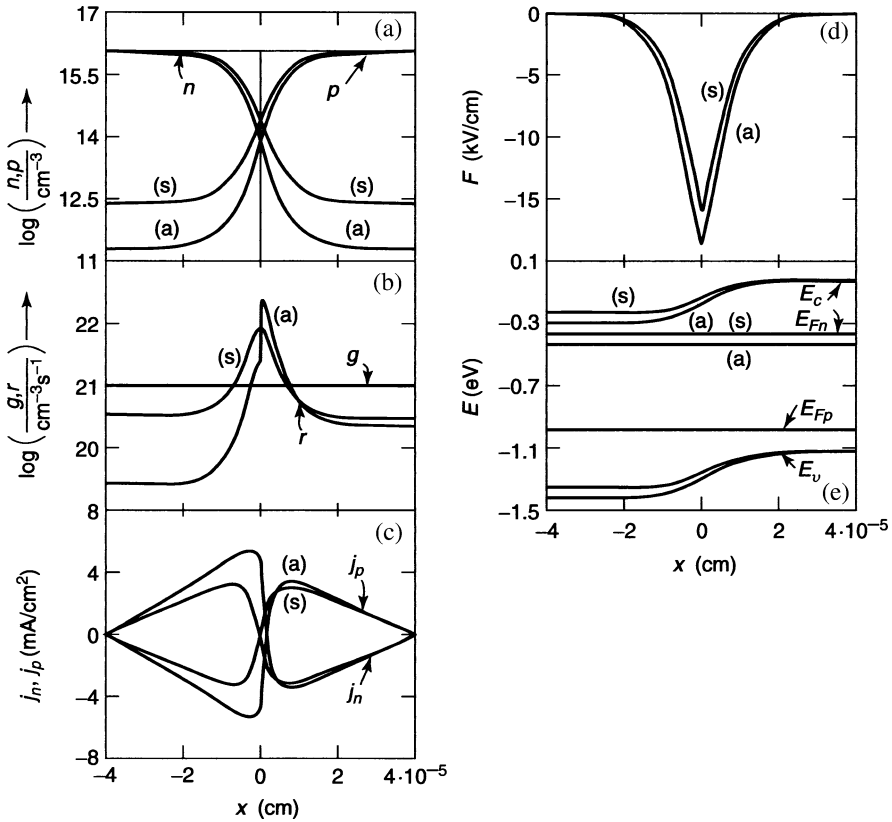


Fig. 32.16 Solution curves as in Fig. 32.14, with asymmetric solution (a) created by a jump in the density of recombination centers from 10^{17} cm^{-3} in the n -type material to 10^{18} cm^{-3} in the p -type material by a factor of 10 at $x = 0$. (s) is the symmetric solution, shown for comparison

32.2.8 Asymmetric Doping

Most junctions are asymmetrically doped with the thinner front side having a substantially higher dopant density. In Fig. 32.18 an example is shown in which the donor density in the left side is increased by a factor of 100. This asymmetry shifts the peak of the recombination overshoot well into the lower doped right side, again coinciding with the position where $n = p$. Thereby, the generation current from the n -type material continues into the p -type part and increases accordingly, while the generation current from the p -type part is reduced. As a consequence of the increased doping there is a major increase in diffusion voltage by 120 mV. However, the open circuit voltage is increased by only ~ 12 mV. The reason for this change is a combination of two effects: the decrease in the density of minority carriers and the increase in the recombination overshoot that almost compensates (except for 12 meV) the expected spread.

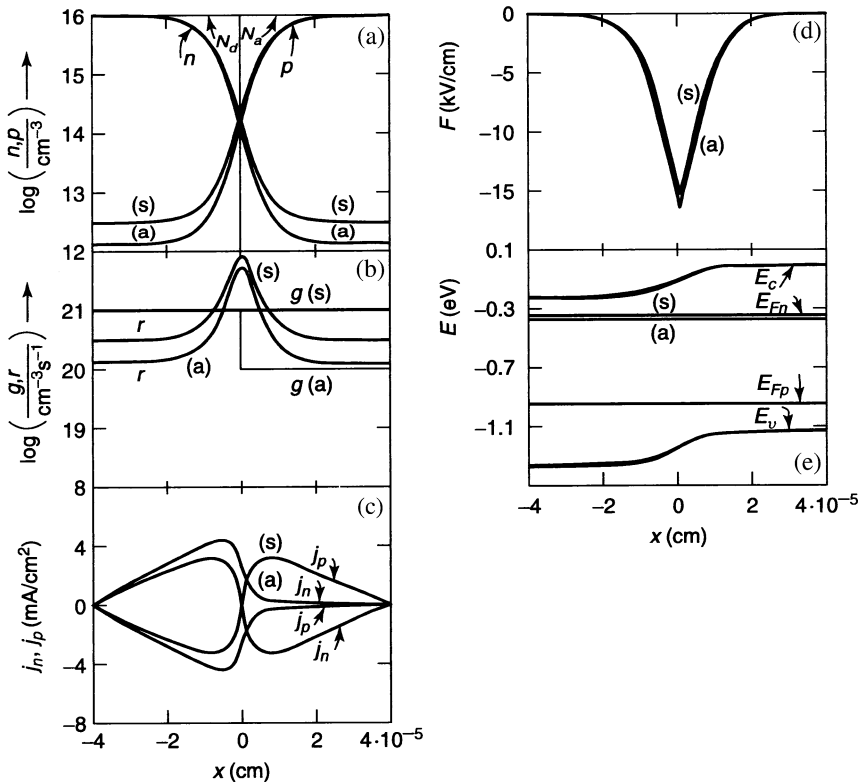


Fig. 32.17 Solution curves as in Fig. 32.14 with asymmetric solution (a) caused by asymmetric generation rates $g_{1,o} = 10^{21}$, $g_{2,o} = 10^{20} \text{ cm}^{-3} \text{ s}^{-1}$. (s) is the symmetric solution, shown for comparison

32.2.9 Thick Asymmetric Devices, Si Solar Cells

We now extend the analysis to an asymmetrically doped device with a thin, heavily doped n -type front layer¹² and a very thick ($d_2 > L_n$) p -type base. A set of solution curves is plotted in Fig. 32.19. As a consequence of the asymmetry we now observe that the cross-over of electron and hole densities shifted away from the junction interface well into the lower doped p -type material, while the peak of the electric field and the change of the space charge remains exactly at the doping interface. We shall emphasize this fact and make sure that we do not misread the position of the pn -junction as the place where $n(x)$ crosses $p(x)$ and j_n crosses j_p force, the electric field peaks at the junction interface (panel d).

¹²The front layer is often referred to as the emitter. We will refrain from doing so, since in solar cells the emission of minority carriers into the junction originates mostly from the much thicker base layer surface. For more see e.g. Lammert and Schwartz (1977), Gray and Schwartz (1984).

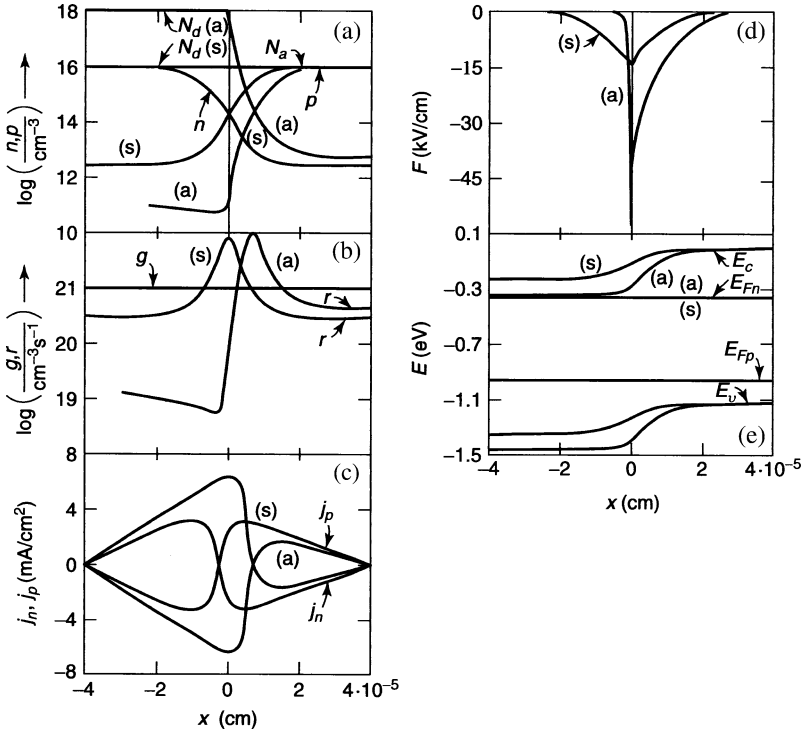


Fig. 32.18 Solution curves as in Fig. 32.14 with asymmetric solution (a) caused by asymmetric doping: $N_d = 10^{16}$ and $N_a = 10^{18} \text{ cm}^{-3}$. (s) is the symmetric solution, shown for comparison

We also shall point out that Fig. 32.19 has a broken abscissa at $2.5 \cdot 10^{-5} \text{ cm}$ (see arrow on top for emphasis) in order to show the behavior in the junction, as well as the bulk and close to the electrodes, which contains several interesting features that will be discussed below.

The jump of the recombination rate at the junction interface is caused by the jump in recombination center densities from $N_r = 10^{17} \text{ cm}^{-3}$ in the heavier doped n -type region to $N_r = 10^{16} \text{ cm}^{-3}$ in the lower doped p -type region. This jump, however, has negligible influence on all other solution curves since $r(x=0) \ll g_o$.

The minority carrier density in the p -type bulk is non monotonic, because of electron diffusion toward the recombination overshoot and of electron out-diffusion for recombination at the outer electrode (Fig. 32.19a). In the bulk the electron density approaches closely its steady state value ($g_o \tau_{n0} = n_{10}$), consequently making the recombination rate here nearly equal to the generation rate and causing near the bulk center a vanishing gr-current (Fig. 32.19c and d).

Observe that closer to the right metal electrode the recombination current changes sign (Fig. 32.19d) and the electron density decreases toward the thermodynamic equilibrium value. The near-bulk recombination rate decreases here below g_o , creating a net generation rate to approach $U = g_o$, and consequently the slope of

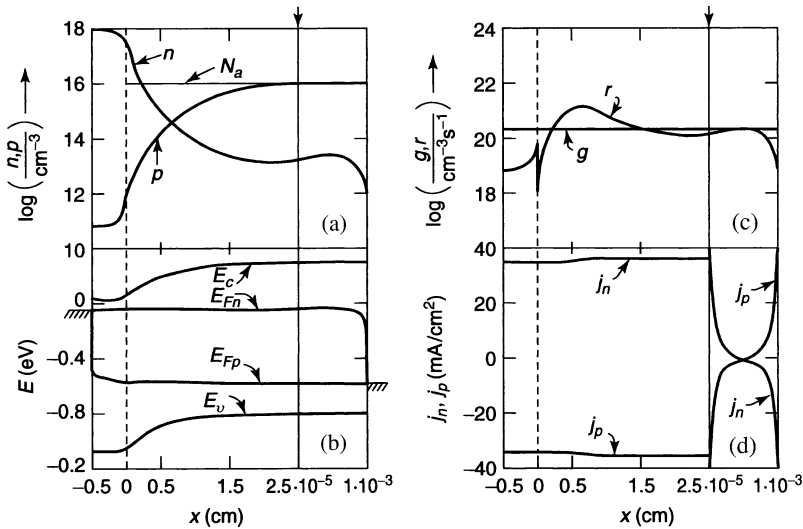


Fig. 32.19 Solution curves of a long asymmetric Si pn -device with complete surface recombination at both electrodes for $g_o = 2 \cdot 10^{20} \text{ cm}^{-3} \text{ s}^{-1}$, $N_{r1} = 10^{17} \text{ cm}^{-3}$, $N_{r2} = 10^{16} \text{ cm}^{-3}$, and $c = 10^{-9} \text{ cm}^{-3} \text{ s}^{-1}$. Observe the broken abscissa in the p -type bulk region (arrow on top of panels (a) and (c))

the recombination currents toward the right electrode rapidly increases to approach the maximum slope $dj_n/dx = -dj_p/dx = eg_o$.

Because of the large width of the p -type bulk, the junction and the right electrode regions are well separated; a large current can flow toward the electrode without substantial reduction of the photo current to the junction.¹³ The recombination current at the right electrode is close to the saturation current and given by:

$$-j_p(d_2) - j_n(d_2) \simeq eg_o L_n \simeq 40 \text{ mA/cm}^2. \quad (32.18)$$

This current is dissipated as

$$j_n(d_2) = e \{ n(d_2) - n_{20}^{th} \} s \simeq en(d_2) v_n^*, \quad (32.19)$$

requiring a density of minority carriers of $n(d_2) \cong 4 \cdot 10^{10} \text{ cm}^{-3}$, which is substantially larger than the thermal equilibrium density

Therefore, one observes a decrease of the minority carrier density from $n_{10} \cong 10^{13} \text{ cm}^{-3}$ to $n(d_2)$ causing a corresponding decrease of the minority quasi-Fermi

¹³This is an artificial condition that is caused by the assumed constant optical generation rate. In actuality $g_o = g_o(x)$ and rapidly decreases from left to right. With $d_2 \gg L_n$, averaging of $g(x)$ can no longer be applied. Therefore most of the gr-current flows toward the junction and much less is collected at the right electrode (the light enters from the left).

level near this surface, with a remaining substantial adjustment of

$$E_{Fn}(d_2) - E_F = kT \ln \left[\frac{n(d_2)}{n_{20}^{th}} \right] \simeq 0.5 \text{ eV}. \quad (32.20)$$

The majority quasi-Fermi level shows only a minute adjustment¹⁴ at $x = d_2$ due to the negligible difference in majority carriers of $\Delta p = 4 \cdot 10^{10} \text{ cm}^{-3}$ that is necessary to maintain the recombination current of $j_p(d_2) = -j_n(d_2)$ compared with the thermal equilibrium value of $p^{th} = 10^{16} \text{ cm}^{-3}$.

At the left electrode the situation is somewhat different. Only a very thin layer of n -type material is available.¹⁵ Here the minority carrier density continues to decrease immediately after passing through the junction toward the thermal equilibrium value.

The slope of $p(x)$ is controlled by the minority carrier current of $\approx 35 \text{ mA/cm}^2$ that is accumulated in the bulk of the p -type material. This current is lower than the saturation current by $\approx 5 \text{ mA/cm}^2$ because of additional recombination in the recombination overshoot region. The recombination at the left electrode results in an adjustment of the minority carrier quasi-Fermi level of $\approx 0.5 \text{ eV}$ that is nearly the same as at the right electrode.

The combined effect of minority carrier leakage to the left electrode and excess recombination because of the recombination over-shoot in the junction reduces the split of the quasi-Fermi level from¹⁶ 0.654 eV to the computed actual split of 0.533 eV shown in Fig. 32.19 panels b and d. The values of the saturation current at the open circuit voltage are close to the one observed in actual in solar cell in full sunlight, even though the model used here is rather crude and needs substantial refinement to describe detail of the experiment.

32.3 Non-vanishing Bias

The general behavior of the solution curves in a pn -junction device with light and non-vanishing bias is qualitatively similar to a non-illuminated diode with respect to the carrier density, space charge, field, and potential distributions. A more careful quantitative analysis, however, reveals typical differences relating to the much increased minority carrier density caused by the optical excitation. In order to discuss the main features, we will first return to a thin symmetrical pn -junction device with homogeneous optical generation.

¹⁴From $E_F - E_{Fp} = kT \ln[(p_{20} + \Delta p)/p_{20}]$, one obtains for this adjustment of the majority quasi-Fermi level approximately 10^{-8} eV .

¹⁵In actuality, the front is covered by a thin grid electrode, rendering this a three-dimensional problem in which most of the minority carriers are generated more than a diffusion length removed from the actual metal.

¹⁶This split is estimated in the lower doped region (see Sect. 32.2.3).

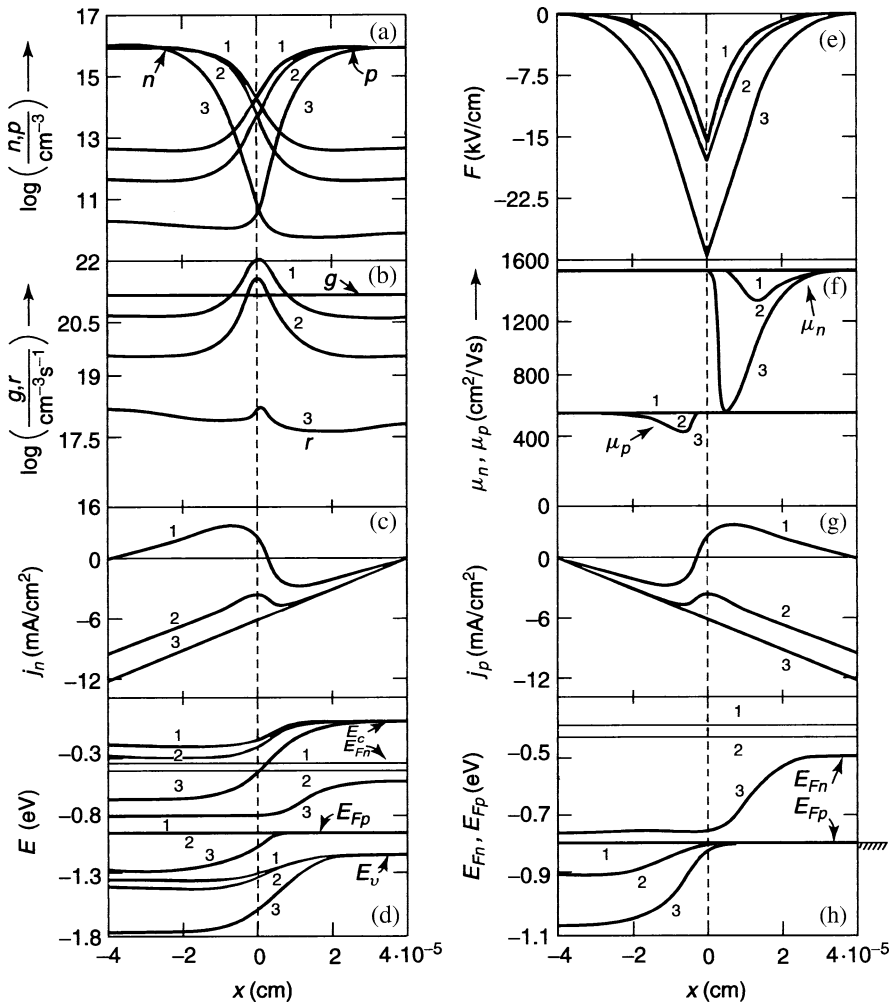


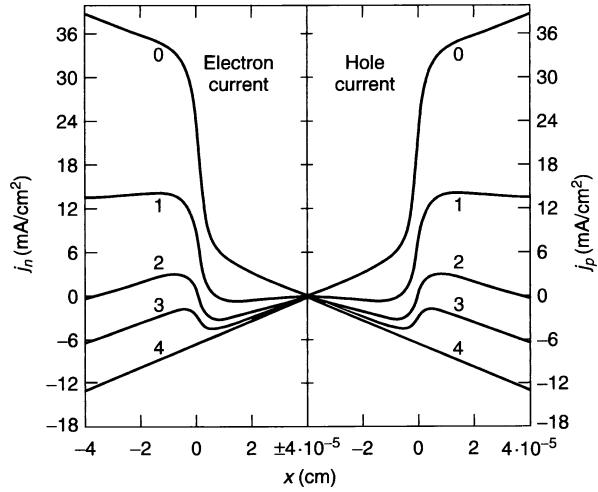
Fig. 32.20 Solution curves computed for a symmetric thin Si pn -junction device with neutral surfaces and $g_o = 10^{21} \text{ cm}^{-3} \text{ s}^{-1}$, $N_r = 10^{17} \text{ cm}^{-3}$. Total current is the family parameter: $j = 14$, 0 , and -12 mA/cm^2 for curves 1–3, respectively. The panel arrangement is the same as in the previous relevant sections to permit easy comparison

32.3.1 Thin Symmetrical pn -Junction Device with Bias

Figure 32.20 shows the set of solution curves for n , p , F , g , r , j_n , j_p , μ_n , μ_p , E_c , E_v , E_{Fn} , and E_{Fp} for the same thin device discussed in Sect. 32.1.1. We have again assumed two neutral surfaces (no surface recombination) and a homogeneous generation rate of $g_o = 10^{21} \text{ cm}^{-3} \text{ s}^{-1}$.

Space charge, field, and electron potential distributions are determined by majority carriers only and have the same qualitative shape as without light. The cor-

Fig. 32.21 Electron and hole current distributions computed as in Fig. 32.20; total current as family parameter (additional curve 0 obtained for 38 mA/cm)



responding currents, however, at which the junction is pulled open are increased by eight orders of magnitude from the dark current of $\sim 10^{-10}$ A/cm² to the photo generated current that is in the 10^{-2} A/cm² range.

In Fig. 32.20b, the optical generation rate and a family of recombination rate distributions are shown with the total current as family parameter. With increased reverse bias, the recombination rate $r(x)$ is pulled down, yielding a larger net generation rate ($U = g_o - r$), until the maximum of $r(x)$ decreases well below g_o , i.e., rendering $U(x) \cong g_o$ and result in reverse current saturation. This is best seen in the $j_n(x)$ or $j_p(x)$ distributions that are separated in different panels to avoid confusion (Figs. 32.20c and g) which, for saturation, straighten out (curves 6), pulling all minority carriers across the junction (current saturation).

The minority carrier density decreases below $n_{10,o} = g_o \tau_p = n_{20,o} = g_o \tau_n = 10^{13}$ cm⁻³ with increasing reverse current.¹⁷

The DRO-range with a strong drop of both quasi-Fermi levels, (Figs. 32.20d and h, curve 6) is seen as a slowly sloping, rather straight segment of $n(x)$ and $p(x)$. This occurs between ± 0.4 and $\pm 1.8 \cdot 10^{-5}$ cm in Fig. 32.20a. The DRO-range appears when current saturation is approached. Here only a minor increase in currents occur (Figs. 32.20c and g), while major changes in bias are computed (Figs. 32.20d and h), as can be seen by comparing curves 5 and 6.

With forward bias, $r(x)$ is shifted upward with a net current (mostly generated in the junction region) in the forward direction. Up to ≈ 15 mA/cm², g_o remains still larger than r in the bulk region; thus a small gr-current of minority carriers flows in the opposite direction toward the junction into the overshoot region. This part of the current is responsible for the diode quality factor $A > 1$ (see Figs. 32.20b and 32.21,

¹⁷The sloping of the density distribution toward the overshoot region is not visible since $(d_1, d_2) \ll (L_p, L_n)$.

curves 1). At high enough forward currents, shown for curve 0 in Fig. 32.21 the current distribution again becomes monotonic.

It is important to go over and over again of this very informative set of panels of Fig. 32.20 to comprehend all detail of the discussion given above and understand cause and result of the described behavior that is typical for such devices.

With forward bias, the bell-shaped $r(x)$ distribution is maintained and determines the step like slope of $j_n(x)$ and $j_p(x)$ according to $dj_n/dx = e_r(x)$ and shown again in Fig. 32.21 that now contains a higher forward bias that was not depicted in the previous figure. With increased forward bias, $r(x)$ increases without bound and causes a stretching of $j_n(x)$ and $j_p(x)$, although with a steeper slope in the junction region (curve 0 near $x = 0$), as the bell-shaped $r(x)$ is maintained.

Next, we will discuss a thin asymmetric Si-photo diode which was introduced in Sect. 32.2.3 (Fig. 32.18) for vanishing bias.

32.3.2 Thin Asymmetric Si pn -Junction Device with Bias

In Fig. 32.22 a set of solution curves is shown for the asymmetrically doped Si pn -junction device with the same parameters as in Sect. 32.2.4, except for a reduced width of the lowly doped region.

In general, the solution curves show no unexpected new features, except for the field distribution that shows a spike where, near the junction interface, $n(x)$ exceeds N_a . This spike, however, has little influence on the potential distribution, except near open circuit conditions, where the area under the spike is non-negligible and causes only a slight steepening of $E_c(x)$ near the junction interface.

However the spike may have significance for field dependent effects since it can easily exceed 60 kV/cm. But we have neglected such high-field effects in this section.

We now proceed to extend the width of the device to a more realistic thick device, with perfect surface recombination at the two electrodes.

32.3.3 Si-Solar Cell with Non-vanishing Bias

This device is identical with the thick, asymmetrical pn -junction device analyzed for zero bias in Sect. 32.2.4. A forward or reverse bias reduces or increases the recombination rate throughout the device in a fashion similar to that in the short device discussed in the preceding section.

With sufficient *reverse bias*, $r(x)$ is reduced well below g_o throughout the entire junction region, and U becomes equal to g_o up to a few diffusion lengths from the junction and from the right surface. In thick devices ($d_2 \gg L_n$), there is a mid-bulk region of $r \cong g_o$ (near $5 \cdot 10^{-4}$ cm in Fig. 32.23c), with negligible U .

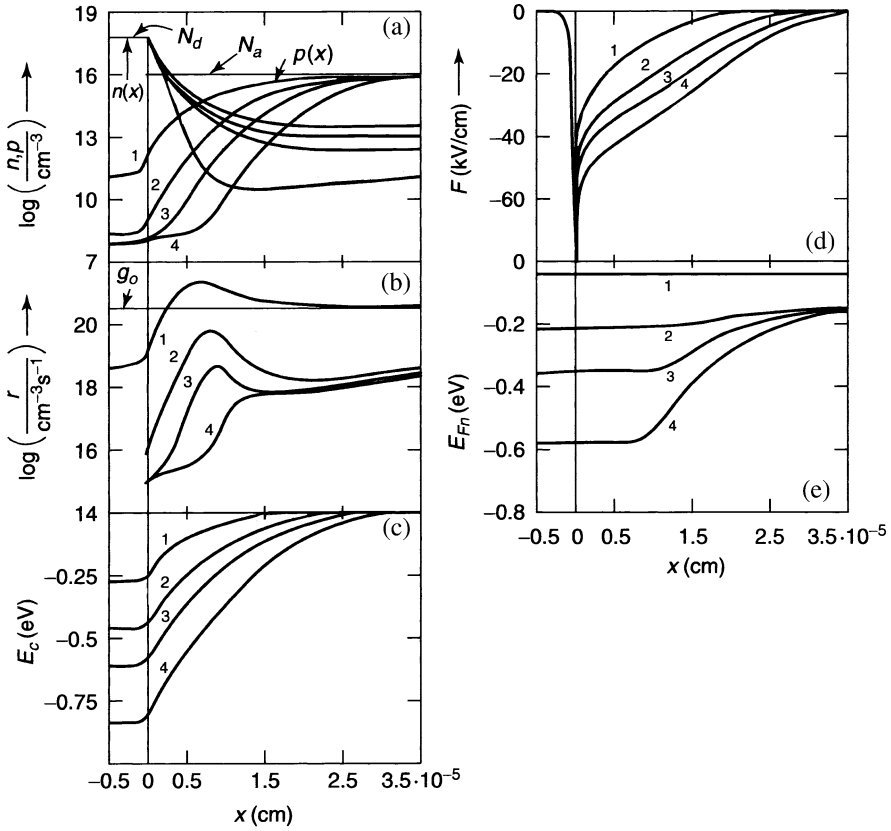


Fig. 32.22 Solution curves for a thin, asymmetrically doped Si pn -junction with the net current as family parameter for $j = 150, -34.5, -35$, and 33.6 mA/cm^2 for curves 1–4, respectively

This inactive region separates the near-junction region from the near-contact region at the right side. The former contributes to the photovoltaic effect, the latter to the surface recombination current.

The current distribution with applied bias becomes highly asymmetric (Fig. 32.23d). A small shift in the hole current distribution, shown near $x = 0$ in an enlarged scale (Fig. 32.23e), indicates the reduction of the surface recombination current from 0.14 to 0.07 mA/cm^2 at the left electrode when current saturation is approached. This concurs with a reduction of $p(d_1)$ from $1.6 \cdot 10^8 \text{ cm}^{-3}$ to $8 \cdot 10^7 \text{ cm}^{-3}$ in accordance with $j_p(d_1) = ev^*p(d_1)$. This surface recombination current, however, is negligible compared to the saturation current j_{sc} of 35.5 mA/cm^2 . Current saturation is almost reached when the DRO-range starts to appear (Figs. 32.23a and b, curves 1 and 2).

The computed current-voltage characteristic of this device is shown in Fig. 32.24 and it is very close to the ideal characteristic that is shown as dashed curve for

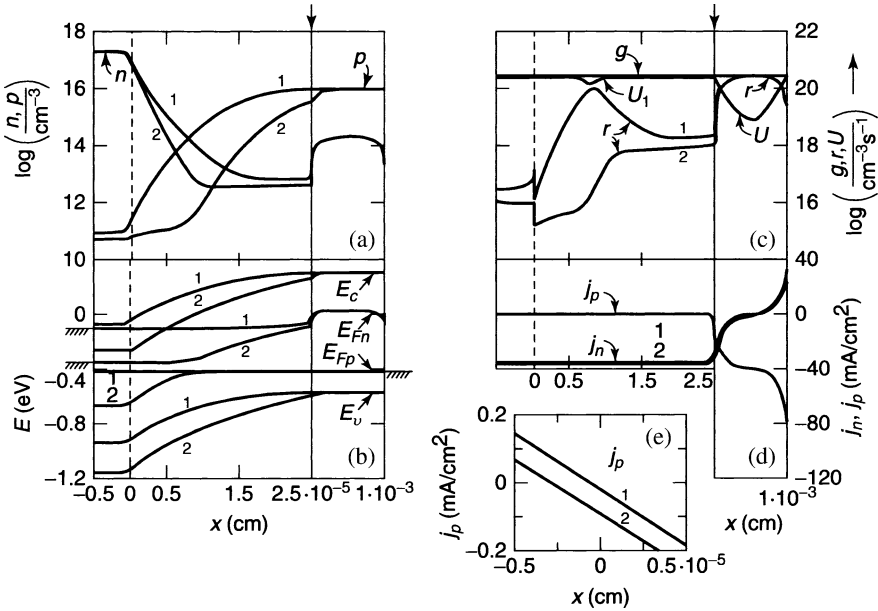


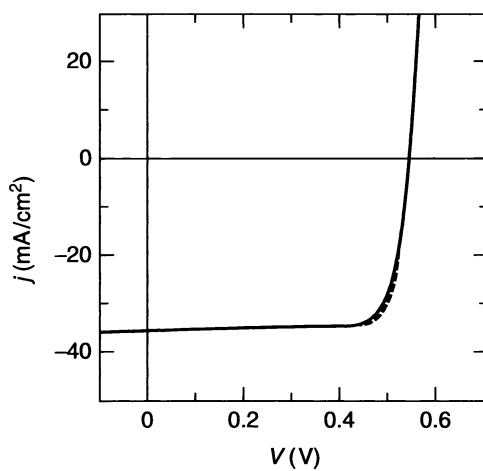
Fig. 32.23 Solution curves for an asymmetric thick Si *pn*-junction solar cell as in Fig. 32.19, however, for two reverse current cases: $j = 35$ and 35.5 mA/cm², and $V = 0.365$ and 0.1 V for curves 1 and 2, respectively. The net generation/recombination rate U for curve 2 in the junction region coincides with g_o within the drawing accuracy, and in the region $x > 2.5 \cdot 10^{-5}$ cm coincides with U for curve 2 as shown $N_{r1} = 10^{17}$, $N_{r2} = 10^{16}$ cm⁻³ and $c = 10^{-9}$ cm⁻³ s⁻¹ on both sides of the junction

comparison. For more on modeling of high-efficient Si solar cells e.g., Banghard (1988).

Numerous device parameters have an influence on the photoelectric conversion efficiency of photo diodes and can be used for device optimization. Some parameters relating to recombination are still insufficiently understood, but may become decisive with specific doping for further improving the device performance by shifting the recombination overshoot into a more benign region. Sensitive balance between electrode separation from the photoelectric active region and permitting optical carrier generation close enough to the junction for nearly perfect minority carrier collection pose geometrical as well as electronic device design challenges.

Fig. 32.24 Current-voltage characteristic obtained from solutions of Figs. 32.23.

Dashed curve represents the ideal diode characteristic shifted by 35.8 mA/cm^2



Chapter 33

The Heterojunction with Light

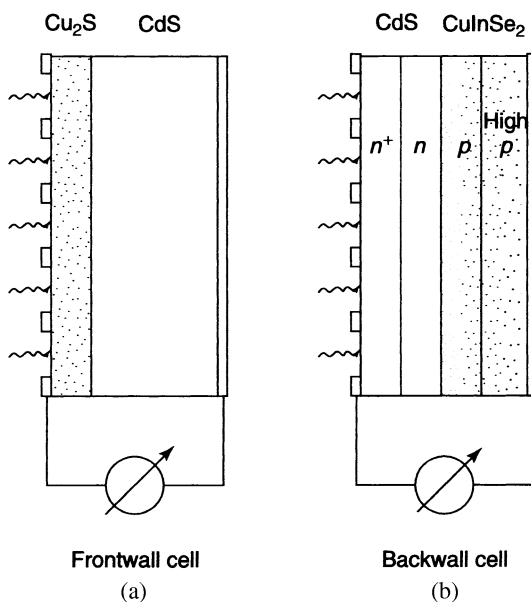
Abstract As an example of the thin heterojunction polycrystalline solar cell, the CdS/Cu₂S cell is chosen. The current voltage characteristic is computed. Space charge effects in the heterojunction are discussed. The influence of electron traps in CdS is shown. The influence of a field enhanced depletion of hole traps is experimentally demonstrated. The influence of field quenching is computed. The Frenkel-Poole effect is identified. Experimental results of kinetic effects of the solar cell characteristics are shown. A Voltage drop kinetic method is introduced. The influence of interface recombination is calculated. Boundary conditions at the interface are introduced. The quality factors *A* and *B* are introduced and measured. Lessons learned from the CdS/Cu₂S solar cell.

Heterojunction solar cells of proper design have an advantage by producing minority carriers close to the junction when light penetrates through the wider band gap material and is absorbed close to the heterojunction and away from performance-deteriorating contacts. Such heterojunctions have the potential for higher conversion efficiencies. A large variety of photo diodes can be formed with heterojunctions either as the photo electrical active junction or as a means for electric control or passivation of adjacent surfaces or electrodes. We will describe here only one example in some detail to illustrate a generic type for such a behavior. We have chosen as an example the Cu₂S/CdS solar cell¹ for which a large volume of experimental evidence is available. With these we can illustrate the principles of the relating effects, even though the cell itself has only limited practical interest for reasons of the high lattice mismatch that creates a high density of interface recombination centers and for the tendency of the copper sulfide to cause cell degradation under sunlight.

In general, all material-related device parameters show a discontinuity at the heterojunction interface. Some of these discontinuities present a disadvantage; an example is the lattice mismatch that produces a dislocation field with enhanced re-

¹We have consistently referred to this cell as a Cu₂S solar cell even though this would indicate that the copper sulfide is a chalcocite, while in actuality it is Djurleite with a stoichiometry closer to 1.98 rather than 2. This also is done in order to indicate that we do not want to use the examples discussed here for more than as possible phenomena rather than staying too close to an actual cell in all the detail discussed here.

Fig. 33.1 Schematic representation of a front wall and a back wall solar cell. Light enters from the *left*. Optical generation rate indicated by *dots*



combination and carrier scattering. Other parameter discontinuities are benign; an example are the bulk carrier mobilities. Some other discontinuities may be used as an advantage, e.g., the discontinuity of the optical generation rate that permits strong optical absorption close to the heterojunction interface when the partner is a direct band gap material.

The discontinuity in optical excitation presents a unique opportunity to design more efficient solar cells by creating most of the minority carriers close to the junction and away from performance-deteriorating contacts or surfaces.

In general, one distinguishes a *heterojunction front wall or back wall solar cell* as devices in which most of the light is absorbed in the front region² or in the region behind the hetero interface, depending on whether the lower band gap material is at the front or back region of the cell. An example for the first is the $\text{Cu}_2\text{S}/\text{CdS}$ solar cell; an example for the second is the $\text{CdS}/\text{CuInSe}_2$ cell. Both devices are shown schematically in Fig. 33.1, with light penetrating each cell from the left.

For reasons mentioned above, we have selected only the first device but leave other, technically highly interesting solar cells to a more sophisticated discussion in the second volume of this book.

²Even though as a heterojunction cell this type seems to miss the obvious advantage of optical absorption close to the heterojunction, it may still be of technical interest because of the ease of fabrication resulting in relatively inexpensive devices that may still show acceptable conversion efficiencies.

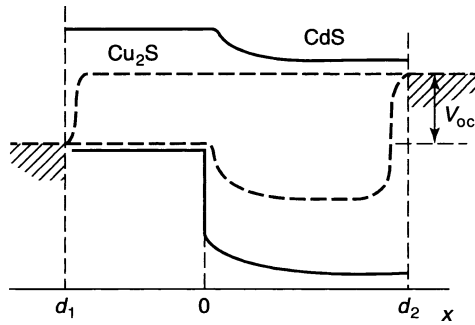


Fig. 33.2 Schematics of the simplified band model of a $\text{Cu}_2\text{S}/\text{CdS}$ heterojunction solar cell with light at open-circuit condition. (The current compensation caused by opposite slopes of the quasi-Fermi levels is not visible in the scale of the shown schematics and therefore should not be interpreted without a further detailed analysis)

33.1 The $\text{Cu}_2\text{S}/\text{CdS}$ Solar Cell

The $\text{Cu}_2\text{S}/\text{CdS}$ solar cell is an example in which the region of minority carrier generation and collection is separated from the barrier region, and both regions, in principle, can be discussed individually. The highly conductive Cu_2S region in which most of the light is absorbed can be regarded as a field-free emitter of minority carriers. The adjacent CdS is much lower doped and contains almost all of the junction which, to a good approximation, can be described electronically as a Schottky barrier, however, without having the performance deteriorating metal electrode as an interface to the Cu_2S . The purpose of the CdS is to divide both types of carriers and separating the electronic active part of the device from the electrode. It is also used to limit the field³ without requiring high purity in the junction region, as will be discussed later.

In Fig. 33.2 we show a simplified band model of the $\text{Cu}_2\text{S}/\text{CdS}$ solar cell with assumed connection of the conduction bands without a jump, and a schematic sketch of the split quasi-Fermi levels with light, at open circuit conditions. The continuous $E_{Fn}(x)$ and $E_c(x)$ indicates the assumed continuity⁴ of $n(x)$ at the $\text{Cu}_2\text{S}/\text{CdS}$ interface (at $x = 0$).

A family of computed minority carrier curves $n(x)$ is shown in Fig. 33.3 for non vanishing bias with the net current (short circuit current) as family parameter. With increased reverse bias (in this simplified model),⁵ the electron density at the $\text{Cu}_2\text{S}/\text{CdS}$ boundary is pulled down from the CdS side of the interface, causing a

³This is a typical characteristic of copper doped CdS by creating a high-field domain.

⁴In actuality, there may be some discontinuities, as discussed in several previous sections, which can be easily introduced but are omitted here to avoid confusion with other effects that are emphasized in this chapter.

⁵Here we assume that the conductivity in the Cu_2S is high enough that any voltage drop here can be neglected.

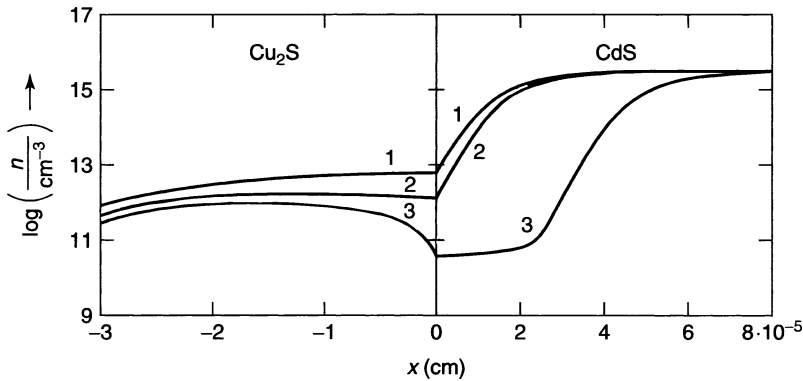


Fig. 33.3 Computed electron density distribution in the $\text{Cu}_2\text{S}/\text{CdS}$ heterojunction solar cell assuming $n(x)$ continuity at $x = 0$ with the electron current as family parameter for $j_n = 17, 0$, and -14 mA/cm^2 for curves 1–3 respectively. Observe the abscissa break at $x = 0$

gradient of $n(x)$ in the Cu_2S with consequent minority carrier diffusion toward the interface.

33.1.1 The Current-Voltage Characteristics

The relation between the applied voltage and the boundary electron density at the $\text{Cu}_2\text{S}/\text{CdS}$ interface can be obtained explicitly from a simple Schottky barrier approximation⁶ (see Sect. 29.3.4) with

$$n_j(x=0) = N_c \exp\left[-\frac{e(\tilde{V}_{Dn} + V_{oc} - V)}{kT}\right], \quad (33.1)$$

and, neglecting the small voltage drop in the highly doped Cu_2S . The diffusion current in Cu_2S is given by [Sect. 27.3.4, Eq. (27.35)] (Böer 1976a, 1976b)

$$j_n = e \frac{L_n}{\tau_n} (n_j - g_o \tau_n) \tanh\left(\frac{x_c}{L_n}\right) \quad (33.2)$$

with $x_c = x_m$ the position of the $n(x)$ maximum in Cu_2S for reverse and $x_c = x_i$ the inflection point in forward bias ($x_c \approx d_1/2$). When combining the voltage drop in the CdS barrier [Eq. (33.1)] with the current created in the Cu_2S emitter [Eq. (33.2)]

⁶The Schottky barrier approximation is well suited for the CdS part of the heterojunction since in the entire CdS one has $p \ll n$, and the Cu_2S is nearly degenerate, thereby acting in some respects as pseudo-electrode.

by eliminating n_j , one obtains directly an essentially ideal current voltage characteristic⁷ (Böer 1980):

$$j_n = eg_o L_n \left\{ \exp \left[\frac{e(V - V_{oc})}{kT} \right] - 1 \right\} \tanh \left(\frac{x_m}{L_n} \right), \quad (33.4)$$

which can be rewritten in the common form

$$\boxed{j_n = j_0 \exp \left(\frac{eV}{kT} \right) - j_s} \quad (33.5)$$

with

$$j_0 = j_{00} \exp \left(-\frac{e\Phi}{kT} \right), \quad (33.6)$$

$$j_{00} = e \frac{L_n}{\tau_n} N_c \tanh \left(\frac{x_c}{L_n} \right), \quad (33.7)$$

$$j_s = eg_o L_n \tanh \left(\frac{x_c}{L_n} \right), \quad (33.8)$$

and

$$\Phi = V_D + V_{oc} \quad (33.9)$$

When written in this form, Eq. (33.5) with its auxiliary formulae [Eqs. (33.3)–(33.9)] it is most instructive as it permits a distinction between the different interacting effects. These are the current generation in Cu₂S and the voltage drop in CdS, resulting in this basic photo diode characteristic. Again this is caused by the fact that the almost degenerate, highly conductive Cu₂S acts almost exclusively to generate the photo electric active minority carriers (electrons), and CdS with much lower donor density has a substantially wider barrier layer with almost all the potential drop of the device generated by electron depletion and little additional photo generation of minority carriers (that are completely neglected in this simple model).⁸

The “ideal characteristic” as obtained in this fashion contains all these approximation. It obviously needs to be modified when comparison with the experiment is desired.

⁷When using the relation

$$\tilde{V}_{Dn} = \frac{kT}{e} \ln \left(\frac{N_c}{n_{j_0}} \right) \quad (33.3)$$

and, inserting for zero current and steady state $n_{j_0} = g_o \tau_n$.

⁸It should be emphasized that a more comprehensive discussion of the characteristic must relate to the distribution of both quasi-Fermi levels that describe the net current. However a realistic computation is exceedingly difficult in typical heterojunctions since the trap distribution and related transition coefficients are insufficiently known.

Beyond this instructive example of a separation of generation and barrier effects, the $\text{Cu}_2\text{S}/\text{CdS}$ solar cell is useful to demonstrate a variety of effects relating to the changes of space charges in the barrier which influence the performance of solar cells, albeit here in a rather transparent form. We will explore some of these effects in the following sections, and it will become evident there why we have selected this heterojunction solar cell for our discussion.

33.1.2 Space Charge Effects in the Heterojunction

Changes in the development of space charges are relatively easy to follow in the $\text{Cu}_2\text{S}/\text{CdS}$ solar cell since the junction can be described as a *single carrier n-type* Schottky barrier (see Fig. 27.1).⁹ These space charges change with changing occupation of various trap levels. Such changes can be influenced by light and bias variation. We will now discuss this behavior in more detail.

33.1.3 Influence of Electron Traps in CdS

We now modify the previous discussion of the Schottky barrier by introducing two sets of donors with a density N_{d1} and N_{d2} and an energy E_{d1} and E_{d2} . Within the barrier layer these donors are sequentially depleted with increased reverse bias, as schematically shown in Fig. 33.4b. This causes a stepwise increase of the space charge and consequent increase in the slope of the electric field (Fig. 33.4d and f). This is compared with a conventional Schottky barrier having only one donor level and is shown in Fig. 33.4a, c and e.

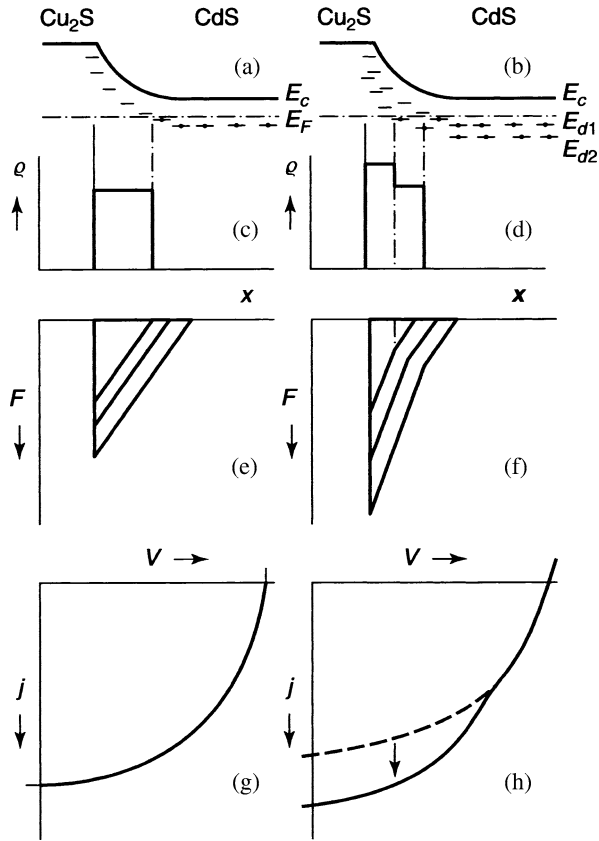
The steeper increase of the high-field region close to the barrier interface (Fig. 33.4f) results in a steeper increase of the current, as indicated in Fig. 33.4h. This can be obtained analytically from the shape factor approximation which yields for the current-voltage characteristics of the heterojunction

$$j = \frac{j_s [\exp\{-\frac{e(V-V_{oc})}{kT}\} - 1]}{1 + \frac{\varepsilon_1 v_D^*}{\varepsilon_2 \mu_{n2} F_j}} \quad (33.10)$$

with indices 1 and 2 for Cu_2S and CdS , respectively and v^* the modified diffusion velocity. Under conditions in which the drift velocity $\mu_{n2} F_j$ at the hetero interface is on the same order as the diffusion velocity v_D , the current becomes proportional

⁹Even considering frozen-in steady state for the minority carriers in the dark and reasonable generation rates and lifetimes under sunlight, the minority carrier density within the CdS will remain well below the electron density within the entire barrier region.

Fig. 33.4 Schematics for the barrier layer at a Cu₂S/CdS heterojunction for a single donor (**a**, **c**, **e** and **g**) and a two-donor model (**b**, **d**, **f** and **h**). Shown are the band model for equilibrium conditions (**a** and **b**); the corresponding space charge distribution (**c** and **d**); the field distribution for three bias conditions (**e** and **f**); and the current-voltage characteristics for cell parameters resulting in an extended square-root branch (**g** and **h**) in the current-voltage characteristics



to F_j which in turn is proportional to the square root of the bias [see Eq. (26.41)]

$$F_j = \sqrt{\frac{2eN_d}{\epsilon_2\epsilon_0}(V_{oc} - V) + F_c} \quad (33.11)$$

with F_c the maximum field in open circuit conditions for a single donor model. In the two-donor model, the space charge distribution can be approximated¹⁰ by a gradual step function

$$\rho(x) = e \left\{ n(x) - N_{d1} \left[1 + 0.5 \frac{N_{d2}}{N_{d1}} (\tanh[C\{V - (\Phi - V_2)\}]) \right] \right\} \quad (33.12)$$

with $C = e/(kT)$ or $C = e/(2kT)$ dependent on the kinetics of the trap filling, and V_2 the area under the triangle of $F(x)$ up to the cross-over point at open circuit.

¹⁰For a more precise evaluation of the sequential trap depletion see the corresponding Sect. 27.2.2 that deals with the dark-diode.

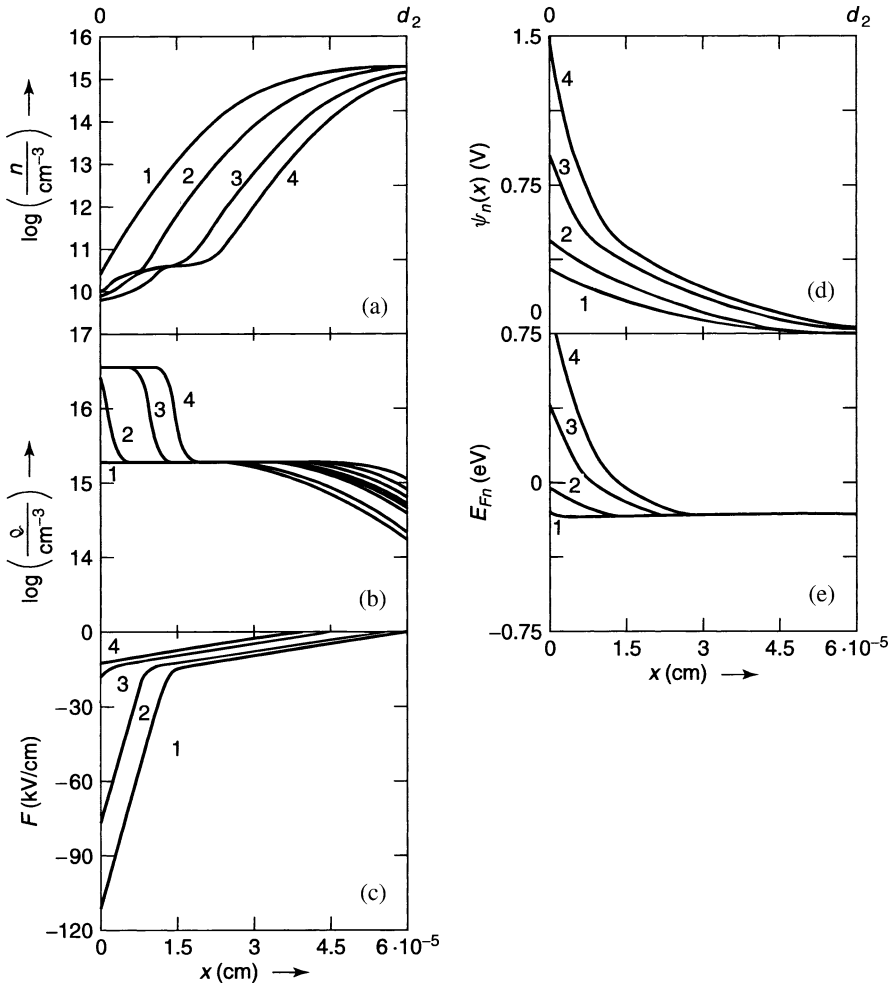


Fig. 33.5 Solution curves of Eqs. (29.12)–(29.18) for a two-donor Schottky barrier model with a space charge modifying function given by Eq. (33.12) and $N_{d1} = 2 \cdot 10^{15} \text{ cm}^{-3}$, $N_{d2} = 5 \cdot 10^{16} \text{ cm}^{-3}$, $V_2 = -0.65 \text{ V}$, $\Phi = 0.9$ and $C = -38$. Family parameter is the current with $j_n = 1, 3, 7$ and 8 mA/cm^2 for curves 1–4, respectively

$\Phi = V_{oc} + V_D$. An example for the computed set of solution curves using such donor depletion function in for a two-level in the basic set of transport equation one obtains the set of curves that are shown in Fig. 33.5. It shows two steps in $n(x)$, $q(x)$, and indicates the field for sufficient reverse bias when the lower donor is being depleted by showing a kink and sharply increasing slope.

A corresponding family of *current-voltage characteristics* is shown in Fig. 33.6. These characteristics develop a step when the parameters are favorable so that an extended square root range exists, and the ratios of N_{d1} and N_{d2} as well as the

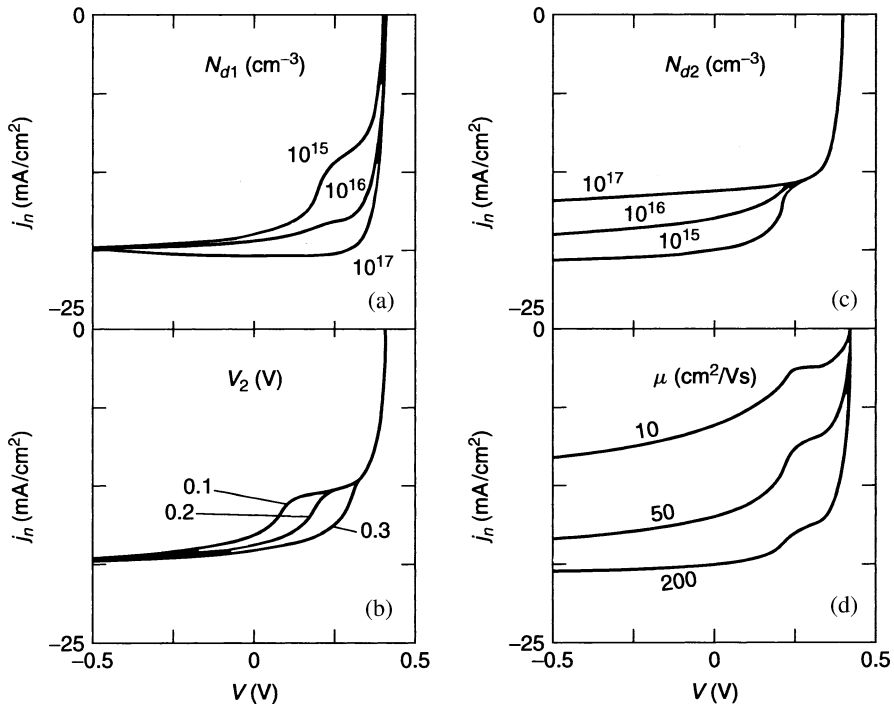


Fig. 33.6 Current-voltage characteristics computed from solution curves corresponding to the ones shown for one example in Fig. 33.5 for $N_{d1} = 2 \cdot 10^{15} \text{ cm}^{-3}$, $N_{d2} = 5 \cdot 10^{16} \text{ cm}^{-3}$, $V_2 = 0.2 \text{ V}$ and $\mu_n = 100 \text{ cm}^2/\text{V s}$ as standard parameters while one of them is changed in steps as shown as a family parameter in each of the panels

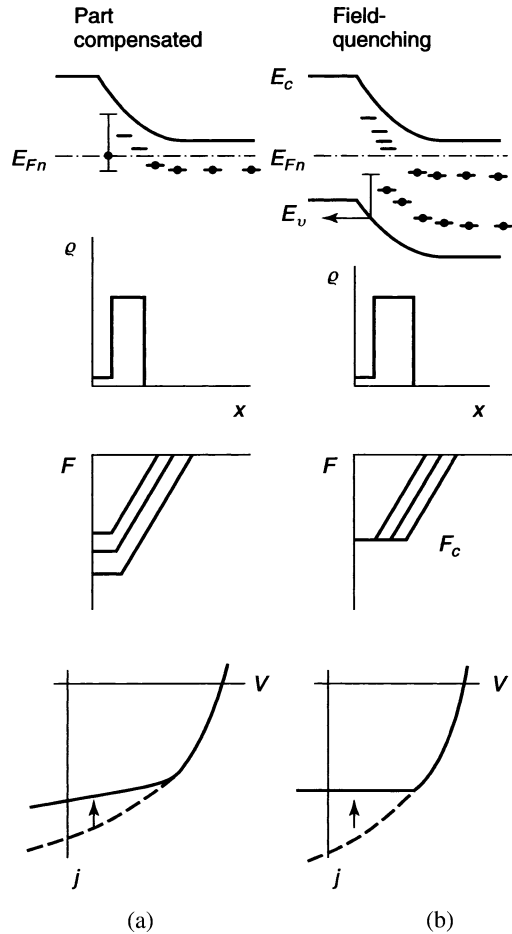
ionization energies are conducive for such a step to develop due to sequential donor depletion.

Steps are indeed occasionally observed and are usually referred to as double-diode characteristics. The case discussed here is another example how careful one has to be in explaining an observed behavior, and how misleading a simple double diode model can be for the search to improve such a cell. Namely, with further cell optimization using treatments to modify the donor distribution, the steps generally disappear as the square root range vanishes and the step-like increase in field slope becomes hidden in the current saturation range.

33.1.4 Influence of a Compensated Layer near the Hetero-Interface

When the region close to the hetero-interface is partially compensated, a lower space charge results. Thereby, the field slope is *reduced*, and the slope of the current-

Fig. 33.7 Schematics of a barrier layer which is partially compensated near the interface (a), or which contains Coulomb-attractive hole traps that permit field quenching above a critical field F_c (b) that forces total compensation at a critical field



voltage characteristic in the DRO-range between the Boltzmann and the saturation range is also reduced.

When this compensated layer comprises only a fraction of the space charge layer, it remains fixed and cannot expand. In such devices only a small parallel shift of the characteristic occurs, as shown in Fig. 33.7a.

33.1.5 Influence of a Field-Induced Depletion of Hole Traps

When Coulomb attractive hole traps (copper centers in CdS) close to the hetero-interface are exposed to fields in excess of the critical field for Frenkel-Poole ionization, these hole traps can be depleted by the action of the field, and the freed holes can be extracted through the adjacent hetero-interface (Fig. 33.7b). This causes a

sharp reduction of the space charge and results in a reduced field slope. Consequently, a wider region becomes exposed to the ionization field (Fig. 33.7b). When the thickness of this hole-depleted region increases beyond the diffusion length, interaction of the freed holes with the electron ensemble must be considered, including modification of the recombination traffic, commonly referred to as field quenching. This is discussed in more detail below.

33.1.6 Influence of Field Quenching

Field quenching in optically excited CdS is well-known (Böer and Dussel 1970), and results in compensation by freeing holes from hole traps to recombine with electrons, thereby lowering their density. This, in turn, lowers the density of positively charged centers, and can essentially eliminate the space charge in the part of the barrier where the field has reached the critical value for field quenching.

It thereby limits field and current and causes a substantial widening of the barrier.¹¹

A typical set of solution curves of the transport equations is shown in Fig. 33.8 which assume the onset of field quenching at 60 kV/cm and a space charge reduction from $5 \cdot 10^{16} \text{ cm}^{-3}$ to a compensated ($N_d - N_a$) value of $\approx 5 \cdot 10^{14} \text{ cm}^{-3}$.

The onset of field quenching can be modeled with a step function

$$\varrho(x) = e \left[n(x) - N_D \left\{ 1 - 0.5 \frac{N_D - N_A}{N_D} (1 + \tanh[Q(F - F_c)]) \right\} \right]. \quad (33.13)$$

Field quenching is a self-compensating process that starts to become marked near the critical field F_c and frees as many holes as necessary for sufficient compensation to limiting the field slightly above F_c . If, however, during this process more acceptors than donors are depleted, the sign of the space charge is inverted, causing a decrease of the field and a reduction of the field quenching, i.e., self-stabilizing the effect.

The leveling of the field causes a rapid widening of the space-charge layer with a fast increasing voltage drop across the barrier without further lowering the carrier density at the barrier interface. This results in substantially improving current saturation with in-creasing compensation for curves 1–4, as shown in Fig. 33.9.

¹¹Such field quenching is of interest for technical applications, since it permits working with semiconductors of lower purity, allowing less expensive fabrication methods. Without field quenching, such semiconductors would easily be driven into a range of excessive barrier fields, with detrimental influence on performance due to tunneling through the barrier, thereby creating leakage currents.

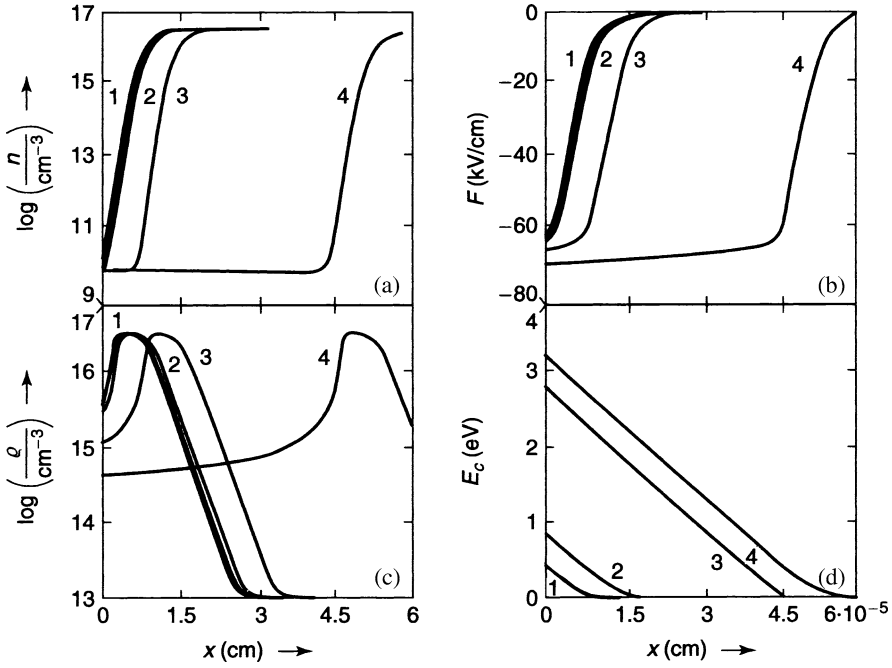


Fig. 33.8 Computed solution curves of Eqs. (7.31)–(7.41) for the CdS barrier in a Cu₂S/CdS solar cell with field quenching causing an effective compensation from $N_d = 5 \cdot 10^{16} \text{ cm}^{-3}$ to $N_d - N_a = 5 \cdot 10^{14} \text{ cm}^{-3}$ at fields in excess of 60 kV/cm. Family parameter is the electron current: $j_n = 2, 6, 6.3$ and 6.5 mA/cm^2 for curves 1–4, respectively

Fig. 33.9 Current-voltage characteristic for a Cu₂S/CdS solar cell with field quenching computed for $n_j = 7 \cdot 10^9 \text{ cm}^{-3}$, $N_d = 5 \cdot 10^{16} \text{ cm}^{-3}$, $F_c = 1.1 \cdot 10^5 \text{ V/cm}$ and $Q = 1.5 \cdot 10^{-4} \text{ cm/V}$ in Eq. (33.13) and with $(N_D - N_A)/N_D = 0.98$; 0.5 and 0.2 as family parameter for curves 1–3, respectively

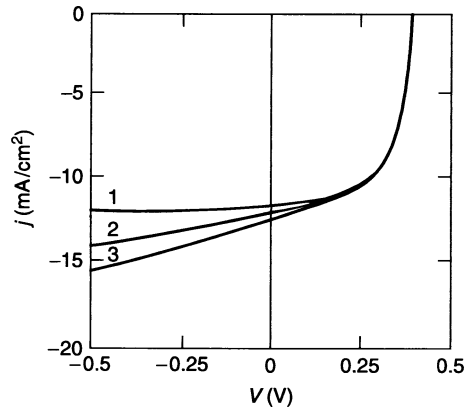
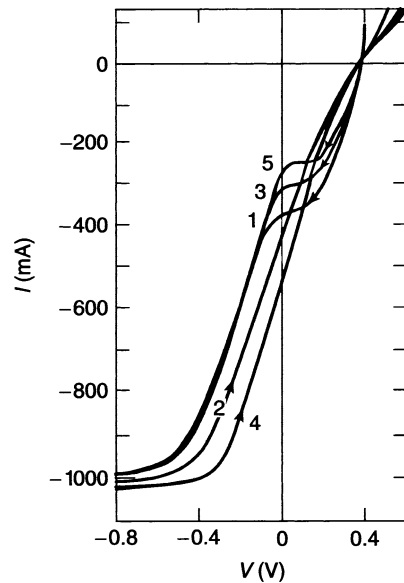


Fig. 33.10 Measured current-voltage characteristics hysteresis of an insufficiently treated $\text{Cu}_2\text{S}/\text{CdS}$ solar cell traversed in direction of the arrow after waiting 5, 10, 15 and 20 s at V_{oc} for curves 1, 3, 5, respectively, or waiting for the same times at -0.8 V for curves 2 and 4, respectively (after Böer 1981a, 1981b, 1981c)



33.1.7 Kinetic Effects of Solar Cell Characteristics

The trapping or release of carriers from traps is a slow process, with a time constant increasing exponentially with trap depth. These processes are initiated when decreasing or increasing the barrier width with changing bias.

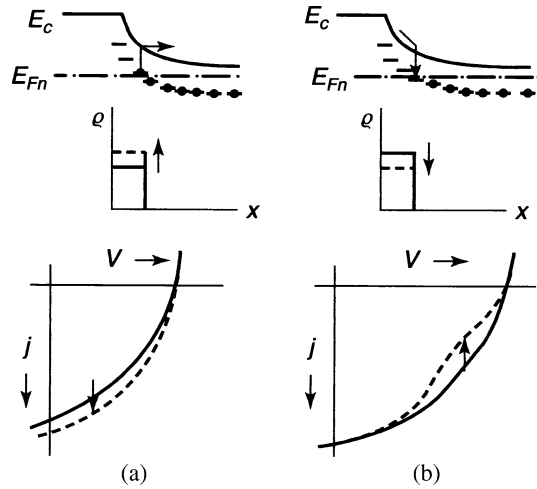
One consequently expects a hysteresis of the current-voltage characteristics when the characteristic is transversed in one or the other direction.

This is indeed observed in $\text{Cu}_2\text{S}/\text{CdS}$ solar cells in characteristics with low fill-factors.¹² Examples of such hysteresis are shown in Fig. 33.10. When traversed in the direction of increased reverse bias, the characteristics show the typical steps indicating deep trap depletion (Sect. 33.1.3). When traversed in the direction of increasing forward bias, the step disappears and an inflection point occurs at V_{oc} with a lower slope at V_{oc} the more traps were depleted while waiting longer at -0.8 V.

The filling or depleting of different types of traps can be more easily analyzed when measuring the kinetics of the voltage drop across the solar cell while maintaining a stepwise increased constant current, as discussed below.

¹²Only in the bias range between the Boltzmann and the saturation branch can such kinetics be observed. Otherwise the structure of interest becomes hidden in the horizontal current saturation branch.

Fig. 33.11 Schematics of a barrier layer kinetics with slow (thermal) trap depletion when waiting in reverse bias (a) and of trap filling when waiting at or near V_{oc} (b)



33.1.8 Voltage Drop Kinetics Method

This method consists of monitoring applied voltage across the cell as a function of time that is necessary to maintain a constant current through the solar cell after the current is changed stepwise, e.g., from zero to a predetermined fixed value (Böer 1981a, 1981b, 1981c). When the current is increased, the space charge is increased, caused by depletion of donors or traps that turn positive (Fig. 33.11a). Conversely, a decrease of the current causes a filling of such centers, neutralizing them and reducing the slope of the characteristic, i.e., causing the voltage drop to decrease (Fig. 33.11b).

If, however, the forced increase in current causes a depletion of acceptors or acceptor-like deep hole traps, e.g., caused by Frenkel-Poole excitation by field quenching causes a reduction in space charge by compensation and thereby an increase in the slope of the characteristics, the opposite behavior as found for depletion of donors.

The changing space charge in part of the barrier is illustrated in Fig. 33.12. In panel a we show a slow depletion of a deep electron trap with higher applied voltage, causing a reduction of the voltage drop (area under the $F(x)$ -curve) as a layer with increased space charge becomes established.

This results in a higher field slope near the interface that can reach the same F_j , thereby maintaining the same current.

When the critical field for field quenching is reached at the interface, the space charge-free field-quenched region with constant critical field F_c expands as shown in Fig. 33.12b. An intermittent region is created with a high field slope where deep electron traps are depleted before quenching starts.

Figure 33.13 shows corresponding experimental results. Three characteristics are given schematically in panel a. When the current is changed to a constant value I_0 , a voltage of ≈ 0.2 V is necessary to maintain this current for curve 1; however, in time

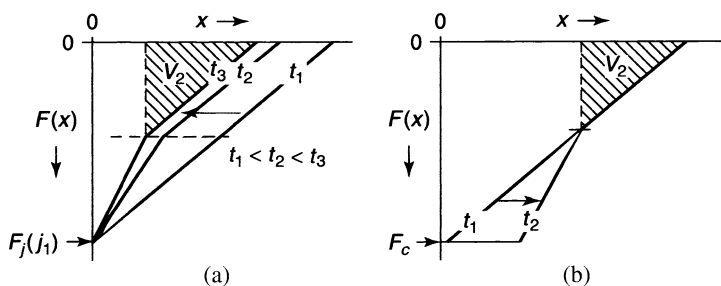


Fig. 33.12 Field distribution kinetics in a barrier layer (a) with gradual depletion of a deep trap; (b) with depletion of a deep trap, but at a field at which field quenching starts to reduce the space charge near the interlayer and therefore limits the field

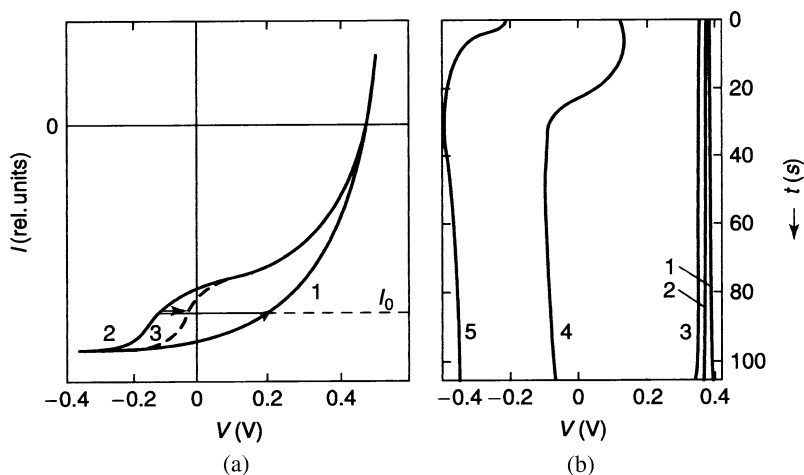


Fig. 33.13 Kinetics of the current-voltage characteristics within the DRO-range. (a) Schematics of three non-stationary characteristics; when constant current I_0 is maintained, the applied voltage changes in time as the characteristic develops from curve 1 through curve 2 to curve 3. (b) Voltage drop as a function of time after the current is changed from zero at V_{oc} for 2 min. to $I_0 = -530, -600, -650, -700, \text{ and } -820$ mA for curves 1–5, respectively (after Böer 1981a, 1981b, 1981c)

the applied voltage needs to be reduced, reaching a minimum at -0.15 (curve 2), and then increased again to -0.05 V (curve 3) to maintain I_0 .

The actual voltage kinetics is shown in Fig. 33.13b for a Cu₂S/CdS cell that shows JV -characteristics with hysteresis similar to the one given in Fig. 33.10. The observed kinetics depends on the degree of preceding trap filling (waiting at a certain point of the characteristic), on the value of I_0 , and on the temperature.

In curves 8 and 7 of Fig. 33.13b, one can discern the three voltage drop ranges shown in panel a. First a shift toward higher negative voltage, indicating trap depletion; this shift is very fast, and barely resolved near $t = 0$ for curve 7. This range overlaps with the voltage decrease caused by the start of field quenching that be-

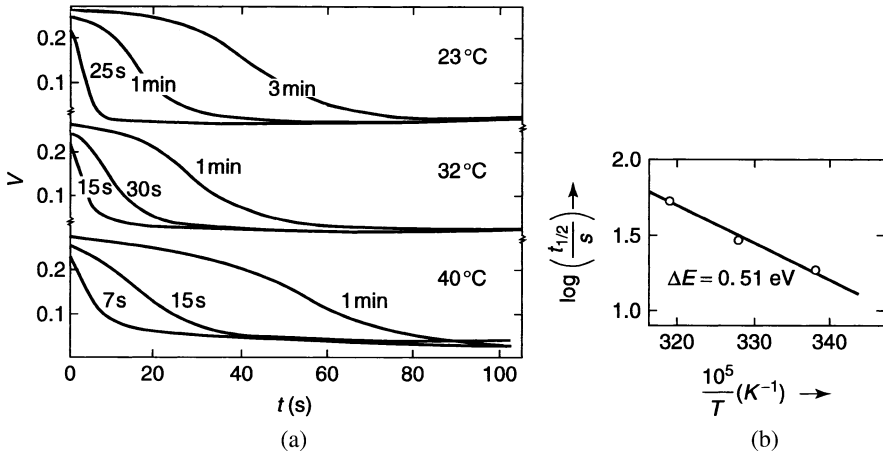


Fig. 33.14 Voltage drop across a $\text{Cu}_2\text{S}/\text{CdS}$ solar cell similar to the one used in Fig. 33.13 after switching from $I = 0$ to 860 mA at the temperatures listed in the three panels and after waiting at V_{oc} for the time indicated at each curve. **(b)** Logarithm of the half-time of the voltage decrease taken from subfigures. **(a)** Curves of 1 min. rest at V_{oc} are used (after Böer 1981a, 1981b, 1981c)

comes dominant near 10 s. It is then followed by a slow rise beyond 40 s; this rise is probably due to an even slower release of electrons from deeper electron traps, thereby lowering the compensation.

When waiting at V_{oc} for different lengths of time (shown as family parameter in Fig. 33.13) and then plotting the time to achieve half of the quenching obtained from the abscissa for different temperatures in a semi-logarithmic plot versus $1/T$ (Fig. 33.14b) one obtains an apparent activation energy of $\approx 0.5 \text{ eV}$ for the filling of deep traps that makes it more time consuming for quenching, the more of these traps are filled.

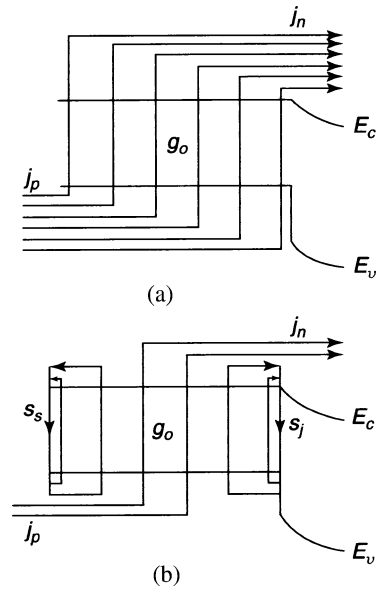
The examples are given here to illustrate the sensitivity of an incompletely filled out current-voltage characteristic to trap kinetics. Any characteristic that has a substantial square-root range (indicating a DRO-range) between the Boltzmann and the current saturation range offers an opportunity to study such kinetics. For example, in this DRO-range, the current-voltage characteristic relates as a simple drift

$$j_n = e\mu_n n_j F_j \quad \text{with} \quad F_j = \sqrt{\frac{2\rho(V_{\text{oc}} - V)}{\varepsilon_2 \varepsilon_0}}, \quad (33.14)$$

which yields for the voltage drop across the solar cell for trap filling with $\rho = e[N_d - n_d(t)]$:

$$\Delta V(t) = V_{\text{oc}} - V(t) = -\frac{j_n^2}{\frac{2e}{\varepsilon_2 \varepsilon_0} (e\mu_n n_j)^2 [N_d - n_d(t)]}. \quad (33.15)$$

Fig. 33.15 Optically generated current (schematically) (a) without and (b) with surface and interface recombination leakage indicating the corresponding current losses. Arrows indicate electron transport



In a similar fashion, the reduction of the space charge due to quenching can be analyzed.

33.1.9 Influence of Interface Recombination

A broadening of the square root branch is caused by interface recombination between Cu₂S and CdS and is probably induced by lattice mismatch resulting in a closely spaced dislocation network that creates a high density of recombination centers.

Such interface recombination provides a leakage path, diverting minority carriers that can no longer pass through the barrier as indicated in Fig. 33.15. As a result, the current is reduced by the interface recombination current and the conversion efficiency is reduced accordingly (see below).

$$j_n(x = 0^+) = j_n(x = 0^-) - en_j s_j \quad (33.16)$$

resulting in a reduced diode current

$$j_n = \frac{j_s [\exp\{-\frac{e(V-V_{oc})}{kT}\} - 1]}{1 + \frac{\varepsilon_1(v_D^* + s_j)}{\varepsilon_2 \mu_n F_j}} \quad (33.17)$$

and a corresponding reduction in the open circuit voltage

$$\Delta V_{oc} = \frac{kT}{e} \ln\left(\frac{v_D^* + s_j}{v_D^*}\right). \quad (33.18)$$

Fig. 33.16 Current-voltage characteristics obtained from Eq. (33.10) for a single donor model with $N_d = 10^{16} \text{ cm}^{-3}$, $\mu_n = 100 \text{ cm}^2/\text{V s}$, $\varepsilon = 10$ and $T = 300 \text{ K}$ and with the interface recombination velocity as family parameter: $s_j = 10^7, 10^6, 3 \cdot 10^5, 10^5, 10^4$, and 0 for curves 1–6, respectively

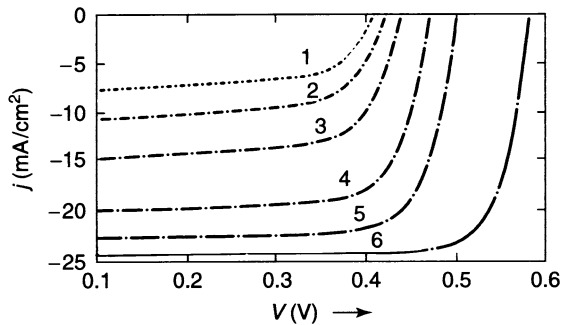


Figure 33.16 shows a family of current-voltage characteristics computed from Eq. (33.17) with the interface recombination velocity as family parameter. This set of curves demonstrate the severity of the performance deterioration with increasing interface losses even for recombination velocities in the low 10^4 cm/s range.

33.1.10 Boundary Condition at the Interface

When we permit the electron density n_j to slide down at the interface, the current-voltage characteristics become modified according to the discussion of Sect. 33.1.8, Eq. (27.48), yielding for a planar hetero interface

$$j_n = \frac{j_s [\exp\{-\frac{e(V-V_{oc})}{kT}\} - 1]}{1 + \frac{\varepsilon_1 (v_D^* + v_n^* + s_j)}{\varepsilon_2 \mu_n F_j}} \quad (33.19)$$

with v^* the modified diffusion velocity given by Eq. (27.41) and adding now in the shape factor in the denominator the much larger modified rms-velocity modified rms-velocity of electrons

$$v^* = v_{n,\text{rms}} / \sqrt{6\pi}.$$

When comparing Eq. (33.19) with Eq. (33.10), one deduces that the square root branch with defect level information widens as the velocity that competes with the drift velocity increases, hence making a defect level analysis easier in the widened DRO-range.

33.1.11 Information from the Exponential A-Factor

We will now devote our attention to the Boltzmann branch near V_{oc} . We assume that a simple characteristics deterioration from a parasitic resistive network can be neglected.

The usually observed deviation from the ideal characteristic is then expressed by the *quality factor* A , as

$$j = j_0 \exp\left(\frac{eV}{AkT}\right) - j_L \quad (33.20)$$

which, for reasons to become obvious below, we will rewrite as¹³

$$j = j_{00} \exp\left(-\frac{e\tilde{V}_{Dn}}{kT}\right) \exp\left[\frac{e(V - V_{oc})}{AkT}\right] - j_L. \quad (33.21)$$

It was pointed out by Shockley and Queisser (1961), that a quality factor $A > 1$ can be related to junction recombination. The Cu₂S/CdS solar cell has an advantage for a simplified analysis, since the dominant junction recombination is localized at the interface and expressed as interface recombination velocity s_j . With it, the parameters of Eq. (33.21) are

$$V_{oc} = V_{oc}^{(0)} - \frac{kT}{e} \ln\left(\frac{v_D^* + s_j}{v_D^*}\right) \quad (33.22)$$

$$j_{00} = eN_{c2}(v_D^* + s_j) \quad (33.23)$$

$$j_L = j_L^{(0)} \frac{v_n^*}{v_n^* + v_D^* + s_j} \quad (33.24)$$

with superscript (0) indicating the parameter for $s_j = 0$. The relevant energy and potential parameters are identified in Fig. 33.17.

A graphical analysis of some typical experimental results will be helpful for guiding further theoretical explanation. In Fig. 33.18 a family of current-voltage characteristics shifted by the short circuit current is shown in a semi-logarithmic scale with the light intensity as family parameter. In order to show the exponential relationship directly, $\ln(j + j_L)$ is plotted versus V . In addition to the excellent fulfillment of the exponential law [Eq. (33.20)] one observes four remarkable properties:

- (1) the quality factor increases with increasing light intensity;
- (2) all curves intersect at a common point at about $I + I_L = 0.5$ A and $V = 0.7$ V;
- (3) $\ln(j_L)$ versus V_{oc} curves also lie on a straight line, but with a different slope B , according to

$$j_L = j_0^* \exp\left(\frac{eV_{oc}}{BkT}\right). \quad (33.25)$$

- (4) The pre-exponential factor j_0 in Eq. (33.20) is related to the saturation current j_L according to a power law

$$J_0 = aj_L^B \quad (33.26)$$

with the exponent B identical to the slope factor in Eq. (33.25).

¹³Observe that we split off an exponential with the diffusion voltage that does not contain A .

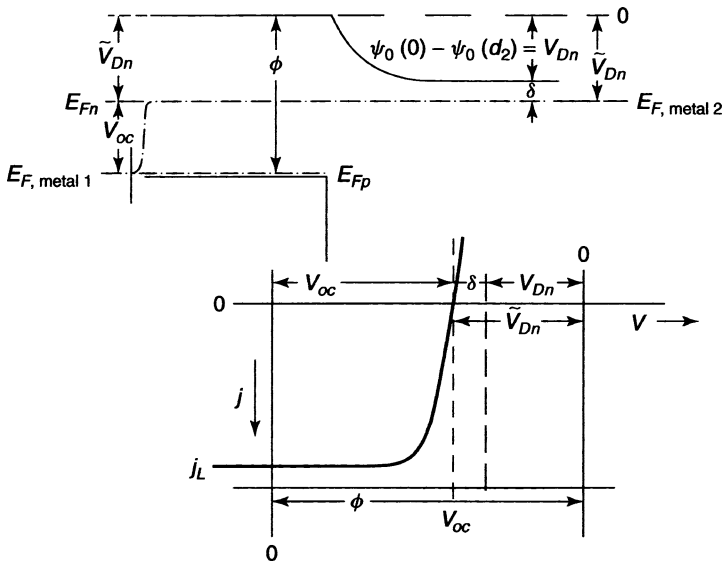
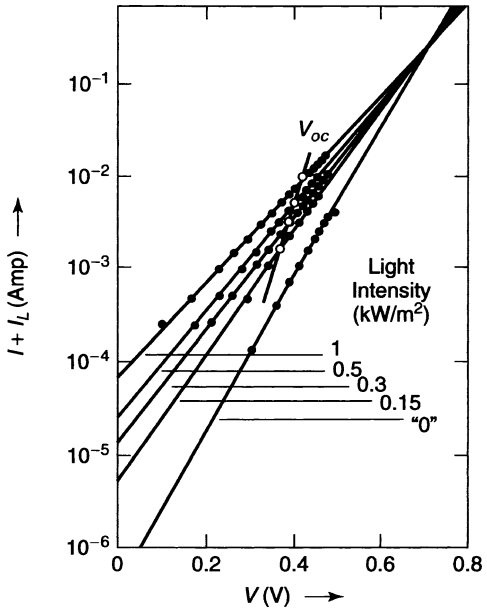


Fig. 33.17 Band model of the $\text{Cu}_2\text{S}/\text{CdS}$ solar cell and corresponding current-voltage characteristics with potential and energy parameters identified

Fig. 33.18 Current-voltage characteristics shifted by the short circuit current versus applied voltage for a $\text{Cu}_2\text{S}/\text{CdS}$ solar cell with the light intensity, expressed in kW/m^2 with air mass 1 sunlight spectrum, as family parameter. Curve “0” measured without intentional illumination except for room stray light. Beyond the range indicated by dots, the measured curves deviate from the exponential law
 $T = 300 \text{ K}$ (after Böer 1981a)



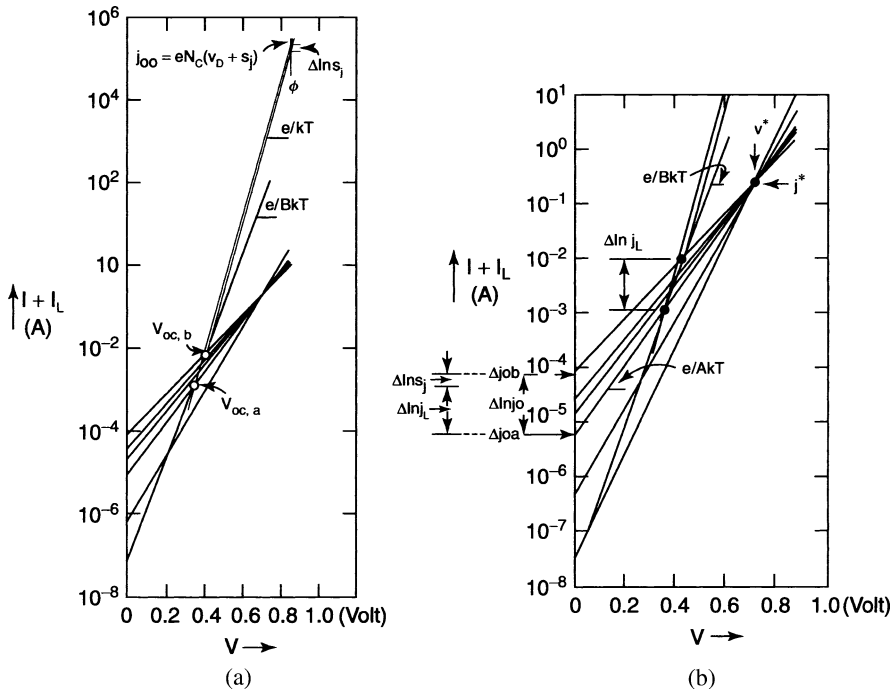


Fig. 33.19 Measured characteristics as in Fig. 33.18. (a) With Boltzmann solution extending from V_{oc} to Φ for two curves (a) and (b), and (b) highlighting the larger spread of j_0 compared to the spread of j_L , causing the fanning-out of $j(V)$ and their intersect at (j^*, V^*)

This can be seen from Fig. 33.19 when extending the curves from V_{oc} at a slope $e/(kT)$ and not $e/(BkT)$ [Eq. (33.21)]. One observes a parallel shift by $\Delta \ln s_j$ as shown in Fig. 33.19a. Such a shift can be explained from

$$j_0 = en_j(V=0)(v_D^* + s_j) \quad (33.27)$$

that results for $s_j \gg v_D^*$ in

$$\Delta j_0 = en_j \Delta s_j + es_j \Delta n_j \quad (33.28)$$

and can be approximated with $j_s = en_j s_j$ and $j_L = en_j v^*$ by

$$\Delta \ln j_0 \simeq \Delta \ln j_s + \Delta \ln j \quad (33.29)$$

in agreement with the geometric picture drawn in Fig. 33.19b, that yields from Eq. (33.26)

$$B \simeq \frac{\Delta \ln j_L + \Delta \ln j_s}{\Delta \ln j_L} \quad (33.30)$$

The larger spreading of j_0 compared to that of j_L and caused by a change in j_s results in the fanning out of the characteristics $j(V)$ and causes the intersect of these curves at $j^*(V^*)$, as identified in Fig. 33.19b.

The quality factor A is related to the slope B (Böer 1980) by

$$A = \frac{-\frac{eV^*}{kT}}{B \ln(\frac{j_L}{j_0}) - \ln(\frac{j^*}{j_0})}, \quad (33.31)$$

and is in reasonable agreement with $A(j_L)$ obtained from the experiment.

A consistent explanation of fanning curves is a slight decrease of the interface recombination velocity (by $\Delta s_j/s_j \simeq 0.7$) when the optical generation rate, and thereby the minority carrier density at V_{oc} is increased (here by a factor of 6.7). Such a decrease of the recombination traffic with increased generation rates indicates a partial clogging of the recombination centers. The fanning of the $\log(j + j_L)$ versus V curve can then be seen as a neat tool and sensitive indication of such partial clogging.

33.2 Lessons Learned from the CdS/Cu₂S Solar Cell

From a current-voltage characteristic that is not deteriorated by a network of series and shunt resistors one can obtain separate information on

- (1) the effective carrier diffusion length,
- (2) carrier trapping and compensation, and
- (3) carrier recombination clogging.

The first and most direct information on bulk carrier diffusion length is obtained from the saturation range, according to $j_s = eg_o L^*$, where L^* may be slightly shortened from the bulk diffusion length in short devices if competition to surface recombination is important.

The second information about the junction can be obtained from the relatively narrow range in a current-voltage characteristic between the Boltzmann and the saturation branch. Here one can obtain kinetic effects and clues about the origin and dynamics of the space charge, such as related to trapping of majority carriers and their slow thermal release, and of compensation from field-induced minority carrier release.

Third, the ideality factor, obtained from the Boltzmann range provides information about the recombination within the junction. Its dependence on optical excitation yields additional clues relating to possible recombination paths and non-linear effects, such as clogging when the current-voltage characteristic is fanning-out, providing in addition to the ideality factor A a factor B relating exponentially the saturation current and the open circuit voltage.

The fact that the Cu₂S/CdS heterojunction cell provides an almost perfect separation of the junction in a wide gap semiconductor that permits easy observation of slow redistribution of carriers over traps, and that it has a dominant recombination interface with well localized interface recombination traffic, is helpful to separate the different influences experimentally.

Chapter 34

The CdS/CdTe Solar Cell

Abstract The CdS/CdTe solar cell is chosen as another thin film polycrystalline cell with ample experimental information, relating to production and treatment methods of the CdS/CdTe cell. Many physical properties of the CdS/CdTe solar cell are given. Its crystallography is discussed. Defect chemistry is indicated from several critical treatment methods. An instructive table of predicted or measured defect levels in CdTe is given. Many different processing methods are given and the associated difference in performance are delineated. Cell degradation is correlated with various production methods. Sensitive and insensitive variables influencing the electrical properties of the CdS/CdTe solar cell are identified. The cell degradation and recuperation in the dark at elevated temperatures is discussed.

The CdS/CdTe solar cell is an example of a thin-film backwall solar cell of high technical and commercial interest. Panels of these cells are produced commercially since the mid 90s. Today multi Gigawatt of these Panels are deployed world wide from a multi billion dollar industry.

The CdS/CdTe solar cell is known as an attractive thin-film cell since its early development, starting in 1976 by Bonnett. It consist now typically as CdS deployed on a conducting glass plate at a thickness of typically 60 nm, covered with a CdTe layer of about 2 μm thickness followed by a copper containing back contact (see Fig. 34.1).

34.1 Production Methods of the CdS/CdTe Cell

There is a wide variety of processes to produce high efficient cells, typically with an efficiency between 14 and 18 %.

(1) As conducting glass a normal soda-lime or borosilicate plate glass is used with a tin oxide or indium tin oxide (ITO) or sometimes the even higher conductive Cd_2SnO_4 (CTO) (Wu 2004) conducting cover layer, the latter with typically $1.5 \times 10^{-4} \Omega\text{cm}$ conductivity, followed by a low conductive thin high resistive layer, such as undoped SnO_2 to minimize shunting. These layers are known to have high transmission in the wavelength range for solar conversion.

Fig. 34.1 Schematic of a typical superstrate CdS/CdTe solar cell

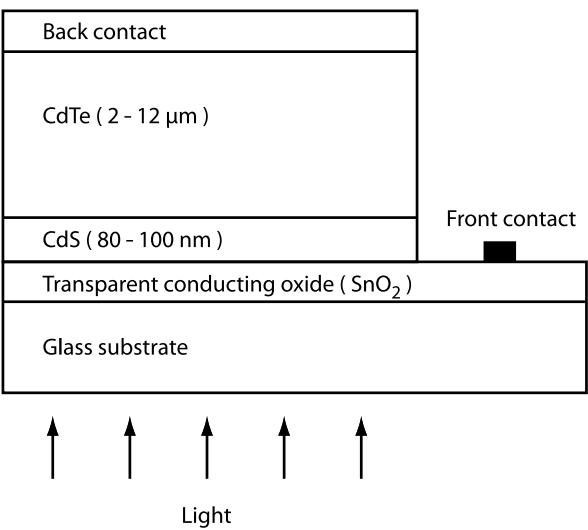
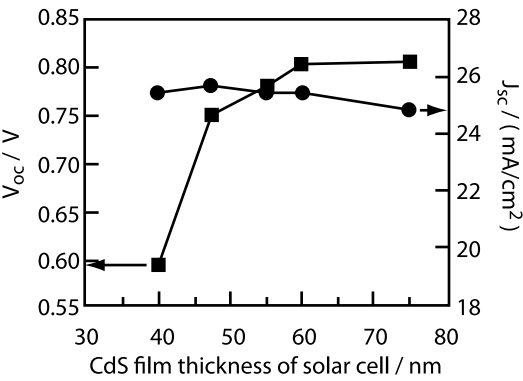


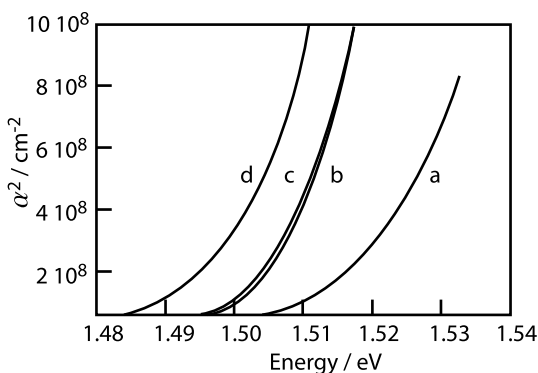
Fig. 34.2 V_{oc} and j_{sc} as a function of the CdS film thickness for a high-efficient CdS/CdTe solar cell (after Wu 2004)



(2) The CdS layer is deposited either by vacuum deposition, vapor transport deposition, sputtering, close space sublimation, or by spray deposition or even by screen printing as polycrystalline sheet, and with the final cell after careful recrystallization remarkably intensity to any of these deposition means. It is typically between 30 and 80 nm thick and may be recrystallized (in some cases before CdTe deposition). Figure 34.2 shows V_{oc} and j_{sc} as function of the CdS thickness for a high-efficient CdS/CdTe cell. The open circuit voltage increases with CdS thickness, the short circuit current decreases, probably because of additional absorption of the optical active light into the CdTe (Wu 2004).

(3) The adjacent CdTe film is deposited by any one of the methods mentioned for CdS deposition, but typical by vacuum or close space evaporation. The CdTe is *p*-type with a hole density of typical 10^{14} – 10^{15} cm⁻³ and a Hall mobility of 50–80 cm²/V s for holes and 500–1000 cm²/V s for electrons, and their effective masses $m_n = 0.09m_0$ and $m_p = 0.35m_0$. Its band gap is E_g (300 K) = 1.5 eV with a tem-

Fig. 34.3 Optical absorption coefficient squared as function of the energy of a 2.5 μm thick CdS/CdTe solar cell with 200 nm CdS (a) as deposited, (b) after high temperature anneal (HTA) at 500 °C for 30 min in argon (c) as (b), followed by CdCl₂ treatment at 420 °C for 20 min in air (d) after CdCl₂ treatment at 420 °C in air alone (after McCandless et al. 1999)



perature coefficient $dE/dT = -0 \text{ eV/K}$. Its static and high frequency dielectric constant is 10 and 7.1 respectively, the thermal expansion coefficient is $50.9 \times 10^{-6}/\text{K}$ (Birkmire and McCandless 1992). For the CdS/CdTe device it is typically between 2 and 8 μm thick.

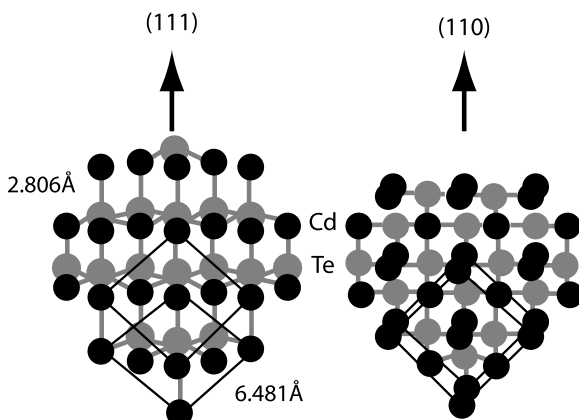
(4) The sandwich is sometimes first high-temperature (500 °C) treated in air (McCandless et al. 1999), or more typically a heat treatment with a thin layer of CdCl₂, in an oxygen containing ambient, or, sometimes with a treatment sequence of bromine methanol (5–10 s at 25 °C) to remove surface contamination and a thin layer CdTe, leaving a terminating Te layer followed by a concentrated dichromate (1 s 25 °C) solution to convert part of it to TeO, that is again converted to a Te layer by dipping in a N₂H₄ (hydrazine) solution (60 s at 40 °C) (Hegedus and McCandless 2005). Typical changes in the optical absorption spectra depending on treatments is shown in Fig. 34.3 (McCandless et al. 1999).

(5) The back electrode is typically a thin tellurium layer followed by a copper layer, followed by etching in a Br₂-methanol solution and then covered with a thicker current carrying Metal contact of Au, Mo or Ni, or alternatively with a Cu and Hg doped graphite inc. Before the back electrode is completed the CdS/CdTe sandwich is baked at a temperature between 300 and 500 °C (e.g. 15 min at 350 °C Kumuzawa et al. 1997) for annealing in a vapor mixture of CdCl₂ and oxygen to facilitate recrystallization and doping of the CdTe (McCandless and Buchanan 2008).

The electrodes and their deposition/treatment techniques have a major influence of the performance of the CdS/CdTe solar cell and its degradation.

A large volume of literature describes slight variation in the deposition and following treatments to achieve high efficiency and stability of these cells. It is beyond the scope of this book to enumerate and evaluate these procedures.

Fig. 34.4 CdTe crystal structure: Zinkblende with Cd atoms in black and Te atoms in gray (from McCandless and Sites 2003)



34.1.1 Physical Properties of the CdS/CdTe Solar Cell

A large variety of properties are reported, from crystallographic, defect chemistry, electrical and life expectancy investigations. We will here summarize the mayor results.

34.1.2 Crystallography

Both CdS and CdTe are hexagonal with the c -axis $\langle 111 \rangle$ as deposited preferably orthogonal to the substrate. The preferred crystal structure is tetrahedral zinkblende (wurzite structure is rarely observed). The Zinkblende Structure of CdTe is shown in Fig. 34.4 (McCandless and Sites 2003).

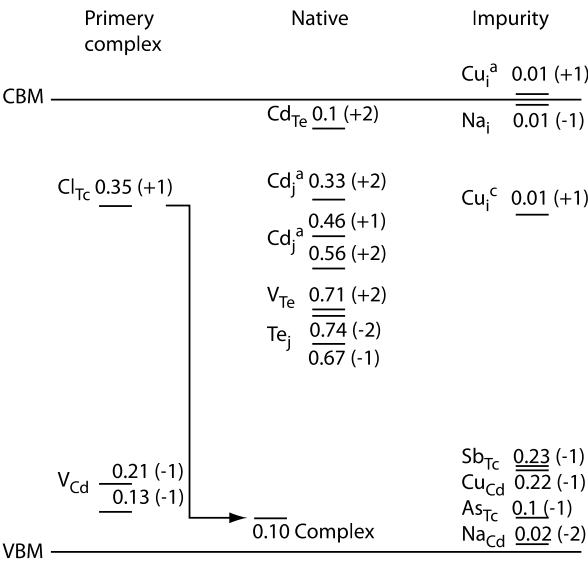
The two layers are contacted directly without a market interlayer. They are initially highly polycrystalline, but recrystallise easily with the help of a thin layer of a flux, typically of CdCl_2 applied from a liquid solution or by evaporation during a heat treatment typically of 30 min in air or oxygen and argon ambient at about 400°C . The cells are then rinsed in an aqueous solution of etchants, typically H_2O_2 or diluted acids to remove surplus Te. They show preferably columnnar structure with grain size on the order of $2\text{--}5\text{ }\mu\text{m}$ (Metzger et al. 2003) and become more randomly oriented (McCandless et al. 1999).

Dependent on the actual deposition and recrystallization/treatment method the size and orientation of the crystallites deviate substantially with significant influence on the cell efficiency.

34.1.3 Defect Chemistry

During the heat treatment there is slight interdiffusion of S and Te close to the boundary but not to an extend to produce a marked layer of a mixed crystal of

Fig. 34.5 CdTe predicted defect levels with charge states for donors (positive) and acceptors (negative) states (McCandless and Sites 2003)



CdS_xTe_y . However, a marked influence of the interface composition can be observed e.g. with S termination of CdS, connected directly to Cd of the CdTe. The actual interface chemistry has a significant influence on the electrical properties of the cell.

Copper is incorporated into CdTe and CdS interstitially and saturates in CdS at about 100 ppm. The electrical properties vary significantly dependent on the reservoir of Cu at the cell surface. Any surplus is etched away with a bromine methanol solution, or hydrazine or diluted acids.

The defect level distribution for copper and other dopands and intrinsic defects is shown in Fig. 34.5.

The back contact is sometimes graphite, doped with Hg and Te, or thin layer of copper followed by the current metals such as gold, nickel, molybdenum, or other metals.

34.1.4 Processing and Performance

Even though the sequence of processing steps, the deposition of a thin layer of CdS onto a conducting glass slide followed by the deposition of a thicker CdTe layer with consequent heat treatment in an ambient containing oxygen, and recrystallization including steps with CdCl_2 and tellurium and copper and finally some etching of the sandwich where similar there was a large degree of variation in the type of deposition, treatment temperature and ambient, as well as recrystallization steps and etching procedures, and finally with the selection of the base electrode. A large body of publication described in detail these procedures and the resulting cell performances (Hegedus and McCandless 2005).

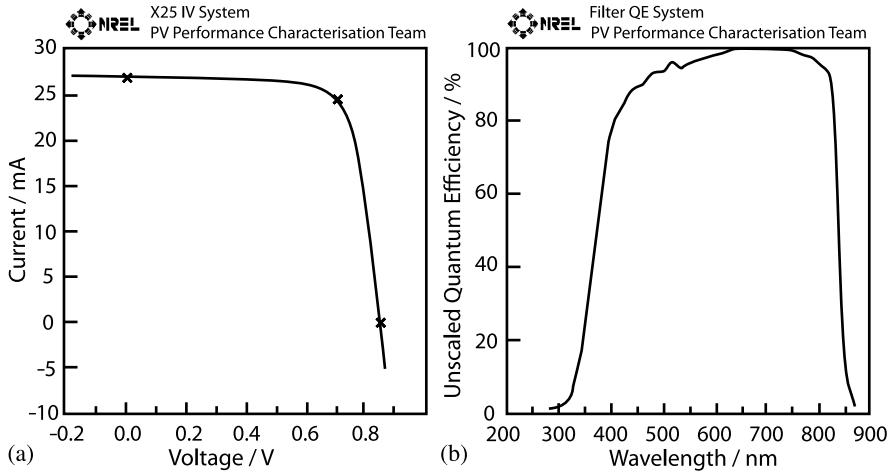


Fig. 34.6 Typical current voltage characteristic (a) and relative quantum efficiency (b) for a high efficient (16.5 %) CdS/CdTe solar cell (Wu 2004)

The difference of performance where significant, but all were lying between 8 and 16 % efficiency, a V_{oc} between 500 and 860 mV, a short circuit current between 16 and 26 mA/cm², and a fill factor between 63 and 76 %. The choice of processing steps was often dictated by economic reasons, using fast processing method with rapid throughput and good process yield of useful cells with similar performance in excess of 85 % (McCandless and Buchanan 2008). For producing large panels in sizes extending beyond one m², additional request of the production steps were imposed, to guarantee total edge-to-edge efficiencies in excess of 10 % and life expectancies within 80 % of the initial performance well in excess of 10 years. With these, large production lines with throughput in excess of 1 Megawatt were established and commercially sold to a number of customers world wide.

34.2 Electrical Properties of the CdS/CdTe Solar Cell

Figure 34.6 shows a high efficient CdS/CdTe cell current voltage characteristic with $V_{oc} = 845$ mV, $j_{sc} = 25.88$ mA and a fill factor of 75.51 % for a total efficiency of 16.5 %. This cell was a typical CdS/CdTe cell, however deposited on conducting glass with a Cadmium stannate (CTO/ZTO)¹ conducting/buffer layer.

In first approximation, the current-voltage characteristics follow the typical diode equation, shifted by the short circuit current, j_L :

$$j = j_0 \exp(-eV/AkT) - j_L \quad (34.1)$$

¹This is a double layer of highly conductive cadmium stannate, Cd₂ SnO₄ followed by a buffer layer ZTO (Cd₂SnO₃).

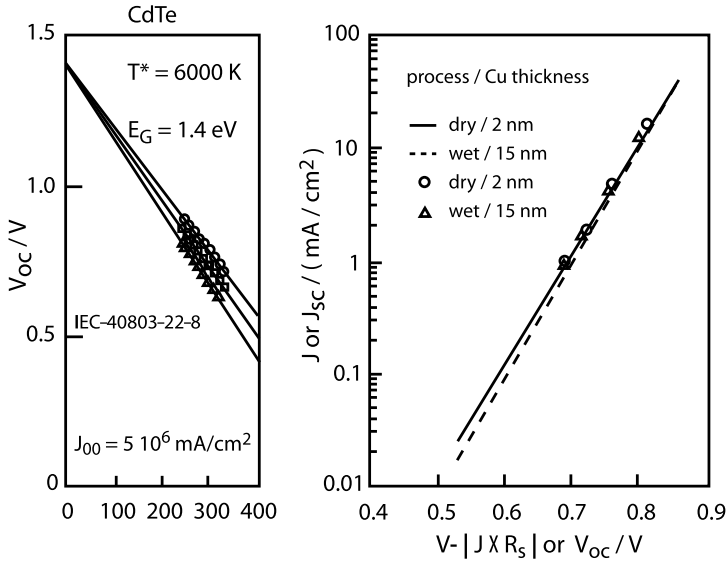


Fig. 34.7 Open circuit voltage as function of the temperature (a) (Phillips et al. 1996a),² and of the logarithm of the shot circuit current (b) (Hegedus and McCandless 2005)

with j_0 the dark current:

$$j_0 = j_{00} \exp -(E_g / A k T) \quad (34.2)$$

if shunt and series resistances can be neglected in better cells. A is the diode ideality factor which is related to interface recombination and E_g is the band gap of the emitter (CdTe).

From Eqs. (34.1) and (34.2) one derives for vanishing current the open circuit voltage as

$$V_{oc} = E_g / e - (A k T / e) \ln (j_{00} / j_L). \quad (34.3)$$

This relation is one criterion of an excellent cell, if V_{oc} approaches the band gap of CdTe when extrapolated to $T = 0$ K (see Fig. 34.7a). From Eq. (34.3) one also concludes the V_{oc} increases with the logarithm of the short circuit current (shown for different base electrodes in Fig. 34.7b).

When including the series resistance with

$$V_{oc} = V + j_R \quad (34.4)$$

one has an easily measurable diode ideality factor from the derivative:

$$dj/dV = (A k T / e) (j / j_L) \quad (34.5)$$

where, from Eqs. (34.4) and (34.5) one obtains the A factor +1.6 and the series resistance of 1.4 and 2.3 Ω cm² for a cell with dry (evaporation of Cu and Te) and wet processing (etching) respectively (see Fig. 34.8). This reflects a more intimate contacting by evaporation compared to the etching (Hegedus and McCandless 2005).

Fig. 34.8 dV/dj as function of the reciprocal current for two CdS/CdTe solar cells with different back contact with sequential tellurium and copper layer as identified within the picture. All similarly produced cells show an ideality factor of 1.6. The curve shift shows the influence of the series resistance (Hegedus and McCandless 2005)

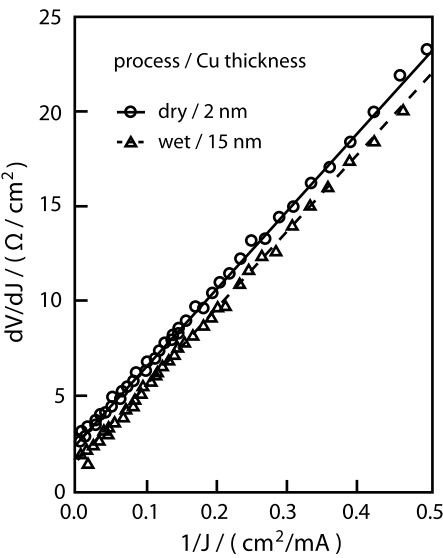
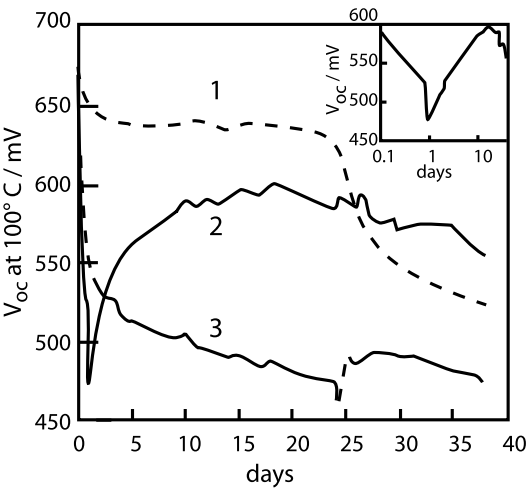


Fig. 34.9 V_{oc} degradation of a CdS/CdTe at 100 °C kept at j_{sc} for 25 days and the switched to V_{oc} kept at V_{oc} for one day and then switched to j_{sc} (curve 2); and kept at V_{oc} for 35 days and then switched to j_{sc} (after Hegedus et al. 2007)



34.2.1 Cell Degradation

The CdS/CdTe solar cell is found to be relatively stable in normal exposure to day/night cycles and loaded close to the maximum power point.

However, a substantial decrease of the open circuit voltage in time can be observed under constant full (AM1) light at slightly elevated temperatures. The main decrease is found when the cell is kept in the open circuit voltage but can (partially) be recovered when returned to short circuit load in the dark (see Fig. 34.9).

Fig. 34.10 Light (AM1) and dark current voltage characteristics before and after degradation at 100 °C at AM1 for 24 days. The figure also contains the same set of curves after recontacting the cells (after Hegedus and McCandless 2005)

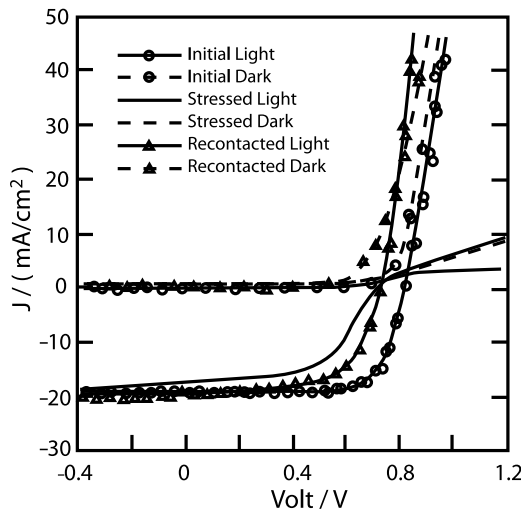
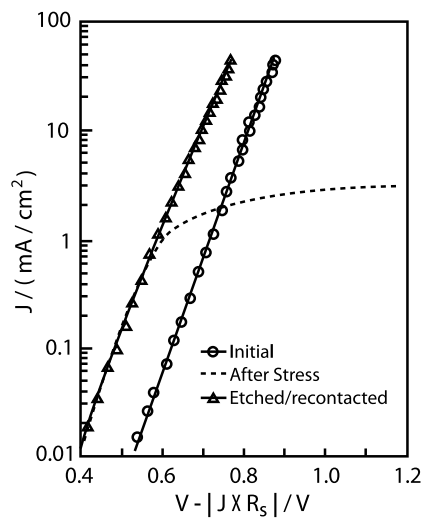


Fig. 34.11 Current–voltage characteristics measured in the dark before and after degradation for 25 days at AM1 and 100 °C and after recontacting (after Hegedus and McCandless 2005)



Cells that were kept at 100 °C and AM1 illumination degraded when in open circuit conditions dependent o back contacts in one month by about 80 mV but recovered nearly fully when left in the dark for a few days. Little degradation was observed at outdoor exposure with day and night cycles. When loaded at maximum power point degradation was further reduced.

The degradation of the current voltage characteristic is shown before and after the exposure to AM1 light at 100 °C for 25 days is shown in Fig. 34.9, measured before and after degradation. They show a reduction in efficiency and bending over at higher bias that is typical for such characteristics. The figure also contains the

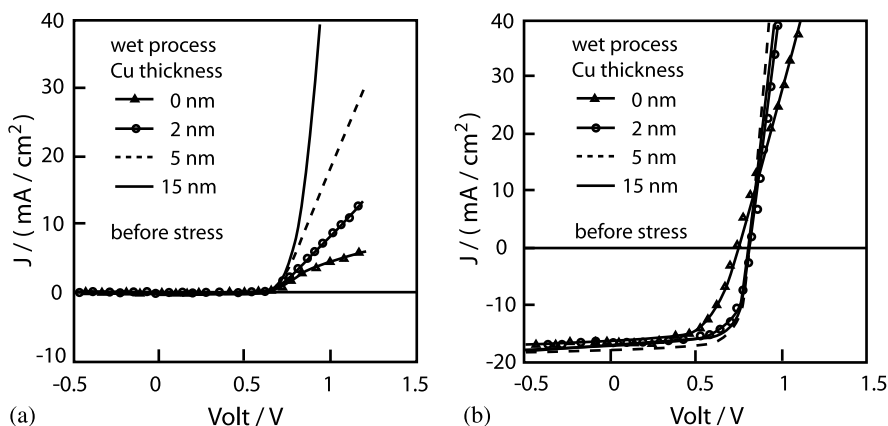


Fig. 34.12 Current-voltage characteristics in the dark (a) and under AM1 illumination for CdS/CdTe solar cells with copper back contacts of different thickness, as indicated in the figures (after Hegedus and McCandless 2005)

same set of dark characteristics showing the strong decrease of the diode effect. The back electrodes of these cells have then etched-off and were recontacted, showing partial restoration of the characteristic, however with remaining degradation of the open circuit voltage.

Degradation after the same light exposure as discussed above shows the degradation in the back contact by shifting the dark current to higher values and substantially reducing the diode effect (bending over at higher bias). The dark current degradation cannot be reversed by recontacting the device after etching away the initial contact (see Fig. 34.10).

The back contact of the CdS has an essential influence on the cell degradation. The difference between wet and vapor deposition of the Te/Cu contact is shown in Figs. 34.10 and 34.11. However, the thickness of the vapor deposited Cu layer is critical. It is especially visible in the dark characteristics Fig. 34.12a where a copper layer of at least 15 nm is required to show reasonable diode characteristics, while the characteristics at AM1 are less sensitive to copper layer thickness and show for copper layers above 2 nm already good conversion efficiencies (see Fig. 34.12b).

For more detail of the sensitivity of the CdS/CdTe solar cell to degradation relating to the specifics of the back contact see the original paper of Hegedus and McCandless (2005).

Chapter 35

CdS/CdTe Analysis and Modeling

Abstract Simple mathematical solar models are introduced, starting from diode models with various amounts of adjustable parameters. Model applications are discussed. Current voltage characteristics are analyzed. Extensive comparison is made with different cell types and different production modes. Encouraging results are obtained from specific diode models with only two adjustable parameters showing surprising agreements with a large number of experiments. These results are compared with the solution curves (current voltage characteristics) of the transport and Poisson equations that contain in addition to some well-known parameters as e.g. band gap, optical absorption constant, and carrier mobility and some derived parameters, as minority carrier life time, most parameters that determine the quasi Fermi levels and band interconnections are missing. Consequently, even though the integration of this set of equations delivers instructive distribution of carrier density, space charges, potential and field distributions, the large quantity of adjustable parameters renders the results questionable and possibly misleading.

An analysis of a thin-film heterojunction solar cell requires the identification of every element of the cell their sizes, interconnection, and defect structure. Except for the most basic parameters, as elements, such as back electrode (Cu/Te) emitter (CdTe) collector (CdS) and front electrode (TiO) with their respective dimensions and crystallography information), little is known about the electronic interconnection that is band connection between the electrodes and CdTe or CdS and the band connection between CdS and CdTe. Little information is available about the defect distribution in energy and space, as well as most of their electronic transition coefficients.

Consequently derived parameters as e.g. Fermi or quasi-Fermi levels are elusive and carrier life times can be derived from experiments only after accepting general basic models. A thorough understanding of the main experimental output, the current-voltage characteristic based on an analysis of transport, Poisson and continuity equations for both carriers is impossible except for assuming a host of these unknown parameters, using general but probable values.

This makes it inadvisable to use packages of solving the complete set of differential equations and inserting parameters that may be plausible, but most of them are unproven by independent experiments. When adjusting the even a few of these

parameters to make the solution curves fit the experiment, usually a current voltage characteristic, one is tempted to attach too much meaning to these results, recognizing that they were produced by one of the most sophisticated computer programs.

On the other hand, assuming relative simple models with more than four adjustable parameters are sufficient to approximate any characteristics within the experimental errors, but conclusions derived from these models are again easily misleading to design device improvements. A typical example is the addition of a network of shunt and series resistors to a basic diode equation, that resulted in agreement with the experiment, but searching for such actual resistors was mostly in vain.

35.1 Simple Mathematical Models

There are a few exceptions to these rules when modeling certain parts of a device that can be separated with specific experiments to give useful indications that can guide certain parts of the production processes that influence these results. This is especially useful if a relation to important device performance parameters, like V_{oc} , j_{sc} , FF , and efficiencies can be established.

In recognizing these limitations, we will here resort to some simple models that are commonly used and permit cell classifications according to measurable parameters.

An early model expresses the collection efficiency η as function of the drift velocity μF_0 and the recombination velocity in the junction region:

$$\eta_c(V) = \mu F_0(V) / [S + \mu F_0(V)]. \quad (35.1)$$

This assumes that the carrier transport in a sufficiently wide junction region is determined by e built-in field within this region and a simple recombination velocity can be defined within the range of interest, e.g. around the maximum power point of the characteristic. We will return to this simple model, requiring only two adjustable parameters, the interface recombination velocity S and the field F , when discussing some experimental results.

The next step is to assume that the Field can be modeled similar to in a simple pn -homojunction as

$$F(V) = [(2eN_A/\epsilon)(V_B - V)]^{1/2} \quad (35.2)$$

with N_A the acceptor density and V_B the built-in potential. Here we assume a voltage dependent depletion width $W(V)$ yielding

$$\eta_c(V) = [1 - \{\exp(\alpha W(V))\} / (1 + \alpha L)] \quad (35.3)$$

where α is the effective optical absorption constant and L is the diffusion length. The voltage dependent depletion width will determine the voltage dependent photoelectric collection efficiency:

$$W(V) = [\{2\epsilon(V_B - V)\} / (eN_A)]^{1/2} \quad (35.4)$$

This model has four parameters that are approximately known for CdTe, hence left are the fitting parameters, αN_A , L and V_D . The absorption constant can be approximate weighted CdTe absorption coefficient that can be obtained from the current-voltage characteristic measured under sunlight.

The losses via recombination in the high-field region within the junction has the form of a Hecht-like equation:

$$\eta_c(V) = X(V)[1 - \exp\{-X(V)^{-1}\}], \quad (35.5)$$

with

$$X(V) = X_C(1 - V/V_0) \quad (35.6)$$

now with only two fitting parameters X_C and V_0 . This equation is widely used for fitting the measured voltage dependent collection efficiency in α -Si and a SiGe p - i - n solar cells (Hegedus 1997).

When the field can be assumed to increase linearly with the applied voltage, as

$$F(V) = (V - V_0)/L \quad (35.7)$$

with some experimental evidence (Hegedus et al. 2007). With the diffusion length on the volume

$$L_C = \mu\tau E(0) \quad (35.8)$$

and

$$X_C = \mu\tau V_B/d^2 \quad (35.9)$$

with d the i -layer thickness, hence the fitting parameter X_C represent the ratio of L_C/L , as seen from

$$X_C = \mu\tau E(0)/d = L_C/d \quad \text{or} \quad \alpha = \tau_R/\tau_D \quad (35.10)$$

Several assumptions about the field distribution that may apply to α -Si n - i - p do certainly not hold for the CdS/CdTe solar cell. Therefore more sophisticated models seem to be required. This has been done by several authors, but requires many more adjustable parameters.

Therefore it seems to be justified to use one of the above given models to relate to the experiments dealing with current-voltage characteristics and derived collection efficiencies, and some useful correlation to experimental formation methods of the CdS/CdTe solar cells may be extracted, as will be discussed below.

35.2 Model Application

We will now apply the simplified models described in the previous section to the measurements of the CdS/CdTe solar cells that were prepared by sequential evaporation and treatments as described in Chap. 36 and had the CdTe layer of 1.7 μm

Fig. 35.1 Current voltage characteristics of CdS/CdTe solar cell with ED back electrode and CdTe thickness of 1.8 μm (Hegedus et al. 2007)

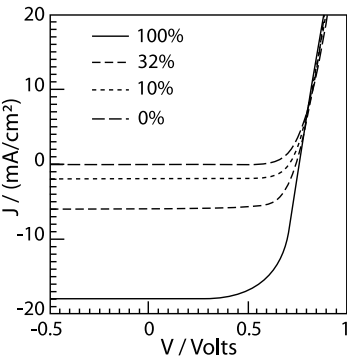
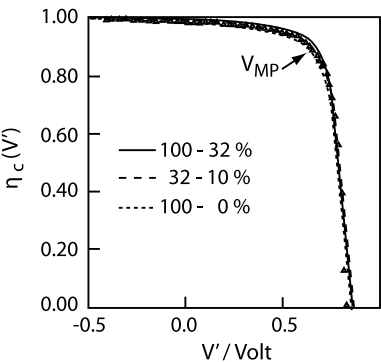


Fig. 35.2 Collection efficiency calculated using Eq. (35.5) using the difference of several pairs of curves from Fig. 35.1 (pairs identified within the figure) (Hegedus et al. 2007)



thickness. They were identical for all measurements except for the contacts which were Tre and Cu either vacuum deposited (VD) or etch deposited (ED) as identified in each case.

For the next experiments we will always refer to the difference of the full AM1 characteristic minus the dark curve to eliminate the influence of the series resistance. We have drawn this a data in Fig. 35.3 and will now attempt to approximate this one curve by the three models IFC, $n-p$, and $n-i-p$ represented by Eqs. (35.2), (35.3) and (35.4) respectively. In this figure the best approximation for these three models are drawn. Neither the ICF model nor the $n-p$ model let us approach the measured curve completely, while the $n-i-p$ model did (Fig. 35.3).

The best fitting parameters for the three approximations: IFC (Eq. (35.3)), $n-p$ (Eq. (35.3)) and $n-i-p$ (Eq. (35.5)) are given below

IFC:	$S = 73 \times 10^4 \text{ cm/s};$ $V_0 = 0.8 \text{ V};$	$\mu = 283 \text{ cm}^2/\text{V s};$ MSE (mean square error) = 0.55	$N_A = 10^{14} \text{ cm}^{-3};$
$n-p$ model:	$\alpha = 1.8 \times 10^4 \text{ cm}^{-1};$ $N_A = 1.5 \times 10^{14} \text{ cm}^{-3};$	$L = 1.1 \times 10^6 \text{ cm};$ $V_0 = 0.7 \text{ V};$	MSE = 0.14;
$n-i-p$ model:	$X_C = 21;$	$V_0 = 0.81 \text{ V};$	MSE = 0.094.

Fig. 35.3 Collection efficiency to fit the 100–0 % curve from Fig. 35.2 for the three models IFC, p - n and p - i - n . For the obtained fitting parameters see text (Hegedus et al. 2007)

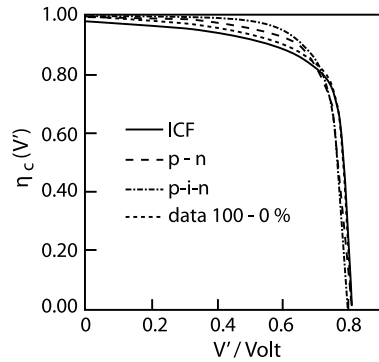
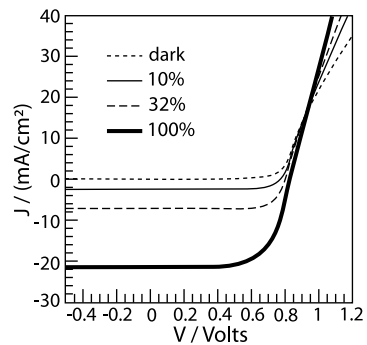


Fig. 35.4 This figure shows an example of the same set of current-voltage characteristics as shown in Fig. 35.1, however taken from a slightly thicker CdS/CdTe cell of 3.5 μ m CdTe thickness and contacted by vacuum treatment (Hegedus et al. 2007)



These parameters are identified by the models with certain physical parameters, as listed. Some are new parameters, some represent the same physics parameters but now have different values to produce best approximations. Examples are N_A and V_0 between the first and second model and V_0 that must be further changed for the third approximation, which interestingly enough is able to approximate best the measured curve *with only two adjustable parameters*.

This may be interpreted that the n - i - p model describes the physics of the CdS/CdTe solar cell operation best, but it deals solely with the collection efficiency curve derived from the characteristics. This important difference is essential to understand the value of the empirical approximations given here, that is, the values of the physical parameters derived from it may actually be quite different when a “correct model” for the cell could be used. This is an essential warning that one should not read too much value into any such parameters. That is different from the specific physical parameters that are directly obtained from the experiment, e.g. the (Hall) mobility from the Hall effect experiment, or the optical absorption constant based on direct optical experiments.

Nevertheless these, and further related measurements described below can have some value for characterization of specific production methods or to improve for further ones.

When converted to collection efficiencies like the previous Fig. 35.2 the curves and approximations look quite similar, however giving substantially different pa-

Fig. 35.5 Current-voltage characteristics of CdS/CdTe solar cells of 7 μm thickness CdTe with Cu/Ni (2) or simple Ni contacts (3). Curve (1) before and curve (2) and (3) after degradation (Hegedus et al. 2007)

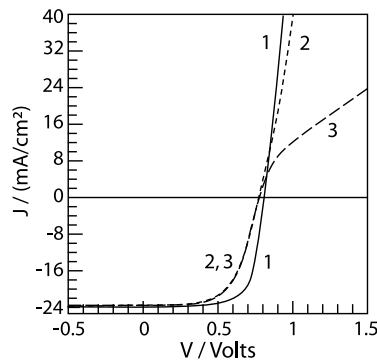


Table 35.1 Hegedus et al. (2007)

Condition	V_{oc} (V)	j_{sc} (mA/cm ²)	FF (5)	Efficiency (η)
As measured	0.805	23.7	69.8	13.3
Corrected for R	0.805	23.7	71.5	12.4
Corrected for R and $\eta(V)$	0.826	23.8	81.9	16.1
j_0 shifted by j_{sc}	0.826	24.0	81.0	16.0

parameter values. So is the diode ideality factor here 1.8 rather than 1.6 as in most of the other cells $X_C = 22.5$ and $V_0 = 0.84$ eV.

Another significant difference between the characteristics is observed after degradation in the dark, here shown as example after 25 days at 80 °C at open circuit condition as shown in Fig. 34.11.

Here, the copper layer is essential to reduce the degradation in open circuit condition. The value for the cell fitting parameters for the n - i - p model are

Cu/Ni	$J_L = 24.4$ mA/cm;	$J_0 = 1.5 \times 10^{-7}$ mA/V/cm;	$A = 1.49$;
	$X_C = 21.2$;	$V_0 = 0.85$ V;	MSE = 0.0086
Cu/Ni, dgr.	$J_L = 24.4$;	$J_0 = 1.66 \times 10^{-7}$;	$A = 1.66$;
	$X_C = 12.5$;	$V_0 = 0.80$;	MSE = 0.0003
Ni only	$J_L = 24.2$;	$J_0 = 1.4 \times 10^{-7}$;	$A = 1.63$;
	$X_C = 13.3$;	$V_0 = 0.80$;	MSE = 0.0056

A systematic data analysis of a large number of samples may give some indication for future cell improvement.

With the measurements shown here it is also easy to correct the measurements for series resistance $\eta(V)$ and for j_D shifted by j_{sc} . The values for V_{oc} , j_{sc} , FF and efficiency η is given in Table 35.1.

Table 35.1 performance of CdS/CdTe solar cell as in Fig. 35.5 with Cu/Ni contact (Hegedus et al. 2007)

For more detail we have to refer to the original paper of Hegedus et al. (2007).

Chapter 36

Basic Physics Discussion of CdS/CdTe

Abstract A basic physics discussion of the CdS/CdTe solar cell is given. Characteristic behavior of a CdTe solar cell when a thin layer of CdS is added to the surface is given. The field distribution in the CdS side of the junction is computed. Field quenching and critical fields are calculated. High field domains are introduced. A Domain analysis is given. The field-of-direction method is introduced. Field limitation at the junction interface are obtained. A reduction in junction leakage is suggested. Experimental evidence of high field domains, using the Franz-Keldysh effect are given. The relevance of high field domains in hetero junctions is demonstrated. The question why only CdS yields such a performance improvement is answered with experimental evidence. Consequences of field quenching for inter band connections are given. Summary and conclusion are given.

In the previous chapters we discussed the performance of solar cells based on an analysis of the current voltage characteristics, using a simple band model and applying transport, Poisson and continuity equations. Since such detailed discussion would require the knowledge of all involved parameters, most of them are not presently available, one resorts to approximations that are based on the diode equation. After using a number of additional approximations one usually arrives at a current-voltage characteristic and related experimental results, that contain in addition to well-known parameters such as the band gap or the carrier mobility only a limited number of adjustable parameters with the help of which the experimental results can be approximated with sufficient accuracy.

As indicated in the previous chapter, such approach assumes the validity of the diode (modified as it may be) as valid for the basis of the discussion. It does not permit simple expansions of this model to encompass specific phenomena that occur within the solar cell and are not included in the diode-type discussion. We will in the following give a few examples as they apply to the CdS/CdTe solar cell (Böer 2009a, 2009b). We will start from a remarkable experimental observation that seems to be characteristic of the combination of an emitter (here CdTe) with cadmium sulfide and cannot easily reproduced with any other compound (Böer 2010).

It is shown that a thin layer of CdS on top of a CdTe Solar Cell improves the efficiency substantially. We will show in this chapter that this is caused by an increase, mainly of the open circuit voltage. This is reasoned as a result of reduced

junction leakage and caused by a limitation of the maximum junction field (Böer 2012a, 2012b). Such a limitation can be achieved by the creation of a high-field domain in the copper-doped CdS, adjacent to the junction (Böer 2011a, 2011b). The domain is initiated by field-quenching, that with further development creates a range of negative differential electron conductivity that forces the domain creation. Within the domain the field is limited to the domain field of about 80 kV/cm, that is well below initiating of any tunneling (Böer and Voss 1968c).

In drawing a band diagram one has to take field-quenching into consideration that forces further separation of the Fermi-level from the conduction band in CdS and hence a separation from the conduction band of the CdTe at the interface when approaching V_{oc} from forward bias. A suggested band diagram of the CdS/CdTe solar cell will be shown (Böer 2010).

The proposed theory is derived from basic principles and distinct from the classic analysis of modeling the IV-characteristics

36.1 Introduction

There are numerous methods to improve the efficiency of CdTe solar cells (McCandless et al. 2005; Hegedus et al. 2007); these are not the subject of comparison in this chapter. We will restrict our discussion to the well-known improvement of the CdTe by a relatively thin (a few 100 Å thick¹) cover layer of CdS (McCandless 2005). In early discussion this was related to a reduction of the mismatch of the index of refraction (reducing sunlight reflection), but it could not explain the significant improvement of the open circuit voltage.

The open circuit voltage of an ideal CdS/CdTe hetero-junction should extrapolate to the band gap E_G of CdTe,

$$V_{oc} = E_G/e - (AkT/e) \ln(J_{00}/J_L). \quad (36.1)$$

This is indeed the case for the CdS covered cell as shown in the lower part of Fig. 36.1 (Thompson et al. 2006), but not in the uncovered CdTe solar cell as shown in the upper part. The puzzle, why CdS was so beneficial, but not any of the other compounds that were tried to replace CdS, was unresolved for more than three decades (Böer 2009b). To obtain more information, it is essential to investigate the intrinsic properties of the CdS and their relevance to the CdS/CdTe hetero junction which will be done in the following section.

36.2 Field Distribution in the CdS Side of the Junction

To help such analysis, we will first discuss the field distribution in the CdS part of the junction for different bias conditions as a family parameter. In first approximation,

¹For thinner cover layers or topographic layer inhomogeneities the reverse bias saturation current starts to increase again.

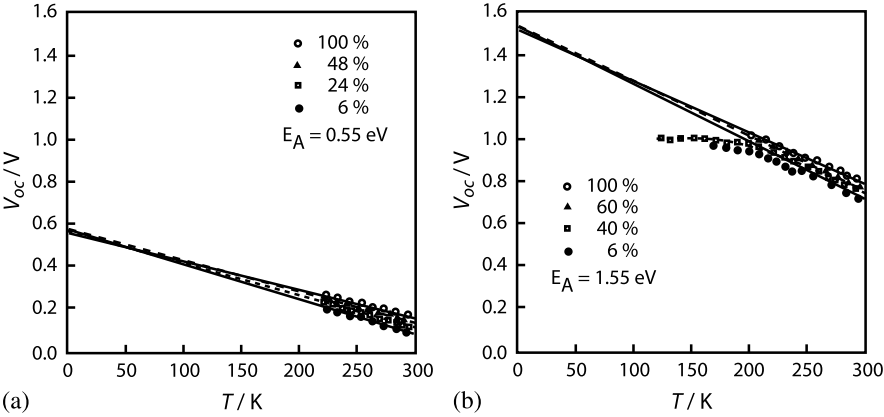
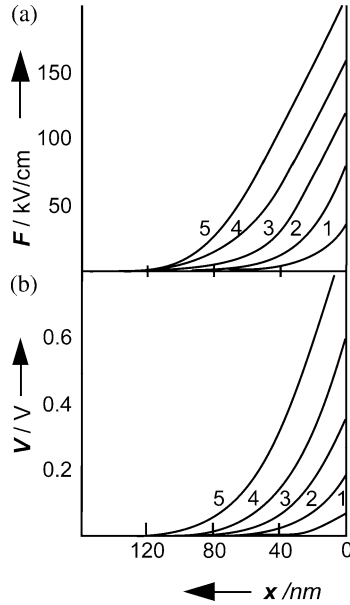


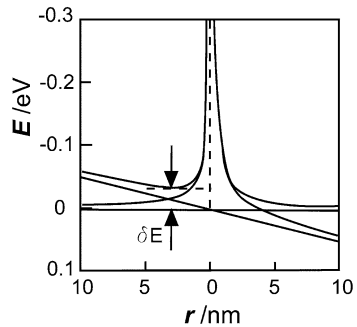
Fig. 36.1 Open circuit Voltage as a function of the temperature for CdTe (*upper figure*) and for CdS/CdTe (*lower figure*) extrapolated to $T = 0$ K, the light intensity is family parameter (Thompson et al. 2006)

Fig. 36.2 Field and potential distribution on the CdS side of the CdS/CdTe hetero junction as function of the distance from the junction; family parameter is the bias across the CdS part of the solar cell (Böer 2008)



this field increases linearly from its bulk value to the junction interface, similar to a Schottky barrier Böer (2008) with a slope, relating to the trap density. For Fig. 36.2 it is calculated for a trap density of 10^{17} cm^{-3} . In forward bias the maximum field at the junction interface is on the order of 20 kV/cm. But it increases rapidly as the open circuit voltage is approached. Toward further reverse bias it can reach tunneling values.

Fig. 36.3 Potential distribution of a Coulomb-attractive hole-trap with and without an electric field, calculated for CdS and a doubly charged Cu. The lowering of the ionization energy with field, δE is indicated (Böer and Dussel 1967a, 1967b)



When the field increases above 20 kV/cm, a new process must be considered, as soon as the ionization energy of a Coulomb-attractive copper center is lowered by Frenkel-Poole excitation, as shown in Fig. 36.3. It is given by

$$\delta E = e(eFZ/\pi\epsilon_{st}\epsilon_0)^{1/2} \quad (36.2)$$

with Z the charge of the center.

A lowering of the barrier by $\delta E = 2kT$ is reached at 23 kV/cm in CdS (Böer and Dussel 1967b). This causes a release of holes trapped in the *slow copper recombination centers* and thereby an increase of the hole density in the valence band, causing an increased recombination via other *fast recombination centers*, hence a reduction in photoconductive electron density. This is called *Field-Quenching*. Above 50 kV/cm the field quenching starts to lower the electron density *markedly* (Böer and Dussel 1967a).

36.2.1 High-Field Domain

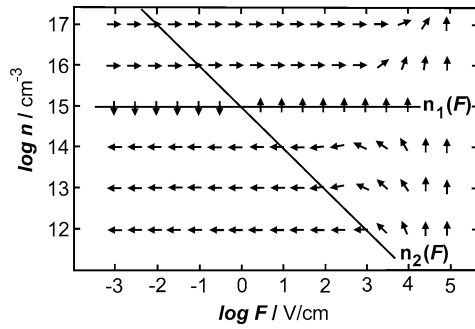
When the field has increased to about 80 kV/cm the electron current decreases more than linearly with increasing field. Now a high-field domain *must* appear (Böer and Voss 1968a). This domain limits any increase of the junction field, as will be discussed below. Further change in the bias is then absorbed in an increase of the width of the domain, rather than an increase in field (Böer and Voss 1968c).

36.2.2 Domain Analysis

The necessity of such a domain to appear can be seen from an analysis of the solution curves of the system of transport and Poisson equation (Böer 1979a) that in its simplest one-dimensional form for electrons reads (the transport equation (1) is rewritten to show both as a system of differential equations):

$$dn/dx = (1/\mu kT)(e\mu nF - j) \quad (36.3)$$

Fig. 36.4 Field-of-direction with n_1 the neutrality electron density, and n_2 the drift current curve with $nF = \text{const}$ (Böer 2009a, 2009b)



$$dF/dx = (e/\varepsilon_{st}\varepsilon_0)\varrho(x). \quad (36.4)$$

For the discussion of the solution curves of this system we will *deviate from the classical approach* that uses a numerical integration, but we will use a *graphic analysis*: We will do this in a two-dimensional rendering by projecting any solution curves $n(x)$ and $F(x)$ into any arbitrary $n - F$ plane, which we will call the “*field-of-directions*” (Böer and Wilhelm 1963a, 1963b). In this field, each point in this field is uniquely characterized by an angle as shown by the short arrows in Fig. 36.4. With the help of two auxiliary functions we can bring some order into this field: by using the neutrality curve, $n_1(F)$ at which $dF/dx \equiv 0$, and the drift current curve $n_2(F)$, at which $dn/dx \equiv 0$. With these auxiliary curves the nF -plane can be divided into the four quadrants of directions (Fig. 36.4) (Böer 2009a, 2009b).

In the first quadrant each direction arrow points up and to the right, in the second quadrant it points up and to the left etc. The neutrality curve can only be crossed vertically, and the drift current curve only horizontally.

Using the field-of-direction approach, we can, as an example, again analyze the Schottky barrier: starting at a given boundary condition, for instance, at $n_c < n_1$ for a blocking electrode. The solution curve has to follow the angle of direction, as shown in Fig. 36.5. That is, F_c must be selected precisely, so that the solution arrives at the bulk where $dn/dx = dF/dx \equiv 0$, that is, at the singular point I in Fig. 36.5, where the electron density and the field is constant.

However, when at higher fields substantial field quenching occurs, the $n_1(F)$ curve decreases as shown in Fig. 36.6. When this decrease becomes over-linear, a *high-field domain* must occur as soon as the drift-current curve $n_2(F)$ crosses $n_1(F)$ again at a given n_c (Böer et al. 1969a).

At this intersection at n_c a second singular point II appears, indicating the development of a *high-field-domain*. This can best be seen in a three-dimensional rendering shown in Fig. 36.7 (Böer 2009a, 2009a).

When the domain is formed, the drift current curve is stuck at II, the current saturates. The solution curve extends flat from the junction interface (in Fig. 36.7 identified as “cathode”) until the excess field is consumed and the field then drops within a few Debye length to the bulk close to the singular point I until it reaches the anode (Böer 2008).

Fig. 36.5 With n_c given at the cathode, the field F_c is uniquely defined in order for the solution to approach asymptotically the constant values of n and F in the bulk, that is at I. For initial points that are slightly off from F_c , the solution curve misses I (*dashed curves*). At higher applied voltage, the drift current curve is shifted up and to the right, and the new solution (b) is shifted accordingly (Böer 2008)

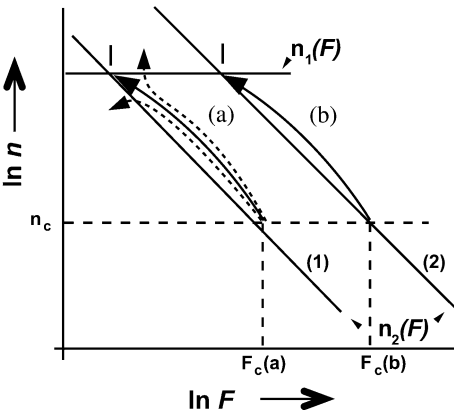


Fig. 36.6 Field of direction representation of a typical Schottky barrier solution (a) and of a high-field domain solution (b), the latter when both n_1 and n_2 cross each other at a new singular point II, that is determined by n_c (Böer 2008)

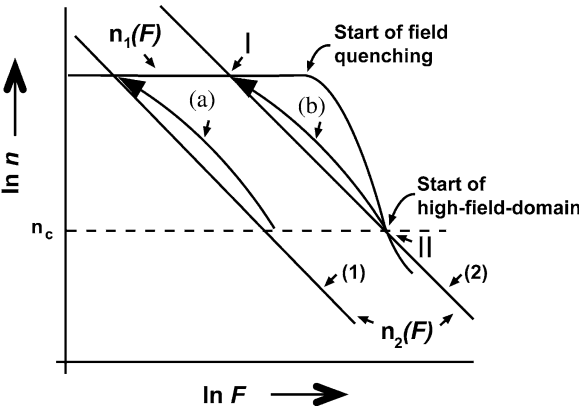


Fig. 36.7 High-field domain shown in perspective rendering; the singular points I and II are identified as crossing points of n_1 and n_2 . When they close again at slightly higher field a third singular point III appears, but is not subject of discussion here

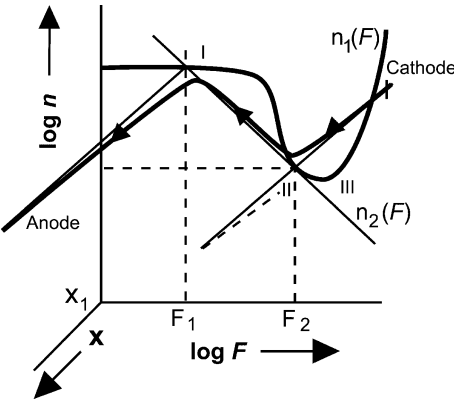
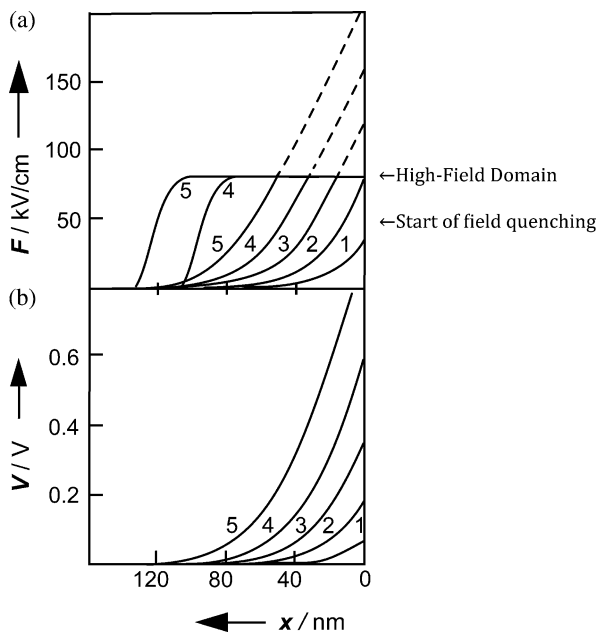


Fig. 36.8 Field and potential distribution as in Fig. 36.2, but now with a domain formation that limits the field to 80 kV/cm (without the domain the field increases further, as shown *dashed* in subfigure (a)) (Böer 2011a)



The field limitation by the high-field domain is shown in Fig. 36.8 (here to about 85 kV/cm—see below).

36.2.3 Direct Experimental Evidence of the High-Field Domain

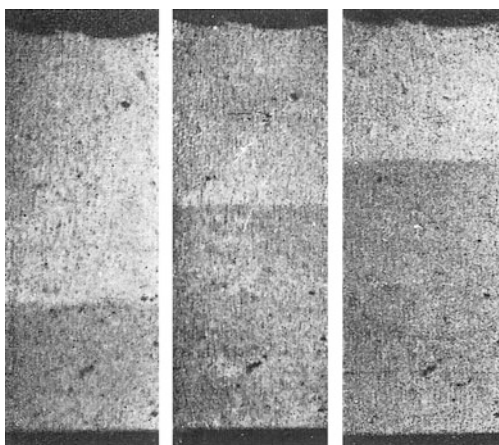
The high-field domain can be observed directly by using the *Franz-Keldysh effect* (a red-shift of the optical absorption edge when tilting the bands with an electric field) as a darkening in the domain-part of a CdS crystal (Böer and Voss 1968c), and is shown in Fig. 36.9.

The field strength of the domain can then be determined from the slope of the linear increase of the domain width with bias (it is 85 kV/cm in Fig. 36.9).

36.2.4 Relevance of the High-Field Domain to the Hetero-Junction

When, in the CdS/CdTe cell, the bias is shifted from forward toward V_{oc} , the field in the CdS at the junction interface increases to first initiate field quenching and then generates the high-field domain before V_{oc} is reached as indicated above. From here on, with further changing bias beyond V_{oc} and toward reverse bias, the field at the junction interface remains constant. The additional voltage drop is absorbed by expanding the high-field domain (Böer 2008).

Fig. 36.9 High-field domain shown in a CdS crystal between cathode (lower electrode) and anode as darkening of the crystal when observed in transmitted monochromatic light at the absorption edge for 5, 10 and 15 kV bias from left to right subfigure (electrode slit width is 0.5 mm) (Böer et al. 1969a)



With field limitation, further leakage through the junction is eliminated, and the open circuit voltage can increase from less than 0.5 V of an untreated CdTe cell at room temperature to 0.85 V as observed in an optimized CdS/CdTe solar cell (as shown in Fig. 36.1 Thompson et al. 2006).

36.2.5 Why is Only CdS such an Advantageous Cover-Layer?

For efficient field-quenching to initiate a sufficiently strong decrease of the electron current, and thereby to initiate the high-field domain, the density of Coulomb-attractive hole centers, that is caused by copper doping, has to be large enough. However, if the centers are too close to each other, their Coulomb funnels overlap too much, and cause a rapid increase in the field that is necessary to initiate Frenkel-Poole excitation. There is a steep optimum for the copper density in CdS of about 50 ppm (see Fig. 36.10) (Böer and Dussel 1970; Hadley et al. 1972).

The copper saturation level in CdS coincides closely with this copper density of 50 ppm. The increased doping shown in Fig. 36.10 was achieved with co-activation caused by additional doping with three-valent Aluminum (Hadley et al. 1972). Such undesired increase of Cu in CdS indicates the need to avoid three-valent impurities in the CdS cover layer.

36.3 Consequences of the Field-Quenching for the Interband Connection

Since, with field quenching, the distance between the Fermi-level and the conduction band increases, the conduction band in CdS close to the CdS/CdTe interface must be moved up with changing bias. Consequently both conduction bands that

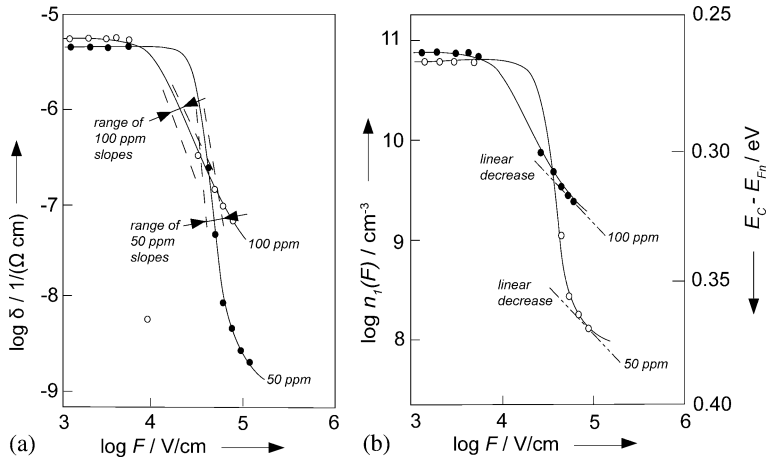


Fig. 36.10 Experimental observation of the electron conductivity (in **a**) and the density, $n_1(F)$ (in **b**) as a function of the field for two copper doping densities in CdS (Hadley et al. 1972): the steepest quenching slope is at copper saturation. The 100 ppm curve is obtained in a CdS crystal co-activated with Al

were connected in forward bias (to ease electron current supply from CdS) they must now become disconnect to the CdTe conduction band, as shown in Fig. 36.11. This separation becomes significant when moving from forward through open circuit into reverse bias (Böer 2009a, 2009b, Böer 2010). Such a band edge discontinuity and shift means a *change in electron affinity* at the interface with changing bias. Presently there is no direct experimental evidence of such a change. However, some indication for a similar change can be obtained from the measured change of the work function (by 0.25 eV) of CdS at a blocking Au contact with changing optical excitation (by a factor of 50) (Böer et al. 1973; Stirn et al. 1973).

A suggested band model in the neighborhood of the junction (excluding outer boundary effects) is shown in a qualitative rendering in Fig. 36.11.

36.4 Summary and Conclusions

Classical Si single crystal and back-contact Swanson solar cells have reached maturity and are theoretically well understood based on Shockley's fundamental theory. Here the most important cell parameters including carrier life time and trap distribution on both sides of the junction can be easily obtained.

Thin-film Hetero-junction cells, however, lack such decisive results and have reached close to 20 % efficiency only by painstaking efforts at the bench by step for step empirical improvements.

Solar cell characterization beyond their efficiency was based on a classification of the characteristics according to short circuit current (collection efficiency), open

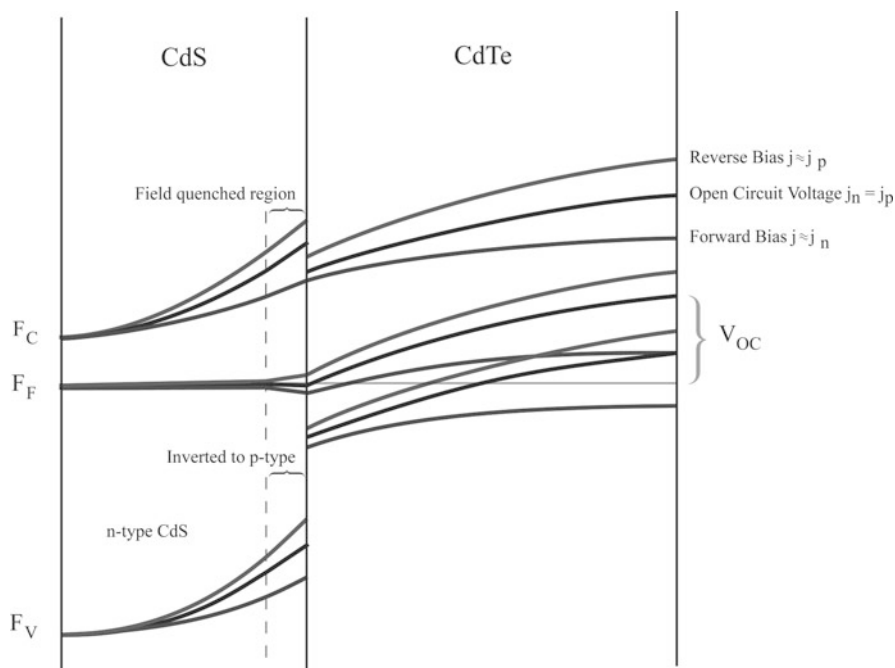


Fig. 36.11 Band model (schematically) shown in the central part of the CdS/CdTe solar cell for different bias as family parameter. Only the Fermi-level is shown, since insufficient information are available to draw the quasi-Fermi-levels (Böer 2009a, 2009b, Böer 2010, Böer 2011a, 2011b, 2011c)

circuit voltage, and fill factor. This was the basis for goal setting, judging empirical improvements.

The theoretical analysis was directed to modeling the current-voltage characteristics, first using networks of resistors and diodes, and later by analyses using transport and Poisson equations. Again, for simple Schottky barriers and basic homo junction single crystal cells this yielded encouraging results. But the more complex cells, such as thin-film hetero-junctions, were handicapped by requiring a set of parameters, only some of which were independently obtained by unique experiments. This posed an often raised question whether, with a sufficient set of *adjustable* parameters, any characteristic could be approximated within the experimental errors.

This, unfortunately, was at times misleading to guide for experimental improvements. A typical example was, some time ago, the conclusion that there may be a shunt or a serious resistance the reason for an undesired characteristic, while the cause was much deeper seated.

We have here resorted to a totally new approach, using basic principles, and neglecting the goal of modeling the entire current-voltage characteristics, but pointing out the main features that influence the cell operation.

This approach, may be discouraging to some experimentalists who expect to see agreement between experiment and theory.

But we are now at the very beginning of this new approach, but still can extract some advice for cell improvement. For instance, special care should be taken to avoid three-valent impurities or complex forming inclusions that may interfere with low-field development of Frenkel-Poole excitation and sufficiently steep reduction of the electron conductivity in CdS to provide for efficient field limitation.

Much more research is encouraged starting with quantitative investigation of field-quenching and high-field-domain formation. For more precise information one may use CdS single crystals and for field measurements the Franz-Keldysh effect. Another area of useful research deals with the interface of CdS and CdTe, again, for transparency done at single crystal interfaces to bring more clarity to changing interface dipoles as a function of the bias

Some guidance for such research may be found in the references cited here, and more comprehensively in the two volume of my recent Springer books (Böer [2008](#), [2009a](#), [2009b](#)). We must await the results of more experiments in order to further substantiate the proposed theory that is presented here.

Chapter 37

Stationary High-Field Domains as Tools

Abstract High field domains are analyzed with the field-of-direction method, applied to the set of transport and Poisson equations. Cathode adjacent stationary high-field domains are inferred. These are directly connected to the metal/CdS interface with constant field and electron density. Thereby they shift the space charge layer that is typically directly attached to the cathode, away from it into the inner part of the crystal. This provides a unique opportunity to study the work function as a function of crystal parameters, e.g. the optical excitation. Also since the domain field can be measured directly, it provides an opportunity to measure the electron mobility as a function of the field when the Hall electrodes are placed within the domain. The domain is measured using the Franz-Keldysh effect to determine the domain width as function of the bias. Since the domain is determined by the work function of the cathode, the method of a virtual cathode by means of a shadow band is introduced. When, with increasing bias the domain starts to fill the entire space between the electrodes, a new stationary domain appears in front of the anode with substantially higher fields. These domains stabilize the current in the pre breakdown range since they limit the field. The conditions for the domains to occur are given. Non stationary, moving high field domains provide additional insight of the properties of CdS at higher fields. Specifically, one obtains that within the domain the otherwise *n*-type CdS is inverted to *p*-type. A summary concludes the chapter.

The stationary high-field domains that were helpful to explain the important function of the thin CdS layer by improving the efficiency of CdS/CdTe solar cells can also be used to clearly identify field-quenched states in CdS. Since this is an important tool that is not otherwise available and can help to characterize copper-doped CdS, we may append this section here and discuss stationary domains in more detail (Böer 2010).

These stationary high-field domains are distinguished as cathode and anode-adjacent domains and permit an unambiguous determination of *electron density and mobility as function of the actual electric field*. The anode-adjacent domain permits additional insight into the high-field properties of CdS in a field range of 100–150 kV/cm that is now stabilized in the pre-breakdown range. Here one finds direct evidence, by using the spectral distribution of the photoconductivity within the domain, of inverting the CdS to *p*-type either by more complete quenching or

by hole injection from the anode (Böer and Ward 1967a). Such observation may also be helpful to indicate the behaviour of CdS close to the interface with CdTe in the CdS/CdTe solar cell.

Both types of stationary domains are determined by the work function of blocking contacts or interfaces and thereby permit a closer analysis of the contact/CdS interface by shifting the space charge region away from the cathode to the bulk-side end of the domain. This allows a more precise determination of the dependence of the work function on the photoconductivity of the adjacent CdS.

The extension of the field-of-direction analysis of the time-independent transport and Poisson equations allows a simple classification of the two types of stationary high-field domains relating to the two singular points in the decreasing branch of the current-voltage characteristic. This permits a transparent discussion of the field distribution of these domains that can be directly observed by the Franz-Keldysh effect in single crystal platelets. Herewith the transition between cathode- to anode-adjacent domains as a function of the applied voltage can be directly followed.

37.1 Introduction

After discovering moving and stationary high-field domains (Böer et al. 1958a, 1958b, 1959) with an electro-optical effect (Böer 1960) which we coined as Franz-Keldysh effect (Franz 1958; Keldysh 1958a), we described these domains as caused by a negative differential conductivity, independent whether caused by a stronger than linear decrease of the electron density (Böer 1960) or the mobility (Böer 1959a) with the electric field. For a first theoretical analysis we used the field-of-direction method in 1961 (Böer and Wilhelm 1963a, 1963b). Soon thereafter a large number of publication started to broaden the field with many theoretical and experimental investigations of the high-field domains (Böer 1959a; Böer and Wilhelm 1964; Böer and Dussel 1967a, 1967b; Böer et al. 1968; Böer and Voss 1968c), and separately of the Franz-Keldysh effect. Except for the further analysis of the stationary high-field domains by the research team of the author (Böer et al. 1968; Böer and Bogus 1968; Böer and Voss 1968c; Böer and Döhler 1969), the moving domains were almost exclusively analyzed by many other groups (Schöll 1987, 2001, 2010; Shaw et al. 1987). They are more easily observed by the kinetic behaviour of the current either by periodic oscillations or by different forms of non-organized fluctuations (Aoki 2000). In parallel, a large number of theoretical studies dealt with a more systematic analysis of the complete system of transport, continuity, and Poisson equations, using detailed analyses of the phase portrait with their singular points and their heteroclinic orbits, yielding pattern formation in bistable systems (Schöll 2010, 2009; Aoki 2000; Amann and Schöll 2005; Hizanidis et al. 2006).

However, stationary high-field domains were often overlooked since they present themselves generally as a small buckle in the current-voltage characteristics before the onset of moving high field domains with starting current oscillations. In reviewing the use of the Franz-Keldysh effect for the measurement of the field in

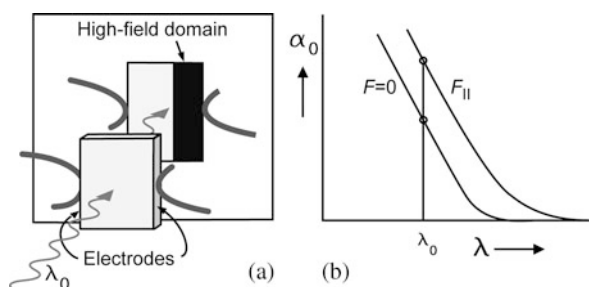


Fig. 37.1 Observation of the shadow picture (a) of the crystal in monochromatic light (b), using the Franz-Keldysh effect, showing the wavelength λ as function of the light intensity α and F as the field strength. In (a) showing the high-field domain as a darkened band. The shading of the band is used as a measure of the acting field (Böer et al. 1958a, 1958b)

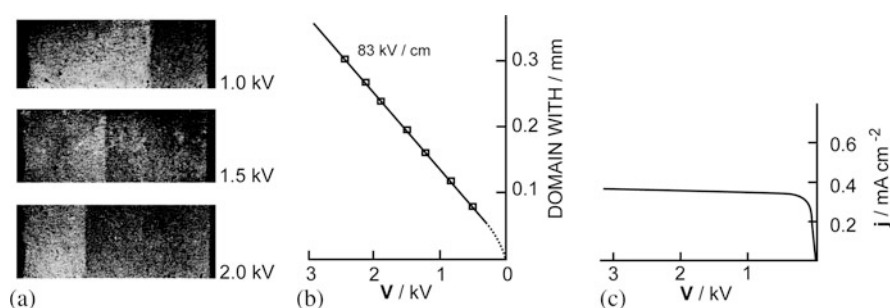


Fig. 37.2 Darkening of part of a CdS crystal platelet photographed at $\lambda = 540 \text{ \AA}$, at three applied voltages (a). The width of the darkened band (the high-field domain) increases linearly with bias (b). While the high-field domain is present, the current through the crystal remains constant (c) (Böer 1961a)

the high-field domains we show the general experimental arrangement in Fig. 37.1, here indicated as stationary domains attached to the cathode in CdS (Böer and Voss 1968c).

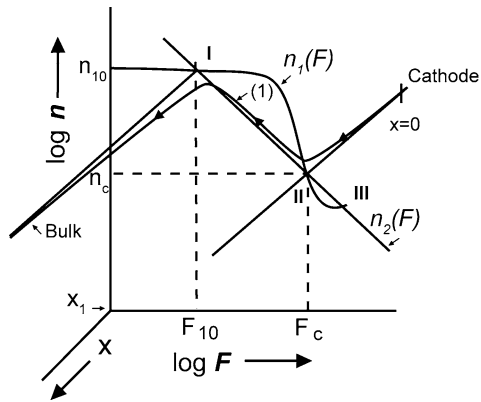
The field in these stationary domains is constant and can easily be determined from the change of their width with increased applied voltage (Fig. 37.2) (Böer and Voss 1968a).

The question at what applied voltage such domain occurs and what determines the field of the domain needs an analysis of the transport and Poisson equations. It is easily seen when using the field-of-direction method (Böer and Dussel 1967b) to distinguish the types of possible solutions.

37.2 Mathematical Analysis (Field-of-Direction-Method)

In this paper the conditions are described that define the states for creating the two kinds of high-field domains. For the first discussion the method of the field-of-

Fig. 37.3 Three dimensional rendering of a typical cathode-adjacent high-field domain initiated at n_c near the singular point II. At the end of the domain the carrier density increased rapidly within a few Debye lengths to the bulk density that is identified here as n_{10}



direction is used that was used in Sect. 36.2.1, based on the set of transport and Poisson equation, that is rewritten here, to show it as a system of differential equations:

$$\frac{dn}{dx} = \left(\frac{1}{\mu kT} \right) (e\mu nF - j) \quad (37.1)$$

$$\frac{dF}{dx} = \left(\frac{1}{\varepsilon_{st}\varepsilon_0} \right) \rho(x) \quad (37.2)$$

$\rho(x)$ is the space charge density which contains in reaction kinetics the different excitation, trapping and recombination processes (usually with mostly unknown transition coefficients).

Without solving numerically the set of equations that would need assumptions about these coefficients, the *types* of possible solution curves can be distinguished from the field-of-direction that was shown in Fig. 37.3.

The only possible solution curves that *must* occur when the electron density decreases stronger than linearly, has a domain character, that is, field and electron density remain constant within the domain and decrease at the end of the high-field domain to the low field bulk value, as shown again here for convenience in Fig. 37.3.

With increased applied voltage the domain width increases without changing the domain field and electron density. The increased bias is absorbed in an increased domain width, as shown already in Fig. 37.2.

The highfield domain is uniquely determined by the electron density at the meal/CdS boundary, and stays constant throughout the domain. Thereby the space charge region that is associated with the Scottky barrier here is now shifted away from this interface into the bulk, at the end of the high-field domain. This presents an opportunity to investigate more closely the properties of the work function (Böer et al. 1973).

37.3 Determination of the Work Function as Function of the Optical Excitation

The work function itself, previously considered independently of the electron density, can now be investigated more closely. Such change of the electron density can be initiated by a change of the optical excitation of the photoconductive CdS. The measurement of the domain field is done again by using the widening of the domain with applied voltage (shown in Fig. 37.4a). Together with the current through the crystal this determines the electron density within the domain, that is now equal to the electron density at the metal/CdS interface. Since the domain has converted the Schottky barrier into a neutral contact, the electron density at this interface changes with optical excitation, one must conclude that also the work changes; as a function of the optical excitation: It decreases typically by 60 meV with an increase of the light intensity by two orders of magnitude (as is shown in Fig. 37.4b) (Stirn et al. 1971; Böer et al. 1973). Different blocking metals show a similar light intensity dependence (shown in Fig. 37.4b). However, for every metal a different CdS crystal (though of similar doping) had to be used. The similarity of the results in Fig. 37.4b, however, indicate that the light intensity dependence is not drastically influenced by slight differences in the defect structure of the CdS.

37.4 Determination of the Field Dependence of the Hall Mobility

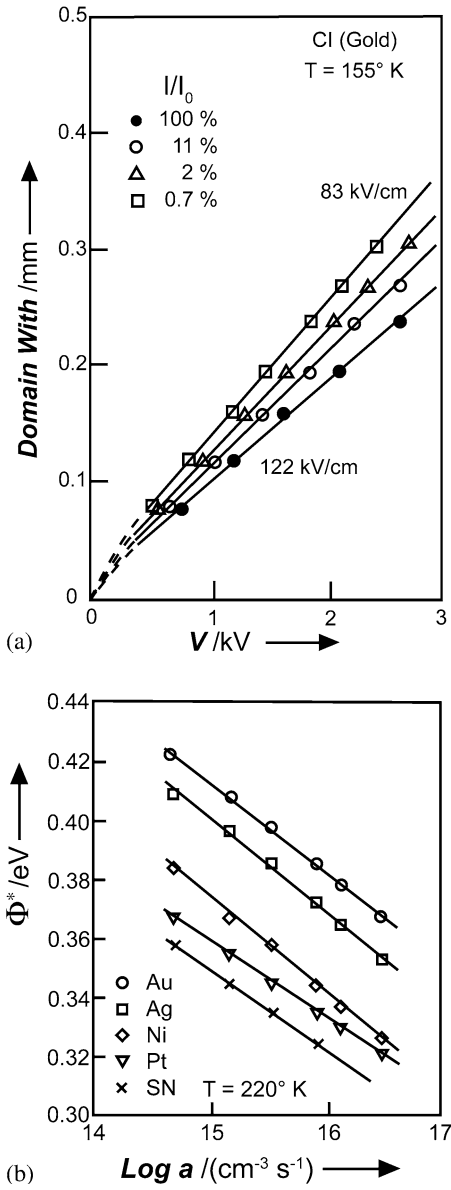
Stationary high-field domain also permit the measurement of the Hall mobility. For this, the applied voltage has to be sufficient to have the domain extending over the entire region between the cathode and extending over the Hall electrodes. Changing the polarity put the measured part of the sample in the low field region. This provides one pair of data points (Böer and Bogus 1968). For each other pair one needs another crystal with electrodes of different work functions, hence different high field values. The similar low-field values at the expected 500 cm²/V s range indicates comparability and a resulting $1/F$ behavior above 30 kV/cm (see Fig. 37.5).

The problem of using different samples for obtaining a wide range of domain fields can be avoided by using a virtual cathode (Böer et al. 1968).

37.5 Stationary Domains Improve Efficiencies of Solar Cells

As mentioned before at length, it is known that a thin layer of CdS on top of a CdTe or CIS solar cell improves their efficiency substantially. This is caused by a stationary high-field domain that is initiated adjacent to the junction interface when the bias is changed from forward to V_{oc} to reverse bias. These domains limit the field at the junction interface below 80 kV/cm and thereby eliminate junction leakage. This causes an almost doubling of the open circuit voltage (Böer 2009a, 2010).

Fig. 37.4 High-field domain width as function of the bias for different light intensities for a Gold contact **(a)** and the work function of different blocking metal contacts as function of the optical generation rate **(b)** (Stirn et al. 1971)



37.5.1 Virtual Cathode

As indicated previously, the field of the domain is uniquely determined by the boundary electron concentration at the cathode. For changing the domain field one needs to change this boundary concentration. This can be done with a quasi-cathode

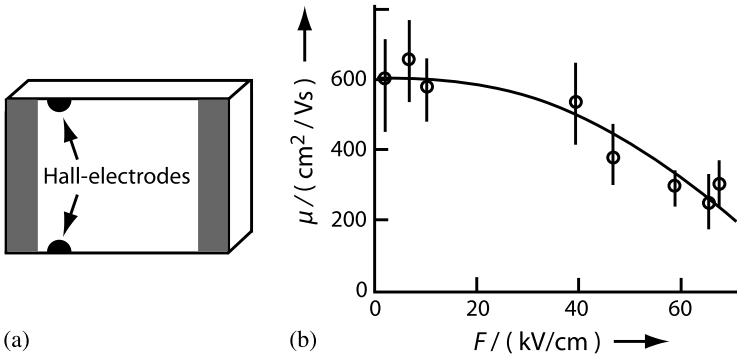
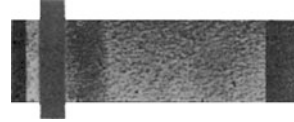


Fig. 37.5 (a) CdS crystal with Hall electrodes, and (b) electron mobility in CdS as function of the field for different high-field domains at 230 K (Böer and Bogus 1968)

Fig. 37.6 Virtual cathode produced by a *shadow band* across the CdS crystal, creating a high-field domain adjacent to it Böer et al. (1968)



with a shadow band in front of the cathode (shown in Fig. 37.6). The electron density here is reduced (Böer et al. 1968).

When the shadow is positioned a few Debye lengths beyond the cathode, it can vary the boundary density n_c^* at the edge of the shadow in a wide range below the bulk electron density n_{10} . This is achieved by reducing the light intensity in the shadow or by adding some quenching light.

With the *virtual cathode* one can produce sequentially high-field domains with different n_c^* (Böer and Voss 1968c) and consequently with different domain fields that can be obtained in each case similar to the procedure shown in Fig. 37.3. Consequently one obtains also the field-quenched electron density (that is equal to n_c^* since the domain-field extends homogeneously from the virtual cathode) from the drift current in each of the domains. The resulting $n_1(F)$ is shown in Fig. 37.7 (Hadley et al. 1972), that is obtained in the same crystal.

When with increasing bias the expanding high-field domain finally fills the entire crystal between both electrodes, an anode-adjacent high-field domain is created that is discussed below.

37.6 Anode-Adjacent Domain at Higher Fields

When extending the neutrality curve in the field-of-direction, it will reach a field range in which field excitation of carriers competes with field quenching and the $n_1(F)$ curve will level-off (Fig. 37.11), or increase again, as shown in the following

Fig. 37.7 Neutrality electron density as function of the actual field (Hadley et al. 1972) obtained from a cathode-adjacent high-field domain analysis, using a virtual cathode (see text)

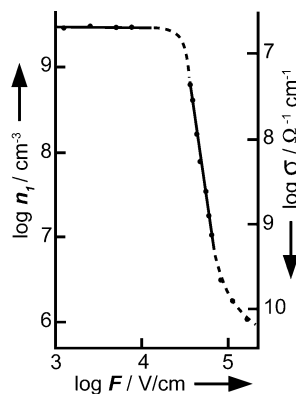
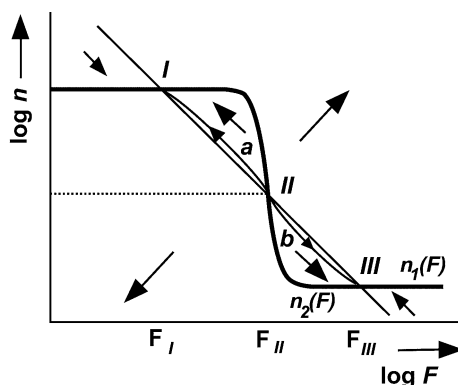


Fig. 37.8 Field-of-direction diagram, extending to higher fields, exposing another singular point III at the third intersection of n_1 and n_2 (Böer and Voss 1968a). Curve a represent the cathode-adjacent curve b represents the anode-adjacent domain



paragraph. This causes a third singular point (III) to occur by intersecting $n_1(F)$ and $n_2(F)$ again.

The solution curve now can no longer approach the singular point I in the bulk but must connect the points II and III. At the third singular point a new type of domain must occur, indicated by a solid arrow (b) in Fig. 37.11. This domain starts at the anode and expands toward the cathode. This second type of domain it now referred to as an *anode-adjacent domain* (Böer and Voss 1968c).

In the three dimensional rendering we can see how the bulk side of the cathode-adjacent domain shrinks until it has only the high-field horizontal branch left within the singular point II. With further increased applied voltage the starting point of the solution is shifted slightly above the point II and then this singular point represents the cathode. The new domain with even higher field will start to grow from the anode side, that is close to the singular point III. This domain will then grow toward the cathode, following the arrow in the second quadrant of Fig. 37.8.

This transition from cathode-to anode-adjacent domain is observed and its three dimensional rendering is shown in Fig. 37.9 using the Franz-Keldysh effect and is shown in Fig. 37.10 (Böer and Voss 1968a).

Fig. 37.9 Three-dimensional rendering of a cathode ($1, 2, s$) and an anode-adjacent ($4, 5, 6$) domain. The direction of the solution curve is indicated by the *arrows*. When the solution contracts to the singular point II, the anode switches around (in this diagram from the left to the right) (Böer 2008)

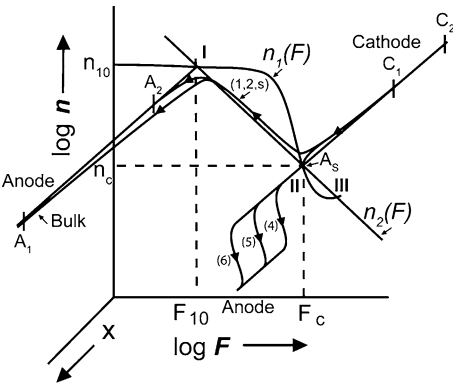


Fig. 37.10 Cathode-adjacent domain extending from 500 to 1,750 V bias, then filling the entire crystal. When increasing the bias further a new high-field domain extends from the anode starting at about 2 kV as shown in the lower row of photos and has substantially higher field as indicated by the increased density of the domain picture (Böer and Voss 1968a)

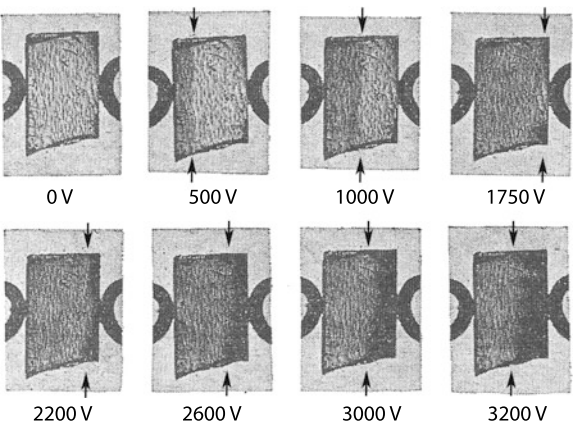
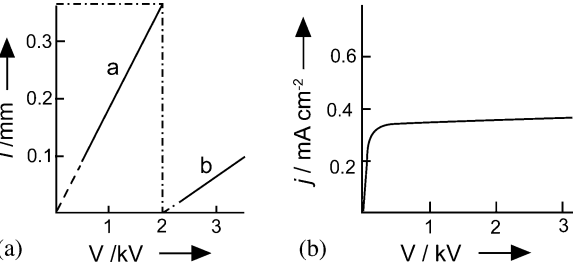


Fig. 37.11 Domain width as a function of the applied voltage (a) for the cathode-adjacent (a) and for the anode-adjacent domain (b). The current-voltage characteristic is taken of the same crystal (b) (Böer and Voss 1968b)

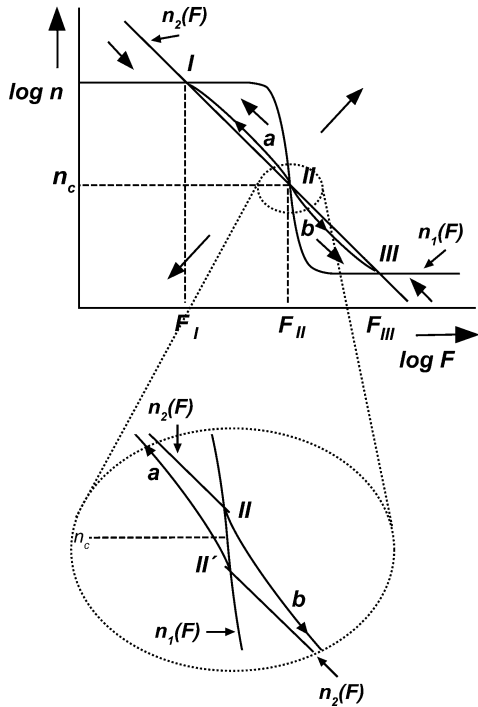


During the transition from the cathode-adjacent to the anode-adjacent domain the current remains saturated without a break visible in the characteristic, since the minute shift from below to above II (see the following section) is not detectable (Fig. 37.14) (Böer and Voss 1968b).

From the slope of the domain width with bias one obtains 80 kV/cm for the field in the cathode-adjacent domain, and 135 kV/cm for the anode-adjacent domain.

This anode-adjacent high-field domain stabilizes the current-voltage characteristic in the pre-breakdown range. It keeps the current lower than it would other-

Fig. 37.12 Enlarged vicinity of the singular point II shown below the original figure of the field-of-direction (Böer 2012a)



wise become when carrier excitation becomes marked. The transition from cathode- to anode-adjacent domain with the solution curve flipping around almost instantaneously needs more explanation that is given below.

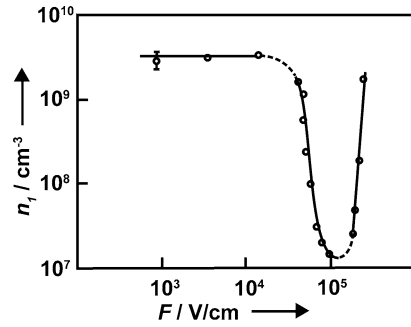
37.7 Transition Between the Two Types of Stationary Domains

At this transition an abrupt change of the direction of the solution is observed: the anode has flipped from the singular point I to the point III.

The transition can be followed in an enlarged diagram of the center part of Fig. 37.12. Here with increased bias, a minute increase of the drift current $n_2(F)$ moves the intersection of $n_1(F)$ and $n_2(F)$ from below to above the singular point II (Fig. 37.12).

At the transition point, the original high-field domain fills the entire crystal, the solution has now degenerated to be contained within the singular point II. When the drift field curve moves with further increased bias very slightly above II, the direction of the solution flips, but the position $n_2(F)$ remains essentially “pinned” near II. It can only move up when the crystal is again entirely filled by the anode-adjacent domain.

Fig. 37.13 CdS crystal with larger donor density showing the steeply increasing branch in the pre-breakdown range that is stabilized and measured sequentially with anode-adjacent high-field domains (Hadley et al. 1972)



37.7.1 Stabilizing by the Domain in the Pre-breakdown Range

The anode-adjacent domain *stabilizes* this part of the pre-breakdown behavior and prevents a run-away current. This again is caused by the thermodynamic principle to maintain the state of lowest current through the crystal (the minimum energy principle). However, the proof of this statement needs an analysis of the dynamic equation that is not the subject of this paper. Only when, with increased bias, the anode-adjacent domain fills the entire crystal, can a run-away breakdown occur, if not prevented by a very large external series resistance.

In a differently doped crystal the anode-adjacent domain is also observed in the steeply increasing branch of the characteristic (Hadley et al. 1972) that is caused by dominating field excitation of electrons, as shown in Fig. 37.13 (Böer 2008).

37.8 Conditions for Stationary High-Field Domains to Occur

In a one-dimensional, homogeneously doped CdS crystal the following conditions can be identified under which stationary high-field domains occur (Böer 2012a):

- (1) The reduction of the electron density with the field must be over-linear.
- (2) The electron density at the electrode boundary must be low enough to fall into the over-linear decrease of conductivity (Schottky barrier condition).
- (3) The range between the first and second singular point must span a region in the forth quadrant of direction (this is not the case for the Gunn effect, hence here stationary domain can not exist [18, 41–43]).
- (4) All external parameters must remain stationary.

Under the following additional conditions, anode-adjacent high-field domains must occur:

- (a) The continuation of the drift current curve intersects the electron neutrality curve a second time at higher fields.
- (b) The region between the second and the third singular point spans a region of the second quadrant of the field of direction.

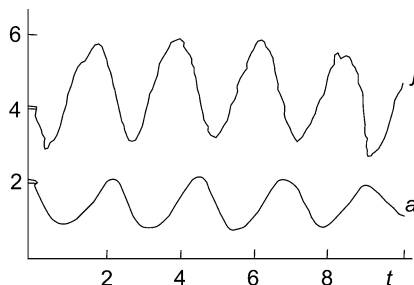


Fig. 37.14 Double trace oscilloscope picture of current (j) and Franz-Keldysh optical absorption (a), the latter obtained through a pinhole focused on a fraction of the primary domain and measured with a photomultiplier (Böer and Ward 1967a)

37.9 Nonstationary (Moving) High-Field Domains

Even though the title of this paper specifies stationary domains, a section of nonstationary domains is included since a few of the moving high-field domains offer additional information about the electronic properties at the third singular point, as given below.

In some CdS crystals relatively broad high-field domains separate from the cathode and are moving slowly toward the anode. Here sub-domains are occasionally observed within the primary domain. These domains move in the opposite direction at a much faster speed and are much darker as seen by the Franz-Keldysh shift of the band edge, hence have a much higher field than the primary domain. When these sub-domains are coordinated and move in phase with a frequency of about 0.5 Hz, they are also connected with faster current oscillations at the same frequency (Böer and Ward 1967a). This correlation can be directly observed by recording simultaneously current and sub-domain motion (see Fig. 37.14).

It should be noted that such domain behavior could not be deduced from the kinetic analysis of the current alone.

There are indications that the conductivity in these sub-domains is inverted to p -type (Böer and Ward 1967a, 1967b). This is shown by an inversion of the infrared induced photocurrent spectrum at higher fields (Fig. 37.15).

Finally, in differently doped CdS, some of these domains do not disappear when they reach the anode but, adjacent to the anode turn much darker indicating a still higher field (see Fig. 37.16 taken from the educational film Böer 1964).

For explanation it is suggested that hole injection from the anode causes such a new domain and flattens the $n_1(F)$ curve to permit a much higher field at the singular point III.

However, all the experimental results given in this paragraph must be analyzed including bipolar transport equations and involve the continuity equation. This is beyond the scope of this paper.

We have to defer for all other discussion of the kinetics of domains since they involve the thermodynamics of the total system (see, e.g., the reviews of Schöll

Fig. 37.15 Photocurrent through a CdS single crystal irradiated with a primary beam at $515\text{ }\mu\text{m}$ as function of the wavelength of a secondary IR irradiation at low bias (50 V), *upper curve, right scale*; and at field-quenching bias (1,000 V), *lower curve, left scale* (Böer and Ward 1967a)

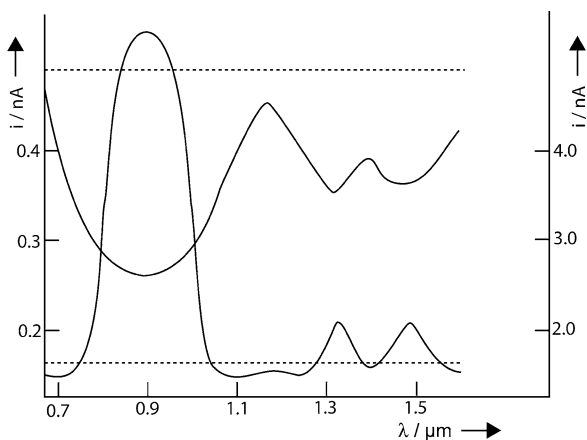
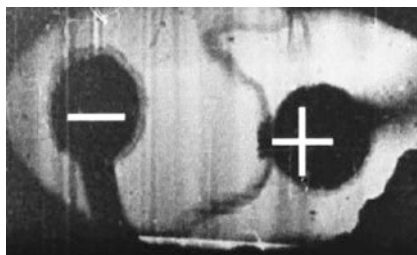


Fig. 37.16 Moving high-field domain that shows a significant stronger darkening (field increase) at the area where the domain starts to contact the anode (Böer 1965)



et al. 1987; Schöll 2001, 2009). Moreover, little information is available from old experiments about the setup since this system included regulated dc generators with a network of capacitor, inductors, and various series resistors.

The information obtained from the CdS experiments permit the field distribution and its kinetics to become directly visible. Thereby other observations that are based on the current behavior alone can now be more precisely categorized. This is especially helpful in CdS, where the conductivity can independently be influenced by the light intensity, temperature and doping (Böer and Borchardt 1953): a wealth of information is available from the movie (Böer 1965) that is attached to the Springer book on the Visualization of Field and Current Distributions in Semiconductors (Böer 2009a).

37.10 Summary

High-field domains can remain stationary, adjacent to a blocking cathode. In one-dimensional, homogeneously doped CdS crystals, stationary high-field domains occur, when the reduction of the electron density with the field is over-linear and the electron density at the cathode boundary is low enough to fall within the over-linear decrease of conductivity.

Stationary high-field domains convert a blocking cathode into a neutral one and move the space charge layer from adjoining the blocking contact to the anode side of the domain. This permits the observation of changes in the work function caused by changes of the optical excitation of the CdS.

Stationary domains can be used to determine unambiguously the electron density and mobility as function of the electric.

Chapter 38

Commercial Use of CdS/CdTe

Abstract The simple production technology and the relatively high stability of the CdS/CdTe solar cell has made it attractive for mass production. It has been one of the first thin-film solar cells. In combination with a thin layer of CdS it is attractive at about 16 % efficiency. Compared to other known solar cells it can be reliably produced in large areas with panel efficiency approaching 15 % and at a production cost of less than \$1/Watt. Currently it is already deployed in many gigaWatt worldwide. Even though Cd is highly toxic, encapsulated it does not present an environmental hazard. Recent studies have confirmed that the terrestrial reserves of Te are sufficient to permit an explosive growth of the industry.

In this chapter we will summarize the technical and economical importance of the CdS/CdTe solar cells on the energy conversion market.

38.1 History of the CdS/CdTe Solar Cell

Since the early 50's Cadmium Telluride was known as a good candidate for solar cells since it could be doped *n*- and *p*-type and its band gap at 1.45 eV is close to optimal for solar energy conversion (Jenny and Bube 1954; Bube 1955). A decade later it was observed that a layer of Cadmium Sulfide on top could increase the conversion efficiency from about 5 % to about 8 % (Cusano 1963; Vodakov et al. 1963). Only in the 1980's solar cells were made by close spaced sublimation of a CdS/CdTe sandwich that achieved 12 % conversion efficiency (Uda et al. 1978; Bube 1978). It took another ten years before one learned that the thickness of the covering CdS layer can be reduced to below 1 μm to prevent it from filtering out a significant part of the solar spectrum beyond its band gap of 2.4 eV (Bonnet 1992a, 1992b; Chu and Chu 1992; Rohatgi 1992; McCandless and Birkmire 1991; Birkmire et al. 1992; McCandless et al. 1996; Nishio et al. 1997; Chu et al. 1996; Ohyma et al. 1997; Aramoto et al. 1997; Bonnet and Herr 1998). The next step was to deposit this sandwich on top of a conducting glass (CTO) layer and further improve the current collection capacity in larger cells and increase the efficiency further. It was in 1991 that Ting L. Chu reached 15 % efficiency (Chu and Chu 1992; McCandless and

Birkmire 1991; Nishio et al. 1997; Aramoto et al. 1997; McCandless et al. 1999; Chu et al. 1991b, 1992; Ban et al. 2006; Barth 2009; Hegedus and McCandless 2005; Ferekides et al. 2000; Asher et al. 2000). This opened the potential for significant commercial interest that was captured by a dozen new start-up companies. However, a continuous production process was not developed, and the early cells showed early degradation problems.

The maximum solar conversion efficiency of the CdS/CdTe cell that was already achieved in 2001 and it stands now, confirmed by NREL at 16.5 % (Hegedus and Shafarman 2004; Desai et al. 2006). With further improved production and cell stability, the conditions were given for a major commercial take-off, that after, several set-backs was achieved by First Solar in 2005 to reach a production capacity of 25 MW/year.

For comparison, another group of promising thin-film solar cells is the CIS group, with its first entrance as CdS/CuInSe₂. But soon thereafter other cells of similar type were produced in which In and Se was replaced by homologous elements or their alloys. The best of these cells surpassed CdS/CdTe cells by a few percentage points (approaching almost 20 %). However, the CdS/CdTe cell became the preferred commercial solar cell because of the ease of reproducible fabrication of large area cells, and their better long-term stability. The production of a large area of these solar cells by relatively simple vacuum deposition has led to a further rapid development of a thin-film solar cell industry.

The CdS/CdTe solar cell is produced by evaporation of a thin CdS layer on top of a conductive glass substrate, followed by another evaporation of a typically 2 μm thick CdTe layer and the deposition of a metal contact layer to complete the initial process. The cell is then treated for a short time at a temperature of about 450° usually with a CdCl₂ flux that causes a partial crystallization of the two semiconductors, and this allows for the copper doping of the CdS in the same process (the flux or other components at the outer interface of the CdTe layer provide the source for this doping) (McCandless et al. 2002). All of these procedures can be performed economically on a semi-automatic production line.

In the last two decades numerous other compounds were investigated in an attempt to replace CdS and achieve similar conversion efficiency improvements, or even surpass CdS. All these attempts failed and only a few materials showed some, but insignificant improvements of the CdTe or CIS type solar cells (McCandless et al. 2001; Metzger et al. 2003; Collins et al. 2009).

The reason why CdS is a good partner to CdTe was first thought by the enhanced optical transmission through the covering CdS layer, that is caused by the lower index of refraction of CdS compared to CdTe, hence one experiences a lower light reflection from the cell surface. However, this “window effect” from which an improvement of the current is expected, is by far surpassed by the substantial increase of the open circuit voltage and the fill factor in the current–voltage characteristics. Thereby the electric power output of these solar cells under solar illumination is almost doubled (Böer 2009a, 2009b, 2010, 2002; Böer and Düssel 1970; Böer and Voss 1968a, 1968b, 1968c).

This remarkable fact of the conversion efficiency enhancement by a thin layer of CdS, which was known for almost three decades, but an explanation of the reasons for it was elusive. In addition more recently, it was observed that the thickness of this layer can be reduced to 200 Å to remain effective (Böer and Voss 1968a, 1968b, 1968c). Only recently a more thorough analysis of the physical behavior of copper-doped CdS helped to clear up this puzzle (Hadley et al. 1972; Böer and Ward 1967a), as we will discuss in the next section.

38.2 Why is Cadmium Sulfide the Only Compound?

Since the replacement of CdS with other compounds was unsuccessful, it became important, to find out why CdS is so beneficial. All earlier attempts of explanation failed. Mostly because one tried to model the actual cell, that is polycrystalline and has a complicated morphology. The involved processes are seemingly too complex to permit a reasonable model computation that shows encouraging agreement with the experiment, i.e. mostly with the measured current–voltage characteristics.

Only recently (Böer and Ward 1967a, 1967b; Böer et al. 1969b) it was recognized that the cause of the enhancement should be researched within the CdS itself, and to do this with sufficient experimental substantiation. One therefore has to first proceed with a simple one-dimensional model, that is, by replacing the actual CdS layer with a thin CdS platelet. Here ample experiments have been performed in the 50's and 60's and provide the basis for an attempt to explain the behavior (for a comprehensive review see Böer et al. 1969b; Fthenakis et al. 2004). From these results it is known that CdS is an *n*-type semiconductor that when doped with copper becomes highly photoconductive. With an optical excitation, as it is exposed in a solar cell, the electron density is on the order of 10^{18} cm^{-3} . Such photoconductivity can easily be quenched (i.e. the electron density can be reduced) by additional low energy excitation, as, e.g., by infrared light, or, what in the case of the solar cell becomes important, by an intermediate electric field. This field causes a Frenkel-Poole excitation (Noufi and Zweibel 2006) of trapped holes¹ (that stem from the optical excitation) from Coulomb attractive hole centers into the valence band. The now set-free holes can be trapped by fast recombination centers from which they can interact with the conduction electrons and by permitting enhanced recombination, thereby reducing their density (Böer and Voss 1968a, 1968b, 1968c). These intermediate electric fields can be reached at the CdS side of the junction to the CdTe, causing in the corresponding thin CdS layer such “field-quenching” to occur (Böer and Voss 1968a, 1968b, 1968c).

It can be shown that the field quenching is one of the reasons for the cell improvement since it can reduce the electron density at the junction interface and hence its back-diffusion into the CdTe, that would represent a junction leakage. Such a

¹Frenkel Poole excitation is caused by the lowering of the Coulomb funnel in field direction by an electric field due to the tilting of the bands in this field, thereby reducing the energy necessary to thermally excite the holes into the valence band.

leakage consequently would result in a lower solar conversion efficiency, as it is observed in the uncoated CdTe cells. However, one must now include several other important factors to more quantitatively explain the behavior.

1. The electric field at the CdS side of the junction is a function of the voltage drop that is observed at various points of the current–voltage characteristics: It is generally low (below 20 kV/cm) in forward bias and increases rapidly when approaching the open circuit voltage, and beyond in reverse bias. This means in sufficient forward bias there is no field quenching, hence electron can travel through the junction easily. However, as the field increases when V_{oc} is approached, field quenching sets-in and substantially reduces such electron leakage (Böer 2009a, 2009b).
2. CdS in the quenched region shows a negative differential conductivity, that is, the photocurrent decreases with increasing applied voltage. When the field quenching is strong enough, a high-field domain is created in which the field is limited to approximately 50 kV/cm. This field is approximately the same in which substantial field quenching is observed. In fact, the field quenching is the cause of the negative differential conductivity that necessary to initiate the high-field domain (Böer and Voss 1968a, 1968b, 1968c). This maximum field near the CdS/CdTe interface is too low to permit electron tunneling through the junction, that otherwise would shunt the junction and reduce the solar cell efficiency.
3. The field quenching near the CdS/CdTe interface can be strong enough to turn the CdS into a *p*-type layer (Böer and Ward 1967a). This causes the Fermi level in this layer to move much closer to the valence band. Since the Fermi Level at open circuit condition must remain horizontal, this means that both valence and conduction bands curved up in the field quenched region and the conduction band at the interface must disconnect from the conduction band of the CdTe, to which it was connected in forward bias (Böer 2009a, 2009b). This again limits the electron back-diffusion into the CdTe.
4. To permit such relative shift of the bands between CdS and CdTe, this requires a change of the dipole moment at the interface, which determines the band connection (or the band offset). There is experimental evidence that in copper doped CdS platelets the dipole moment that is involved in a Schottky barrier to a metal electrode can be changed by changing the photoconductivity (Böer et al. 1969b). That seems to justify the assumption that such a change of the dipole moment at an even ‘softer’ interface can occur.

With these conditions one can draw the band diagram of a CdS/CdTe solar cell close to the junction interface (Böer 2009a, 2009b) as it was shown in the previous chapter (Fig. 36.11).

As discussed before, the thin cover layer of CdS permits a substantial improvement of the conversion efficiency of the CdS/CdTe solar cell. For this it is essential that the field-quenching is initiated at a field of about 50 kV/cm. Field quenching is quite sensitive to the distance between Coulomb attractive centers that are produced

by copper doping² (Böer and Dussel, 1970). If this density is too low, then the quenching is not efficient enough to reduce the electron density markedly. If, on the other hand, the density is too high, then these centers become too close and the critical field for Frenkel-Poole excitation becomes much higher. Accidentally, the saturation level of copper in CdS is about 100 ppm, that brings the distance between the copper atoms to its optimal value (Böer and Dussel 1970).

Though in some other semiconductors one can induce such field quenching and consequently negative differential conductivity, but one has to design the doping just to the right level. This is too complicated to achieve over large enough areas, causing this alternative layer to become highly inhomogeneous and its beneficial effect limited to a small percentage of the solar cell area.

38.3 Economical Aspects of Thin-Film Solar Cells

Compared with the classical silicon solar cells these CdS/CdTe or other CdS/CIS type solar cells have a somewhat smaller conversion efficiency but a substantially lower material electrical power demand for production. Specifically laboratory size cells thin-film cells have approximately 15 % while single crystal silicon cells often exceed 20 % efficiency. Large panels fully assembled of thin-film cells have approximately 10 % while silicon panels have approximately 17 % and panels assembled from polycrystalline silicon have about 12 % efficiency.

However, the material demand for silicon cells is at least 10 times that of thin-film cells, and the energy consumption per unit area of the final panel is at least twice as large. This relates to a substantial cost advantage for the thin-film material, even though the material supply of the raw material for silicon cells is of unlimited supply (sand and charcoal) while some of the other elements such as Cd, Te, In, Ga and As have limited supply in the minable earth crust, but are still plentiful for decades of future thin-film production. The limited supply compensates for some of the material demand factors. In addition, the necessary encapsulation, e.g. glass and framing of the panels tend to even out some of the costs. Therefore, presently the selling price for the assembled panels is approximately \$2 for thin-film and \$4 for crystalline silicon cells per peak Watt. Taking the larger area into consideration to achieve the same wattage of the installed panels, that is larger by the inverse ration of the efficiency, this tends to further even out the cost for the consumer. Furthermore the silicon cell panels are on the market now for at least four decades, while large scale CdS/CdTe panels have taken off into the multi-Megawatt per year production range only less than a decade ago. This has an impact on the reliability confidence that is guaranteed for silicon often to 25 years, with older panels on rooftop exposure have exceeded mostly that warranty range significantly. Even though the manufacturers of the CdS/CdTe cells claim confidence in their product, one simply has to await actual field data to gain such experience.

²Saturation can be shifted by adding co-activators, e.g., Al during doping.

Dependent on the size and the place of the installation one has to add approximately \$2 to \$5 per Watt to the cost of the total installation. This results in a cost for the consumer on his house roof to about \$7,000 to 9,000 per installed kW, minus a percentage of tax incentives that differs from state to state, and together with federal tax incentives can amount to 30 to 50 % of this value.

Depending on the geographic location and assuming an average 50 % of utility electric power savings this means the need of a 2 to 5 kW installation on a single family home, or a \$ 14,000 to \$ 45,000 initial cost, with an average of 40 % tax savings to about \$5,000 to \$ 30,000 initial capital outlay,

Giving an electric power saving of, in average 10 cents per kW and an annual average of 3 hours per day total sunshine, one obtains with \$ 100 per year savings an amortization period of about 10 to 15 years for such an installation.³

For large area installations the prorated installation costs are smaller, but then again dependent on the state and other local considerations the tax incentives are smaller. It exceeds the intent of this presentation to go further into the economical detail.

Irrespective of the unquestionable advantage of the installation of solar panels by reducing the emission of greenhouse gases, the investment into such solar system may make already economical sense, recognizing that it will increase the value of the house and the electrical energy harvested will be essentially free after the amortization period.

38.4 Cd Toxicity and Te Supply

Cadmium is one of the most toxic metals and has long ago banned to be as sulfide or selenide the pigment of paint. Its use was consequently banned by the European Union's RoHS regulation. Consequently the use in solar cells is subject to stringent recycling procedures.⁴ The additional costs for recycling, including transport is estimated at \$0.05 per Watt. Also exposure to fire of the glass encapsulated cells does not allow cadmium release.

The tellurium supply is still questionable, since presently only 800 metric tons per year is available, since it was not in high demand in the past. In 2007 the global production has increased to 135 metric tons [59], but was barely sufficient for much more than 1 gigaWatt CdS/CdTe solar panel installation,⁵ However in the meantime new Telluri (Tellurium, Mineral commodities, 2008) rich ore has been discovered

³This number was calculated for cells of 10.7 % efficiency, yielding 107 W/m² multiplied with a \$1.04 per Watt, yielding \$111 per m².

⁴Recycle First Solar Modules, First Solar.

⁵With CdTe at 5.85 g/cm³ of which Te is 3.1 g/cm³. In 1 m² of CdS/CdTe cells et 3 μm CdTe thickness this yields a use of 3.1 g/m² of Te. Therefore the production of 1 GW of such cells with 100 km² area requires approximately 95 metric tons of Te.

in Xinju, China (Hein et al. 2003) and at several other places in the world. Other resources of abundant tellurium are now discovered on undersea ridges which promise a further increased supply potential, sufficient for more solar cell panels than can be expected to be produced to supply most of the global electric energy demand (Hein et al. 2003).

38.5 Larger Recent CdS/CdTe Panel Deployments

Up to the writing of this paper, more than 2 GW of CdS/CdTe panels have been deployed, the latest part of it from First Solar 40 MW at Waldpolenz in Germany at a price of €3,250 per kW, and the 7.5 MW system installed by Blythe, CA, where the California Public Utility Commission has an agreed power delivery price of 12 cent per kWh. Other large installations of First Solar include a contract with Southern California Edison to install a total of 250 MW, at a installation price of \$3.50/W with Tax incentives.

Chapter 39

The CdS/CuInSe₂ Solar Cell

Abstract Copper indium diselenid that could be doped to be *n*- and *p*-type and has a band-gap of 1.04 eV attractive as a solar cell. The history of its development, and the early observation that covered with a thin layer of CdS the conversion efficiency was considerably increased. The crystal structure is described and a table of many electrical and optical parameters is given. The defect structure is discussed which is surprisingly independent of producing the cell. The ease with which the material either by simultaneous evaporation of the elements, or by selenizing a copper/indium metal layer encouraged to seek for other similar compounds that have a slightly higher band gap. Very early the Cu(InGa)Te₂ was made with a slightly higher band gap and excellent electrical and optical properties. From then on almost all attention was devoted, and many similar compounds were synthesized. For this reason a separate, following chapter was assigned to these materials.

39.1 Introduction

There is a large number of devices of ABC₂, where A stands for copper, B stands for Ga, or In or any alloy thereof and C stands for S or Se. All of these ternary chalcopyrite compounds show ability to become *n*- or *p*-type, and in connection with a cover layer of CdS are solar cells of various technical attraction. Mass fabrication is eased due to the advantages of thin films for low-cost, high-rate semiconductor deposition over large areas using layers only a few micrometers thick and for fabrication of monolithically interconnected modules. They are light weight and can be easily mass fabricated with module efficiencies exceeding 16 %.

39.2 History

The first CdS/CuInSe₂ solar cells were made by evaporating *n*-type CdS onto *p*-type single crystals (Wagner et al. 1974). These ternary chalcopyrites are direct band-gap semiconductors that have a broader spectral response with higher absorption than Si

(Derived from Review of Shafarman et al. 2011).

Table 39.1 Selected properties of CuInSe₂

Property		Value	Units	Reference
Lattice constants	<i>a</i>	5.78	Å	(Suri et al. 1989)
	<i>c</i>	11.62	Å	
Density		5.75	g/cm ³	(Suri et al. 1989)
Melting temperature		986	°C	(Ciszek 1984)
Thermal expansion coefficients at room temperature	(<i>a</i> axis)	11.23 × 10 ^{−6}	1/K	(Bondar and Orlova 1985)
	(<i>c</i> axis)	7.90 × 10 ^{−6}	1/K	
Thermal conductivity at 273 K		0.086	W/(cm K)	(Neumann 1986)
Dielectric constant	Low frequency	13.6		(Li et al. 1979)
	High frequency	70.3–7.75		(Chattopadhyay et al. 1991)
Effective mass [<i>m_e</i>]	Electrons-exp.	0.08	<i>m_{e0}</i>	(Arushanov et al. 1993)
	Theory (<i>c</i> -axis)	0.08	<i>m_{e0}</i>	(Persson 2008)
	(<i>a</i> -axis)	0.09	<i>m_{e0}</i>	
	Holes (heavy)-exp.	0.72	<i>m_{e0}</i>	(Chattopadhyay et al. 1991)
	Holes (light)-exp.	0.09	<i>m_{e0}</i>	(Neumann et al. 1981)
	Theory (<i>c</i> -axis)	0.66, 0.12	<i>m_{e0}</i>	(Persson 2008)
	(<i>a</i> -axis)	0.14, 0.25	<i>m_{e0}</i>	
Energy gap [<i>E_g</i>]		1.04	eV	(Hahn et al. 1953)
Energy gap temperature coefficient		−1.1 × 10 ^{−4}	eV/K	(Nakanishi et al. 1987)

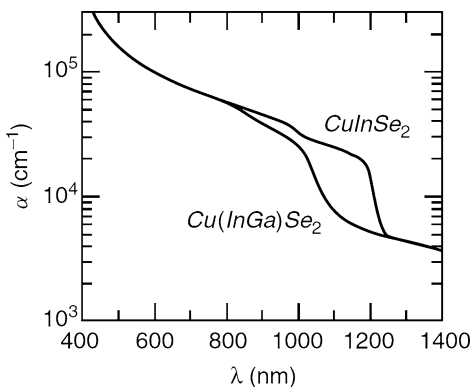
photo-detectors. With some optimization the efficiency for solar cells increased to 12 %, measured under outdoor illumination (Shay et al. 1975). The first thin film CdS/CuInSe₂ devices were fabricated by Kazmerski et al. using films deposited by evaporation of CuInSe₂ with excess Se added (Kazmerski et al. 1976). CuInSe₂ of 9.4 % efficiency were produced by Boeing (Mickelsen and Chen 1981) with co-evaporation of the elements, using separate sources (Mickelsen and Chen 1982), onto ceramic substrates coated with a Mo back electrode. These devices were completed with evaporated undoped CdS followed by an In-doped CdS that served as the main current-carrying material (Mickelsen and Chen 1982).

ARCO Solar on the other used a precursor reaction process with Cu and In deposition at a low temperature followed by a reactive anneal in H₂Se. These two approaches remain as the common deposition methods, and produce the highest device and module efficiencies.

39.3 Material Properties

Effective masses for electrons in CuInSe₂ are 0.1*m_o* (Weinert et al. 1977; Arushanov et al. 1993) and 0.7*m_o* for the holes (Ruckh et al. 1996a; Schroeder and Rockett

Fig. 39.1 Optical absorption coefficient of CuInSe₂ and Cu(InGa)Se₂



1997). These experimental values agree with recently refined local density approximation calculations, which show anisotropy of the hole effective masses with a factor of 4 difference between parallel and perpendicular to the c -axis. CuInSe₂ has the lower effective hole mass perpendicular to the c -axis (see Table 39.1).

39.4 Electronic Properties

CuInSe₂ with excess Cu is always p -type, however In-rich films can be made p -type or n -type depending on the Se content (Noufi et al. 1984). By annealing in a high pressure selenium atmosphere, n -type material can be converted to p -type, and conversely, p -type material becomes n -type by annealing at low selenium pressure (Neumann and Tomlinson 1990). However CuGaSe₂ is always p -type (Siebentritt 2002).

For CuInSe₂, the highest values of hole mobilities of 200 $\text{cm}^2/\text{V s}$ have been measured for epitaxial films. Up to 250 $\text{cm}^2/\text{V s}$ was found in pure CuGaSe₂ (Siebentritt 2005) (see Fig. 39.1). Photoluminescence measurements have shown that only very little Ga changes the symmetry of the valence band from CuInSe₂-like to CuGaSe₂-like (Hönes et al. 2008).

Crystals have shown hole mobilities in the range 15–150 $\text{cm}^2/\text{V s}$ with electron mobilities ranging from 90 to 900 $\text{cm}^2/\text{V s}$ (Neumann and Tomlinson 1990). In solar cells, giving values of 5–20 $\text{cm}^2/\text{V s}$ (Siebentritt 2005).

With a large number of intrinsic defects in the chalcopyrite structure, numerous electronic transitions have been observed by photoluminescence, temperature dependent Hall measurements, photoconductivity, photo voltage, optical absorption, or capacitance measurements. Comparison of photoluminescence in bulk crystals, epitaxial films and polycrystalline films reveal nearly the same spectral features, indicating identical shallow defects in materials prepared under very different conditions.

Chapter 40

The CdS/Cu(InGa)Se₂ Solar Cells

Abstract Derived from the early Various cells have been explored in which In was alloyed with Ga to make Cu(In_xGa_{1-x})Se₂ with various degree of composition, or others in which S was substituted for Se, or Ag was substituted for Cu. The electrical and optical properties are analyzed and the performance of solar cell made of these materials are discussed. Models for the operation are suggested. Attention is paid to the electrodes, deposition, treatment methods and the doping. Reasons to use soda lime glass as the preferred substrate are given. The role of Cu and Na for the cell operation is discussed. Models of the defect structure are given and the energies of traps and recombination centers are tabulated and their measurements are enumerated. The influence of grain boundaries and their passivation is described. The electrical solar cell performance and degradation under various conditions and long-term outdoor deployment is discussed. Economical aspects for mass productions are enumerated.

40.1 Introduction

Of the ABC₂ compounds the CdS/(InGa)Se₂ cell has become very attractive for cost-effective power generation; best cell efficiencies measured at NREL are 20.3 % (Green et al. 2009a). Mass fabrication is eased by low-cost thin film, high-rate deposition over large areas for fabrication of monolithically interconnected modules. The CdS/Cu(InGa)Se₂ cells are radiation resistant and their life expectancies well exceeds that of other thin-film solar cells.

40.2 History

Boeing and ARCO Solar used alloying In with Ga, thereby producing a Cu(In_xGa_{1-x})Se₂ layer with a bandgap increased from 1.04 eV for CuInSe₂ to 1.1–1.2 eV by the partial substitution of In with Ga, leading to a substantial increase

Derived from the review of Shafarman et al. (2011).

in efficiency (Chen et al. 1987a). They also reduced the thickness of top CdS layer from 2 μm to 50 nm and used ZnO instead of CdS:In as a current carrier layer (Potter 1986). This increased the short-wavelength response. Later, a soda-lime glass was used as substrate for its good thermal expansion-match to CuInSe₂, but also for some diffusion of sodium from the glass (Hedström et al. 1993).

Cu(InGa)Se₂ is a very forgiving material, since high-efficiency cells can be made with a wide range in Cu(InGa)Se₂ composition (Rocheleau et al. 1987b; Mitchell et al. 1990a). Grain boundaries are inherently passive so that even films with grain sizes less than 1 μm can produce efficient solar cells. The device behavior is insensitive to defects at the junction caused by lattice mismatch or impurities between Cu(InGa)Se₂ and CdS. This permitted exposure to air before CdS is deposited, yielding solar cells with efficiencies of 18 %.

The solar cell, using a soda-lime glass substrate, is coated with a sputtered layer of Mo. After Cu(InGa)Se₂ deposition, the junction is formed by chemical bath-deposited CdS with of thickness ~ 50 nm. Then a high-resistance ZnO buffer layer is followed by a transparent doped ZnO or indium tin oxide (ITO), that are deposited, either by sputtering or chemical vapor deposition. A current-collecting grid or monolithic series interconnection completes the device or module, respectively.

40.3 Material Properties

40.3.1 Structure and Composition

CuInSe₂ and CuGaSe₂ have chalcopyrite lattice structure with a ratio c/a close to 2 (see Table 40.1). The deviation from $c/a = 2$, the tetragonal distortion, is caused by different strengths of the Cu–Se and the In–Se or Ga–Se bonds.

Cu(InGa)Se₂ can accommodate large variations in composition *without* appreciable differences in optoelectronic properties. This tolerance is essential for the use of Cu(InGa)Se₂ for efficient and low-cost photovoltaic modules. Solar cells with high performance can be fabricated with Cu/(In + Ga) ratios from 0.7 to nearly 1.0. This can be understood from the fact that two Cu vacancies with an In on Cu antisite defect have a low formation energy, and is electrically inactive (Zhang et al. 1997). Thus, these defect complexes can accommodate the Cu deficiency in Cu-poor/In-rich compositions of CuInSe₂ without adverse effects on the photovoltaic performance.

The effect of Na in the CuInSe₂, calculated by Wei et al. (1999), replacing InCu antisite defects, reduces the density of compensating donors and increases the net acceptor density (Schuler et al. 2004). Together with the tendency for Na to occupy Cu vacancies, the reduced formation of antisite defects also suppresses the formation of an ordered defect compound. This is observed with an increase in compositional with single-phase chalcopyrite exists with increased conductivity (Wei et al. 1999; Ruckh et al. 1996a).

40.3.2 Optical Properties and Electronic Structure

The absorption coefficient α of CuInSe₂ is larger than $3 \times 10^4/\text{cm}$ for higher than 1.3 eV energy (Alonso et al. 2001, 2002; Paulson et al. 2003) with 95 % of the incident solar illumination absorbed in films of 1 μm thickness. The energy (E) dependence of the fundamental absorption edge can be approximately described by

$$\alpha = A(E - E_g)^{1/2}/E \quad (40.1)$$

for a direct band gap semiconductor, where A is a function of the density of states. The optical properties, including band-gap and critical points of CuInSe₂, CuGaSe₂ and other Cu-ternary chalcopyrites is given in reference (Alonso et al. 2001). Spectroscopic ellipsometry and the dielectric functions were obtained from single crystals and of Cu(InGa)Se₂ with a compositions from $0 \leq x \leq 1$ as bulk polycrystalline ingots (Alonso et al. 2002) and polycrystalline thin films (Paulson et al. 2003).

The composition dependence of the band-gap can be fit to an empirical equation with a quadratic dependence on x . For the thin films with an In, Ga alloy (Paulson et al. 2003) this is

$$E_g = 1.04 + 0.65x - 0.26x(1 - x) \quad (40.2)$$

with a bowing parameter $b = 0.264$; the band gap of CuInSe₂ is 1.035 eV and of CuGaSe₂ is 1.68 eV.

The electronic structure of CuInSe₂ and other chalcopyrite semiconductors shows the degeneracy of the valence band maximum removed. This is unlike the degeneracy in common semiconductors such as Si, III–V or II–VI compounds, where the heavy and the light hole bands are degenerate at the center of the Brillouin zone and only the third band is split off by spin–orbit coupling.

Chalcopyrites have an additional crystal field splitting due to the tetragonal distortion (Shay et al. 1975) that can be seen by different absorption edges for light polarized parallel or perpendicular to the c -axis (Persson 2008; Hönes et al. 2008). The effective mass in solar cells that are made from Cu(InGa)Se₂ is lower parallel to the c -axis.

40.3.3 Electronic Properties

The effective mass, is determined by the curvature of the bands at the Γ -point, and influences the carrier mobility. Cu(InGa)Se₂ films, grown with the excess Se, are p -type with a carrier densities of $\sim 10^{15}$ – 10^{16} cm^{-3} (Heath et al. 2004).

CuInSe₂ and Cu(InGa)Se₂ have the same type of intrinsic defects, such as three vacancies, three interstitials, and six antisites, of which the ones with lowest formation energies are formed. These are, depending on the composition, the Cu vacancy, the In or Ga vacancy, the CuIII or III_{Cu} antisite and the Se vacancy (Wei et al. 1998, 1999).

The Se vacancy are amphoteric defect (Lany and Zunger 2004), which could explain some metastable effects in solar cells. The III_{Cu} antisite defect is related to a DX center (Lany and Zunger 2008), that could limit doping in wide band gap Cu(InGa)Se₂.

Photoluminescence and Hall effect on epitaxial film show four dominating shallow defects, i.e. three acceptors and one donor (Bauknecht et al. 2001; Siebentritt et al. 2004a, 2005). Defect spectroscopy by photoluminescence is more useful in material with Cu-excess (Dirnstorfer et al. 1998; Bauknecht et al. 2001; Shklovskii et al. 1989).

Capacitance measurements identify two dominant deep defects in all Cu(InGa)Se₂ samples: one, sometimes labeled N2, at an energy of 250–300 meV from the valence band (Turcu et al. 2002a), and a deeper one at 800 meV from the valence band (Heath et al. 2002). The N2 defect is far enough away from the mid-gap for all Ga/In ratios and does not act as recombination center. However, the 800 meV defect becomes a mid-gap defect for high Ga contents and may act as recombination center in alloys with larger Ga content.

40.3.4 Surface and Grain Boundaries

Surface morphology and grain structure are seen by scanning electron microscopy (SEM). The films used in devices have grain diameters on the order of 1 μm, but the grain size and morphology can vary greatly, depending on fabrication method and conditions.

The composition changes gradually from bulk to the surface of the films due to Cu migration (Klein et al. 2007). The surface Fermi level approaches the conduction band due to surface defects, adsorbates or junction formation. Reduced Cu concentration has then been interpreted as the formation of Cu vacancies, which becomes more favorable with higher Fermi level (Zhang et al. 1997). There can also be a band bending induced by surface charges that drive electro-migrating Cu into the bulk, leaving the surface depleted of Cu (Herberholz et al. 1999). This depletion is stopped when the composition is that of CuIn₃Se₅, since further depletion requires a structural change of the material. Electro-migration of Cu in CuInSe₂ has been correlated with type conversion of the chalcopyrite (Gartsman et al. 1997). Copper diffusion into the bulk is reduced when oxides form on the surface as the material is exposed to air. The surface oxidation is enhanced by Na (Ruckh et al. 1996a). Compounds that have been identified for extended oxidation include In₂O₃, Ga₂O₃, SeO_x, and Na₂CO₃ (Kylner 1999).

Post-treatment in air, typically at 200 °C, completes Cu(InGa)Se₂ solar cell. After CdS or (CdZn)S is vacuum-deposited to form the junction, annealing was extended for several hours for optimization (Mickelsen and Chen 1981; Damaskinos et al. 1987). Oxygen passivates the selenium vacancies on the surface of grains (Cahen and Noufi 1989). This indicates that the donor-type selenium vacancy act as recombination center. The positive charge of these donor-type defect reduces the ef-

fective hole concentration, hence the inter-grain carrier transport is impeded. When oxygen substitutes the missing selenium, this impediment is canceled.

The beneficial effect of Na on the performance of Cu(InGa)Se₂ solar cells, however, lacks a complete explanation. It could be a catalytic effect of Na on oxidation, by enhanced dissociation of molecular oxygen into atomic oxygen, that makes the passivation of V_{Se} more effective (Kronik et al. 1998). This is consistent with the observation that Na and O are predominantly found at the grain boundaries rather than in the bulk of the grains in CuInSe₂ (Niles et al. 1999). However, with little compositional difference between the interior and the boundary (Boyd and Thompson 1980; Kessler et al. 2005).

The insensitivity of Cu(InGa)Se₂ solar cells to grain size and morphology indicates that there is no significant recombination loss at grain boundaries. Even polycrystalline Cu(InGa)Te₂ solar cells outperform single-crystalline solar cells, and may suggest that grain boundaries are actually beneficial for solar cells.

40.4 Deposition Methods

40.4.1 Substrate Effects

Three effects of the substrate of polycrystalline Cu(InGa)Se₂ influence their properties: (1) thermal expansion, (2) chemical effects, and (3) surface influence on nucleation, each depend on the substrate, whether it is glass, a flexible metal foil or a plastic web.

Soda-lime window glass is mostly used for Cu(InGa)Se₂ since it is available in large quantities at low cost, contains the Na for diffusion into the cell, and has been used to make the highest-efficiency devices. Cu(InGa)Se₂ deposition requires a high substrate temperature of at least 350 °C up to 750 °C for the highest-efficiency cells. But it is also the highest temperature at which the glass substrate shows softening. Soda-lime glass has a thermal expansion coefficient of $9 \times 10^{-6}/K$ (Boyd and Thompson 1980), that matches closely the expansion coefficient of $9 \times 10^{-6}/K$ of the Cu(InGa)Se₂. Hence there is little stress during cool-down.

A CuInSe₂ film deposited on a substrate with a lower thermal expansion coefficient, such as borosilicate glass, will be under increasing tensile stress during cool-down. Typically, such films exhibit voids and micro-cracks (Chen et al. 1992). When the expansion coefficient of the substrate, like polyimide, is higher than that of CuInSe₂, it will be under compressive stress, that may lead to adhesion failures.

The glass composition includes various oxides such as Na₂O, K₂O (and CaO), that provide alkali to the Cu(InGa)Se₂. Sodium from the glass can also diffuse through the Mo back contact and requires control of the deposition of Mo (Bodegård et al. 1999).

The incorporation of Na influences the microstructure of Cu(InGa)Se₂ with larger grains and a higher degree of orientation with (112) parallel to the glass surface (Wei et al. 1999). Though the orientation is influenced by the incorporation of

Na, it is also directly correlated to the orientation of the Mo film (Schlenker et al. 2005). A comparison between Cu(InGa)Se₂ grown on Mo-coated substrates and directly on soda-lime glass, shows a more pronounced (112) orientation on glass (Hedström et al. 1993). The preferred orientation of the Cu(InGa)Se₂ film has also been shown to be directly correlated to the orientation of the Mo film (Schlenker et al. 2005). Other orientations like (220)(204) have also been observed in highly efficient cells (Contreras et al. 1999).

A more controllable supply of Na can be achieved by blocking sodium from the substrate with a diffusion barrier such as SiO_x, Al₂O₃, or SiN (Herz et al. 2003; Palm et al. 2003). Then, on the barrier-coated glass or flexible substrate, Na can be directly provided to the Cu(InGa)Se₂ growth process by depositing a sodium containing precursor, typically NaF with thickness of the order of 10 nm onto the Mo film (Probst et al. 1994). Alternatively, Na can be co-deposited with the Cu(InGa)Se₂ (Bodegård et al. 2000). A post-deposition Na treatment gave the same increased cell performance as Na provided during deposition Rudmann et al. (2005).

Metal foils can withstand higher temperatures, but are electrically conductive and may be reactive with the Se, used in the Cu(InGa)Se₂ process. While a variety of metal foil substrates have been used (Kessler et al. 2005), stainless steel is the mostly used and has produced the highest efficiency flexible Cu(InGa)Se₂ cells (Contreras et al. 1999).

40.4.2 Back Contact

The Mo back contact is mostly deposited by dc-sputtering. The Mo thickness is adjusted to the resistance requirements for the specific cell or module. A Mo film with thickness 1 μm will typically have a sheet resistance of 0.1–0.2 Ω/squ, that is a factor of 2–4 higher than bulk Mo. Sputter deposition of the Mo layer requires careful control of the pressure to control stress in the film (Vink et al. 1991) and to prevent poor adhesion. During the following Cu(InGa)Se₂ deposition, a MoSe₂ layer forms at the interface (Wada et al. 2001). Less MoSe₂ is formed on dense Mo, that is sputter-deposited under low pressures (Wada 1997). This interfacial layer does not degrade the device performance and may even promote the formation of an ohmic contact. Comparable cell performance are obtained with other Metals, such as Ta and W (Orgassa et al. 2003).

40.4.3 Deposition Methods

Deposition methods of Cu(InGa)Se₂ thin films are selected, that can be completed at low cost while maintaining a high deposition or processing rate, and high compositional uniformity over large areas.

For absorption of the incident light, the Cu(InGa)Se_2 layer should be at least 1 μm thick. Two general approaches for producing commercially highly efficient solar cells or panels can be distinguished:

(1) The first is a simultaneous vapor deposition of all constituents—Cu, In, Ga, and Se—onto a substrate between 450 and 600 °C. Here the Cu(InGa)Se film is formed in a single growth process. This co-evaporation from elemental sources uses Knudsen-effusion cells or open-boat sources (Matsuda 1998), with typical evaporation temperature ranges are 1300–1400 °C for Cu, 1000–1100 °C for In, 1150–1250 °C for Ga, and 250–350 °C for Se (see Fig. 40.5). The sticking coefficients of Cu, In, and Ga are very high, so the film composition and growth rate are determined by the flux distribution and effusion rate from each source.

As long as there is sufficient Se available, the composition of the film tends to follow the pseudo-binary tie-line between $(\text{InGa})_2\text{Se}_3$ and Cu_2Se , according to the relative concentration of Cu compared with In and Ga. The relative concentrations of In and Ga determine the band-gap of the film, according to Eq. (40.2).

Se has a much higher vapor pressure and lower sticking coefficient, therefore it is always evaporated in excess of what is needed for the film. Insufficient Se can result in a loss of In and Ga in the form of In_2Se or Ga_2Se (Jackson et al. 1987).

The advantage of elemental co-evaporation is its flexibility to control film composition and band-gap. However, there is some difficulty controlling the desired Cu-evaporation. Therefore, the bulk of the film is grown with Cu-rich overall composition and contains a Cu_xSe phase in addition to Cu(InGa)Se_2 (Mickelsen and Chen 1981).

(2) Second is an in-line process, in which the flux distribution results from the substrate moving sequentially over the constantly effusing Cu, Ga, and In sources. This has been implemented by several companies. This process may not give good reproducibility, since the Cu source that is at the highest temperature. Consequently, *in situ* measurement of the fluxes is used to control the evaporation sources. Electron impact spectroscopy (Mickelsen and Chen 1981), mass spectroscopy (Stolt et al. 1985), and atomic absorption spectroscopy (Powalla et al. 1997) have all been successfully implemented. In addition, the process can be monitored by *in situ* film thickness measurement using a quartz crystal monitor, optical spectroscopy, or X-ray fluorescence of the growing film (Eisgruber et al. 2002). The latter can also be used to measure composition. When the process includes a transition from Cu-rich to Cu-poor composition near the end of the deposition, it can be monitored by a change in the film structure using laser light scattering (Scheer et al. 2003) a change in the emissivity or temperature of the film (Nishitani et al. 1995) or by the infrared transmission (Negami et al. 1996).

40.4.4 Precursor Reaction Processes

Another approach to Cu(InGa)Se_2 film formation is a two-step process in which a precursor film containing Cu, In, and Ga is deposited and then reacted at high tem-

perature to form Cu(InGa)Se₂. This is sometimes referred to selenization though S is also added in many cases as described below. This approach was first demonstrated by Grindle et al. (1979) who sputtered Cu/In layers and reacted them in hydrogen sulfide to form CuInS₂. This was then adapted to CuInSe₂ by Chu et al. (1984). The highest-efficiency Cu(InGa)Se₂ using precursor reaction is 16.5 % (Alberts 2007).

The highest efficiency of any monolithically-interconnected large-area Cu(InGa)Se₂ module was produced with a sputtered precursors by Showa Shell (Kushiya et al. 2009). The precursor contains the Cu, Ga, In, and in some cases Se or S. It determines the final composition of the film. Sputtering is attractive since it is easily scalable. It provides good uniformity over large areas with high deposition rates, but material utilization is limited. Electro-deposition can also provide high material utilization at low cost. Application of particles in an ink or spray can also provide high utilization and uniformity. All of these methods are being developed for commercial use.

Reaction of the precursor films to form Cu(InGa)Se₂ can be done in H₂Se at 400–500 °C at times up to 60 min. Poor adhesion (Kapur et al. 1987) and excessive formation of a MoSe₂ layer at the Mo/Cu(InGa)Se₂ interface limits the reaction time and temperature (Sato et al. 1993). Reaction in H₂Se at atmospheric pressure and can be precisely controlled, but it is highly toxic. Reaction with diethylselenium, that is less toxic has also been used (Sugiyama et al. 2006).

Still other approaches for depositing CuInSe₂-based films have been used. These include reactive sputtering (Thornton et al. 1988), hybrid sputtering in which Cu, In, and Ga are sputtered while Se is evaporated (Talieh and Rockett 1989), closed-space sublimation (Guenoun et al. 1998), chemical bath deposition (CBD) (Murali 1988), laser evaporation (Galindo et al. 1989), and spray pyrolysis (Abernathy et al. 1984). Great effort was made to explore different thin film deposition techniques. For early attempts see (Rockett and Birkmire 1991).

40.5 Junction and Device Formation Using CdS

The first device with CuInSe₂ high-performance solar cells was a heterojunction cell between *p*-type single-crystal CuInSe₂ and a thin film of *n*-type CdS (Wagner et al. 1974; Shay et al. 1975). Consequently, most later thin film junction were formed by depositing CdS onto the CuInSe₂ films (Kazmerski et al. 1978), indicating that a similar mechanism as discussed in earlier chapters occurred in CdS to improve the efficiency. Later, an undoped layer of CdS, followed by CdS doped with In (Michaelson (1972). Further improvement was achieved by replacing the doped CdS with doped ZnO (Potter et al. 1985). The undoped CdS layer adjacent to the Cu(InGa)Se₂ film was reduced in thickness to ~50 nm to maximize the optical transmission.

A pinhole-free coating of the thin CdS layer can be obtained by chemical bath deposition, also referred to as solution growth. The thin CdS layer grows ion-by-ion, resulting in dense homogeneous films (Lincot et al. 1993) with mixed cubic/hexagonal or predominantly hexagonal lattice structure (Wada 1997; Lincot

et al. 1993; Nakada and Kunioka 1999). The films consist of crystallites with a grain size of the order of tens of nanometers (Lincot et al. 1993).

Deviation from stoichiometry of CdS is commonly observed: films tend to be cadmium-rich and contain substantial amounts of oxygen, hydrogen, carbon and nitrogen (Kylner et al. 1996a; Hashimoto et al. 1998).

40.5.1 Interface Effects

The interface between the Cu(InGa)Se_2 and the CdS is pseudo-epitaxial with some intermixing of the elements. Chemical bath deposited CdS on Cu(InGa)Se_2 films is epitaxial with (112) chalcopyrite Cu(InGa)Se_2 planes parallel to the (111) cubic or (002) hexagonal CdS planes (Wada 1997; Nakada and Kunioka 1999). The lattice mismatch is very small for pure CuInSe_2 with a (112) spacing of 0.334 nm compared with a spacing of 0.336 nm for (111) cubic and (002) hexagonal CdS. The lattice mismatch increases with Ga content. $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ and $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ have (112) spacings of 0.331 and 0.328 nm, respectively.

When Cu(InGa)Se_2 films are immersed in the chemical bath for deposition of CdS, they cause some chemical etching. Thereby native oxides are removed. This cleans the Cu(InGa)Se_2 surface and promotes the epitaxial growth of the CdS layer. Cu(InGa)Se_2 exposed to chemical baths without thiourea shows some diffusion or electro-migration of Cd (Ramanathan et al. 1998).

40.5.2 Transparent Contacts

High conductivity for lateral current collection is provided from a transparent conducting oxide (TCO). There are three main materials in this class, doped SnO_2 , $\text{In}_2\text{O}_3\text{:Sn}$ (ITO), and doped ZnO. SnO_2 requires undesired high deposition temperatures above 250 °C. However, ITO and ZnO can both be used, but ZnO is favored by potentially lower material costs. Mostly a low-temperature sputtering deposition is used for TCO films.

ITO layers are routinely fabricated by sputtering from ceramic ITO targets in an Ar:O_2 mixture, and at sputter rates range between 0.1 and 10 nm/s (Lewis and Paine 2000). Sputtering of doped ZnO films is preferred for depositing the transparent front contact on Cu(InGa)Se_2 solar cells.

ZnO:Al films are deposited by rf magnetron sputtering from ceramic $\text{ZnO:Al}_2\text{O}_3$ targets with 1 or 2 weight% Al_2O_3 . But dc sputtering from ceramic targets is favored for higher deposition rates (Menner et al. 1998).

Reactive dc sputtering from Al/Zn alloy has also been used for $\text{Cu(InGa)Se}_2/\text{CdS}$ devices with the same performance as with rf sputtered ZnO:Al (Ruckh et al. 1996a). The use of Zn/Al alloy targets allows lower costs, but the reactive sputtering requires precise process control because of an hysteresis effect (Westwood 1990). Optimal

optoelectronic properties are achieved only within a narrow process window. Deposition rates are in the 5–10 nm/s range.

Chemical vapor deposition of ZnO is another deposition option and is used by at least one commercial manufacturer of Cu(InGa)Se₂ modules (Kushiya et al. 2009). The reaction occurs at atmospheric pressure between water vapor and diethylzinc and the films are doped with fluorine or boron.

The sheet resistance of the transparent contact is usually controlled by the layer thickness. Small-area cells use layers with 20–50 Ω/squ and thicknesses of 100–500 nm. Commercial modules may require 5–10 Ω/squ with correspondingly larger thickness. With increasing thickness and lower resistance a loss in transparency occurs due to free carrier absorption.

40.5.3 High-Resistance Buffer-Layers

An interlayer of undoped high-resistivity (HR) ZnO is often used before sputter deposition of the TCO layer. Depending on the deposition method and conditions, this layer may have a resistivity of 10^5 times the one of the transparent contact. Typically, this HR interlayer is rf magnetron sputtered of 50 nm thickness from an oxide target.

The gain in performance by using an HR ZnO HR layer is related to the CdS thickness (Ruckh et al. 1996a; Rau and Schock 2001; Kessler et al. 2000). The role of an HR ZnO layer may be locally non-uniform electronic quality of the Cu(InGa)Se₂ layer or by pinholes in the CdS layer, which create parallel diodes with a Cu(InGa)Se₂/ZnO junction. This HR interlayer increases the open circuit voltage. However, this is not observed when the CBD–CdS layer is thick enough (Kessler et al. 2000).

40.5.4 Device Completion

For completion, a metal contact is deposited onto the TCO layer, as a grid with minimum shadow to allow maximum light penetration. The metal grid contact is made by first evaporating some tens of nanometers of Cr or Ni to prevent the formation of a high-resistance aluminum oxide layer of the following Al. Deposition is through an aperture mask to about a micrometer thickness or preferably through a photo-lithographically defined grid (Jackson et al. 2007).

The cell area is defined by removing the layers on top of the Mo outside this area by mechanical scribing or laser patterning. Alternatively, the layers on top of the Cu(InGa)Se₂ can be removed by photolithography and etching. Or the TCO layer can be deposited through an aperture mask to define the cell area.

Finally, the highest-efficiency solar cells have an antireflection coating to minimize optical losses. Typically this is an evaporated MgF₂ layer with thickness of ~ 100 nm. However, this is not done for modules that are covered with glass or encapsulated otherwise.

40.6 Device Operation

Cu(InGa)Se₂ solar cells of more than 20 % efficiency were made in laboratory-scale devices, largely by empirical processing improvements. In recent years considerable effort has gone to developing models of the effects of interfaces, grain boundaries, point defects, etc. to enable both a better understanding and identification of pathways for further improvements.

Cu(InGa)Se₂/CdS solar cells are characterized by high quantum efficiency (QE) and short-circuit current. The open-circuit voltage increases with the band-gap of the absorber layer and is rather insensitive to grain boundaries and defects at the Cu(InGa)Se₂/CdS interface.

The loss mechanisms can be divided into optical losses that limit the short-circuit photocurrent (J_{sc}), recombination losses that limit the open-circuit voltage (V_{oc}) and the fill factor (FF). In addition parasitic losses, such as series resistance, shunt conductance, and voltage-dependent current collection occur, which mostly reduce the FF but may also reduce J_{sc} and V_{oc} .

One model suggests that the voltage is limited by recombination through bulk recombination centers in the space-charge region of the Cu(InGa)Se₂ absorber layer. Recombination at the Cu(InGa)Se/CdS interface is minimized by a domain-related field limitation in CdS (Böer 2010). Processing-dependent exceptions to this behavior, for example, when the voltage is limited by interface recombination, seem to confirm this basic understanding. Characterization of the metastable response to light exposure respond to kinetics of carrier trapping and release as function of the acting field. Current injection is another possibility contributing to an understanding of the device physics.

40.6.1 Light-Generated Current

The best Cu(InGa)Se₂ cells have $J_{sc} = 36 \text{ mA/cm}^2$ (Repins et al. 2008) out of a possible 42.8 mA/cm^2 calculated for a bandgap of 1.12 eV under AM1.5 global illumination. The light-generated current is the integral of the product of the external quantum efficiency (QE_{ext}) and the illumination spectrum. QE_{ext} is controlled by the band-gap of the Cu(InGa)Se₂ absorber layer, the CdS and ZnO window layers, and a number of loss mechanisms. These losses are illustrated in Fig. 40.1 where typical QE curves at two different voltage biases, 0 and -1 V , are shown.

The QE curve at -1 V is slightly higher at longer wavelengths, because of the increased space charge layer width under reverse bias, which causes the effective collection length to increase.

However, each of these losses depend on the device design and optical properties of the specific layers. These losses include:

1. Shading from a collection grid or the area for the interconnect.
2. Front surface reflection.

Fig. 40.1 Quantum efficiency (*solid curve*) at 0 and -1 V and optical losses for a Cu(InGa)Te₂/CdS/ZnO solar cell with a band gap of 1.12 eV

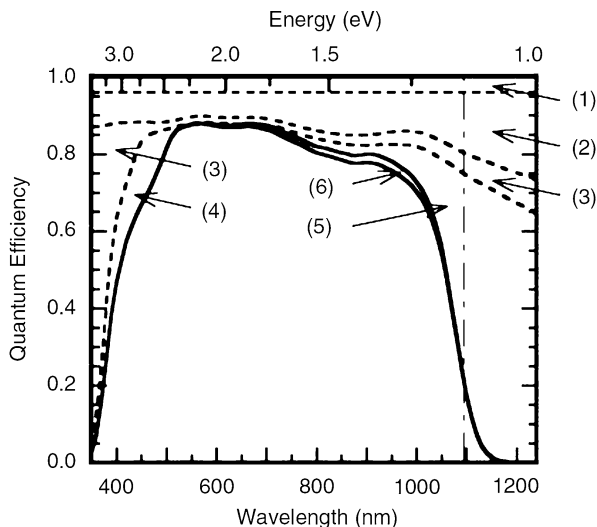


Table 40.1 Current loss, ΔJ , for $E > 1.12$ eV due to the optical and collection losses for a typical Cu(InGa)Se₂/CdS/ZnO solar cell as shown in Fig. 40.1

Region in Fig. 40.1	Optical loss mechanism	ΔJ (mA/cm ²)
(1)	Shading from grid with 4 % area coverage	1.7
(2)	Reflection from Cu(InGa)Se ₂ /CdS/ZnO	3.8
(3)	Absorption in ZnO	1.8
(4)	Absorption in CdS	0.8
(5)	Incomplete generation in Cu(InGa)Se ₂	1.9
(6)	Incomplete collection in Cu(InGa)Se ₂	0.4

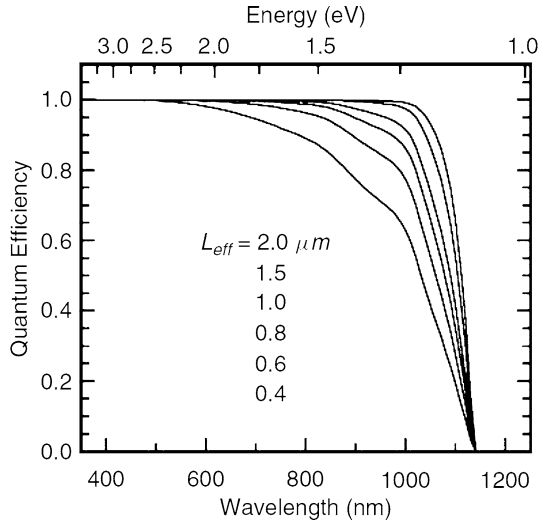
3. Absorption in the ZnO layer typically with 1–3 % absorption in the visible wavelengths range, which is influenced at $\lambda > 900$ nm by free-carrier absorption, and for $\lambda < 400$ nm by band-to-band absorption.
4. Absorption in the CdS layer that increase steeply at wavelengths below the band gap of 2.42 eV.
5. Incomplete absorption in the Cu(InGa)Se₂ layer near the Cu(InGa)Se₂ band gap.
6. Incomplete collection of photo-generated carriers in the Cu(InGa)Se₂, as discussed below.

The external quantum efficiency QE_{ext} is given by

$$QE_{\text{ext}}(\lambda, V) = [1 - R(\lambda)][1 - A_{\text{ZnO}}(\lambda)][1 - A_{\text{CdS}}(\lambda)](QE_{\text{int}}(\lambda, V)) \quad (40.3)$$

where R is the total reflection, including grid shading, A_{ZnO} is the absorption in the ZnO and A_{CdS} is the absorption in the CdS. QE_{int} , the internal quantum effi-

Fig. 40.2 Calculated internal quantum efficiency
 $QE = 1 - \exp[-\alpha(\lambda)L_{\text{eff}}]$
 for Cu(InGa)Se₂ with
 $g = 1.12$ eV and collection
 lengths from 0.4 μm (*bottom*)
 to 2 μm (*top*), using
 absorption coefficient data
 from reference (Paulson et al.
 2003)



ciency, is the ratio of photo-generated carriers collected, to the photon flux that can be approximated by Jackson et al. (2007)

$$QE_{\text{int}}(\lambda, V) = 1 - \exp[-\alpha(\lambda)(W(V) + L_{\text{diff}})] \quad (40.4)$$

where α is the Cu(InGa)Se₂ absorption coefficient, W is the space-charge width in the Cu(InGa)Se₂, and L_{diff} the minority-carrier diffusion length. This approximation assumes that all carriers generated in the space-charge region are collected for cells at 0 V.

Internal quantum efficiencies, calculated from Eq. (40.4) are shown in Fig. 40.2.

The incomplete collection can be significant for Cu(InGa)Se₂ (Mitchell et al. 1985; Shafarman et al. 1996a). The effect of $J_L(V)$ on the current–voltage characteristic increases, since the collection length decreases with forward voltage bias and therefore has its largest effect on the fill factor and on V_{oc} (Eron and Rothwarf 1984; Ohnesorge et al. 1998). This analysis of current collection holds for sufficiently thick Cu(InGa)Se₂ to absorb all light.

40.6.2 Recombination

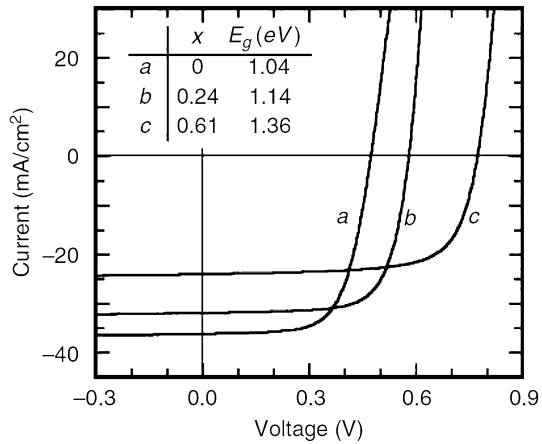
The current–voltage characteristic of Cu(InGa)Se₂/CdS can be described by a general diode equation:

$$J = J_D - J_L = J_O \exp\left\{\left[e/(AkT)\right](V - R_S J) + G(V - R_S J)\right\} - J_L \quad (40.5)$$

with the diode current J_O given by:

$$J_O = J_{OO} \exp[-\Phi_b/(AkT)]. \quad (40.6)$$

Fig. 40.3 Current–voltage curves for Cu(InGa)Se₂/CdS solar cells with different relative Ga content giving (a) $E_g = 1.04$, (b) 1.14, and (c) 1.36 eV



The ideality factor A , barrier height Φ_b , and prefactor J_{00} depend on the recombination mechanism that dominates J_0 , while the series resistance R_s and shunt conductance G are losses with the primary diode. General expressions for A , Φ_b , and J_{00} in the cases of recombination through the interface, space-charge region, or bulk of the absorber layer can be found earlier in this Handbook.

Changes of the band-gap due to variation of the In to Ga ratio of Cu(In _{x} Ga _{$1-x$})Se₂/CdS solar cells is instructive as shown in Fig. 40.2 for three devices with $x = 0$, 0.24, and 0.61, corresponding to $E_g = 1.04$, 1.14, and 1.36 eV, respectively (Shafarman et al. 1996a).

Thus with the barrier height $\Phi_b = E_g$ combining Eqs. (40.5) and (40.6) and assuming $G \ll J_L/V_{oc}$, the open-circuit voltage becomes

$$V_{oc} = E_g/e - AkT/e \ln(J_{00}J_L). \quad (40.7)$$

Therefore, for Zero Temperature the open circuit Voltage extrapolates to the band-gap (see Fig. 40.3)

$$T \rightarrow 0, \quad V_{oc} \rightarrow E_g/e. \quad (40.8)$$

For a wide range of thin film solar cells with an ideality factor $1 < A < 2$, it was shown, that $V_{oc}(T \rightarrow 0) = E_g/e$.

Values of Φ_b and A indicate different recombination paths, with the dominant recombination mechanism in the bulk, in the space charge region of the Cu(InGa)Se₂, or at the Cu(InGa)Se₂/CdS interface (Phillips et al. 1996a; Turcu et al. 2002a; Klenk 2001). Each of the curves in Fig. 40.2 can be fit to Eq. (40.5) with $A = 1.5 \pm 0.3$ similar to the data above. Measured values of $\Phi_b = E_g$ have been reported for CuInSe₂ (Mitchell and Liu 1988; Roy et al. 1988) and many Cu(In _{x} Ga _{$1-x$})(SeS)₂ (Turcu et al. 2002a) solar cells, independent of the band gap of the (CdZn)S cover layer (Roy et al. 1988), and for a variety of different absorber-layer deposition processes and alloy ratios (x) (Shafarman and Phillips 1993).

These results for Φ_b and A indicate that Cu(In _{x} Ga _{$1-x$})Se₂/CdS solar cells operate with the diode current controlled by Shockley–Read–Hall-type recombination

centers in the $\text{Cu}(\text{In}_x\text{Ga}_{1-x})\text{Se}_2$ layer and eV_{oc} extrapolates to E_g independent of composition x . The recombination is largest through deep trap states in the space-charge region of the $\text{Cu}(\text{InGa})\text{Se}_2$ where $p \approx n$. The variation in A between 1 and 2 depends on the energies of the deep trap states (Sah et al. 1957). Some very high efficiency devices show low values of $A \approx 1.1$ – 1.3 (Repins et al. 2008). Here a dominance of bulk recombination may be seen as an indicator that recombination at the $\text{Cu}(\text{InGa})\text{Se}_2/\text{CdS}$ interface does not limit V_{oc} , in spite of the fact that during processing of $\text{Cu}(\text{In}_x\text{Ga}_{1-x})\text{Se}_2$ solar cells, no efforts are made to reduce interface defects, and the devices are often exposed to air between the $\text{Cu}(\text{In}_x\text{Ga}_{1-x})\text{Se}_2$ and CdS depositions. This is an indication that the deposition of CdS itself helps to clean the surface to epitaxial quality, and to prevent interface recombination or diode leakage, probably by limiting the field at the junction interface through the creation of high-field domains (Böer 2010).

However, when the absorber layer is processed without Cu supply for some wide-band-gap devices, especially those using $\text{Cu}(\text{InGa})\text{Se}_2$ absorbers (Scheer et al. 1993), regardless of the band gap, these devices have lower V_{oc} and $\Phi_b < E_g$ which is indicative that interface recombination has become dominant (Shafarman et al. 1996a; Turcu et al. 2002a), and enables further increase of interface fields and therefore diode leakage (Böer and Voss 1968c; Böer 2011a). $\text{Cu}(\text{InGa})\text{Se}_2$ devices with a diffusion barrier that restricted Na diffusion from the glass substrate had the open circuit voltage reduced by 120 mV from Φ_g the absorber band-gap (Thompson et al. 2008).

The temperature dependence of A was explained by enhancement of the recombination current, particularly at reduced temperatures (Rau 1999). Transient photocurrent (Nishio et al. 1997) and time-resolved photoluminescence (Ohnesorge et al. 1998; Metzger et al. 2008) were used to determine lifetimes in the range 10–250 ns for high-efficiency solar cells. However, one cannot decide which of the defects, discussed in Sect. 40.2, that is responsible for the recombination and limits the voltage in the devices.

40.6.3 The $\text{Cu}(\text{InGa})\text{Se}_2/\text{CdS}$ Interface

The bulk of $\text{Cu}(\text{In}_x\text{Ga}_{1-x})\text{Se}_2$ is p -type with E_g depending on the relative Ga concentration; the CdS layer is n -type with $E_g = 2.4$ eV and is totally depleted, and the bulk ZnO n^+ -layer has $E_g = 3.2$ eV. The HR ZnO layer between the n^+ -ZnO layer and the CdS is also assumed to be depleted. Positive ΔE_C indicates a spike in the conduction band, that is, the conduction-band minimum in CdS is at higher energy than the conduction-band minimum of the $\text{Cu}(\text{InGa})\text{Se}_2$. We assume also a -0.3 eV conduction-band offset between the ZnO and the CdS (Scheer et al. 1993). Simulation of current transport and recombination has considered the effect of ΔE_C (Niemegeers et al. 1995; Liu and Sites 1996; Minemoto et al. 2001). These models show that if ΔE_C is larger than about 0.5 eV, the collection of photo-generated electrons in the $\text{Cu}(\text{InGa})\text{Se}_2$ is impeded and J_{sc} and FF is reduced

sharply. With a smaller spike, electrons can be transported across the interface assisted by thermionic emission (Niemegeers et al. 1995). Because of its importance for Cu(In_xGa_{1-x})Se₂/CdS devices, several efforts have been made to calculate or measure ΔE_C with varying results (Wei and Zunger 1993).

Experimentally accessible are the valence band offsets via photoemission spectroscopy (XPS, UPS or synchrotron based). For unoxidized Cu(InGa)Se₂ interfaces with CdS a valence (band offset of -0.9 eV was found. The same valence-band offset was found for pure CuInSe₂ polycrystalline (Scheer et al. 1993) or epitaxial (Schuler et al. 2004) films, or single-crystals (Loher et al. 1995), independent of the surface orientation or the deposition of the CdS film (Hunger et al. 2007).

40.6.4 Wide and Graded Band-Gap Solar Cells

While the highest efficiency solar cells generally have (In_xGa_{1-x}) with $x \approx 0.1-0.3$ yielding $E_g \approx 1.1-1.2$ eV, efforts have been made to develop high-efficiency solar cells from wider-band-gap alloys. These result in a lower temperature coefficient for the output power (Kniese et al. 2006), which will improve performance at elevated temperatures in most terrestrial applications. Wide-band-gap devices could also be used as the top cell in a tandem or multi-junction cell structure.

Wider band-gap materials Cu(InGa)Se₂ and CuInS₂ have attracted most attention. CuGaSe₂ has a band-gap of $E_g = 1.68$ eV, which is suited for a tandem structure. CuInS₂ has $E_g = 1.53$ eV, which is nearly optimum for a single-junction solar cell. CuInS₂ is deposited with Cu-rich composition and then the excess Cu, that forms a Cu_xS second phase, is etched away before CdS deposition (Scheer et al. 1993). Cu(InAl)Se₂ solar cells have achieved 17 % efficiency with $E_g = 1.15$ eV. The CuAlSe₂ has a band gap of $E_g = 2.7$ eV. Other promising results have been obtained for (AgCu)(InGa)Se₂ films (Nakada et al. 2005; Hanket et al. 2009), where the replacement of Cu with Ag enables the band-gap to be increased while the alloy melting temperature is lowered, and relatively high V_{oc} have recently been reported. The highest-efficiency of wide-band-gap solar cells with different alloys are listed in Table 40.2.

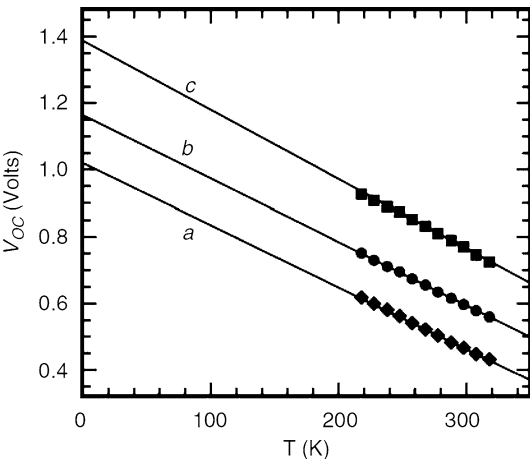
The addition of a small amount of Ga to CuInSe₂ increased the open circuit voltage, even when the Ga was confined to the back of the absorber and did not increase the band-gap in the space-charge region (Jensen et al. 1993). Improved adhesion with Ga addition was also observed with S (Ohashi et al. 2001) and Al (Shafarman et al. 1996a).

The effect of increasing band-gap in Cu(InGa)Se₂/CdS solar cells on V_{oc} and efficiency is shown in Fig. 40.4. Here it is seen that the efficiency is nearly independent of the band-gap for $E_g < 1.3$ eV. For Ga_xIn_{1-x} compounds with $x < 0.4$ (Shafarman et al. 1996a) the open circuit voltage V_{oc} increases approximately linearly with E_g . With even wider-band-gap absorbers, V_{oc} increases to values greater than 0.8 V, but the efficiency decreases due to increased recombination that reduces V_{oc} below that expected from Eq. (40.7) (Rau and Schock 2001; Phillips et al. 1996a);

Table 40.2 Highest total area efficiencies for wide-band-gap devices with different alloy absorber layers. The record-efficiency low-band-gap CuInSe₂ and Cu(InGa)Se₂ cells shown for comparison

Material	E_g [eV]	Efficiency [%]	V_{oc} [mV]	J_{sc} [mA/cm ²]	FF [%]	Reference
CuInSe ₂	1.02	14.5	491	41.1	71.9	(AbuShama et al. 2004)
Cu(InGa)Se ₂	1.12	20.0	692	35.7	81.0	(Green et al. 2009a)
CuGaSe ₂	1.68	9.5	905	14.9	70.8	(Young et al. 2003)
Cu(InGa)S ₂	1.53	12.9	832	22.9	67.0	(Merdès et al. 2009)
Cu(InAl)Se ₂	1.51	9.9	750	20.1	65.8	(Shafarman et al. 2002)
(AgCu)(InGa)Se ₂	1.6	13.0	890	20.5	71.3	(Hanket et al. 2009)
Ag (InGa)Se ₂	1.7	9.3	949	17.0	58	(Nakada et al. 2005)

Fig. 40.4 Shows the temperature dependence of V_{oc} for these devices. In each case, as shown in Eq. (40.7) for the same cells as in Fig. 40.2

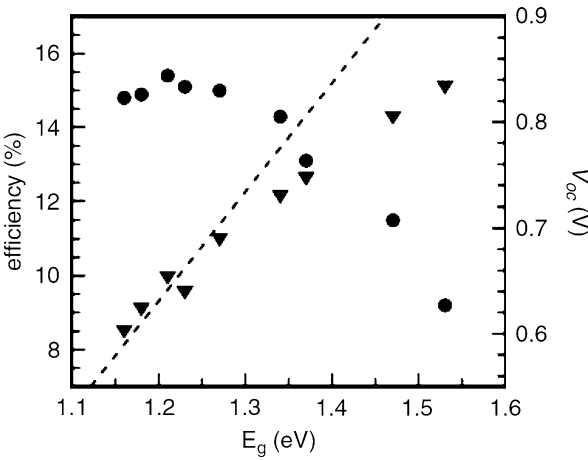


a voltage-dependent current collection (Shafarman et al. 1996a) causes the fill factor to decrease. The dashed line in Fig. 40.4 has a slope $\Delta V_{oc}/\Delta E_g = 1$. However, devices with $E_g > 1.3$ eV fall below this slope due to the dependence on J_L in the second term of Eq. (40.7).

Admittance spectroscopy of Cu(In_xGa_{1-x})Se₂ shows that, with increasing concentration of Ga recombination becomes marked with defects of an activation energy ~ 0.3 eV (Hanna et al. 2001). The defect band centered at 0.8 eV from the valence band moves closer to mid-gap for increasing band-gap and therefore becomes more efficient as a recombination center (Heath et al. 2002). As expected, the ideality factor A increases toward $A = 2$ with increasing Ga content (Hanna et al. 2001; Sah et al. 1957).

Band-gap gradients formed by controlled incorporation of Ga or S have been proposed as a means to increase device efficiency by separately reducing recombination and collection losses (Gabor et al. 1996; Gray and Lee 1994; Topic et al. 1996; Dullweber et al. 2001a). A gradient from wider band-gap at the Cu(InGa)Se₂/CdS interface to narrower band-gap at the edge of the space charge region, could re-

Fig. 40.5 Efficiency (●) and V_{oc} (▼) as a function of Cu(InGa)Se₂ band-gap, varied by increasing the relative Ga content (Shafarman et al. 1996a). The dashed line has slope $\Delta V_{oc}/\Delta E_g = 1$



duce recombination and increase V_{oc} . In this case, the smaller band-gap in the bulk portion of the device enables higher optical absorption and J_{sc} (Gabor et al. 1996; Dullweber et al. 2001a).

Chapter 41

Amorphous Silicon Solar Cells

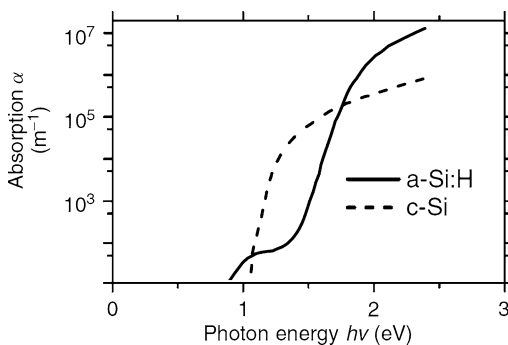
Abstract After a short introduction of the basics of producing these cells from an amorphous silicon layer and depositing a much thinner n and p layer on each side of this i -layer. Typical electro-optical properties are discussed, including the drift mobilities of electrons and holes and the optical absorption spectrum. Band-edges, band-gaps and band-tailings are analyzed. The two common production procedures are given and the properties of the resulting layers as function of the production steps are discussed. Atomic and electric properties of the defect structure are given. The specific influence of incorporated hydrogen is described. The doping process is described and the reasons given why a phosphorous doping of α -Si:H is totally different from a P-doping of crystalline Si. The growth-related defect structure and its influence of the carrier transport in α -Si:H is elaborated. The reasons for a special geometry of α -Si:H is discussed with a central i -layer of ~ 100 times the thickness of the outer n - and p -layers. Modern pin -cell performances are analyzed. The influence of the built-in field on the selection of the best device geometry is described. The deposition methods and properties of micro-crystalline (mc-Si:H) and nano-crystalline (nc-Si:H) Si are given. Solar cell degradation under light deployment (laboratory or outdoor), the Staebler–Wronski effect, is described and means to minimize cell degradations are indicated. Defect meta-stability is analyzed. The different deposition methods are described. Alloying α -Si:H including the changing defect structure are described and the reasons for it are analyzed. Various multi-junction Si:H based solar cells are listed and their performance is analyzed.

41.1 History of Amorphous Silicon Solar Cells

Amorphous silicon can be deposited as a thin film on substrates inserted into the silane (SiH_4) gas discharge and contains about 10 atomic% hydrogen. Its electron mobility is approximately $10 \text{ cm}^2/\text{V s}$. Amorphous silicon can be made n -type by mixing silane with phosphine (PH_3) or p -type by mixing it with diborane (B_2H_6) (Spear and LeComber 1975). However, the doping is less efficient to produce conduction electrons than in crystalline silicon. In α -Si:H sulfur is threefold coordi-

Derived from the review of Schiff et al. (2011).

Fig. 41.1 Spectra of the optical absorption coefficient $\alpha(h\nu)$ as a function of photon energy $h\nu$ for crystalline silicon (c-Si) and for hydrogenated amorphous silicon (α -Si:H)



nated with electrons in p-orbitals, while the two remaining valence electrons are paired and relatively tightly bond in s orbitals. Only a small percentage of P atoms are fourfold bond and contribute one electron to the conduction band. But these also generate dangling bonds that act as compensating electron traps. Similarly Borane doping is complex.

The first solar cells based on amorphous Si were made in RCA (Carlson 1957) and showed a conversion efficiencies of 2.4 % (Carlson and Wronski 1976). A significant amount of hydrogen is incorporated in amorphous silicon when it is useful for solar cells, while amorphous silicon made from evaporated silicon is not. The deposition of the hydrogenated form of amorphous silicon and its doping with phosphorus and boron is simple and inexpensive. The optical absorption spectrum of hydrogenated amorphous silicon (α -Si:H) is attractive for solar cells since it is transparent up to 1.7 eV and highly absorptive starting at 2 eV with absorption constants approaching 10^7 cm^{-1} . As a direct band gap material, a significant fraction of the sun light is absorbed in a thin layer of only a few μm thickness (Fritzsche 2001). On the other hand, crystalline silicon as an indirect band gap material is transparent in this range even in crystals of 100 μm thickness (see Fig. 41.1). All these properties opened a rapidly increasing interest in these solar cells (Carasco and Spear 1983).

41.2 Designs of Modern α -Si:H Solar Cells

High-efficiency devices deviate from the typical design of *pn*-solar cells by including a relatively thick intrinsic layer between the much thinner *p*- and *n*-type layers forming a *pin* photodiode.

Since within the *n*- or *p*-type layers the diffusion length is very small, one prefers that most of photo-generate electrons and holes in the *i*-layer that contains a high built-in electric field to separate these carriers and generate the photo emf that can be extracted through the adjacent *n*- or *p*-type layers. Typically the *n*- or *p*-type layers are about 10 nm thick, while the separating undoped α -Si:H layer, that has a much larger diffusion length for both carriers, has a thickness of up to several hundred nm. Since the electrons have a larger diffusion length than the holes in the *i*-layer, it is

advantageous to place the p -layer toward the light, and the n -layer toward the metal back electrode.

The α -Si:H layer can be produced in a high frequency ac-gas discharge (also referred to as Plasma Enhanced Chemical Vapor Deposition (PECVD)). The used ac frequency is usually 13.56 MHz (permitted by federal and international authorities for industrial processing) with pressure ranges between 0.1 and 1 Torr, RF Power between 10 and 100 mW/cm² substrate temperatures between 150 and 300 °C, electrode spacing between 5 and 1 cm, active gas flow between 0.02 and 0.002 sc cm/cm², and hydrogen dilution between 100 and 1 (the more hydrogen the higher the deposition rate and substrate temperature is). Typical deposition rates are between 1 and 20 Å/s. For lower frequencies, toward dc glow discharges, it is difficult to maintain homogeneity, and at much higher frequencies the opto-electronic properties are inferior.

41.3 α -Si:H-Related Solar Cells

41.3.1 *Multijunction Solar Cells*

The conversion efficiency of the α -Si:H *pin* photodiode can be significantly improved by depositing two or three such photodiodes of different band-gap, one on top of another, to create a “multijunction” device. The main advantage to the tandem design over the single-junction is due to “spectrum splitting” of the solar illumination (Dalal and Fagen 1980), e.g. by using the α -Si:H with a band gap of 1.9 eV as front layer, followed by an α -SiGe:H alloy with lower band gap. More recently multi-junction cells of three consecutive layers with stepwise decreasing band gap have been used.

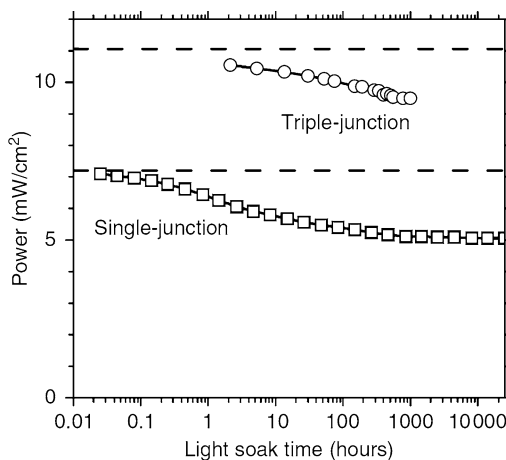
41.3.2 *α -Si:H Followed by a Micro-crystalline Si Layer*

The micro-crystalline Si layer has also a smaller band gap than α -Si:H and increases the conversion efficiency substantially. These new layers are also referred to as nanocrystalline layers and are produced similarly to the α -Si:H layer in a high frequency ac-gas discharge at 13.56 MHz, however using a larger current density.

41.3.3 *Staebler–Wronski Effect*

Amorphous silicon-based solar cells exhibit a significant decline in their efficiency during their first few hundred hours of illumination; however, the degradation of multiple layer solar cells and of nanocrystalline silicon cells is much lower. The

Fig. 41.2 Decease of the efficiency of α -Si:H solar cells as a function of the time of illumination with 100 mW/cm² simulated sunlight (Guha 1999; Guha et al. 1993)



single-junction cell loses about 30 % of its initial efficiency after about 1000 hours; the triple-junction module loses about 15 % of its initial efficiency (see Fig. 41.2).

All amorphous silicon-based solar cells exhibit such degradation with light, which is called the Staebler–Wronski effect (Staebler and Wronski 1977a, 1977b). The effect anneals out nearly completely within a few minutes at temperatures of about 160 °C, and anneals substantially in outdoor deployment at summer operating temperatures of 60 °C.

The Staebler–Wronski effect contributes to noticeable seasonal variations in the conversion efficiency of α -Si:H as observed for modules in the field in Switzerland (since during the winter season the daytime temperature was insufficient for annealing), but there was no discernible, permanent degradation of this module over the three-year extent of this test; one study over ten years does suggest degradation of about 0.7 % per year (Gregg et al. 2005), which is comparable to the long-term degradation of c-Si cells.

41.4 Atomic and Electronic Structure of α -Si:H

41.4.1 Atomic Structure

Silicon atoms in amorphous silicon mostly have the same basic structure that they have in crystal silicon: each silicon atom is connected by covalent bonds to four other silicon atoms arranged as a tetrahedron around it. However, amorphous Si has numerous atoms with only 3 bonds satisfied, the fourth bond unempty, it is a “dangling” bond, consequently the lattice is deformed, there is no long-rang order.

In hydrogenated amorphous silicon (α -Si:H), an hydrogen atom is attached to the dangling bond. This hydrogen is invisible to X-rays, but is evident in proton magnetic resonance (Reimer and Petrich 1989) and infrared spectroscopy (Zhao et al.

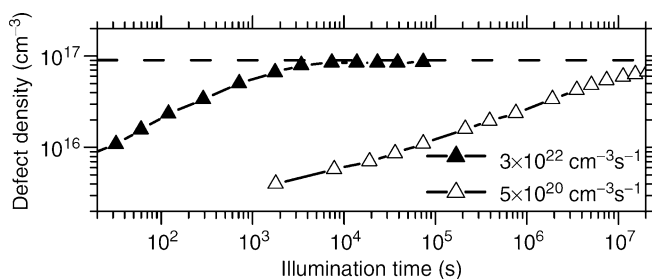


Fig. 41.3 Defect (*dangling bond*) density as a function of illumination time of an α -Si:H film as measured by Park et al. (1989). The intensity of illumination is indicated in the legend

1995), secondary ion mass-spectroscopy (Santos et al. 1991), and can be collected in hydrogen evolution during annealing (Beyer et al. 1991).

Several configurations for the hydrogen in α -Si:H are possible. One is the *dilute* phase where each hydrogen atom is about 1 nm away from any other hydrogen atom; the other phase is the *clustered* phase where two or more hydrogen atoms are in close proximity. The densities of hydrogen in each of the individual phases is different from each other. In the bulk of α -Si:H the total density of hydrogen depends on the conditions under which it is made.

41.4.2 Defects and Metastability

The electronic and optical properties of the material depend on this configuration and the chemical bonding of its defects. A single defect may be a dangling bond and is referred to as the *D-center*. It dominates most of the properties in undoped α -Si:H (Street 1991), and can be created by removing a hydrogen atom in the diluted phase. This is confirmed by an increase of dangling bonds when hydrogen is removed from α -Si:H by heating. However, the density of dangling bonds is usually much lower than the density of hydrogen lost from the bulk. This is attributed to an additional removal of some hydrogen from clustered-phase sites, which does not create dangling bonds.

Figure 41.3 shows the increase of the dangling bond density as a function of the illumination time up to 10^7 s. This time evolution is similar to decrease of the solar conversion efficiency shown in Fig. 41.2, as a measure of the Staebler–Wronski effect which stabilizes after 10,000 s, as does the dangling bond density at 10^{17} cm^{-3} for high density illumination (similar to sunlight) (Zafar and Schiff 1991; Fritzsche 2001; Branz 1999). This indicates that the hydrogen shifts from dilute to the clustered phase.

Both, the Staebler–Wronski effect and the shifting of hydrogen are reversible at elevated temperatures in the dark. The motion of hydrogen from the diluted to the clustered configuration and returns at about 150 °C to its original state points to the

creation of a metastable phase in α -Si:H under light (Zafar and Schiff 1991; Branz 1999).

A similar behavior of the Staebler–Wronski suggests a metastable here, and confirms that the Staebler–Wronski effect can be mitigated in α -Si:H solar cells by changing its preparation.

41.4.3 Electronic Density-of-States

The optical and electronic properties of semiconductors are determined by the electronic density-of-states, $g(E)$ that can be measured by electron photoemission (Ley 1989; Jackson et al. 1985), optical absorption (Cody et al. 1981), and electron or drift mobilities (Tiedje 1984).

41.4.4 Band Tails, Band Edges, and Band-Gaps

α -Si:H shows conduction and valence bands with an energy gap where the density-of-states is very low. For perfect crystals, the valence and conduction band edges E_V and E_C are well defined, as is the *band-gap* $E_G = E_C - E_V$. In disordered semiconductors there is an exponential distribution of band tail states near the band edges. For instance, the valence band tail is given by

$$g(E) = g_V \exp(-(E - E_V)/\Delta E_V). \quad (41.1)$$

The width ΔE_V of this exponential distribution is identified as “Urbach” tail of the spectrum. For α -Si:H, a typical value is $\Delta E_V = 50 \times 10^{-3}$ eV. The band tail accounts for a low hole mobility; (Tiedje 1984; Gu et al. 1994). The conduction band tail width ΔE_C is smaller; for the best α -Si:H it is about 22×10^{-3} eV, but increases markedly for amorphous silicon–germanium (Wang et al. 1993).

An analysis of the drift-mobility supports the concept of a well-defined band edge (Tiedje 1984; Gu et al. 1995), to be defined as the energy that separates localized electrons from delocalized. The band edges are correspondingly termed the conduction and valence band *mobility edges** (Mott 1987). These are slightly different from the optical band-gap. The optical absorption coefficient $\alpha(h\nu)$ yields this “optical” or “Tauc” band-gap E_T (Tauc 1972):

$$\alpha(h\nu) = (A/h\nu)(h\nu - E_T)^2. \quad (41.2)$$

The Tauc bandgap E_T is found from the intercept of a graph of $(h\nu\alpha)^{1/2}$ versus $(h\nu)$. The proportionality constant A incorporates several effects, and is not usually studied separately.

The measured Tauc band-gap is typically about 1.75 eV in α -Si:H, but does vary with deposition conditions. Alloying with germanium or carbon causes sizable changes. A simpler procedure than that of Tauc is to define the band-gap

to be the photon energy corresponding to an optical absorption coefficient of $\alpha = 3 \times 10^3 \text{ cm}^{-1}$ that is denoted as $E_{3.5}$. The difference between the optical band-gap and the electrical band-gap $E_G = E_C - E_V$ can be measured by internal photoemission, (Chen and Wronski 1995) and shows that the mobility band-gap is larger than the Tauc band-gap by typical 50–100 meV.

41.4.5 Defects and Gap States

Between the band tails lie defect levels; in un-doped α -Si:H, these levels are due primarily to the dangling bonds (*D*-centers) measured by electron spin resonance. For example, infrared absorption at around 1.2 eV excites an electron from such defect and is proportional to the *D*-center density (Jackson and Amer 1982).

The *D*-center is “amphoteric:” there are three charge states (with $+e$, 0, and $-e$), leading to two levels (transitions between the 0/+ and $-/0$). The $(+/0)$ level is about 0.6 eV below E_C in low-defect-density, undoped α -Si:H (Antoniadis and Schiff 1992). The $(+/0)$ level lies about 0.3 eV below the $(-/0)$ levels; the difference between the two levels is termed the “correlation energy” of the *D*-center (Antoniadis and Schiff 1992).

The level positions vary between doped and intrinsic α -Si:H (Street 1991), and between intrinsic samples of varying densities of *D*-centers (Antoniadis and Schiff 1992), and possibly also between dark and illuminated states (Han et al. 1993). These effects are usually explained with a “defect pool” model (Street 1991).

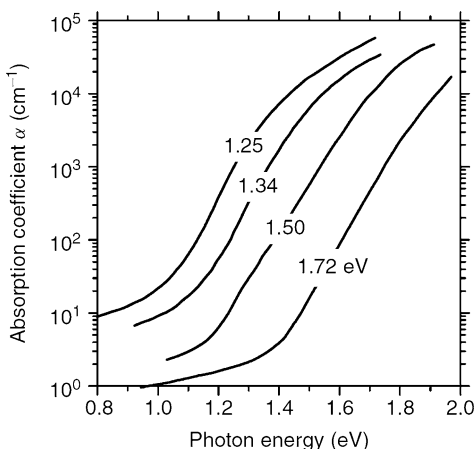
41.4.6 Phosphorus Doping Puzzle

In crystalline silicon (c-Si) phosphorus (P) substitutes for a silicon atoms with 4 valence bonds in the crystal lattice. P has five valence electrons, so in the “fourfold coordinated” sites of the Si lattice, four electrons participate in the bonding and the fifth excess electron occupies a state just below the bottom of the conduction band and acts as a donor to render c-Si *n*-type.

In α -Si:H, however, most phosphorus atoms bond to only three silicon neighbors; they are in *threefold coordinated* sites. This configuration is chemically advantageous; phosphorus atoms normally form only three bonds (involving the three valence electrons in *p* atomic orbitals). The other two electrons are paired in *s* atomic orbitals, remain tightly bond to the P atom. The reason for the more favorable bonding in α -Si, but not in c-Si, is the absence of a rigid lattice. During growth of α -Si, the network of bonds adjusts to incorporate impurity atoms in nearly ideal chemical arrangement.

Thus phosphorus doping is a paradox in amorphous silicon. On the other hand independent formation of both a positively charged, fourfold coordinated *P* and a negatively charged dangling bond *D* can occur occasionally instead of the more ideal threefold coordination (Street 1991).

Fig. 41.4 The absorption coefficient for $\alpha\text{-Si}_x\text{Ge}_{1-x}$ alloys. The optical band-gaps and corresponding Ge fractions x are respectively: 1.25–0.58, 1.34–0.48, 1.50–0.30, 1.72–0.0 (Hama et al. 1983)



Most dopant P atoms do not contribute a “free” electron, because only if fourfold coordinated, it would contribute an electron, but then there is a balancing Si dangling bond to receive it. Therefore any fourfold-coordinated phosphorus would be compensated by a D defect in $\alpha\text{-Si:H}$, and is not effective as a dopant, it does not change the charge type of the sample. The same is true for the threefold bond P atom as discussed earlier (the tightly bond electrons are too far away from the conduction band). Hence the incorporation of phosphorus in $\alpha\text{-Si:H}$ does not act as a dopant in the sense that it does in c-Si, where it renders the crystal n -type.

41.4.7 Alloying and Optical Properties

The structural and optical properties of $\alpha\text{-Si:H}$ can be varied substantially by changing its deposition, such as changing the substrate temperature or the dilution of silane by hydrogen in a plasma deposition. These changes in the microstructure of $\alpha\text{-Si:H}$ can cause a change of the optical band-gap between 1.6–1.8 eV (Hama et al. 1983).

Larger band-gap changes can be produced by alloying with Ge, C, O, and N. This is readily accomplished by mixing the silane (SiH_4) gas with GeH_4 , CH_4 , O_2 , NO_2 , or NH_3 . The resulting alloys have very wide ranges of band-gaps. For example an $\alpha\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ can have on optical band-gaps down to about 1.45 eV and can be used as absorber layer in a multi-junction *pin* cell: The narrow band-gap of the alloy allows for increased absorption of photons with lower energies (Guha et al. 1987). Figure 41.4 shows the absorption coefficient $\alpha(h\nu)$ as a function of the changes of the concentration ratio x in $\alpha\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ indicating substantially different optical band-gaps. However, all absorptions show nearly the same Urbach slopes of about 50 meV. But the plateau of the absorption coefficient at the lowest photon energies increases with increasing ratio x , indicating that the *defect density* increases as the band-gap decreases.

The role of Ge-induced alloying on optoelectronic properties indicates that *structural inhomogeneities* resulting in a two-phase material, are responsible for the degradation of these properties in Ge-alloys (Mackenzie et al. 1998).

The band-gap decreases by about 0.7 eV as the Ge-ratio x increases from 0 to 1. The band-gap increases also with the atomic fraction of hydrogen. However, only limited ranges of x and of the atomic fraction of hydrogen yield useful absorber layers (Stutzmann et al. 1989). Boron-doped α -SiC is used extensively as a p -type window layer (Arya et al. 1986) and α -SiO and α -SiN are used as insulators in thin film transistors (Tsukada 2000), but are not major components in solar cells.

41.4.8 Nanocrystalline Silicon

The same deposition processes that are used to make amorphous silicon can also be used to make hydrogenated “nano-crystalline” silicon (nc-Si:H). Here fine silicon crystallites with a diameter of several nanometers are bound with a hydrogenated amorphous silicon matrix. This nano-crystalline silicon is also referred to as “micro-crystalline” silicon for many years.

Below 1.6 eV, nano-crystalline silicon (nc-Si:H) has a stronger optical absorption than α -Si:H, and is similar to c-Si. This makes nc-Si:H interesting as the infrared absorber in multi-junction solar cells, or tandem cells that are sometimes called “micromorph” (Curtins et al. 1987). The Staebler–Wronski degradation is much weaker in nc-Si:H than in α -Si:H, despite the presence of a fraction of α -Si:H.

41.5 Depositing Amorphous Silicon

41.5.1 Deposition Techniques

The first preparations of α -Si:H by Chittick and Sterling (1985) and by Spear and LeComber (Spear and LeComber 1972), using a silane-based glow discharge at radio frequencies (RF) is often called plasma enhanced chemical vapor deposition (PECVD). Other deposition methods are using higher frequencies: RF-PECVD with 13.56-MHz that is widely used today. However, emerging film deposition methods for higher deposition rates or to making improved nc-Si:H, have been extensively explored in recent years. These are PECVD with very high frequency (VHF) and hot-wire (HW) catalytic deposition as described below.

41.5.2 RF Plasma-Enhanced Chemical Vapor Deposition (RF-PECVD) at 13.56 MHz

The growth of α -Si and nc-Si by PECVD is determined by electron density and energy distribution in the plasma, gas phase reaction chemistry, precursor transport to the growth surface, and surface reactions.

A mixture of SiH_4 and H_2 is adjusted into a chamber with power from an RF supply. The gas pressure is adjusted for the given RF voltage to initiate the plasma, that ionizes and decomposes the gas. The α -Si:H film grows on a substrate that may be mounted on one or both of the electrodes that are heated to 150–300 °C.

Thermally activated surface diffusion of ad-atoms is used for optimum film quality (Chapman 1980; Luft and Tsuo 1993; Kushner 1988). At lower substrate temperature, more H is incorporated that increases the band gap of α -Si:H slightly. At higher substrate temperature, less hydrogen is incorporated and the band-gap is reduced.

The pressure range is usually between 0.5 and 1 Torr. Lower pressure permits more uniform deposition, higher pressure permits higher growth rates.

The RF power usually is set to 10–100 mW/cm². Power above 100 mW/cm² causes rapid reactions in the gas and can create silicon polyhydride powder that contaminates the growing Si film.

Optimum spacing (d) between the RF electrode and the substrate is usually between 1 and 5 cm for α -Si deposition, with smaller spacing for a uniform deposition, however, larger spacing is easier for maintaining the plasma.

Important for the growth of high-quality α -Si films is the reduction of contaminants, such as oxygen, carbon, nitrogen, or metals. But, because of the flexibility of the bonding network, the tolerance for contaminants in α -Si is much higher than in its crystalline counterpart. However, when the contaminants in the i -layer exceed for $\text{O} < 10^{19}$, $\text{C} < 10^{18}$, and $\text{N} < 10^{17}/\text{cm}^3$, the fill factor of the resulting solar cell is reduced because of the reduced lifetime of photo-generated carriers (Kinoshita et al. 1996).

41.5.3 PECVD at Different Frequencies

Higher excitation frequencies ($f = 40$ –100 MHz) permit the deposition of α -Si and nc-Si films that are more stable at high deposition rates ($> 10 \text{ Å/s}$) without creating polyhydride powder. In contrast, film and device quality, and stability suffer when deposition rates are larger than $> 3 \text{ Å/s}$ by increasing RF power at 13.56 MHz (Shafarman et al. 2003). High-quality devices have been obtained using VHF deposition by a number of groups (Smets et al. 2008; Takatsuka et al. 2004; Fujioka et al. 2006).

With increasing plasma frequency, the electron energy decreases and its density increases (Wertheimer and Moisan 1985). With higher electron concentration more beneficial radicals provide selective etching of disordered amorphous phase, reducing defects and voids, and provide fast growth of crystalline grains. Both are beneficial to nc-Si growth.

Glow discharge deposition at frequency of 2.45 GHz permits very high deposition rates (Kato et al. 1982; Hudgens et al. 1985). Generally, however, the structural and optoelectronic properties of MW-deposited α -Si-based films are worse than RF-deposited films.

41.5.4 Hot-Wire Chemical Vapor Deposition

With an improved hot-wire chemical vapor deposition (HWCVD), “device quality” α -Si films were produced (Matsumura 1986; Wiesmann et al. 1979; Mahan et al. 1991). The set-up for a HWCVD system is similar to RF-PECVD except that the RF electrode is replaced with a Pt, W, or Ta filament that is heated to around 1800–2000 °C. In the HW process, SiH₄ gas or a mixture of SiH₄ and other gases such as H₂ or He are used. The silicon radicals then diffuse and deposit onto a substrate placed a few centimeters away and heated to 150–450 °C. Mahan et al. (1991) demonstrated that HWCVD α -Si materials show relatively lower H content in the film and improved stability against light-induced degradation compared with RF PECVD films (Mahan et al. 1991). The improved HWCVD α -Si has resulted in an *n-i-p* solar cell as the intrinsic layer of solar cells with ~10 % initial efficiency (Bauer et al. 1997). HWCVD is now considered promising. The ability to deposit α -Si and α -SiGe films at high rates (~up to 150–300 Å/s) (Mahan et al. 2001) has attracted much interest. HWCVD is also effective in making nc-Si and polycrystalline silicon. With it, single junction nc-Si, triple-junction α -Si/ α -SiGe/nc-Si, and α -Si/nc-Si/nc-Si (no Ge) devices on flexible stainless steel have shown *stabilized* efficiencies of 8.6, 10.6, and 10.6 %, respectively (Schmid et al. 2009). However, the HW films are of slightly lower quality than that of RF PECVD films (Osono et al. 2006) and have not yet achieved the same performance as cells prepared with low rate RF PECVD.

41.5.5 Other Deposition Methods

Other deposition processes have been explored for α -Si films. Here only those are listed for which solar cell results were reported. These include

- (1) reactive sputter deposition from silicon targets using a mixture of hydrogen and argon (Moustakas et al. 1985);
- (2) photo-CVD using ultraviolet excitation and mercury sensitization (Konagai et al. 1987; Rocheleau et al. 1987a, 1987b);
- (3) remote plasma chemical vapor deposition (Park et al. 1988);
- (4) electron cyclotron resonance (ECR) microwave deposition (Sakamoto 1977; Dalal et al. 1997); and
- (5) gas jet deposition (Jones et al. 2000).

These depositions yielded worse α -Si films or solar cells, or they could not be easily scaled to provide large-area uniform films, and therefore, are not used in large-scale α -Si PV production.

41.5.6 Hydrogen Dilution

Hydrogen dilution of the silane gas mixture during α -Si deposition has been found to reduce the density of defect states and improve the stability of the material against light-induced degradation. Solar cells with *i*-layers deposited using high H₂ dilution ratios showed improved performance and stability (Guha et al. 1981; Okamoto et al. 1996).

For higher dilutions, the growing thin film initially adopts an amorphous structure, called the “protocrystalline” regime. As the film thickens, crystallites form in the amorphous matrix (creating a “mixed phase”). The crystallites improve the stability (Kamei et al. 1999). Ultimately, the film becomes entirely nano-crystalline.

Due to their lower absorption with an indirect band-gap ~ 1.1 eV, nc-Si films must be 5–10 times thicker than α -Si films. When incorporated as the bottom cell of a multi-junction cell structure, this requires a 5–10 times increase of the deposition rate to maintain production throughput (Guo et al. 1998; Rech et al. 2006). There is a very narrow process window for achieving high growth rates and high efficiency and larger area uniformity.

41.5.7 Alloys and Doping

As was discussed in Sect. 41.4.7, α -Si-based alloys can be deposited using a gas mixture of SiH₄ with other gases such as GeH₄, CH₄, O₂, or NO₂, and NH₃ for obtaining α -SiGe_{*x*}, α -SiC_{*x*}, α -SiO_{*x*} and α -SiN_{*x*}, respectively. Among these alloys, only α -SiC, as a wide band-gap *p*-layer, and α -SiGe, as a low-band-gap absorber layer, have been used to produce solar cells. But α -SiGe with a band-gap below 1.3 eV is difficult to deposit with uniformity (Mackenzie et al. 1998; Paul et al. 1993). By taking advantage of the similar dissociation rate of GeH₄ and disilane (Si₂H₆), a mixture of these gases permitted the fabrication of α -SiGe alloy with uniform films (Guha et al. 1987). As discussed in Sect. 41.4.6, α -Si can be doped *n*-type by mixing phosphine (PH₃) or doped *p*-type by mixing it with diborane (B₂H₆), BF₃, or trimethylboron [TMB, B(CH₃)₃] during deposition. Most cells have either μ c-Si or α -SiC as the uppermost *p*-layer. Amorphous SiC *p*-layers in *p-i-n* devices are usually deposited using a mixture of SiH₄ and CH₄ diluted in hydrogen (Tawada et al. 1982), leading to bandgaps of 1.85–1.95 eV. The μ c-Si *p*-layer for *n-i-p* devices is mostly made by PECVD, using high H dilution with high RF power at relatively low temperature. The optimum *p*-layer for α -Si *n-i-p* solar cells is a mixed phase of amorphous and nano-crystalline (Pearce et al. 2007; Rath and Schropp 1998) and is essential to improve V_{oc} .

In solar cells made on stainless steel in the *nip* growth sequence, the final *p*-layer yielding the best open-circuit voltage is a boron-doped “nanocrystalline” silicon film (Guha et al. 1986). In superstrate cells, usually made on TCO-coated glass, the best open-circuit voltages have been achieved using boron-doped amorphous silicon–carbon alloys (α -SiC:H:B). High efficient solar cells with high open-circuit

voltages use α -SiC:H:B *p*-layers and also include a thin (<10 nm) “buffer layer” of un-doped α -SiC:H between the *p*-layer and the intrinsic-layer of the cell (Arya et al. 1986; Hegedus et al. 1988; Sakai et al. 1990).

41.6 Theory of the α -Si *pin* Cells

41.6.1 Electronic Structure of a *pin* cell

Due to the presence of a “built-in” electric field $F(x)$ within the α -Si:H-based *pin* solar cell device, the bands are tilted, for E_C according to $eF(x) = \partial E_C(x)/\partial x$; however, these built-in fields cannot be measured directly.

The built-in fields across the *i*-layer stems from the space charges created between the *n* and *p* layers on both sides. This is caused by the connection of the Fermi energies at both sides (as connected to the respective electrodes). With electrons donated from the *n*-layer to the *p*-layer a built-in potential V_{bi} can be read. With light, electrons and holes are generated that will drift in the built-in field toward the respective electrodes.

Several computer programs were developed for solar cell calculations with α -Si:H and nc-Si:H (Burgelman et al. 2004; Zhu et al. 1999); in amorphous semiconductors, band tail states may determine some opto-electronic properties (for a review see Schropp and Zeman 1998).

41.6.2 Influence of Thickness on Power Generation

The power generation is determined by the depth of the absorption for the more than 70 % of the blue components (this depth is approximately first 200 nm), and by the distance a photo-generated carrier can travel before it recombines. This distance is given by $\Delta x = \mu_D F \tau$ with μ_D the drift mobility, F the acting field, and τ the carrier lifetime.

The $\mu\tau$ product is larger for electrons than for holes and depends on the structure of the α -Si:H. However, in nc-Si the distance a hole can travel is larger than in α -Si:H by at least a factor 100 (Schiff 2004). The drift mobility of a hole is on the order of $0.01 \text{ cm}^2/\text{V s}$ and for electrons is $\sim 2 \text{ cm}^2/\text{V s}$ in α -Si:H, and for holes in nc-Si:H it is, at $\sim 1 \text{ cm}^2/\text{V s}$, i.e. still smaller than the electron drift mobility. The low drift-mobility is due to trapping of the holes by the valence band-tail states (Scher et al. 1991) and affects the operation of a solar cell markedly (Schiff 2003).

This means that photo-generated holes near the *p*-layer are more likely to be collected than the electrons in the *n*-layer. Therefore a *pin* cell is more efficient than an *nip* solar cell.

There is a “collection zone” with $R \sim 0$ that extends from the *p*-layer interface; carriers generated in this zone contribute to the photocurrent (and power) from the

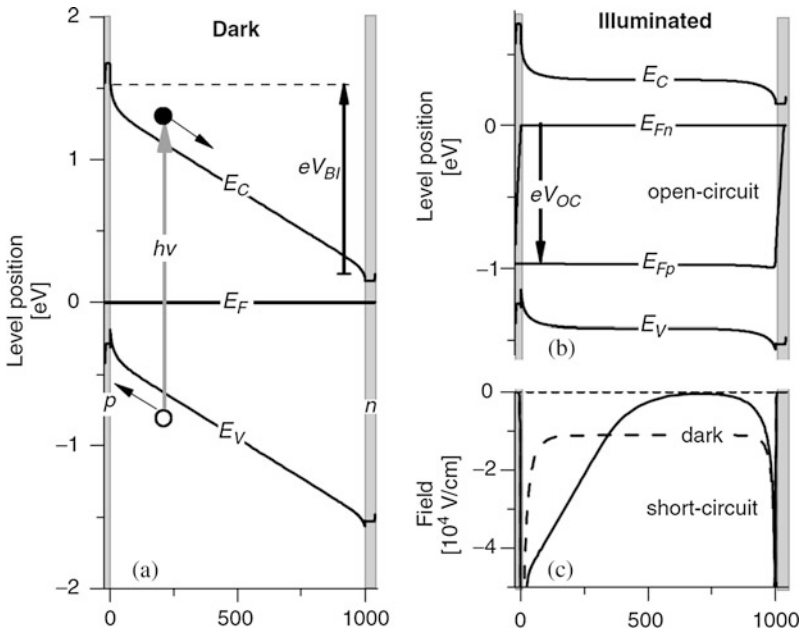


Fig. 41.5 Calculated profiles for electron level positions and for electric fields in a *pin* solar cell as a function of the position within the cell (scale in nm). **(a)** Levels in the *dark*; note the built-in potential V_{bi} and that the *p*-layer has a slightly (0.2 eV) larger band-gap than the *i*-layer. **(b)** Open-circuit voltage under illumination (uniform photo-generation with $g = 3 \times 10^{21} \text{ cm}^{-3} \text{ s}^{-1}$); showing the two quasi-Fermi levels and the open-circuit voltage V_{oc} . **(c)** Short-circuit electric field, which collapses under illumination from near-uniformity in the *dark* (dashed) to a width $d_C \sim 400$ nm (solid curve)

cell. Beyond the collection zone is a recombination region, where carriers are more likely to recombine instead of contributing to the cell's power (see Fig. 41.5). The width of the collection zone at which $R/g = 0.5$, increases from about 200 to 400 nm as the hole band mobility increases from 0.1 to $1.0 \text{ cm}^2/\text{V s}$. The open circuit voltage (given at room temperature) increases with the band gap, according to $V_{oc} = E_g/e - 0.8$, with 0.8 the V_{oc} deficit in α -Si:H. This deficit decreases to ~ 0.55 in nc-Si:H, because of the shrinking of the band tails.

41.6.3 Optical Design of α -Si:H and nc-Si:H Solar Cells

Back reflectors and substrate texturing are used to improve the power output of most thin film solar cells. Figure 41.6a shows the “quantum efficiencies” measured for a 250-nm-thick α -Si:H solar cell with varying texturing and back reflectors (Hegedus et al. 1996), along with absorptances calculated from the optical absorption coefficient spectrum for α -Si:H. The dashed absorptance curve labeled “no light trapping”

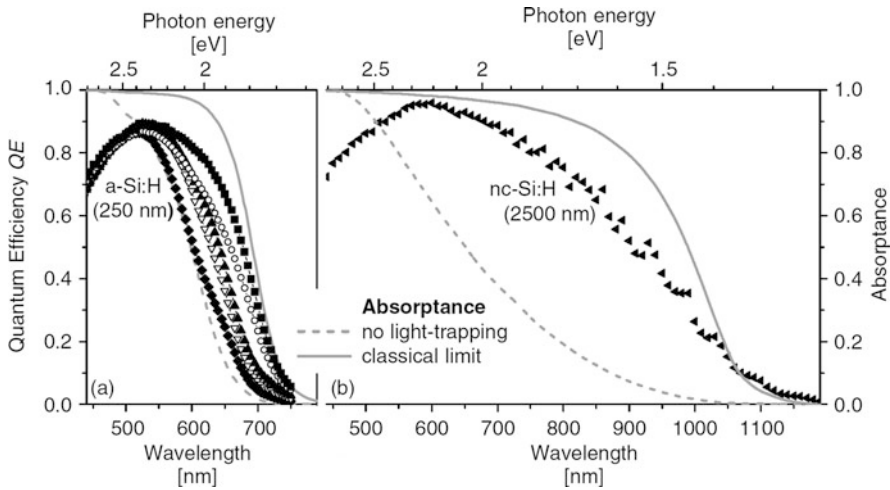


Fig. 41.6 (a) Absorption spectra calculated for a 250 nm α -Si:H, and quantum efficiency spectra measured for a series of α -Si:H *nip* solar cells with a 250 nm thick *i*-layer and varying substrates and back reflectors (Hegedus et al. 1996). ◇: (untextured, none); ∇: (untextured, untext.); ▲ untextured, textured), (textured, none); ■ (textured, untextured). (b) Calculated absorption spectra and quantum efficiency measured for a nc-Si:H solar cell (Yan et al. 2010)

corresponds to $A(\lambda) = 1 - \exp(-\alpha(\lambda)d)$, and is the fraction of light that is absorbed by a 250 nm layer of α -Si:H assuming normal incidence and neglecting reflection from both the front and rear interfaces. This absorbance falls with increasing wavelength, which corresponds to the absorption coefficient spectrum of Fig. 41.2 and the thickness of 250 nm.

The quantum efficiency (QE) of the solar cell is defined as the ratio, at a specific wavelength, of the photocurrent density j (A/cm^2) to the incident photon flux f ($cm^{-2} s^{-1}$):

$$QE(\lambda) = j(\lambda)/[ef(\lambda)]. \quad (41.3)$$

Electrons generated in a *p*-layer are more likely to be captured by a dopant or a dangling bond than to escape to the *i*-layer, and similarly for holes generated in an *n*-layer. Figure 41.6 shows, that the introduction of a back reflector doubles the QE for the longer wavelengths, which are weakly absorbed. The other curves show that “texturing” of the substrate and of the back reflector further increases the QE from the cells, by allowing light to traverse more. The substrate texturing also leads to a modest improvement of the QE in the blue spectral region (beyond 2.5 eV), which is due to a reduction in the front-surface reflectance of the cell. For α -Si:H, the best texturing increases the short-circuit current by about 25 % (Hegedus et al. 1996; Lechner et al. 2000). The texturing and back reflectors and of a front antireflection coating, vary substantially between superstrate and substrate cells. Superstrate cells usually have a textured, transparent conductive oxide (TCO) coating on the transparent substrate (usually glass). The back reflector deposited on top of the semiconductor layers is often a thin TCO layer, followed by the reflective metal (typically

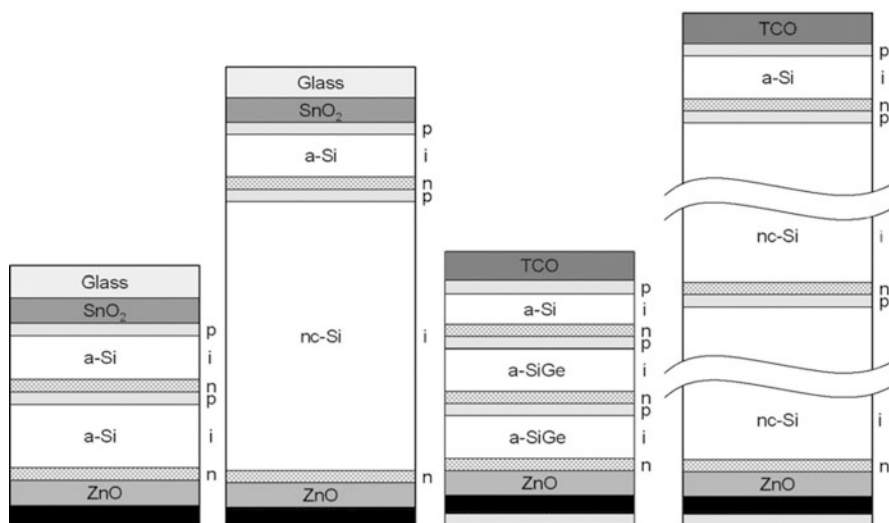


Fig. 41.7 Multi-junction solar cells: (a) α -Si/ α -Si superstrate tandem; (b) α -Si/nc-Si “micro-morph” superstrate tandem; (c) α -Si/ α -SiGe/ α -SiGe substrate triple; and (d) α -Si/nc-Si/nc-Si substrate triple. The light enters from the top. The *black region* is the metal contact. TCO as ITO or ZnO. The differences of the *i*-layer thickness for the different cell types is indicated

Ag, for best reflectivity, or Al, for improved production yield). Substrate cells are deposited onto the back reflector, a textured silver or aluminum metallization and then a textured TCO (Banerjee and Guha 1991).

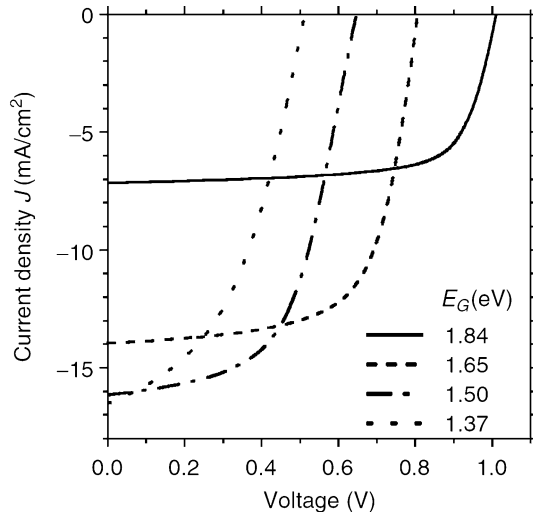
41.7 Multijunction Solar Cells

41.7.1 Advantages of Multi-junction Solar Cells

A-Si:H solar cells can be fabricated in a stacked structure to form multi-junction solar cells. Figure 41.7(1) shows a tandem cell with two junctions (i.e. two *pin* photodiodes) in series. These multi-junction cells can have higher solar conversion efficiency than single-junction cells and are presently used in most commercial modules. Mostly multi-junction α -Si:H based solar cells were tandem or triple junctions with an α -SiGe low band-gap absorber. Since the early 70’s, tandem “micromorph” cells and cells with α -Si/nc Si multiple band-gap tandem modules are widely used

Multi-junction solar cells are spectrum splitting. The thickness of the top *pin* junction is adjusted so that it filters out about half of the photons that would otherwise have been absorbed in the bottom *pin* junction. The top material has a larger band-gap to absorb photons at larger energies, and produces a larger open-circuit voltage than the bottom part of the cell. In this two-terminal multi-junction cell the same electrical current flows through the series-connected cells. Aside from the

Fig. 41.8 Current-voltage characteristics of α -Si and α -SiGe *nip* solar cells with different Ge concentrations in the *i*-layer, with the band gaps indicated in the legend. The fill factors for these cells are 0.70, 0.62, 0.55, and 0.43 for the cells with *i*-layer band-gaps of 1.84, 1.65, 1.50, and 1.37 eV, respectively (Agarwal et al. 2002)



spectrum-splitting effect, the upper cell is thinner than in single-junction cells, causing an improved fill factor, and since a multi-junction cell delivers its power at a higher voltage and lower current, the resistive losses are reduced. Most desirable, is a higher stabilized output for multiple-junction cells (Minemoto et al. 2007).

41.7.2 Alloys to Vary the Band Gap

The band-gap of α -SiGe alloys can be continuously adjusted between 1.7 and 1.1 eV by varying the percentage of Ge. However, the optoelectronic quality (i.e. defects and carrier transport) of α -SiGe degrades rapidly when the α -SiGe bandgap is reduced below about 1.4 eV. Figure 41.8 shows the J - V characteristics of a series of α -SiGe solar cells with different Ge concentrations in the *i*-layer (of constant thickness, and without a back reflector) (Agarwal et al. 2002).

As the band-gap is reduced, V_{oc} is reduced and J_{sc} increases, since the narrower-band-gap absorbs more sunlight. But also the fill factor decreases as the band-gap decreases, probably because of a reduced hole drift-mobility or an increase in the defect density, hence lower lifetime and collection.

41.7.3 Bandgap Grading of α -SiGe *i*-Layers and of α -SiC

To enhance the fill factor of cells with α -SiGe *i*-layers, band gap *grading* is used to enhance the collection of holes (Guha et al. 1989; Zimmer et al. 1998). An asymmetric *V*-shaped band-gap profile is created by adjusting the Ge content across the *i*-layer. Wider-band-gap material is deposited closest to the *p*-layer.

Such a grading allows more light to be absorbed near the p -layer so that “slower” holes do not have to travel far to get collected. Also, the tilting of the valence band creates an electric field that assists holes generated in the middle or near the n -side of the i -layer to move toward the p -layer. With appropriate hydrogen dilution during growth and band-gap grading, α -SiGe cells can generate up to 27 mA/cm² under AM1.5 light. The advantage of these graded band-gap junction is the improved light stability (Yang et al. 1991)

The bandgap of α -SiC can be adjusted between 1.7 and 2.2 eV, depending on the C concentration (Bullot and Schmidt 1987). However, α -SiC with enough C to increase the band-gap appreciably suffers significant decrease in electron drift mobility (Gu et al. 1994) and became highly defective after light-soaking (Li 1993).

41.7.4 α -Si/ α -SiGe Tandem and α -Si/ α -SiGe/ α -SiGe Triple-Junction Solar Cells

Dual-junction α -Si/ α -Si (same band-gap tandem) solar cells have lower material cost (no GeH₄) than tandem cells using α -SiGe, and have slightly higher efficiencies (0.5–1 % absolute) than α -Si single junction cells. Same band-gap α -Si/ α -Si tandems have been in production for decades. Multiband-gap dual junction (α -Si/ α -SiGe: Doughty and Gallagher 1990, or α -Si/nc-Si Yamamoto et al. 2004; Meier et al. 2007) and triple-junction (α -Si/ α -SiGe/ α -SiGe or α -Si/ α -SiGe/nc-Si) solar cells use spectrum-splitting. They achieve higher conversion efficiencies, usually over 10 % stabilized for small area <1 cm² cells (Doughty and Gallagher 1990; Kroll et al. 2007; Fujioka et al. 2006; Mahan et al. 2001). While all-amorphous α -Si (1.8 eV)/ α -SiGe (1.6 eV)/ α -SiGe (1.4 eV) triple-junction solar cells have produced the most efficient α -Si-based cells today (Yang et al. 1997), triple junctions based on α -Si/ α -SiGe/nc-Si or α -Si/nc-Si/nc-Si (no Ge) have produced nearly equivalent stabilized efficiencies (Kroll et al. 2007; Mahan et al. 2001; Yang et al. 2005).

Appendix A

Important Formulae

A.1 General Formulae

Wave vector, electron energy (quasi-free electron):

$$\mathbf{k} = \frac{m_0 \mathbf{v}}{\hbar} = \frac{\mathbf{P}}{\hbar}, \quad E = \frac{m_0}{2} v^2 = \frac{p^2}{2m_0} = \frac{\hbar^2 k^2}{2m_0}$$

Photon momentum:

$$p_{\text{phot}} = \frac{h}{\lambda} = \frac{h\nu}{c} = \hbar k$$

Group velocity v_g , phase velocity v_s :

$$v_g = \Delta_k \omega(\mathbf{k}) = \frac{1}{\hbar} \frac{dE}{dk}, \quad v_s = \frac{\omega}{k}$$

The rms velocity of electrons:

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m_n}} = 1.18 \times 10^7 \sqrt{\frac{m_0}{m_n}} \sqrt{\frac{T(\text{K})}{300}} \text{ (cm/s)}$$

De Broglie wavelength:

$$\lambda_{\text{DB}} = \frac{h}{|p|} = \frac{h}{m_0 v} = 7.27 \frac{1}{v \text{ (cm/s)}} \text{ (cm)}$$

$$\lambda_{\text{DB}} = \frac{h}{\sqrt{2m_0 E}} = 12.26 \frac{1}{\sqrt{E \text{ (eV)}}} \text{ (\AA)}$$

A.2 Characteristic Lengths in Solids

Debye length:

$$\lambda_D = \sqrt{\frac{\varepsilon_{\text{st}} \varepsilon_0 k T}{e^2 n}} = 1205 \sqrt{\frac{\varepsilon_{\text{st}}}{10} \frac{T}{300} \frac{10^{15}}{n}} \text{ (\AA)}$$

Thomas–Fermi length:

$$\lambda_{\text{TF}} = \pi^{2/3} \frac{\hbar}{e} \sqrt{\frac{\varepsilon_{\text{st}} \varepsilon_0}{m_n (3n)^{1/3}}} = 1.16 \sqrt{\frac{\varepsilon_{\text{st}}}{10} \frac{m_0}{m_n} \left(\frac{10^{18}}{n} \right)^{1/3}} \text{ (\AA)}$$

Drift length or *Schubweg*:

$$l_c = \mu_c \tau_c F \quad \text{with } c = n \text{ or } p$$

Diffusion length:

$$L_c = \sqrt{\frac{\mu_c k T}{e}} \tau_c = 5.1 \sqrt{\frac{\mu_c}{10^3 \text{ (cm}^2/\text{V s)}} \frac{T}{300 \text{ (K)}} \frac{\tau_c}{10^{-8} \text{ (s)}}} \text{ (\mu m)}$$

Upstream and downstream diffusion lengths:

$$L_{c(u,d)} = L_c \frac{2L_c}{\sqrt{4L_c^2 + l_c^2} \pm l_c}$$

Mean free path:

$$\lambda_{\text{sc}} = v_{\text{rms}} \tau_{\text{sc}} = \frac{1}{s_n N_{\text{sc}}}$$

A.3 Effective Masses

Effective carrier mass:

$$m_n = \frac{\hbar^2}{\frac{d^2 E}{dk^2} |_{E_c}}, \quad m_p = -\frac{\hbar^2}{\frac{d^2 E}{dk^2} |_{E_v}}$$

Density of state masses:

$$m_{\text{nds}}^{3/2} = \nu_D (m_{n\parallel} m_{n\perp}^2)^{1/2}$$

$$m_{\text{pds}}^{3/2} = m_{\text{pl}}^{3/2} + m_{\text{ph}}^{3/2}$$

Mobility effective masses:

$$\frac{1}{m_{n\mu}} = \frac{1}{3} \left(\frac{2}{m_{n\perp}} + \frac{1}{m_{n\parallel}} \right)$$

$$\frac{1}{m_{p\mu}} = \frac{1}{2} \left(\frac{2}{m_{p\parallel}} + \frac{1}{m_{p\perp}} \right)$$

Reduced effective mass:

$$\frac{1}{m_r} = \frac{1}{m_n} + \frac{1}{m_p}$$

A.4 Phonons, IR Dispersion, and Thermal Properties

Phonon dispersion equation:

$$\omega_{\pm}^2 = \frac{\beta_s(M_1 + M_2)}{M_1 M_2} \left[1 \pm \sqrt{1 - \frac{4M_1 M_2 \sin^2(qa)}{M_1 + M_2}} \right]$$

Dispersion equation neglecting damping

$$\varepsilon = \varepsilon_{\text{opt}} + \frac{(\varepsilon_{\text{st}} - \varepsilon_{\text{opt}})\omega_{\text{TO}}^2}{\omega_{\text{TO}}^2 - \omega^2}$$

Complex dielectric constant and conductivity:

$$\left. \begin{aligned} \varepsilon' &= n_r^2 - \kappa^2 \\ \varepsilon'' &= \frac{\sigma}{\varepsilon_0 \omega} = 2n_r \kappa \end{aligned} \right\} \quad \varepsilon = \varepsilon' + i\varepsilon''$$

$$\varepsilon'(\omega) = \varepsilon_{\text{opt}} + \omega_p^2 \frac{\omega_{\text{TO}}^2 - \omega^2}{(\omega_{\text{TO}}^2 - \omega^2)^2 + \gamma^2 \omega^2}$$

$$\varepsilon''(\omega) = \omega_p^2 \frac{\omega \gamma}{(\omega_{\text{TO}}^2 - \omega^2)^2 + \gamma^2 \omega^2}$$

Kramers–Kronig relations:

$$\varepsilon'(\omega_a) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega \varepsilon''(\omega)}{\omega^2 - \omega_a^2} d\omega$$

$$\varepsilon''(\omega_a) = -\frac{2\omega_a}{\pi} P \int_0^\infty \frac{\varepsilon'(\omega)}{\omega^2 - \omega_a^2} d\omega$$

Line width:

$$Q = \frac{\Delta\omega}{\omega_0} \simeq \frac{1}{\tan \delta} = \frac{\varepsilon'}{\varepsilon''} = \frac{\varepsilon\varepsilon_0\omega_0}{\sigma} = \omega_0\tau_\sigma$$

Complex conductivity:

$$\left. \begin{aligned} \sigma' &= \varepsilon''\varepsilon_0\omega = \sigma_0 \\ \sigma'' &= \varepsilon'\varepsilon_0\omega = \varepsilon_0\omega(n_r^2 - \kappa^2) \end{aligned} \right\} \quad \sigma = \sigma' + i\sigma''$$

Lyddane–Sachs–Teller relationship:

$$\frac{\omega_{\text{LO}}}{\omega_{\text{TO}}} = \sqrt{\frac{\varepsilon_{\text{st}}}{\varepsilon_{\text{opt}}}}$$

Debye-specific heat:

$$C_v = \begin{cases} 233.78R(\frac{T}{\Theta})^3 & \text{for } T \ll \Theta \\ 3R[1 - 0.05(\frac{\Theta}{T})^2] & \text{for } T \gtrsim 0.5\Theta \end{cases}$$

Maximum thermal expansion:

$$\left(\frac{\Delta l}{l}\right)_{T_m} \simeq 0.07, \quad \alpha \simeq \frac{0.07}{T_m}$$

Melting point:

$$T_m = \frac{k}{9\hbar^2} M \Theta^2 f_{\text{max}}^2 a^2$$

Thermal conductivity:

$$\kappa = \frac{1}{3} C_v v_s \lambda$$

A.5 Electron-Lattice Interaction

Coupling constant:

$$\alpha_c = \sqrt{\frac{\frac{e^2}{8\pi\varepsilon^*\varepsilon_0 r_p}}{\hbar\omega_{\text{LO}}}} = \frac{e^2\sqrt{m_n}}{4\sqrt{2}\pi\hbar\sqrt{k}\Theta} \frac{1}{\varepsilon_0\varepsilon^*} = 22.88\sqrt{\frac{m_n}{m_0}}\sqrt{\frac{300}{\Theta(\text{K})}} \frac{1}{\varepsilon^*}$$

Huang–Rhys factor:

$$S = \frac{E_r - E_c}{\hbar\omega_b} = \frac{\frac{1}{2}M_r\omega_b^2(Q_2 - Q_1)^2}{\hbar\omega_b}$$

Effective dielectric constant, reduced mass:

$$\frac{1}{\varepsilon^*} = \frac{1}{\varepsilon_{\text{opt}}} - \frac{1}{\varepsilon_{\text{st}}}, \quad \frac{1}{M_r} = \frac{1}{M_1} + \frac{1}{M_2}$$

Effective polaron mass:

$$m_{\text{pol}} = \frac{m_n}{(1 - \frac{\alpha_c}{6})}$$

Large polaron energy and polaron radius:

$$E_{\text{pol}} = \alpha_c \hbar \omega_{\text{LO}} = E_{\text{qH}} \left(\frac{\varepsilon_{\text{st}}}{\varepsilon^*} \right)^2 \frac{m_{\text{pol}}}{m_n}$$

$$r_{\text{pol}} = \frac{4\pi \varepsilon_0 \hbar^2}{m_0 e^2} \varepsilon^* \frac{m_0}{m_{\text{pol}}} = a_{\text{qH}} \frac{\varepsilon^*}{\varepsilon_{\text{st}}} \frac{m_n}{m_{\text{pol}}} = \frac{4\pi \varepsilon^* \varepsilon_0 \hbar^2}{m_{\text{pol}} e^2}$$

Yukawa potential:

$$V(r) = \left(\frac{e}{\varepsilon^* r} \right) \exp\left(-\frac{r}{\lambda_s}\right)$$

Callen effective charge:

$$e_c = \omega_{\text{TO}} \sqrt{\varepsilon_0 \frac{\varepsilon_{\text{st}} - \varepsilon_{\text{opt}}}{\varepsilon_{\text{opt}}^2} M_r a^3}$$

Szigetti effective charge:

$$e_s = e_c \frac{3\varepsilon_{\text{opt}}}{\varepsilon_{\text{st}} + 2}$$

A.6 Optical Properties

Optical absorption coefficient:

$$\alpha_0 = \frac{2\omega\kappa}{c} = \frac{4\pi}{\lambda} \kappa$$

Normal incidence reflectance:

$$R_0 = \frac{(n_r - 1)^2 + \kappa^2}{(n_r + 1)^2 + \kappa^2}$$

Average transmissivity and reflectivity:

$$\overline{T} \simeq (1 - R_0)^2 \exp(-\alpha d)$$

$$\overline{R} = R_0(1 + \overline{T} \exp(-\alpha_0 d))$$

Direct absorption edge:

$$\begin{aligned} \alpha_{o,vc} &= \frac{2\sqrt{2}\pi^2 e^2 m_r^{3/2}}{m_0^2 \varepsilon_0 h^2 c} \frac{\sqrt{h\nu - E_g}}{n_r} M_{vc} \\ &= 7.64 \cdot 10^5 \left(\frac{m_r}{m_0}\right)^{3/2} M_{vc} \frac{\sqrt{h\nu - E_g \text{ (eV)}}}{n_r} \text{ (cm}^{-1}\text{)} \end{aligned}$$

Indirect absorption edge:

$$\alpha_{o,\text{ind}} \propto f_{\hbar\omega} (h\nu + \hbar\omega - E_g)^2 + (1 - f_{\hbar\omega}) (h\nu - \hbar\omega - E_g)^2$$

Forbidden edge transitions:

$$\begin{aligned} \alpha_{o,\text{dir,forb}} &\propto (h\nu - E_g)^{3/2} \\ \alpha_{o,\text{ind,forb}} &\propto (h\nu \pm \hbar\omega - E_g)^3 \end{aligned}$$

Urbach tail:

$$\alpha_o = \alpha_{o0} \exp\left(\frac{h\nu - E_g}{E_0}\right)$$

Line shape: Lorentzian:

$$g(\nu - \nu_0) = \frac{\gamma}{2\pi} \frac{1}{(\nu - \nu_0)^2 + (\frac{\gamma}{2})^2}$$

Gaussian:

$$g(\nu - \nu_0) = \frac{1}{\sqrt{2\pi} \gamma} \exp\left[-\left(\frac{\nu - \nu_0}{2\gamma}\right)^2\right]$$

A.7 Quasi-hydrogen and Deep Well States

Quasi-hydrogen radius:

$$a_{qH} = \frac{4\pi \varepsilon_0 \hbar^2}{m_0 e^2} \varepsilon_{st} \frac{m_0}{m_n} n_q^2 = 0.529 \varepsilon_{st} \frac{m_0}{m_n} n_q^2 \text{ (\AA)}$$

Quasi-hydrogen energy:

$$E_{qH}^{(n_q)} = \frac{m_0 e^4}{2(4\pi \varepsilon_0 \hbar)^2} \frac{m_n}{m_0} \frac{1}{\varepsilon_{st}^2} \frac{1}{n_q^2} = 13.6 \left(\frac{m_n}{m_0} \frac{1}{\varepsilon_{st}^2}\right) \text{ (eV)}$$

Wannier–Mott excitons:

$$E_{\text{exc}} = E_g + \frac{\hbar^2 k^2}{2m_r} - \frac{m_r}{\varepsilon_r^2} R_H \frac{1}{n_q^2}$$

Superlattice eigenstates:

$$E_n = \frac{\hbar^2 k^2}{2m_n} = \frac{\hbar^2 \pi^2}{2m_n l_z^2} n_q^2, \quad \text{where } n_q = 1, 2$$

A.8 Equilibrium Densities, Energies, Velocities

Density of states (for parabolic bands):

$$g_n(E) dE = \frac{1}{2\pi^2} \left(\frac{2m_n}{\hbar^2} \right)^{3/2} \sqrt{E - E_c} dE$$

Effective level density:

$$N_c = 2 \left(\frac{m_{\text{nds}} kT}{2\pi \hbar^2} \right)^{3/2} = 2.5 \times 10^{19} \left(\frac{m_{\text{nds}}}{m_0} \frac{T \text{ (K)}}{300} \right)^{3/2}$$

$$N_v = 2 \left(\frac{m_{\text{pds}} kT}{2\pi \hbar^2} \right)^{3/2} = 2.5 \times 10^{19} \left(\frac{m_{\text{pds}}}{m_0} \frac{T \text{ (K)}}{300} \right)^{3/2}$$

2D density of states:

$$N_{2c} = \frac{m^* kT}{\pi \hbar^2}$$

Intrinsic Fermi level, carrier density:

$$E_F = \frac{E_c + E_v}{2} - kT \ln \left(\frac{m_n}{m_p} \right)^{3/4}$$

$$n_i = \sqrt{N_c N_v} \exp \left(-\frac{E_c - E_v}{2kT} \right)$$

Fermi gas:

$$E_F = 50.1 \text{ (eV)} (r_s/a_0)^{-2}$$

$$k_F = 3.63 \text{ (\AA}^{-1}\text{)} (r_s/a_0)^{-1}$$

$$\sigma_F = 4.20 \times 10^8 \text{ (cm/s)} (r_s/a_0)^{-1}$$

$$T_F = 5.82 \times 10^5 \text{ (K)} (r_s/a_0)^{-2}$$

with

$$\frac{r_s}{a_0} = 5.44 \left(\frac{n \text{ (cm}^{-3}\text{)}}{10^{22}} \right)^{-1/3}$$

Density of Frenkel or Schottky defects in equilibrium:

$$N_F = \sqrt{N_L N_i} \exp\left(-\frac{E_{Fr}}{2kT}\right), \quad N_S = N_L \exp\left(-\frac{E_S}{2kT}\right)$$

A.9 Transport Properties

Interstitial diffusion in cubic lattices:

$$D = D_0 \exp\left(-\frac{\Delta E_i}{kT}\right) \quad \text{with } D_0 = a^2 \frac{v_0}{6}$$

Boltzmann equation for electrons:

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \dot{\mathbf{k}} \nabla_{\mathbf{k}} f = \dot{\mathbf{r}} \nabla_{\mathbf{r}} f = \left(\frac{\partial f}{\partial t} \right)_{\text{coll}}$$

Field and Lorentz force:

$$\vec{\mathcal{F}} = \hbar \frac{d\mathbf{k}}{dt} = e(\mathbf{F} + \mathbf{v} \times \mathbf{B})$$

Deformed Boltzmann distribution (low fields):

$$f = f_0 \left(1 - \frac{e}{kT} \tau_m \mathbf{F} \cdot \mathbf{v} \right)$$

Randomizing scattering:

$$\tau_m = \frac{\tau_{\text{sc}}}{\langle 1 - \cos \theta \rangle}$$

Energy and momentum relaxation:

$$\left(\frac{\tau_e}{\tau_m} \right)_{\text{ion}} = \frac{m_n}{M_i} \quad \text{or} \quad \left(\frac{\tau_e}{\tau_m} \right)_{\text{ac,ph}} = \frac{3v_s^2}{v_n^2}$$

Total current:

$$j_n = e\mu_n n F + eD_n \frac{dn}{dx}, \quad j_p = e\mu_p p F - eD_p \frac{dp}{dx}, \quad j = j_n + j_p$$

Carrier currents:

$$j_n = \sigma_n \frac{\partial \varphi_n}{\partial x}, \quad j_p = \sigma_p \frac{\partial \varphi_p}{\partial x}$$

$$j_{n,\text{drift}} = \sigma_n \frac{\partial \psi_n}{\partial x}, \quad j_{p,\text{drift}} = \sigma_p \frac{\partial \psi_p}{\partial x}$$

$$j_{n,\text{diff}} = \sigma_n \frac{\partial(\varphi_n - \psi_n)}{\partial x}, \quad j_{p,\text{diff}} = \sigma_p \frac{\partial(\varphi_p - \psi_p)}{\partial x}$$

Carrier mobility:

$$\mu = \frac{e}{m_n} \tau_{\text{sc}} = \frac{e}{m_n} \frac{\lambda}{v_{\text{rms}}} = \mu = 1.5 \cdot \lambda \text{ (Å)} \left(\frac{m_0}{m_n} \right)^{3/2} \left(\frac{300}{T \text{ (K)}} \right)^{1/2} (\text{cm}^2/\text{V s})$$

Nernst–Einstein relation:

$$v_i = \frac{e}{kT} D_i$$

Carrier mobility:

$$\boxed{\mu_n = \frac{e}{m_n} \tau_{\text{sc}} = \frac{e}{m_n} \frac{\lambda}{v_{\text{rms}}}}$$

$$\mu_n = 1.5 \times \lambda \text{ (Å)} \left(\frac{m_0}{m_n} \right)^{3/2} \left(\frac{300}{T \text{ (K)}} \right)^{1/2} (\text{cm}^2/\text{V s})$$

Current continuity:

$$\frac{dn}{dt} = g_n - r_n - \frac{1}{e} \frac{dj_n}{dx}, \quad \frac{dp}{dt} = g_p - r_p - \frac{1}{e} \frac{dj_p}{dx}$$

Saturation drift current and velocity:

$$j_{n,\text{diff,max}} = en v D_s \quad \text{with } v D_s = \sqrt{\frac{3k\Theta}{4m^*} \tanh \frac{\Theta}{2T_L}}$$

Poisson equation:

$$\frac{dF_i}{dx} = \frac{\rho}{\epsilon \epsilon_0}$$

Anderson–Mott localization; semiconductor–metal: transition

$$N_{\text{AM}}^{1/3} a_{\text{qH}} \simeq 0.2$$

Minimum metallic conductivity:

$$\sigma_{\text{min}} = \frac{1}{2\pi^2} \frac{e^2}{\hbar} \frac{1}{a} \simeq \frac{12}{a \text{ (Å)}} (\Omega^{-1} \text{ cm}^{-1})$$

Electric fields:

$$F = F_i + F_e$$

A.10 Characteristic Times and Frequencies

Reststrahl frequency:

$$\omega_{\text{TO}} \simeq \sqrt{\frac{\beta}{M_r}}$$

Plasma frequency:

$$\omega_p = \sqrt{\frac{ne^2}{\epsilon_{\text{opt}}\epsilon_0 m_n}}$$

$$\hbar\omega_p = 38.9 \sqrt{\frac{n}{10^{16}} \frac{10}{\epsilon_{\text{opt}}} \frac{m_0}{m_n}} \text{ (meV)}$$

Cyclotron frequency:

$$\omega_c = \frac{eB_0}{m^*} = 17.84 \frac{m_0}{m^*} B_0 \text{ (GHz/kG)}$$

Dielectric relaxation time:

$$\tau_\sigma = \frac{\epsilon\epsilon_0}{\sigma} = 8.8 \times 10^{-13} \frac{\epsilon}{10} \frac{(\Omega \text{ cm})}{\sigma} \text{ (s)}$$

Decay time (τ_l) and carrier lifetime:

$$\tau = \tau_n \left(1 + \frac{dn_t}{dn} \right)$$

$$\frac{\tau_l}{\tau_n} = 1 + \frac{N_t(E)kT}{n}$$

Rise and decay times of photoconductivity:

$$\tau_t = \frac{1}{c_{\text{ct}} N_t}, \quad \tau_1 = \frac{1}{c_{\text{cv}} n}$$

Time between scattering events:

$$\tau_{\text{sc}} = \frac{1}{v_{\text{rms}} s_n N_{\text{sc}}}$$

Thermal noise, shot noise:

$$\overline{j_{\text{th}}^2} = \frac{4kT}{R} \Delta\nu, \quad \overline{j_{\text{sh}}^2} = 2ej \Delta\nu$$

A.11 Photoconductivity

Recombination cross section:

$$s_n = \frac{\omega_r}{2\pi} \frac{1}{N_c v_{\text{rms}}} \exp\left(-\frac{E_n}{kT}\right)$$

Emission and capture rates:

$$\begin{aligned} \frac{e_{\text{tc}}}{c_{\text{ct}}} &= \exp\left(-\frac{E_c - E_t}{kT}\right) \\ e_{\text{tc}} &= \frac{v_t}{N_c} \exp\left(-\frac{E_c - E_t}{kT}\right) \\ c_{\text{ct}} &= s_n v_{\text{rms}} \end{aligned}$$

Carrier density for photoconductivity:

$$n = \sqrt{\frac{g_o}{c_{\text{ca}}}} \quad \text{or} \quad n = \frac{g_o}{c_{\text{ca}} N_t}$$

Photoelectric gain:

$$G_o = \mu_n \tau_n \frac{V}{d^2} = \frac{\tau_n}{t_n} = \frac{l_n}{d}.$$

Carrier kinetics:

$$\frac{dn}{dt} = g_n - r_n - \frac{1}{e} \frac{dj_n}{dx}, \quad \frac{dp}{dt} = g_p - r_p - \frac{1}{e} \frac{dj_p}{dx}$$

Net carrier flow through Shockley–Read–Hall center:

$$U = \frac{c_{\text{ct}} c_{\text{tv}} N_t (np - n_i^2)}{c_{\text{ct}} [n + n_i \exp(\frac{E_t - E_i}{kT})] + c_{\text{tv}} [p + n_i \exp(\frac{E_i - E_t}{kT})]}$$

Rise of photocarrier density:

$$n(t) = n_0 \left\{ 1 - \exp\left(-\frac{t - t_0}{\tau}\right) \right\} \quad \text{with} \quad \tau = \begin{cases} \tau_t = \frac{1}{c_{\text{ct}} N_t} \\ \tau_l = \frac{1}{c_{\text{cv}} n} \end{cases}$$

Decay of photocarrier density:

$$n(t) = n_0 \exp\left(-\frac{t - t_1}{\tau_1}\right) \quad \text{or} \quad n(t) = n_0 \frac{\tau_1}{t - t_1}$$

Trap depth from glow (TSC) maximum:

$$E_c - E_t \simeq 25kT_{\text{max}}$$

A.12 Field Effects

Impact ionization distribution function:

$$f(E) = A^* \exp \left[- \left(\frac{4\hbar\omega_{\text{LO}}}{(e\lambda)^2} \frac{E}{F^2} \right) \right]$$

Fowler–Nordheim tunneling:

$$j_n = \frac{e^3 m_n^{1/2} d}{2\sqrt{2}\pi^3 \hbar^2 E_g^{1/2}} F^2 \exp \left(- \frac{\pi m_n^{1/2} E_g^{3/2}}{2\sqrt{2}e\hbar F} \right)$$

$$j_n = 1.011 \times 10^{-8} \left(\frac{F}{10^6} \right)^2 \left(\frac{m_n}{m_0} \right)^{1/2} \left(\frac{d}{100 \text{ \AA}} \right) \frac{1}{\sqrt{E_g}} \exp \left(- \frac{F_0}{F} \right) (\text{A/cm}^2)$$

$$F_0 = 4.04 \times 10^7 \left(\frac{m_n}{m_0} \right)^{1/2} E_g^{3.2} (\text{V/cm})$$

Franz–Keldysh shift:

$$\Delta E_{g,\text{opt}} = E_g - \hbar\nu = \left(\frac{3}{4} eF \sqrt{\frac{\hbar^2}{2m}} \right)^{2/3} = 7.25 \times 10^{-6} [F (\text{V/cm})]^{2/3}$$

A.13 Tables of Constants

Table A.1 Table of Constants^a

Symbol	Value (Units)	Item					
GENERAL							
c	$2.9979 \cdot 10^{10}$ (cm s ⁻¹)	Light velocity					
e	$1.60217733 \cdot 10^{-19}$ (As)	Elementary charge					
$\hbar = h/(2\pi)$	$1.0545727 \cdot 10^{-34}$ (W s ²)	Reduced Planck's constant					
m_0	$9.1093897 \cdot 10^{-35}$ (W s ³ cm ⁻²)	Electron rest mass					
	$9.1096 \cdot 10^{-28}$ (g)						
k	$1.3806513 \cdot 10^{-23}$ (W s/K)	Boltzmann constant					
V_0	22414 (cm ³ mole ⁻¹)	Normal volume of ideal gas					
N_{Av}	$6.0221367 \cdot 10^{23}$ (mole ⁻¹)	Avogadro's number					
$N_{\text{Lo}} = N_{\text{Av}}/V_0$	$2.6873 \cdot 10^{19}$ (cm ⁻³)	Loschmidt's number					
M_p/m_0	1836.152701	Proton/electron mass ratio					
M_p	$1.6725 \cdot 10^{-24}$ (g)	Proton rest mass					
M_n	$1.6748 \cdot 10^{-24}$ (g)	Neutron rest mass					
$T(\text{ice})$	273.150 (K)						
DERIVED							
ϵ_0	$8.8543 \cdot 10^{-14}$ (As V ⁻¹ cm ⁻¹)	Permittivity of free space					
$\mu_0 = 1/(\epsilon_0 c^2)$	$1.2560 \cdot 10^{-8}$ (Vs A ⁻¹ cm ⁻¹)	Permeability of free space					
$a_H = 4\pi \epsilon_0 \hbar^2/(m_0 e^2)$	0.5292 (Å)	Bohr radius					
$F = eN_{\text{Av}}$	96485.309 (As mole ⁻¹)	Faraday constant					
$R_H = m_0 e^4/[2(4\pi \epsilon_0 \hbar)^2]$	13.607 (eV)	Rydberg energy					
$\mu_B = e\hbar/2m_0$	$5.788 \cdot 10^{-6}$ (eV/kG)	Bohr magneton					
$\alpha^{-1} = c/v_n = \hbar c/e^2$	137.0359895	Reciprocal of fine structure constant					
ENERGY RELATIONS							
1 (V As)	$2.38845 \cdot 10^{-4}$ (kcal)	1 Joule equivalent					
1 (eV)	$1.6022 \cdot 10^{-19}$ (Ws = J)	Energy associated with 1 eV					
1 (eV)	$1.6022 \cdot 10^{-12}$ (erg)	Energy associated with 1 eV					
1 (eV)	23.053 (kcal/mol)	Energy associated with 1 eV					
λ (1 eV)	1.23975 (μm)	Wavelength ^b					
$\bar{\nu}$ (1 eV)	8066.14 (cm ⁻¹)	Wavenumber ^b					
ν (1 eV)	$2.418 \cdot 10^{14}$ (s ⁻¹)	Frequency					
T (1 eV)	11.605 (K)	Temperature					
v (1 eV)	$5.931 \cdot 10^7$ (cm s ⁻¹)	Velocity					
k ($T = 300$ K)	25.848833 (meV)	Thermal voltage					
$\bar{\nu} = 1$	0.1236 (meV)	Energy associated with 1 wavenumber					
PREFIXES							
deca (da)	10	giga (G)	10 ⁹	deci (d)	10 ⁻¹	nano (n)	10 ⁻⁹
hecto (h)	10 ²	tera (T)	10 ¹²	centi (c)	10 ⁻²	pico (p)	10 ⁻¹²
kilo (k)	10 ³	peta (P)	10 ¹⁵	milli (m)	10 ⁻³	femto (f)	10 ⁻¹⁵
mega (M)	10 ⁶	exa (E)	10 ¹⁸	micro (μ)	10 ⁻⁶	atto (a)	10 ⁻¹⁸

^aUpdated: CODATA, 1986. Bulletin 63, Pergamon Press and Moldover et al. (1988)

^bIn vacua

Table A.2 Properties of Ge, Si, GaAs, CdS

Properties	Ge	Si	GaAs	CdS
Atoms/cm ³	4.42×10^{22}	5.00×10^{22}	4.42×10^{22}	$3.48 \cdot 10^{22}$
Atomic weight	72.60	28.09	144.63	144.476
Crystal structure	Diamond	Diamond	Zincblende	Wurtzite
Lattice constant (Å)	5.65791	5.43095	5.6533	a = 4.1368; c = 6.7163
Density (g/cm ³) at 300 K	5.3234	2.3290	5.317	4.824
Dielectric constant ϵ_{st}	16.2	11.9	12.9	$\epsilon_{11} = 8.45$; $\epsilon_{33} = 9.12$
ϵ_{opt}	16.2	11.9	10.9	$\epsilon_{11} = 5.33$; $\epsilon_{33} = 5.5$
μ_n (cm ² /Vs)	3900	1450	8500	350
μ_p (cm ² /Vs)	1800	500	400	50
$m_{eff,n}$	$m_{\perp}(L) = 0.08152$ $m_{\parallel}(L) = 1.588$ $m_n(\Gamma) = 0.04$	$m_{\perp}(\Delta) = 0.9163$ $m_{\parallel}(\Delta) = 0.1905$	$m_n(\Gamma) = 0.067$ $m_n(\Delta)_{\perp} = 0.37$, $m_n(\Delta)_{\parallel} = 1.98$ $m_n(L)_{\perp} = 0.075$, $m_n(L)_{\parallel} = 1.19$	0.20 (isotropic)
$m_{eff,p}$	$m_{lp} = 0.044$ $m_{hp} = 0.28$ $m_{nds} = 0.22$ $m_{pds} = 0.18$	$m_{lp} = 0.153$ $m_{hp} = 0.537$ $m_{nds} = 1.18$ $m_{pds} = 0.591$	$m_{lp} = 0.082$ $m_{hp} = 0.50$ $m_{nds} = 0.067$ $m_{pds} = 0.53$	$m_{p\perp}^A = 0.7$; $m_{p\perp}^B = 1.1$ $m_{p\parallel}^A \sim 2.5$ $m_{nds} = 0.2$ $m_{pds} \simeq 1$
Density of state mass	1.54×10^{19} 1.9×10^{18}	2.8×10^{19} 1.02×10^{19}	4.3×10^{17} 8.1×10^{18}	$2.24 \cdot 10^{18}$ $2.5 \cdot 10^{19}$
N_c (cm ⁻³)				
N_v (cm ⁻³)				
Energy gap (eV) at 300 K	0.664	1.12	1.424	2.489
Spin orbit splitting (eV)	0.28	0.044	0.340	$\Delta_{so} 0.0635$, $\Delta_{cf} 0.027$
Temp. coeff. $\partial E_g / \partial T$ (meV/deg)	-0.37	-0.28	-0.39	-0.38
Press. coeff. $\partial E_g / \partial p$ (μeV/bar)	3	-1.41	12	4.5

Table A.2 (Continued)

Properties	Ge	Si	GaAs	CdS								
n_i (300 K) (cm ⁻³)	2.33×10^{13}	1.02×10^{10}	2.1×10^6	$1.03 \cdot 10^{-4}$								
Electron affinity, χ (V)	4.0	4.05	4.07									
Lin. therm. expans. coeff. (deg.)	5.6×10^{-6}	2.59×10^{-6}	6.86×10^{-6}	$\perp c = 6.52 \cdot 10^{-6}$								
Linear compressibility (10 ⁻⁷ bar ⁻¹)		3.15		$\perp c = 5.26 \parallel c = 5.15$								
Melting point (°C)	937	1415	1238	1475 at 3.8 atm.								
Minority carrier lifetime (s)	10 ⁻³	2.5×10^{-3}	$\sim 10^{-8}$	$\sim 10^{-7}$; sensitized: 10 ⁻³								
Debye temperature Θ (K)	366	658	345	215								
	Γ X L	Γ X L	Γ L	$\Gamma_{5\perp c}$ $\Gamma_{4\parallel c}$ $\Gamma_{4\perp c}$								
$\hbar\omega_{\text{TO}}$ (meV)	37.2	34.0	34.6	60.4	32.7	30	29.5	25.8	24.5			
$\hbar\omega_{\text{LO}}$ (meV)	37.2	28.4	30.5	50.8	51.9	36.2						
$\hbar\omega_{\text{TA}}$ (meV)	0	10.1	8.0	0	18.5	14.1	0	9.8	7.9	37.8	37.3	$\Gamma_{6\perp c}$: 31
$\hbar\omega_{\text{LA}}$ (meV)	0	18.4	26.6	0	50.8	46.7	0	27.8	18.7	TA ₁ : 6.94	TA ₃ : 5.58	
Sound velocity (cm/s)	$v_1 = 8.4332$, $v_2 = 5.8446$, $v_3 = 9.1333$, $v_4 = 5.8442$, $v_5 = 4.6740$	$v_l = 5.8 \cdot 10^5$, $v_l = 8.4 \cdot 10^5$	$v_l = 3.3 \cdot 10^5$, $v_l = 4.7 \cdot 10^5$	$v_l = 4.42 \cdot 10^5$, $v_l = 1.76 \cdot 10^5$								
Specific heat (J/g °C)	0.31	0.7	0.35	0.58								
Thermal conductivity at 300 K (W/cm °C)	0.6	1.5	0.46	0.20; $\kappa_{\text{max}}(T = 10 \text{ K}) = 6$								
Thermal diffusivity (cm ² /s)	0.36	0.9	0.44									
Vapor pressure p (atm)	1 at 1330 °C 10 ⁻⁶ at 760 °C	1 at 1650 °C 10 ⁻⁶ at 900 °C	100 at 1050 °C 1 at 900 °C	4 at 1480 °C								

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Index

Symbols

(111) axial symmetry, 210

8 – N rule, 34, 40, 57

α -Si:H, 42

II–VI compounds, 12, 30, 110, 167, 169, 192, 195, 208, 213, 215

III–IV compounds, 116

III–V compound semiconductors, 117, 357

III–V compounds, 14, 185, 198

A

A high-field domain, 668

A photo-generated current, 571

A surplus or accumulation space, 431

AB-compounds, 19, 31, 106, 128, 168

Abac chart, 356

ABC₂ compounds, 703

Abrupt Ge pn-junction, 551

Abrupt pn-homo-junction, 544

Abrupt Step-Junction, 429

Absorption, 208

Absorption coefficient, 705

Acceptor, 51, 54, 55

Acoustic phonon-induced deformations, 230

Acoustic phonons, 255, 306

Acoustic waves, 257, 300

Acousto-electric effects, 257

Activator, 408

Actual pn-junction device, 551

Additional recombination traffic, 572

Adiabatic approximation, 99, 374

Adiabatic expansion, 6

Airy functions, 332

Alkali halide, 75, 172, 180, 183

Allowed energy range, 86

Alloy, 16, 19, 34, 110, 692

Alloy formation, 42, 128

Alloying, 728

AM 1 sunlight, 477

Ambipolar, 408

Ambipolar diffusion coefficient, 540

Amorphous chalcogen compounds, 40

Amorphous chalcogenides, 229

Amorphous configuration, 89

Amorphous semiconductor, 38, 40, 42, 85, 101, 146, 227, 229, 234, 238, 372

Amorphous silicon, 721

Amphoterics defect, 706

Anderson localization, 236

Anderson-Mott density, 238

Anion molecule, 74

Anion vacancies, 180, 208

Anisotropic, 115, 210

Anisotropic growth rate, 47

Anisotropic shielding, 161

Anisotropy, 115

Anisotropy factor, 162, 312

Annealing, 78, 216, 234

Annealing of centers in the dark, 78

Annihilation, 79, 303

Anode-adjacent domain, 684

Antibonding state, 8, 186

Antiferromagnetic, 16

Antiparallel spin, 7

Antiphase defect, 59

Antisite defects, 185

Aperiodic repetition, 43

Asymmetric Doping, 614

Asymmetric Recombination, 611

Atomic clusters, 42

Atomic displacement, 192, 214, 305

Atomic electronegativity, 174

Atomic point defects, 307

Atomic radii, 3, 16, 30

Auger coefficient, 379
 Auger matrix, 378
 Auger recombination, 376, 379
 Average momentum relaxation time, 254

B

Back contact, 708
 Back reflectors, 734
 Balance equations, 409
 Ballistic creation, 75
 Band edge, 101, 140, 143
 Band gap, 137, 138, 145, 341
 Band gap bowing, 35
 Band gap grading, 737
 Band structure of semiconductors, 29
 Band tailing, 217
 Band tails, 227
 Band-to-band recombination, 373
 Band-to-band tunneling, 329
 Barrier field at zero current, 453
 Barrier height, 69, 70
 Barrier layer thickness, 454
 Barrier material, 241, 470
 Basic field-enhanced-diffusion, 510
 Bethe lattice, 42
 Bias, 265, 291, 325
 Bimolecular recombination, 407
 Binary crystal, 19
 Binding energy, 5, 128, 161, 188
 Bloch electron, 108, 139, 150, 156, 157, 236, 286, 309
 Bloch functions, 156, 165, 176
 Bloch oscillation, 99, 100
 Bloch-functions, 91
 Bohr magneton, 286
 Bohr radius, 157, 161, 220, 240, 371
 Boltzmann distribution, 248, 263, 452, 468
 Boltzmann distribution of minority carriers, 530
 Boltzmann equation, 271
 Boltzmann function, 441
 Boltzmann gas, 254, 551
 Boltzmann range, 452
 Boltzmann region, 468
 Boltzmann solution, 459
 Boltzmann solution for holes, 530
 Bombardment, 215
 Bond angle, 40, 87, 229
 Bond length, 9, 19, 21, 41, 43, 229
 Bond length variation, 20
 Bond-stretching and bond-bending, 22
 Bonding forces, 23
 Bonding state, 7, 9, 106
 Bonding-antibonding pair, 186

Born approximation, 312
 Born forces, 4
 Born-Haber cycle, 6
 Born-von Karman boundary condition, 150
 Boundaries, special angle, twin, 66
 Boundary conditions, 527
 Bowing, 35, 110, 129, 131
 Bragg reflections, 91
 Bravais lattice, 24, 25
 Bravais lattice identifier, 26
 Brewster angle, 351, 353
 Bridgeman technique, 47
 Bridging hydrogen structure, 89
 Brillouin zone, 23, 28, 89, 95, 114, 140, 156, 172, 259, 298
 Brillouin zones, mini-, 35
 Brownian motion, 249, 260
 Building block, 23
 Building blocks, atomic, 40
 Built-in field, 247, 259, 265, 267, 437, 439, 441, 733
 Built-in strains, 241
 Bulk contribution, 550
 Bulk recombination, 717
 Bulk regions, 548
 Bulk relaxation time, 319
 Bulk semiconductors, 239, 432
 Burgers vector, 58, 62, 63, 66, 242
 Burstein-Moss effect, 138, 222–224
 Burstein-Moss shift, 225

C

Callen effective charge, 305
 Capture cross section, 368, 415, 476, 533
 Carrier distribution, 149, 267, 383, 398, 405, 439, 473, 483, 530
 Carrier gas, 265, 266, 273, 313, 437, 438
 Carrier generation, 474
 Carrier heating, 266, 268, 289, 438, 471
 Carrier injection, 245, 446
 Carrier inversion, 537
 Carrier lifetime, 395, 488
 Carrier mobility, 18, 66, 240, 252, 280, 295, 397, 440
 Carrier motion, 249, 295
 Carrier recombination, 171, 318, 367, 423, 474
 Carrier redistribution, 387
 Carrier scattering, 51, 295, 307
 Carrier transport, 271, 315, 429, 473, 509, 660
 Carrier-scattering relaxation, 387
 Cation interstitials, 169
 Cation vacancies, 74, 180, 208
 Cd^xS^x configuration, 12
 CdS/CuInSe₂, 699

- Center, anisotropic, 53
- Cessation of optical excitation, 75
- Chaffing of ZnO-based white paint, 78
- Chain-like structure, 41
- Chains of electrons, 417
- Chalcogen, 40, 106, 209, 210, 230, 233
- Chalcogenide amorphous semiconductors, 193
- Chalcogenide glasses, 227, 231, 232
- Chalcopyrite semiconductors, 705
- Chalcopyrites, 32
- Charge character, 54, 55, 181, 184, 193–195, 198, 230, 382, 412, 483
- Charge contour plot, 6
- Charge density distribution, 187, 189
- Charge distribution, 64
- Charge transfer pair, 80
- Charged defects, 64, 229, 308
- Charges of partially covalent AB-compounds, 12
- Chemical environment, 20
- Chemical shift, 162
- Chemical valence force, 11
- Cinnabar structure, 31
- Classical diode equation, 462
- Climb, 62
- Climb over, 62
- Close packed layer, 64
- Close-packed structures, 14
- Cluster, 74, 86–88, 90, 101, 176, 213
- Cluster calculations, 176
- Clustering, 211
- Clusters of defects, 316, 317
- Co-evaporation, 709
- Coherence length, 106
- Coherent phonon waves, 257
- Coherent scattering, 313
- Cohesion strength, 47
- Cohesive energy, 5, 11
- Collection efficiency, 507
- Collective behavior, 87
- Collision broadening, 106
- Collision time, 308
- Colloidal distribution, 211
- Colloids, 76
- Color centers, 180, 183
- Compensating defects, 68
- Competing effects, 398
- Complex conductivity, 348, 349
- Complex dielectric constant, 342, 345, 358, 359
- Complex index of refraction, 345
- Complex space-charge effects, 427
- Compositional superlattices, 241, 244
- Compressibility, 6, 14, 301
- Compression and expansion at hetero-interface, 67
- Concentration gradient, 260
- Conduction band, 54, 114, 117, 127, 131, 137, 394
- Conductivity, anisotropic, 37
- Confinement energy, 145
- Conservation laws, 273
- Constraints, over-constraints, 41
- Contact potential, 69
- Continuum, 86, 173, 241, 290, 329, 342, 345
- Controlled Excitation, 393
- Cooling the cell, 587
- Coordination number, 5, 14, 30, 41, 184, 229, 230, 235, 242
- Coordination number, average, 40
- Corbino disk, 283
- Correction energy term, 208
- Correspondence principle, 97
- Coulomb attraction, 4
- Coulomb contributions, 188
- Coulomb energy, 193
- Coulomb potential, 156, 159, 173, 174, 307, 311, 370, 371
- Coulomb radius, 310, 311
- Coulomb-attractive center, 167, 218, 311, 369, 372, 415
- Coulomb-repulsive centers, 412
- Counting etch pits, 61
- Covalent, 4
- Covalent bonding, 6, 11
- Covalent crystals, 183, 193, 203, 238
- Covalent forces, 11, 46
- Covalent molecule, 74
- Covalent monatomic crystal, 107
- Covalent state of $\text{Cd}^{2-}\text{S}^{++}$, 12
- Covalent (tetraivalent) crystal, 106
- Critical bias, 228
- Critical distance, 241
- Critical field for field quenching, 638
- Critical size, 45
- Critical size of latent image, 78
- Cross-over of electron and hole densities, 536
- Crystal classification, 26
- Crystal defects, 3, 51, 62, 155, 192, 207, 249
- Crystal field, 16, 117, 178, 179, 195, 336
- Crystal growth, 57
- Crystal lattice, 23, 229
- Crystal momentum, 99
- Crystal structure, 23
- Crystal system, 24, 25
- Crystal-field splitting, 198
- Crystalline semiconductor, 23, 90, 228, 233, 234, 238

- Crystallite boundaries, 64
- Crystallization, strees to enhanced, 48
- Crystallization, using chemical reactions, 48
- Crystallization from solution, 47
- Crystallographic classification, 27
- Crystallographic directions, 68
- Crystals in equilibrium, 23
- Cu-nodule growth, 76
- Cu₂S/CdS solar cell, 627
- Cubic, 28
- Cubic crystal, 113, 132, 210
- Cubic lattice, 114
- Cu(In_xGa_{1-x})Se₂, 703
- Cumulative trap-filling, 403
- Current continuity, 421
- Current voltage characteristic, 444
- Curved lattice regions, 64
- Cyclotron frequency, 122, 123, 281, 284, 286
- Cyclotron resonance, 122–124, 284
- Czochralski method, 47
- D**
- D-center, 231
- Damped wave equation, 344
- Dangling bond, 15, 40, 59, 80, 183, 193, 230, 231
- Dark current, 580
- Darkconductivity, 75
- Dawson's integral, 457
- De Broglie wavelength, 90, 91, 99, 122, 308
- Debye length, 68, 244, 311, 317, 452, 454
- Debye temperature, 303–305
- Decelerate, 99
- Deep center, 75, 159, 176, 191, 193, 194, 373, 374, 398
- Deep impurities, 177
- Deep level centers, 171
- Deep level defect, 177, 233
- Deep level transient spectroscopy, 61
- Deep levels, 172, 174, 177, 183, 191, 198, 398
- Deep states, 172, 193
- Deeper tail states, 220, 221
- Defect, chemical nature, 55
- Defect associates, higher, 52
- Defect center, 53, 54, 165, 166, 176, 192, 196, 211, 336, 368, 408
- Defect center pairs, 207
- Defect cluster, 316
- Defect eigenfunction, 240
- Defect level spectrum, 155, 173, 197, 211
- Defect pairs, 52
- Defects, 51
- Defects, amphoteric, 53
- Defects, antisites, 52
- Defects, intrinsic, native, 52
- Defects, lines, 51
- Defects, orientation, 60
- Defects, surface, 51
- Defects, volume, 51
- Deformation potential, 296, 301–303, 305, 316
- Deformation wave, 300
- Deformed distribution, 273
- Degenerate oscillators, 86
- Degenerate semiconductor, 289
- Degradation, 724
- DeHaas-van Alphen effect, 289
- Delamination, 67
- Demarcation line, 381, 382, 482, 483, 536
- Density of depleted donors, 469
- Density of recombination centers, 603
- Detailed balance principle, 475
- Detectivity, 419
- Development, 77
- Deviations from an optimal bonding configuration, 231
- Dexter-Klick-Russell rule, 375
- Diamagnetic, 233, 287
- Diamagnetic interactions, 286
- Diamond lattice, 30, 31
- Diatomic oxygen centers, 210
- Dielectric constant, 18, 156, 157, 160, 161, 163, 221, 240, 309, 332, 342, 349
- Difference in electron affinities at heterojunction, 69
- Different contributions, 560
- Diffusion coefficient, 260, 261
- Diffusion current, 247, 260–262, 267, 436, 439, 445, 509
- Diffusion length, 73
- Diffusion of free electron to nucleation site, 78
- Diffusion velocity, 497
- Diffusion-limited Schottky diode equation, 466
- Dihedral angle, 42
- Dimer, 77
- Diode equation, 580
- Diode quality factor, 585
- Dipole moment, 13, 15, 68, 302, 305
- Dipole-dipole interaction, 15
- Dirac delta function, 299
- Disassociation energy, 211
- Disclinations, 64
- Dislocation decoration, 61
- Dislocation density, 61
- Dislocation loops, 63
- Dislocation network, 68
- Dislocation velocity, 62
- Dislocations, 51
- Dislocations, electronic states, 60

- Dislocations array, 65
- Disordered atom, 102, 213, 307
- Disordered lattices, 217
- Dispersion relation, 93
- Displaced lattice atoms, 101
- Displacement current, 348
- Dissociation energy, 6
- Dissociation of a defect-associate, 75
- Distant pairs, 53
- Distribution of traps, 396
- Divalent metals, 109
- Divergence-free, 514
- Divergence-free current, 519
- Divergence-free electron current, 533
- Divergence-free hole current, 533
- DLTS, 61, 172
- DO-range, 557
- Donor, 51, 54, 427, 537
- Donor-acceptor pair, 74, 207
- Donors, 163
- Donors and acceptors, 54
- Dopants, 149, 168, 191, 201, 217, 228, 233, 239
- Doping, 79, 125, 160, 211, 223, 233, 378, 415, 543
- Doping superlattice, 239, 244
- DOS, 187
- Double donors, 189
- Double layer “at” the metal, 464
- Double-diode characteristics, 633
- Doubly negatively charged activators, 412
- Downstream diffusion length, 511
- Drift and diffusion, 247, 248, 263, 436, 439, 452, 519
- Drift current, 253, 258, 264, 267, 431, 432, 436, 439, 445, 468
- Drift length, 418, 510
- Drift velocity, 250, 253, 254, 257, 269, 281, 370, 440, 441, 468, 660
- Drift-assisted gr-currents, 511
- DRO-range, 469, 557
- Drude approximation, 252
- Drude equation, 254
- DX* center, 191
- E**
- EBIC, 61
- Edge dislocation, 58, 62, 315
- Effective carrier mass, 279
- Effective charge concept, 12
- Effective density of states, 434
- Effective diffusion velocity, 502, 509
- Effective electron mass, 98
- Effective ion charge, 12
- Effective mass, 53, 99, 115, 117, 123, 126, 132, 138, 139, 161, 163, 167, 187, 223, 255, 266, 286, 291, 302, 332, 438
- Eigenfunctions, 7, 11, 16, 88, 138, 141, 155, 156, 160, 161, 167, 175, 176, 178, 207, 208, 221, 234, 235, 372
- Eigenstates, 53, 85–87, 91, 103, 109, 141, 157, 162, 167, 173, 176, 181, 188, 217, 237, 299, 328, 336, 387
- Einstein relation, 262, 263
- EL2 center, 185
- EL2 defect, 191, 194
- Elastic scattering, 298
- Elastic tensor, 301
- Electric conductivity, 342, 405
- Electrical conductivity, 38, 108, 109, 232, 258, 274, 348, 403
- Electro-reflectance, 334, 335
- Electrochemical driving forces, 37
- Electrochemical potential, 274, 434–437, 471
- Electromechanical coupling constant, 302
- Electron affinity, 6, 67
- Electron and hole traps, 480
- Electron bridge, 6, 12
- Electron conductivity, 250, 251, 675
- Electron demarcation line, 382, 483
- Electron density, 3, 186, 377, 395, 447, 627, 668, 677, 678
- Electron diffusion potential, 434, 450, 453
- Electron drag, 257
- Electron eigenvalue spectrum, 178
- Electron exit, 70
- Electron mobility, 233, 251, 301, 306
- Electron paramagnetic resonance, 287
- Electron rest mass, 90, 173
- Electron spin relaxation, 387
- Electron spin resonance, 287
- Electron transport, 107
- Electron trapping transition, 373
- Electron tunneling, 321
- Electron wave, 90
- Electron-electron interaction, 179
- Electron-lattice coupling, 75
- Electron-lattice interaction, 180, 192, 232
- Electron-paramagnetic resonance, 203
- Electron-phonon interaction, 131
- Electron-traps, 381
- Electronic ionization, 214
- Electronic level structure, 172
- Electronic noise, 419
- Electroplastic effect, 63
- Electrostatic electron potential, 432, 436
- Electrostatic forces, 3

- Electrostatic potential, 249, 258, 261, 264, 433, 435, 437, 461
- Elemental semiconductors, 30
- Emission, 69, 122, 132, 172, 211, 341, 372, 401, 465
- Emission from traps, 392
- Emission of multiple phonons, 376
- Empty state, 107, 108
- ENDOR, 159, 172
- Energy balance, 587
- Energy bands, 86
- Energy eigenvalues, 88
- Energy flux, 345, 352
- Energy level structure, 176
- Energy loss, 255
- Energy relaxation time, 255, 256
- Energy-dependent effective mass, 125
- Epitaxy, molecular beam, 36, 47
- Epitaxy, vapor phase, 36, 47
- Equal energy surfaces, 113
- Equi-energy surfaces, 113–115, 272, 279, 280, 282
- Equilibrium distance, 3
- Equivalent circuit of a solar cell, 585
- Equivalent phonon mass, 255
- Erginsoy approximation, 308
- ESR, 159, 229, 287
- Ewald's method, 5
- EXAFS, 172
- Excited states, 82, 141, 158, 160, 161, 163, 167, 169, 171, 173, 196, 210, 400
- Exciton in alkali halide, 75
- Exciton state, 222
- Excitons, 35
- Expectation values, 99
- Exponential decay, 608
- Extensive dispersion equation, 121
- External field, 249, 251, 260, 263, 265, 268, 324, 437, 439–441, 512, 514
- External surfaces, 318
- Extra lattice plane, 57
- Extra planes required, 58
- Extrinsic Cooper pair, 192
- Extrinsic photoconductivity, 408
- F**
- F-center, 76, 82, 172, 180, 181, 183, 211
- F-center with adjacent R-center, 76
- Famatinites, 34
- Fast photoconductive devices, 397
- Fast recombination centers, 668
- Favorable polarization, 74
- Fermi distribution, 223, 326, 263, 264, 272, 439
- Fermi energy, 153, 272, 434, 483
- Fermi gas, 218
- Fermi level, 75, 110, 156, 247, 259, 291, 436, 694
- Fermi potential, 258, 264, 434
- Fermi surface, 114, 123, 288, 289
- Fermi-Dirac distribution, 153
- Fermi-surface, 135
- Field distributions, 432
- Field effect in superlattices, 337
- Field ionization, 478
- Field-effect transistors, 191, 318
- Field-of-directions, 669
- Field-quenching, 668
- Field-stimulated conductivity, 406
- Figures of merit, 418
- Fill factor, 584
- Fill their outer shells, 3
- Film Sensitivity and Sensitization, 77
- Finite cluster approach, 89
- First Brillouin zone, 28
- Fixation of picture, 77
- Fixation process, 77
- For scattering, 249
- Forbidden zones, 86
- Foreign atoms, 42, 233, 307
- Form-elasticity, 38
- Forward bias, 521
- Fourier transformation, 348
- Fractional Quantum Hall Effect, 292
- Frank-Read source, 63
- Franz-Keldysh effect, 330–332, 335, 671, 675, 678, 684
- Franz-Keldysh oscillations, 333
- Free electron, 77, 90, 91, 93–95, 99, 219, 434, 487
- Free path, 102, 106, 236, 249, 250, 261, 262, 284, 312, 313, 316–319, 371, 465, 479
- Freeze-in disordered state, 46
- Frenkel excitons, 16, 336
- Frenkel pair, 76, 214, 231
- Frenkel-Poole type, 336
- Frequency response, 420
- Fresnel's equations, 352
- Fröhlich interaction, 305
- Fronts of ordered crystal growth, 48
- Frozen-in, amorphous, 38
- Frozen-in liquids, 38
- Frozen-in strain, 230
- Frustration, 40

G

Gain of a photoconductor, 417
 Gapless semiconductors, 111
 Gas discharge, 216, 453
 Gas-kinetic model, 252, 253, 369
 Gels, crystallization, 48
 Geminate recombination, 367, 368, 372
 Generation, 494, 513
 Generation current, 548
 Generation/recombination current, 423
 Germanium, 107
 Giant oscillations, 74
 Giant relaxation oscillators, 75
 Glass transition temperatures, 38
 Glass-forming matrix, 233
 Glasses, 38
 Glide motion, 62
 Glide plane, 57
 Glide set, 58
 Glissile, 63
 Glowcurve, 401
 Golden rule, 217
 Goldschmidt radii, 16
 Gr-current, 519, 534, 558
 Graded band-gap, 259
 Grain boundaries, 57, 65, 66, 77, 296, 315, 317, 318, 585
 Grain boundaries, low angle, 65
 Grain structure, 706
 Green's function, 177, 180, 186, 198
 Green's function calculations, 177
 Grimm-Sommerfeld rule, 11
 Ground-state, 162, 163, 166–169, 210, 212, 235, 400
 Ground-state energy, 162, 163, 166–168, 212
 Group velocity, 98, 127, 165, 272
 Growth from vapor phase, 47
 Growth habit, 45
 Growth of a semiconductor, 45
 Growth of microcrystallites, 48
 Growth perpendicular to surfaces, 46
 Growth spiral, 57

H

H-center, 82, 183
 H_2 molecule, 8
 Hall angle, 279, 280
 Hall constant, 279, 280
 Hall effect, 272, 274, 278, 279, 283, 292, 293, 407
 Hall field, 280
 Hall mobility, 280, 284, 681
 Hall-Shockley-Read center, 384, 385
 Halogen defects, 183

Hard-sphere collisions, 213
 Harrison mo, 68
 Heat of reaction, 70
 Heat of sublimation, 6
 Heavily doped semiconductors, 135, 221, 222
 Heavy hole bands, 119
 Heisenberg's uncertainty principle, 86
 Hermann-Mauguin nomenclature, 26
 Hermann-Mauguin symbol, 25
 Hetero-boundaries, 64, 66
 Heterojunction front wall or back wall solar cell, 626
 Heterojunction solar cells, 625
 Hexagonal lattices, 28
 High-efficient Si solar cells, 623
 High-energy particles, 337
 High-field tunneling, 69
 Higher excited states of the F-center, 82
 Hole conductivity, 251
 Hole demarcation line, 382
 Hole-traps, 381
 Homogeneous semiconductor, 239, 248, 257, 265, 270, 573 386, 493
 Honey-like consistency, 38
 Host matrix, 42
 Hubbard correlation energy, 192
 Hund's rule, 194, 197
 HWCVD, 731
 Hybrid function, 11
 Hybridization, 9, 11, 105, 106, 109, 130
 Hydrogen bonding, 3, 15
 Hydrogen dilution, 732
 Hydrogen in Si, 185
 Hydrogen pairing in silicon, 210
 Hydrogen-like centers, 189, 238
 Hydrogen-like defect, 53, 155, 156, 163, 167, 173, 336
 Hydrogen-like states, 187, 210
 Hydrophobic chains, 37
 Hydrostatic pressure, 110, 128, 171, 189, 242, 243
 Hyperfine interaction, 159
 Hyperfine structure, 234
 Hypergeometric functions, 92

I

I-center, 183
 Ideal lattice, 51, 102, 103, 156, 181, 217–219, 248, 296
 Ideal photovoltaic current-voltage characteristic, 582
 Impact ionization, 479
 Impacting electron, 75, 214
 Imperfect growth techniques, 233

- Impurities, isocoric, 53
- Impurities, isovalent, 53
- Impurity, 20, 22, 52, 53, 158, 169, 174–176, 178, 183, 186, 187, 191, 192, 195, 196, 203, 223, 240, 241, 287, 308, 309, 336, 338
- Impurity band, 237
- Impurity scattering, 277
- Incremental tunneling, 328
- Incremental velocity, 250
- Index of refraction, 345, 349, 350, 356, 358, 692
- Indirect band-gap materials, 329
- Inelastic collisions, 251
- Inelastic events, 311
- Inelastic scattering, 249, 295, 298, 305, 372
- Influence of the device thickness, 515
- Influence of traps, 390, 409
- Inhomogeneous doping, 427
- Inhomogeneous optical excitation, 608
- Inter-grain barriers, 318
- Interatomic distance, 3, 8, 14, 18, 87, 88, 102, 106, 235, 303, 305
- Intercalating atoms, diffusivity, 37
- Intercalation, 37
- Interface recombination, 641
- Interfacial layer, 708
- Interference effects, 99
- Interference pattern, 355, 356
- Interlayer, 712
- Intermediate valence bonding, 16
- Internal field, 266, 267, 437–439
- Internal quantum efficiencies, 715
- Interspersed forbidden gaps, 94
- Interstitial pairs, 210
- Interstitial site, 34, 102, 169, 195
- Interstitials, 52
- Interstitials, split, 52
- Intracenter transitions, 197, 198
- Intrinsic defect, 52, 183, 207, 231, 307
- Intrinsic energy level, 485
- Intrinsic layers, 244
- Intrinsic photoconductivity, 407
- Intrinsic point defect, 103, 307
- Intrinsic properties, 23, 341, 666
- Intrinsic semiconductor, 149
- Intrinsic workfunction of semiconductors, 70
- Inversion, 26
- Inversion layer, 537
- Ion bombardment, 216
- Ionic bonding, 4
- Ionic crystals, 4, 172
- Ionic radii, 14, 16–18
- Ionic radii in metals, 14
- Ionic state is $\text{Cd}^{++}\text{S}^{--}$, 12
- Ionicity, degree of, 12
- Ionization energy, 6, 119, 159, 168, 181, 189, 192, 197, 308, 393, 400, 668
- Ionized impurity, 277, 280
- Ionized impurity scattering, 312
- Irradiation, 211, 403
- Isoelectronic center pairs, 209
- Isoelectronic defects, 188
- Isoelectronic traps, 188
- Isomorph, 27
- Isothermal and adiabatic galvanomagnetic effects, 274
- Isothermal compression, 6
- Isothermal Hall effect, 278
- ITO layers, 711
- J**
- Jahn-Teller, 172, 178, 184, 194, 195, 198
- Jahn-Teller effect, 178, 187, 194, 195, 198
- Joule's heating, 251, 256, 257
- Jump of the valence band, 68
- Junction capacitance, 547
- Junction region, 549
- K**
- Kakhenberg method, 49
- Kelvin relation, 277
- Kind of electron trap, 382
- Kinetic effects, 150, 387
- Kinetic experiments, 75
- Kramers-Kronig analysis, 359
- Kröger-Vink notation, 55
- Kronig-Penney, 92
- Kronig-Penney potential, 92, 93, 95, 139, 235
- L**
- Landau diamagnetism, 288
- Landau level, 122, 284–289, 291–293
- Landau quantum number, 288
- Landau-level splitting, 290
- Lande g -factor, 286, 287
- Langmuir-Blodgett films, 37
- Large band-gap material, 239, 240
- Large defect associates, 211
- Large lattice defects, 315
- Larmor frequency, 286
- Laser-excited luminescence, 287
- Latent picture, 77
- Lattice constant, 7, 6, 19, 27, 35, 67, 91, 101, 106, 128, 132, 157, 158, 181, 208, 242–244, 305
- Lattice defects, 74, 75, 111, 149, 180, 184, 192, 211, 214, 216, 217, 220, 252, 268, 296, 315, 317, 387, 440

- Lattice direction, 27
- Lattice mismatch, 36, 67, 711
- Lattice perturbation, 181
- Lattice plane, 27
- Lattice point, 27
- Lattice relaxation, 53
- Lattice vectors, 24
- Lattice vibration, 305, 372
- Laughlin states, 293
- Layered lattices, 10
- Lazarevicites, 34
- Leak out, 427
- Leakage current, 509
- Lifshitz tail, 217
- Ligands, 30
- Light hole band, 117
- Linearly doped junction, 568
- Local currents, 474
- Local heating, 75
- Local stress-relief, 230
- Localization, 87
- Long wavelength cut-off, 225
- Long-range Coulomb forces, 308
- Long-range periodicity, 85
- Longitudinal acoustic phonons, 300
- Longitudinal optical phonons, 289, 306
- Lorentz force, 122, 278, 285, 286
- Lorentz number, 277
- Loss mechanisms, 713
- Low angle grain boundaries, 64
- Low optical generation, 593
- Luminescence, 54, 61, 80, 136, 172, 183, 192, 211, 245, 368, 400–402, 404
- Luminophore, 400
- Luttinger band parameters, 122
- M**
- Madelung constant, 5
- Magnetic field, 122, 123, 159, 211, 212, 271, 273, 274, 284, 286, 288–290, 342
- Magnetic induction, 122–124, 271, 272, 278, 280, 282–286, 288–292
- Magnetic momentum, 234, 286
- Magnetic permeability, 342
- Magnetic subbands, 286
- Magnetic susceptibility, 271, 288, 289
- Magnetization, 271
- Magneto-conductivity tensor, 279
- Magneto-optical experiments, 110
- Magneto-resistance, 272, 280, 282–284, 289, 290, 292, 293
- Magneto-resistance coefficient, 282, 283
- Main group metal, 106
- Majority carriers, 573
- Many-body effects, 222
- Mathiessen's rule, 296
- Maximum GR-Currents, 498
- Maxwell's equations, 341, 342, 348
- Mean free path, 252
- Measurement of Optical Parameters, 349
- Melt, 38, 47–49, 211, 238
- Memory-erasing collisions, 309
- Metal contacts, large area, 69
- Metal impurities, 171, 180, 194, 198, 203
- Metal ions, 57
- Metal/semiconductor boundary, 64, 319, 463
- Metal/semiconductor interface, 69, 524
- Metallic bonding, 4, 14
- Metastability, 193, 194
- Metastable, 73, 75, 82, 168, 184, 185, 214, 242
- Microcrystallite boundaries, 233, 316
- Microcrystallite formed, 46
- Microscopic order or long-range, 38
- Miller indices, 27
- Mini-bands, 100, 139–141, 143
- Minibands, 244
- Minority carrier currents, 493
- Minority carrier depletion, 536
- Minority carrier diffusion equation, 495
- Minority carriers, 473, 573
- Mirror plane, 26
- Mismatch dislocation, 67, 68, 241
- Mismatch dislocation field, 67
- Missing charges, 431
- Missing lattice atom, 52, 217
- Mixed bonding, 4, 12–14, 56
- Mixed dislocation, 58
- Mixed-bond crystals, 11
- Modified boundary condition, 465
- Modified Schottky Barrier, 462
- Modified Schottky diode equation, 466
- Modifying elements, 228
- Modulation reflection spectrum, 359
- Modulation spectroscopy, 358
- Mohs hardness, 19
- Molecular crystals, 23
- Molecular pairs, 210
- Momentum effective mass, 126
- Momentum matrix element, 332, 359
- Monochromatic light, 477
- Monomolecular recombination, 408
- Monovalent metals, 109
- Morphologies, 45
- Morphology of crystals, 27
- Morphotrop, 27
- Multijunction solar cells, 736
- Multijunction device, 723

N

N defect states, 233
N-type, 63, 186, 191, 197, 210, 240, 259, 277, 280, 328, 382, 451, 561, 562
n-type, 223–225, 228, 408, 483
N-type Ge, 60
N-type semiconductor, 447
 Nano-crystalline silicon, 729
 Negative effective mass, 108
 Negative *U*-center, 186, 191–193, 227, 232
 Negative-*U* character, 80
 Net thermal generation, 486
 Net-generation rates, 523
 Network of dislocations, 67
 Neutral activators, 413
 Neutral lattice defects, 307
 Newton's second law, 97
 No hole traps, 536
 Noble metal configuration, 203
 Non-magnetic, nonconductive dielectrics, 343
 Non-thermal carrier, 383
 Nonequilibrium states, 23
 Nonequilibrium steady state, 383
 Nonhydrogenated, 234
 Nonlocalized Bloch wavefunctions, 234
 Nonradiative capture, 372
 Nonradiative recombination, 367, 368, 375, 376
 Nonresonant interactions, 341
 Nonsaturable Coulomb forces, 4
 Nonstoichiometric, 221
 Notation, Kröger, Vink, Schottky, 55
 Novotny-Juza compounds, 31, 34
 Nuclear particles, 337
 Nuclear spins, 287
 Nucleus, overcritical size, 45

O

Odd-numbered rings, 40
 ODMR, 172
 Of quantum-confined Stark effects, 336
 Ohm's law, 251
 Opposite strain at outer surfaces, 67
 Optical absorption, 141, 218, 333, 341
 Optical absorption coefficient, 348, 726
 Optical absorption spectrum, 75
 Optical dielectric constant, 156
 Optical excitation near the front surface, 608
 Optical generation, 491
 Optical generation rate, 603
 Optical phonon, 256, 277, 298, 303–305
 Optical quenching, 398
 Optical spectra, 180
 Order, intermediate range, 41

Orientation relaxation, 387
 Over-coordinated, 231
 Oxygen centers, 210
 Oxygen in GaP, 190
 Oxygen-related centers, 191

P

p-orbitals, 11
P-states, 11, 109, 189
p-states, 117, 160
P-type, 60, 155
p-type, 228
 Pair energy, 208
 Parabolic approximation, 125
 Parabolic barrier, 324
 Paramagnetic, 16
 Paramagnetic interaction, 286, 287
 Paramagnetic resonance, 60, 231
 Partial dislocations, 58
 Particle flux, 109
 Pauli operator, 119
 Pauli principle, 7, 107
 Pauli spin paramagnetism, 287
 Peltier coefficient, 277
 Penalty, 192, 266, 438, 439
 Penrose tiling, 43
 Periodic lattice, 90, 95, 99, 101, 235, 299
 Periodic lattice potential, 95, 99, 235
 Periodic modulation, 244
 Periodic potential, 90–92, 94, 95, 138, 139, 235, 237, 240, 248, 299
 Periodicity, 23, 29, 35, 39, 65, 85, 91, 92, 94, 95, 114, 138, 139, 146, 181, 235, 296, 302, 307
 Permeable, 144, 240
 Persistent photoconductivity, 423
 Perturbation, 96, 160, 176, 178, 182, 209, 217, 223, 236, 272, 275, 299
 Perturbed potential, 235
 Phase segregation, 48, 207, 211, 259
 Phase transition, 242
 Phenomenological theory, 342
 Phonon, 75, 149, 295, 299, 329
 Phonon dispersion relation, 298
 Phonon drag, 257
 Phonon relaxation, 387
 Phonon spectrum, 221, 266, 329, 438
 Phonon-assisted Auger transitions, 376
 Phosphor, 400, 401, 403
 Phosphorescence, 400
 Phosphorescent material, 400
 Phosphorus, 54, 156, 190, 208
 Phosphorus (P) substituents, 727
 Photo chromatic processes, 76

Photo diode current, 493
 Photo-emf, 574
 Photochemical reaction, 73, 78
 Photochemical reaction product, 75
 Photoconductivity, 54, 61, 394
 Photoconductors, 573
 Photocurrent, 574
 Photodetectivity, 418
 Photoemission measurements, 68
 Photographic process, 77, 211
 Photon noise, 420
 Photon-assisted tunneling, 330, 331
 Photoplastic effect, 63
 Photosensitivity, 416
 Photovoltaic current, 580
 Photovoltaic devices, 574
 Photovoltaic effect, 571
 Piezoelectric crystals, 302, 315
pin cell, 733
 Pinhole-free coating, 710
 Pinning of dislocations, 63, 64
pin photodiode, 722
 Plasma deposition, 728
 Plasmon-induced recombination, 380
 Plastic deformation, 60
Pn-homojunction, 543
Pn-junction, 51, 383, 544, 552, 591, 606
pn-junction, 444
 Pnictide, 33
 Pnictogen, 106, 230, 233
 Point contacts, 69
 Point defects, 52, 54, 55, 57, 60, 203, 207,
 217–219, 239, 296, 315, 316
 Point group, 24
 Point lattice, 23
 Poisson equation, 266, 317, 428, 433, 438,
 445, 450, 452, 454, 525, 545
 Poisson ratio, 242
 Polarizability, 27
 Polarization, 198, 210, 271, 279, 287, 305,
 343, 349, 350
 Polarization rotation, 400
 Polaron mass, 99
 Polychromatic light, 477
 Polycrystalline devices, 585
 Polycrystals, 46
 Polytype, 31
 Polytype structures, 65
 Potential wells, 239
 Power conversion efficiency, 585
 Poynting vector, 344
 Precrystallization, 233
 Precursor film, 709
 Preferred lattice structure, 19

Primitive unit cell, 23
 Print-Out Effect, 77
 Pseudo-momentum, 126
 Pseudo-orbitals, 177
 Pseudopotential method, 172
 Pseudoternary compounds, 34
 Pure generation current, 499

Q

Quality factor, 550
 Quantized Hall effect, 289
 Quantum boxes, 144
 Quantum number, 101
 Quantum well structure, 290
 Quantum wires, 144
 Quantum-mechanical exchange, 87
 Quantum-mechanical model, 141, 248
 Quantum-mechanical theory, 220
 Quantum-well structures, 145
 Quasi Fermi level, 473
 Quasi-cathode, 682
 Quasi-Fermi level, 264, 382, 563, 534, 564
 Quasi-Fermi levels collapse, 535
 Quasi-free electrons, 145, 218, 279, 281
 Quasi-neutrality condition, 409
 Quasi-particles, 16, 342
 Quasicrystals, 42
 Quenching transition, 398

R

R-center, 75
 Radiation damage, 212–214
 Radiative recombination, 367, 374
 Reaction kinetic equations, 388, 572
 Reaction-kinetic, 79, 393, 395, 421
 Reciprocal lattice, 27, 28
 Recombination, 73, 74, 78, 79, 149, 368, 370,
 372, 376, 379, 380, 482, 561, 562, 564,
 573, 660
 Recombination center density, 600
 Recombination centers, 51, 381, 412
 Recombination centers are annihilated, 79
 Recombination current, 548
 Recombination leakage current, 565
 Recombination overshoot, 594, 597
 Reconstruction, core, 60
 Recrystallization, 49, 234
 Recrystallization, flux-enhanced, 48
 Rectangular barrier, 321, 322
 Rectifying characteristic, 442
 Redistribution of carriers, 240, 387, 388, 573
 Reflectance and absorption coefficient, 356
 Reflection, 26
 Relative workfunction, 69
 Relaxation, neighbor, position, 52

- Relaxation parameter, 20–22
- Relaxation time, 253, 254, 284, 295, 296, 310, 313, 318, 397
- Repulsive center, 218
- Repulsive interatomic forces, 4
- Repulsive potential softness parameters, 18
- Resonance absorption, 287, 344
- Resonance effects, 241
- Resonant absorption, 287, 341
- Resonant states, 181
- Resonant transitions, 341
- Responsivity, 418
- Reverse bias, 468, 521
- RF-PECVD, 729
- Richardson-Dushman current, 262
- Richardson-Dushman emission, 464
- Rings, even numbered, 40
- Roto-inversion, 26
- Rs-bands, 304
- Rutherford scattering, 214
- Rydberg energy, 161
- S**
- S-orbital, 11
- Saddle points, 100
- Saturable bonding, 11
- Scattering cross section, 252, 307, 308, 310, 311
- Scattering of carriers, 249, 305, 313
- Schönflies symbol, 25
- Schottky approximation, 450–452, 455
- Schottky barrier, 432, 447, 460, 461, 518
- Schottky-barrier device, 525
- Schottky-Read-Hall centers, 485
- Schrödinger equation, 88, 90–95, 156, 157, 161, 173, 175, 284–286, 300
- Schubweg, 510, 522
- Screw dislocation, 57
- Seed, two dimensional, 46
- Segregated phases, 36
- Segregation, 36, 49, 211
- Self-interstitial, 184–186, 231
- Semi-classical approach, 87
- Semiclassical model, 218
- Semiconductor alloys, 221
- Semiconductor plate, 354
- Semiconductors with a direct band gap, 298
- Semimagnetic semiconductors, 16
- Semimetals, 110, 111
- Sensitive photoconductor, 412, 413
- Sensitization, 415
- Seraphin coefficients, 358
- Series resistance, 586
- Series resistance limitation, 569
- Series-resistance limited, 444
- Sessile, 63
- Several relaxation times, 397
- Shallow traps, 410
- Shape factor, 467
- Shear strain, 304
- Shell number, 208, 209
- Shifted Boltzmann distribution, 153
- Shockley-Frank-Read approximation, 533
- Shockley-Read-Hall model, 534
- Short-range repulsion, 3
- Shubnikov-DeHaas effect, 289
- Shuffle set, 58
- Shunt resistance, 587
- Si *pn*-junction, 591
- Silver interstitial diffusion, 76
- Silver-halide, 76
- Simple drift current, 515
- Simple one-band model, 186
- Simple Schottky diode equation, 582
- Simultaneous vapor deposition, 709
- Single atomic layer, 241
- Single carrier n-type Schottky barrier, 630
- Single crystal grow, 46
- Single donor model, 631
- Singular point, 429
- Slips of lattice planes, 47
- Slow copper recombination centers, 668
- Small doping step, 430
- Snell's law, 351
- Softness of the ionic spheres, 18
- Softness parameter, 4
- Solar cell degradation, 73
- Solar cell performance, 51
- Solar cells, 574, 583
- Solid semiconductor, 85
- Solidification, 211
- Solubility, 49, 128, 195, 211
- sp*³-bonding, 89
- sp*³-hybridization, 105
- Space charge, 51, 68, 171, 240, 427, 518, 551, 625, 630
- Space groups, 26
- Space-charge cloud, 316
- Space-charge limited current, 444
- Space-charge-limited current equation, 446
- Specific resistivity, 251
- Spectral range extended by absorbing organic dyes, 78
- Spin density, 234
- Spin resonance, 159, 183, 193, 229, 234, 287
- Spin-flip electromagnetic resonance experiment, 234
- Spin-orbit coupling, 180

- Spin-orbit interaction, 117, 305
- Spin-orbit split-off band, 117
- Splat cooling, 39
- Splicing boundary, 523
- Split quasi-Fermi levels, 596
- Sputter deposition, 708
- Sputtered precursors, 710
- Square Well potential, 172
- Stacking fault, 65, 64
- Stacking single layers, 143
- Staebler–Wronski effect, 78, 724
- Standing wave, 99
- Stannites, 34
- Stark effect, 336
- Stark shift, 336
- Stationary high-field domain, 681
- Statistical distribution, 150, 218, 248, 296
- Steady-state current continuity equations, 421
- Sticking of ion pairs, 46
- Stoichiometry, 47
- Stokes shifts, 191
- Strain, remaining, 67
- Strain-related defects, 229, 230
- Strained layer systems, 64
- Structure, matrix-like, 41
- Structure, network-like, 41
- Subbands, 105
- Subimage, 77
- Sublattice, 35, 128, 131, 188, 208, 221, 259
- Sublimation, 47
- Substitutionals, 53, 56, 186
- Sulphur-containing gelatin, 78
- Sum of free and trapped charges, 536
- Sunlight absorption, 576
- Supercell technique, 176
- Superlattice, 23, 35, 138, 240, 336
- Superlinearity, 416
- Supersaturation, 47
- Supershell approach, 101
- Superstrate CdS/CdTe solar cell, 650
- Supply of minority carriers, 603
- Surface charges, 432
- Surface energy, 45
- Surface recombination, 599
- Surface recombination current, 499, 558
- Surfaces, 64
- Symmetry of the lattice, 23
- Symmetry operation, 24
- Symmetry points, 28
- T**
- Tail of band states, 217
- Tailing of band states, 222, 225
- Tathogen, 230
- Tauc band-gap, 726
- Temperature gradient, 257, 271, 277
- Tensor ellipsoid, 115
- Ternary and quaternary compounds, 32
- Tetragonal glasses, 233
- Tetrahedral covalent radii, 17
- Tetrahedral lattice, 32
- Tetrahedrally bound amorphous semiconductors, 228, 229
- Tetrahedrally bound semiconductors, 230
- Tetravalent elements, 10
- Thermal distribution, 253
- Thermal donors, 210
- Thermal equilibrium, 248, 249, 261–264, 266, 272, 369, 380, 383, 385, 427, 434, 438, 440, 475, 476, 483, 484, 565
- Thermal excitation, 475
- Thermal GR-Current, 500
- Thermal ionization, 400
- Thermal phonons, 230
- Thermally stimulated current, 403
- Thermionic emission current, 262
- Thermo-emf, 278
- Thicker slab, 506
- Thin slab, 506
- Three-band model, 127
- Three-dimensional dispersion relation, 112
- Three-dimensional lattice, 325
- Three-step process, 330
- Tight-binding approach, 88
- Tight-binding approximation, 194
- Tolman experiment, 108
- Topology, local, 41
- Total area efficiencies, 719
- Total carrier current, 270
- Total current, 247, 262, 263, 269, 348, 436, 445, 561, 562, 564
- Total current-voltage characteristic, 550
- Total electron current, 263, 264
- Total hole current, 513
- Total incremental current, 486
- Totally filled valence band, 107
- Transition Character, 197
- Transition coefficient, 389, 475
- Transition metal, 15, 16, 53, 109, 192, 194, 198, 228
- Transition metal impurities, 194
- Transition rate, 402, 475
- Translational symmetry, 222
- Transmission electron microscopy, 61
- Transmuted elements, doping, 32
- Transparent conducting oxide, 711
- Transport equations, 273, 274, 592
- Transverse magneto-resistance, 283

Trap availability factor, 410
 Trap distribution, 411
 Trap-filling, 391, 392, 396, 404
 Trapping, 103
 Trapping a carrier causes violent oscillations, 75
 Triangular barrier, 323–325
 Triangular shape, 323
 Triple and higher defect centers, 211
 Triplet state, 183
 Trivalent metals, 109
 Trochoids, 290, 291
 True glasses, 233
 TS C measurements, 374
 TSC, 403–405
 TSL, 403, 404
 Tunability, 245
 Tunnel spectroscopy, 329
 Tunneling, 144, 247, 325
 Twin boundaries, 64
 Two sets of donors, 630
 Two-carrier model, 517
 Two-dimensional hydrogen problem, 336
 Two-dimensional (layered) lattices, 10
 Two-donor model, 631
 Two-step tunneling, 330
 Type-I pairs, 208
 Types of scattering centers, 296
 Typical photoconductors, 573

U

Ultrathin superlattices, 36
 Umklapp processes, 298
 Uncompensated spins, 193, 287
 Uniaxial stress, 132
 Unit cell, 23, 24, 28, 32, 43
 Unit cells, two, 43
 Unit polarization vector, 332
 Unpaired spin, 60, 80, 229, 234
 Upstream diffusion length, 511
 Urbach tail, 218, 220, 221, 229

V

V-center, 183
 V-shaped potential well, 241

Vacancies, 52
 Vacancies and interstitials, 56
 Valence alternation, 193, 232
 Valence angles, 30
 Valence band, 54
 Van der Waals, 3, 10, 15, 17
 Virtual cathode, 683
 Viscosity near surface, 46
 Vk-center, 183
 Voltage drop kinetics method, 638

W

Waals forces, 10
 Wannier functions, 176
 Wave crest, 300
 Wave numbers, 322
 Wave packet, 96, 98, 99, 156, 158, 165, 272
 Wave vector, 28, 90, 127, 151, 300, 312, 323, 324
 Wavefunction, 28, 98, 157, 160, 171, 198, 220, 236, 240, 300, 321
 Wavenumber, 28
 Weak bond breaking, 80
 Wide band gap material, 180
 Wiedemann-Franz law, 277
 Wigner-Seitz cell, 28
 WKB approximation, 323
 Workfunction of metals, 69
 Wurtzite, zincblende, 64
 Wurtzite lattice, 31
 Wurtzite structure, 31

X

X-ray photons, 337
 X-valley, 190

Y

Yukawa potential, 311, 312
 Yukawa-type, 306

Z

Zero band gap semiconductors, 128
 Zincblende, 31
 ZnS lattice, 32
 Zone rectification, 49