

Siegfried Hofmann

Auger- and X-Ray Photoelectron Spectroscopy in Materials Science

A User-Oriented Guide



Springer

SPRINGER SERIES IN SURFACE SCIENCES

Series Editors: G. Ertl, H. Lüth and D.L. Mills

This series covers the whole spectrum of surface sciences, including structure and dynamics of clean and adsorbate-covered surfaces, thin films, basic surface effects, analytical methods and also the physics and chemistry of interfaces. Written by leading researchers in the field, the books are intended primarily for researchers in academia and industry and for graduate students.

Please view available titles in *Springer Series in Surface Sciences*
on series homepage <http://www.springer.com/series/409>

Siegfried Hofmann

Auger- and X-Ray Photoelectron Spectroscopy in Materials Science

A User-Oriented Guide

With 262 Figures

 Springer

Professor Dr. Siegfried Hofmann

Max-Planck-Institute for Intelligent Systems
(formerly Max-Planck-Institute for Metals Research)
Heisenbergstrasse 3, 70569 Stuttgart, Germany
s.hofmann@mf.mpg.de or s.hofmann@is.mpg.de

Series Editors:

Professor Dr. Gerhard Ertl

Fritz-Haber-Institute der Max-Planck-Gesellschaft, Faradayweg 4-6,
14195 Berlin, Germany

Professor Dr. Hans Lüth

Institut für Schicht- und Ionentechnik
Forschungszentrum Jülich GmbH,
52425 Jülich, Germany

Professor Douglas L. Mills, Ph.D.

Department of Physics, University of California,
Irvine, CA 92717, USA

Springer Series in Surface Sciences ISSN 0931-5195
ISBN 978-3-642-27380-3 ISBN 978-3-642-27381-0 (eBook)
DOI 10.1007/978-3-642-27381-0
Springer Heidelberg New York Dordrecht London

Library of Congress Control Number: 2012942909

© Springer-Verlag Berlin Heidelberg 2013

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed. Exempted from this legal reservation are brief excerpts in connection with reviews or scholarly analysis or material supplied specifically for the purpose of being entered and executed on a computer system, for exclusive use by the purchaser of the work. Duplication of this publication or parts thereof is permitted only under the provisions of the Copyright Law of the Publisher's location, in its current version, and permission for use must always be obtained from Springer. Permissions for use may be obtained through RightsLink at the Copyright Clearance Center. Violations are liable to prosecution under the respective Copyright Law.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

While the advice and information in this book are believed to be true and accurate at the date of publication, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)



*Dedicated to the Memory of my Father
Georg Adam Hofmann,
Müllermeister in Dietenhofen/Moosmühle
13. April 1901 †15. December 1969

Foreword

Surface chemical analysis is used extensively for a wide range of purposes in science and technology. Technologically, surface and interface properties are crucial for the fabrication and performance of a wide range of advanced materials (e.g., ceramics, composites, alloys, polymers, superconductors, diamond-like thin films, and biomaterials), semiconductor devices, optoelectronic materials, high-density magnetic-storage media, sensors, thin films, and coatings. Surface or interface integrity is critical for many properties or processes, such as the electrical behavior of a semiconductor device, the wear or corrosion of an automobile part, or the degradation of an implant material in the human body. Surface analysis is used in these applications for failure analysis in manufacturing or of a component in its service environment as well as for monitoring steps in product fabrication or process development. The surface composition may be required for product quality control or may be usefully correlated with specific material properties, processes, or phenomena (e.g., corrosion, adhesion, lubrication, wear, segregation of bulk impurities to interfaces, and diffusion, among many others) so that improvements can be developed. Surface and interface properties are also critical in many areas of public concern ranging from new sources of energy (e.g., photovoltaics and fuel cells) to defence systems (e.g., sensors and stability of high-power laser optical components) and health and environmental problems (e.g., particulate pollutants in the atmosphere and the stability of stored nuclear waste). Two of the most commonly used surface analysis techniques are Auger-electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). These techniques are utilized in different modes to obtain information on the near-surface composition and, in conjunction with ion sputtering or other methods to remove surface layers, to determine the composition of the material as a function of depth from the original surface. For many advanced materials (e.g., semiconductor devices, magnetic storage media, and new classes of nanostructures and nanomaterials), the materials are fabricated with critical dimensions on the nanometer scale and there is little distinction between surface, bulk, thin film, and interface properties. A growing need in these applications is to determine composition as a function of position, particularly in the vicinity of surfaces and interfaces for materials that may have complex morphologies.

Commercial instruments for AES and XPS became available some four decades ago, and the instrumental capabilities (e.g., in sensitivity, spatial resolution, and imaging) have improved dramatically over the years. While the early instruments were controlled manually and information was obtained with analogue systems, modern instruments are controlled by computers with advanced software for instrument setup, operation, data acquisition, and data analysis. The principles of AES and XPS are relatively easy to understand, but it can nevertheless be difficult to select instrumental operating conditions to obtain the desired information as efficiently as possible. Many artifacts can arise in data acquisition and there can be complexities in the interpretation and analysis of acquired data, particularly for inhomogeneous specimens. This welcome book by Siegfried Hofmann provides extensive guidance to novice as well as experienced surface analysts. Throughout his distinguished career, Hofmann has made numerous significant contributions to applied surface, ranging from the development of new methods to applications in materials science. He recognized early the importance of surfaces, interfaces, and thin films in many fields, and developed analytical methods of increasing sophistication and detail to obtain quantitative information for the solution of a wide range of practical problems. Hofmann has distilled his extensive knowledge and experience into an extremely useful book. Hofmann's book provides a comprehensive account of the basic principles of AES and XPS (Chaps. 1 and 3), the available instrumentation (Chap. 2), and the many factors that need to be considered in surface analyses by these techniques. The two longest chapters, Chap. 4 on quantitative analysis (data evaluation)" and Chap. 7 on quantitative compositional depth profiling, contain a clear description of factors affecting the measured signal intensities as well as how the intensities are modified by specimen inhomogeneities. Worked examples are provided with typical data to illustrate concepts and the application of different analytical approaches. Other chapters give guidance on optimizing experimental conditions (Chap. 5), on optimizing certainty and the detection limit (Chap. 6), and on developing an analytical strategy for AES and XPS measurements (Chap. 8). Finally, Chap. 9 gives examples of typical AES and XPS applications in materials science. While AES and XPS are extensively used for qualitative purposes, this book provides the best and clearest account I am aware of on how to make different types of quantitative AES and XPS analyses for various types of samples. Readers will also welcome the author's focus on using the instruments as effectively and efficiently as possible and on solving different types of practical problems. Most AES and XPS analysts will find this book to be a valuable resource. I recommend it strongly.

Cedric J. Powell

Preface

The aim of this book is mainly to help the practical analyst in his daily work on a rather basic level. Furthermore, it should serve as a guide for students working for their master's or Ph.D. thesis in materials science by teaching them about capabilities and limitations of applied surface analysis using AES and XPS in their special field. The reader may ask: why another book on a topic that is already covered by excellent books such as Briggs and Seah (1990) [1], Briggs and Grant [2], and Watts and Wolstenhome [3]. The answer is manifold: Book [1] is still excellent but outdated in some special although important aspects of quantitative analysis or depth profiling; book [2], thought as a replacement of [1] after 13 years, in many aspects is too much detailed and theoretically based for practical applications, a book aimed at the advanced spectroscopist. Book [3] is highly recommended as an introduction for the beginner but as such lacks the quantitative information and data needed for the practical researcher in daily work. In short, the author's intention is to provide a compendium that fulfills the gap between [2] and [3]. In addition, the above argument for [2] may hold here too, since at least a few topics were introduced only in recent years, such as the surface excitation parameter (SEP) or the backscattering correction factor (BCF). Furthermore, I adopt the point of view already mentioned by René Descartes in 1637 (p. 11 of Ref. [4]): "...there is often less perfection in works composed of several parts, and made by the hands of a variety of contributors, than in those one which only one person has worked on ...". After having established the surface and interface analysis group in the Max Planck Institute on Metals Research in Stuttgart, the author has worked more than 30 years in application of AES and XPS to Materials Science. This seems to be an advantage at first sight, but it bears an inevitable disadvantage: personally unique experience leaves everybody somehow biased about the importance and the treatment of specific topics. Therefore, the book appears like a homunculus picture in psychology, where the size of an organ is displayed according to the volume the brain needs for its operation. Thus, I have to apologize that the contents may appear somehow imbalanced to many colleagues. For example, sputter depth profiling is highly emphasized, as are the practical issues of quantification, signal-to-noise and detection limit, at the cost of

the more cursorily presented theoretical background. The book frequently refers to the original, pioneering work that is easier to understand and most often is best understood today. The intention is to build a bridge to the more recent research on the same topic where the full range of possibilities of modern instrumentation and new theory is revealed. I have always tried to follow the four basic rules of scientific research as postulated by René Descartes in his famous *Discourse on Method* [4]: (1) Do not believe anything that you did not think about thoroughly and with utmost scrutiny, (2) always try to decompose complex problems into smaller, less complex parts, (3) after having solved the partial problems, put them together again to solve the original task, and (4) always be as quantitative as possible. For me, rules (1) and (4) seem to be the bottom line of any scientific approach. Therefore I recommend that the reader applies these rules, in particular rule (1), to the book too, and I can only hope that the outcome is not unfavorable for the book. This mutual problem was addressed already by one of the first German physicists, Georg Christoph Lichtenberg (1742–1799), when he said: *Wenn ein Buch und ein Kopf zusammenstoßen und es klingt hohl, ist das allemal im Buch?*, which means: *If there is a collision of a book and a head and it sounds hollow, will this sound always be caused by the book?*

The ten chapters of the book are strongly cross-linked with each other. The reader is guided from the broader, introductory issues, such as historical background and basic principles (Chap. 1), to more special topics like instrumentation (Chap. 2) and qualitative analysis (Chap. 3), and to the most essential topics such as quantitative analysis (Chap. 4). Extending that issue to optimizing signal intensity (Chap. 5), which considers angular relations and roughness effects, the general role of signal-to-noise ratio in optimization of certainty and detection limit is outlined in Chap. 6. Being the focus of any surface (and thin film) analysis, quantitative compositional depth profiling (destructive and non-destructive) is presented Chap. 7. The following chapters are of more qualitative character but are nevertheless important for the analytical strategy. The latter topic is addressed in practical aspects of surface and interface analysis (Chap. 8), which contains many hints and tips for sample handling and for solving problems such as charging and beam damage effects. Some typical examples (Chap. 9) illustrate proper usage of the previous chapters (Chaps. 3–8). The final chapter, related surface analysis techniques (Chap. 10), gives an outlook to various methods which often are complementary to AES and XPS.

Thus, I like to encourage the reader to read the book critically but with open mind and optimism. My hopes were already expressed by Friedrich Nietzsche (1844–1900) in his book *Die froehliche Wissenschaft (The Joyful Science)*:

Wagt's mit meiner Kost ihr Esser
Morgen schmeckt sie euch schon besser
Und schon uebermorgen gut.

Approximately this means:

Be courageous, taste this book
Tomorrow you may like it better
And later you may think it's good.

Stuttgart

Siegfried Hofmann

References

1. D. Briggs, M.P. Seah (eds.), *Practical Surface Analysis vol. 1 (AES and XPS)*, 2nd edn. (Wiley, Chichester, 1990)
2. D. Briggs, J.T. Grant (eds.), *Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy* (IM Publ., Chichester, 2003)
3. J.F. Watts, J. Wolstenholme, *An Introduction to Surface Analysis by XPS and AES* (Wiley, Chichester, 2003)
4. R. Descartes, in *Discourse on Method and Other Writings*, ed. by R. Clarke. Penguin Classics (Penguin, London, 1999)

Acknowledgment

I am indebted to many friends and colleagues who supported me professionally and who directly and indirectly helped me to write up the book chapters. First of all, I like to thank my former doctorate students and long time coworkers Anton Zalar (who much too early died in 2009), Jose Maria Sanz, Joachim Steffen and, above all, Pavel Lejček. Without their scientific talent, skill, and toughness I could never have accomplished the core of my work presented here. Pavel Lejček first came to my group as a postdoc in 1988. Since then, we worked together in the field of quantitative grain boundary segregation in a well balanced team spirit, resulting in more than 35 coauthored publications. In addition, Pavel supported me by constant encouragement and by tremendous technical assistance in writing up this book, which I could not have finished without his help.

Like the scientific community at large, I myself in particular owe a lot to the outstanding giants in surface analysis, Martin Seah and Cedric Powell. Their fundamental work had and still has an enormous influence in the development and current status of quantitative surface analysis. Often feeling like Newton's dwarf, during many years I had the chance of receiving their critical opinion on my work in a fair and open way, and our scientific exchange led to many new ideas on my side. In addition, Cedric Powell gave me the honor of writing a foreword to this book.

Of course, I am grateful for support to many more people, and I like to mention here just a few of them. In the early days of my scientific career, Alfred Benninghoven, Helmut Werner, and Helmut Seiler helped me in entering the topic of depth profiling and of electron spectroscopy. A close cooperation with John Thomas III in the group of Rick Honig at the former David Sarnoff Research Center of RCA in Princeton gave me much insight in applied materials research. During a stay at the University of Florida in 1984, I learned a lot from Paul Holloway about many special effects in practical surface and in-depth analysis (including deep seawater fishing). In the extremely cold winter in 1994 at NIST in Gaithersburg, I had the pleasure of receiving the warming point of views of Cedric Powell and the late Joe Fine concerning basic surface science and analysis, including heat induced techniques to remove thick ice layers from windshields. My colleagues and friends

of the ECASIA conferences community always were ready to discuss with me my work and to support me in many ways, and I am especially grateful to Hans-Jörg Mathieu, Jacques Cazaux, Francis Degrève, Philippe Marcus, László Kövér, and Miklós Menyhard.

With many thanks and great respect I am looking back to several years of close and fruitful cooperation with my Japanese friends and colleagues, foremost with Ryuichi Shimizu, Kazuhiro Yoshihara, Shingo Ichimura, and Kazuo Kajiwara, who always supported me and my work. During my stay at NRIM (now NIMS) in Tsukuba (1996–1998), Kazuhiro Yoshihara was my constant, friendly, and patient advisor and helped me a lot to overcome cultural discrepancies. The support of my English-speaking secretary at that time, Kayoko Horiuchi, is gratefully acknowledged. In recent years, Kenichi Shimizu of Keio University widened my scientific horizon at special conferences and in many discussions. I am grateful to Ze-jun Ding, Heifei University, for discussions on electron backscattering.

Last but not least, I like to thank my excellent coworkers who helped me a lot in topics which are frequently referred to in the book: Juergen Erlewein in starting our surface segregation work, Johan Malherbe in the early days of depth profiling and ion implantation, Hermann Jehn in characterization of metallurgical coatings, and Jiang Yong Wang with recent modifications of the MRI model. Special thanks are due to my successor as head of the Surface Analysis group at the former Max Planck Institute for Metals Research, Lars Jeurgens, for many discussions and for good cooperation including help for this book. Skilful technical assistance of Bernhard Siegle, Michaela Wieland and Martin Noah is gratefully acknowledged.

I like to thank Claus Ascheron from Springer Verlag for his valuable hints and constant patience for many years.

Finally, I apologize for not having mentioned those whom I should have mentioned in addition but, for some reason or other, I simply forgot to do so.

Stuttgart

Siegfried Hofmann

Contents

1	Introduction and Outline	1
1.1	Historical Background	1
1.1.1	X-Ray-Induced Photoelectron Spectroscopy (XPS)	2
1.1.2	Auger Electron Spectroscopy (AES)	3
1.2	Outline of Electron Spectroscopy	5
1.2.1	Outline of X-Ray Photoelectron Spectroscopy (XPS)	7
1.2.2	Outline of Auger Electron Spectroscopy (AES)	7
1.3	State of the Art and Future Development	8
	References	9
2	Instrumentation	11
2.1	Vacuum System	11
2.1.1	Basic Pressure Requirements	13
2.1.2	Attainment and Maintenance of Ultrahigh Vacuum (UHV)	15
2.2	X-Ray Source	18
2.2.1	Conventional X-Ray Source	18
2.2.2	Monochromatic X-Ray Source	19
2.2.3	Small-Spot X-Ray Source and Scanning XPS Microscopy	20
2.2.4	Synchrotron X-Ray Source	22
2.3	Electron Gun	23
2.4	Ion Gun	26
2.5	Electron Energy Analyzer	29
2.5.1	The Cylindrical Mirror Analyzer (CMA)	30
2.5.2	The Concentric Hemispherical Analyzer (CHA)	33
2.5.3	Multichannel Detection	36
2.5.4	Imaging XPS	37
2.6	Software	39
	References	40

3	Qualitative Analysis (Principle and Spectral Interpretation)	43
3.1	Introduction: Notation of Atomic Electron Levels	43
3.2	Qualitative XPS	43
3.2.1	Principle of XPS Analysis	43
3.2.2	Photoelectron Spectra: Elemental Identification	45
3.2.3	Chemical Shift of Photoelectron Peak Energy	48
3.2.4	Auger Parameter	49
3.2.5	Valence Band Spectra	52
3.2.6	Satellite Peaks	52
3.2.7	XPS Line Shapes	54
3.2.8	Emission Angle Effects	58
3.3	Qualitative AES	63
3.3.1	Principle of AES Analysis	63
3.3.2	Auger Spectra and Elemental Identification	64
3.3.3	Direct and Derivative Spectra	66
3.3.4	Recognition and Influence of Chemical Bonding	68
3.3.5	Electron Backscattering, Channeling, and Diffraction	71
	References	74
4	Quantitative Analysis (Data Evaluation)	77
4.1	Measurement and Determination of Intensities	77
4.1.1	Background Subtraction	79
4.1.2	Differential (Derivative) Spectra (APPH in AES)	81
4.1.3	Decomposition of Overlapping Peaks	83
4.1.4	Factor Analysis and Principal Component Analysis	83
4.2	Quantification Using Intensities	84
4.2.1	Quantification Principles Using Elemental Relative Sensitivity Factors (E-RSFs)	84
4.2.2	Key Parameters: Inelastic Mean Free Path (IMFP) and Effective Attenuation Length (EAL)	87
4.3	Quantitative XPS	104
4.3.1	Fundamental Quantities for XPS	104
4.3.2	Quantitative XPS Analysis of Homogeneous Material	109
4.3.3	Quantitative XPS Analysis of Thin Surface Layers	135
4.4	Quantitative AES	172
4.4.1	Fundamental Quantities for AES	172
4.4.2	Quantitative AES Analysis of Homogeneous Material	179
4.4.3	Quantitative AES Analysis of Thin Surface Layers	189
4.5	Summary and Conclusion	200
	References	201
5	Optimizing Measured Signal Intensity: Emission Angle, Incidence Angle and Surface Roughness	205
5.1	XPS: Intensity Dependence on Emission and Incidence Angles	205
5.1.1	Sample Tilt Using CHA	208
5.1.2	Double-Pass Cylindrical Mirror Analyzer (DP-CMA) and Thetaprobe (CHA)	209

5.1.3	Total Reflection XPS (TR-XPS)	213
5.1.4	XPS Intensity Dependence on Surface Roughness	214
5.2	AES: Intensity Dependence on Emission and Incidence Angles ..	227
5.2.1	Sample Tilt Using CHA for AES	227
5.2.2	Sample Tilt Using CMA	235
5.2.3	AES Intensity Dependence on Surface Roughness	239
5.3	Summary and Conclusion.....	255
	References.....	256
6	Optimizing Certainty and the Detection Limit: Signal-to-Noise Ratio	259
6.1	Introduction and Definitions for Pulse-Counting Systems	259
6.1.1	Definitions and Explanations	260
6.1.2	Role of Peak-to-Background (<i>P/B</i>) Ratio	263
6.2	Parameters Affecting <i>P/B</i> and Singal-to-Noise (<i>S/N</i>) Ratios.....	266
6.2.1	Emission and Incidence Angle Dependencies of <i>P/B</i> and <i>S/N</i> for XPS and AES.....	266
6.2.2	Analyzer Resolution	270
6.2.3	Surface Roughness	275
6.2.4	Detector Efficiency and Scattered Electrons	275
6.2.5	Excitation Intensity (Primary Beam Current) and Total Measurement Time per Channel	275
6.2.6	Detection Limit	279
6.2.7	<i>S/N</i> Ratio and Uncertainty in Peak Measurements.....	281
6.2.8	<i>S/N</i> in Multichannel Detection.....	286
6.2.9	Uncertainty in Quantified Data and Strategy for Data Acquisition	289
6.3	<i>S/N</i> Ratio for Analog Systems	293
	References.....	295
7	Quantitative Compositional Depth Profiling	297
7.1	Sputter Depth Profiling	298
7.1.1	Instrumentation and Experimental Setup.....	298
7.1.2	Basic Quantification of Composition and Sputtered Depth	302
7.1.3	Depth Resolution: Definition and Measurement	314
7.1.4	Factors Limiting Depth Resolution and Profile Accuracy	319
7.1.5	Depth Dependence of Depth Resolution: Superposition of Different Contributions.....	338
7.1.6	Optimized Depth Profiling Conditions	339
7.1.7	Modeling, Deconvolution, and Reconstruction of Depth Profiles	344
7.1.8	The MRI Model and Its Modifications	348
7.1.9	Special Sputter Depth Profiling Techniques.....	371

7.2	Nondestructive Depth Profiling	382
7.2.1	Angle-Resolved XPS and AES	382
7.2.2	Depth Profiling by Variation of the Excitation Energy ...	398
7.2.3	Depth Profiling Using Background Information (Peak-Shape Analysis)	400
7.3	Conclusion: Comparison of Nondestructive and Destructive Depth Profiling Methods	402
	References	402
8	Practice of Surface and Interface Analysis with AES and XPS	409
8.1	Analytical Strategy	409
8.2	Sample Properties	411
8.2.1	Type of Material	411
8.2.2	Size, Shape, Morphology, and Roughness	412
8.2.3	Inhomogeneous Structure and Composition	412
8.2.4	Electrical Conductivity	413
8.2.5	Likelihood of Electron- or Photon-Beam- Induced Damage	413
8.3	Sample Preparation	414
8.3.1	Outside (“ <i>Ex Situ</i> ”) Preparation	414
8.3.2	Inside (“ <i>In Situ</i> ”) Preparation	417
8.4	Setting Up the Instrument and Measurement	420
8.4.1	Calibration of the Energy and Intensity Scales	420
8.4.2	Mounting and Alignment of the Sample	422
8.4.3	Measurement Sequence	423
8.5	AES and XPS on Insulators	424
8.5.1	Charging and Charge Compensation in XPS	424
8.5.2	Charging and Charge Compensation in AES	426
8.6	Electron and Photon-Beam Damage During AES and XPS Analyses	434
8.6.1	AES: Electron Beam Stimulated Changes in Composition and Structure	435
8.6.2	XPS: X-Ray-Induced Changes in Composition	441
	References	446
9	Typical Applications of AES and XPS	451
9.1	<i>Ex Situ</i> Sample Preparation	451
9.1.1	Coatings and Layered Structures	452
9.1.2	Corrosion and High-Temperature Oxidation	454
9.1.3	Interfacial Reactions and Diffusion	460
9.1.4	Interfacial Segregation	460
9.1.5	Implantation Layers	465
9.1.6	Further Methods and Materials	468
9.2	<i>In Situ</i> Sample Preparation	469
9.2.1	Surface Layer Formation by Deposition	469
9.2.2	Early Stages of Oxidation	471

9.2.3	Altered Layers by Ion Bombardment	476
9.2.4	Deposited Layer Structure	479
9.2.5	Surface Segregation	479
9.3	Treatment of AES and XPS Data by Factor Analysis	481
	References	482
10	Surface Analysis Techniques Related to AES and XPS	487
10.1	Overview of Surface Analysis Methods	487
10.2	Photon-Beam Excitation	488
10.2.1	Detection of Photons	488
10.2.2	Detection of Electrons	489
10.2.3	Detection of Ions and Neutral Particles	490
10.3	Electron-Beam Excitation	491
10.3.1	Detection of Photons	491
10.3.2	Detection of Electrons	491
10.3.3	Detection of Ions and Neutrals	494
10.4	Ion-Beam Excitation	494
10.4.1	Detection of Photons	494
10.4.2	Detection of Electrons	495
10.4.3	Detection of Ions and Neutrals	495
10.5	Excitation by Electric Field or Heat	497
10.5.1	Detection of Photons	497
10.5.2	Detection of Electrons	497
10.5.3	Detection of Ions and Neutral Particles	498
10.5.4	Detection of Forces	498
10.6	Comparison of the Principal Surface Chemical Analysis Techniques	499
10.6.1	Main Features of AES, XPS, SIMS and ISS	499
10.6.2	Combination of Techniques	501
	References	501
Index		505

Chapter 1

Introduction and Outline

By the middle of the last century, it became obvious that the chemical composition of surfaces and interfaces in atomic dimensions determines many properties of materials. For example, corrosion and oxidation, intergranular brittle fracture, wear and friction, and electronic properties strongly depend on surface and interfacial microchemistry [1.1]. Therefore, there was a growing demand for analysis on the atomic layer scale. This fact enhanced the rapid development of surface analysis methods based on ion and electron spectroscopy. Auger electron spectroscopy (AES) was the first technique used for surface analysis of solids, followed by X-ray-induced photoelectron spectroscopy (XPS). Both techniques have outstanding features when compared with other surface and interface analysis techniques (see Chap. 10). They are characterized by a relatively small matrix effect, by the capability of easy elemental identification and the detection of chemical bonds, and they are principally nondestructive. Furthermore, particularly in AES, an outstanding spatial resolution and, in XPS, a high energy-resolution enable mapping of elements and of chemical states. AES and XPS can be easily combined with ion sputtering to obtain high-resolution compositional depth profiles in thin films. Today, surface analysis methods using AES and XPS are the backbone of any materials research laboratory. By their application, a large number of topics in materials science can be successfully treated, as compiled in Table 1.1. By this book, the reader is provided with the knowledge necessary to understand AES and XPS and to successfully apply these techniques to solve typical problems.

1.1 Historical Background

Although AES and XPS have a different historical background, it is obvious that both are electron spectroscopies with a similar energy range, and, therefore, they have much in common. Over the years, there was a steady convergence with respect to instrumentation, and the use of modern hemispherical analyzers in both

Table 1.1 Application of surface analysis methods to topics in materials science

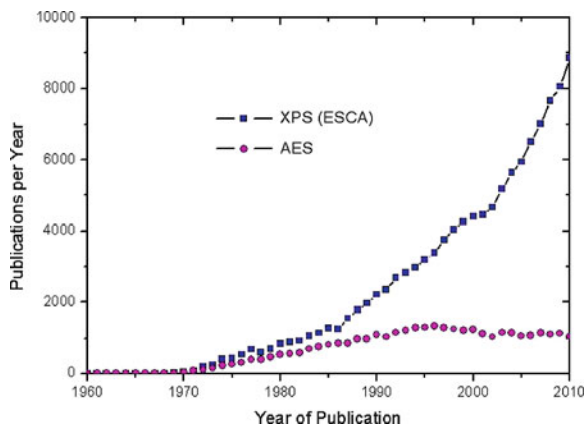
Surfaces	Interfaces	Thin films
<i>Direct</i>	<i>Via fracture and/or profiling</i>	<i>Depth profiling</i>
Segregation	Segregation	Interdiffusion
Diffusion	Diffusion	Implantation
Contamination	Embrittlement	Interfacial reaction layers
Adsorption	Intercrystalline corrosion	Evaporation layers
Oxidation	Sintering	Coatings
Passivation	Adhesion	Layered nanostructures
Catalysis	Composites	Electronic device structures
Friction and wear		

techniques has come to a point where by adding an X-ray source to an Auger spectrometer or an electron gun to an XPS instrument is practically all one needs to have a combination instrument. Historically, the foundations of XPS were laid much earlier than that of AES. Let us first have a brief look at the historical development [1.2].

1.1.1 X-Ray-Induced Photoelectron Spectroscopy (XPS)

In 1887, Heinrich Hertz discovered the effect of light on the generation of electric sparks [1.3]. Hallwachs [1.4] as well as Lenard and Wolf [1.5] studied this phenomenon in more detail, and Philipp Lenard [1.6] was the first to correctly describe the light-induced electron emission on metal surfaces including the work function that could not be understood by the classical wave theory of light. After the quantum theoretical explanation of the photoelectric effect by Einstein in 1905 [1.7], it was clear that the energy of the emitted photoelectron contains information of the solid from which it is emitted. In 1914, Rutherford and coworkers [1.8, 1.9] recognized that the kinetic energy of the emitted electron is the difference between X-ray energy and electron binding energy. The following decades saw X-ray-induced photoelectron spectroscopy left far behind the development of X-ray spectroscopy, mainly because of the greater experimental difficulties of the former. A major step forward in photoelectron spectrometry was the work of Robinson [1.10] (1923) and of Robinson and Young [1.11], who in 1930 clearly observed the line shift caused by chemical bonding (“chemical shift”) that was most important for further applications of XPS. The development of precision electron spectrometers by Steinhardt and Serfass at Lehigh University [1.12] and above all in Uppsala by Kai Siegbahn led to the first XPS spectra with high resolution in the 1950s. In the subsequent decades, Siegbahn’s group investigated core level binding energies and their shifts due to chemical bonding. Siegbahn coined the acronym ESCA (electron spectroscopy for chemical analysis), that includes Auger electrons besides photoelectrons, published a famous book with that title in 1967 [1.13] and received

Fig. 1.1 Development of AES and XPS as monitored by publications per year. (Database Chemical Abstracts Service (CAS), with correction for AES used as an acronym for atomic emission spectrometry) (Courtesy of W. Marx, Max-Planck-Institute for Solid State Research, Stuttgart)



the Nobel Prize in physics in 1981 for his achievements in ESCA (see appraisal in Ref. [1.14]).

The first commercial AES instruments for surface analysis of solids appeared by the end of the 1960s and triggered a similar development in XPS (Fig. 1.1). XPS (ESCA) became quickly popular within the large chemistry community. Furthermore, AES is more difficult to interpret and to quantify, and beam effects are more pronounced. Due to the relatively low signal-to-noise level of the first-generation spectrometers and the low excitation density of the X-ray source, XPS was a “slow” technique when compared to AES. This was a particular disadvantage in the time of analog instruments (the 1970s). With the development of digital instruments with multichannel detection and with higher analyzer transmission, the use of XPS in materials increased dramatically around 1985 at an accelerating pace, whereas that of AES appears to have attained a saturation already around 1995, as can be concluded from Fig. 1.1.

1.1.2 Auger Electron Spectroscopy (AES)

Auger electron spectroscopy (AES) has its name from the French physicist Pierre Victor Auger (1899–1993) who first studied the respective phenomena [1.15], although there is some controversy about the possible contribution of Lise Meitner [1.16]. In 1923, while studying electron emission induced by X-ray excitation in a Wilson cloud chamber, Auger observed, besides photoelectrons, electrons emitted with constant energy independent of the X-ray energy. Further experiments and the correct theoretical explanation were summarized in 1926 in his doctoral thesis [1.15, 1.17]. For a long time, Auger electrons were considered only as a special topic in atomic physics and as an unwanted side effect in practical X-ray spectroscopy. In 1953, Lander first mentioned the possibility of performing surface analysis by determination of characteristic Auger electron peaks, which he observed

in the secondary electron emission spectrum of electron-irradiated solids [1.18]. However, the intensity of those Auger peaks was too low to be used for practical analysis. This obstacle was overcome by the pioneering work of Harris in 1965 (published 1968 [1.19, 1.20]). Using a 127° energy analyzer, Harris showed that the electronically differentiated energy distribution greatly enhances the signal-to-noise ratio of the Auger electron peaks. In 1967, Weber and Peria [1.21] recognized that the same techniques could be adopted for conventional LEED optics which was already in use in about a 100 laboratories working on surface research. This was the breakthrough of AES as a surface analytical tool and the onset of the rapid development of commercially available instruments. The next major step forward was the introduction of the cylindrical mirror analyzer by Palmberg, Bohn, and Tracy in 1969 [1.22]. This device increased the sensitivity toward the detection limit of typically 0.1% of an atomic monolayer. Further development in the lens system of the primary electron beam improved the lateral resolution, and by scanning the electron beam, Auger electron images of the surface became available. In 1970, MacDonald [1.23] showed the principal possibility of high spatial resolution and scanning AES, and in 1973, the first scanning Auger microprobe with 5- μm lateral resolution was on the market. Since that time, commercial instruments for practical surface analysis are of the scanning Auger microscopy (SAM) type (Sect. 2.3). By the end of the 1970s, better electron optics and the use of lanthanum hexaboride filaments improved the spatial resolution to about 50 nm. Introduction of Schottky field emitters about 10 years later finally led to spatial resolution values of about 3–10 nm that today are typical for instruments from the major manufacturers (JEOL, Kratos, Omicron, PHI, and Thermo Scientific).

Along with the development of increased spatial resolution was that of more powerful energy analyzers with several detectors for parallel detection capability, and of digital data acquisition and completely computer-based spectrometer operation. Today, all this is standard equipment. Although the cylindrical mirror analyzer (CMA) has superior point transmission as compared to the concentric hemispheres analyzer (CHA) (see Sects. 2.5.1 and 2.5.2), the advantage of the latter with respect to higher energy resolution has favored its use in the majority of today's instruments.

Parallel with the development of powerful Auger spectrometers, the combination of AES with sputtering by ion bombardment revealed its capability for in-depth analysis of thin films, as proposed by Palmberg and Marcus in 1969 [1.24]. Since then, ion guns with rastered beam and differential pumping were introduced, to provide a flat sputter crater bottom and ease of operation, respectively (see Sect. 2.4). A major step forward in sputter depth profiling was the introduction of sample rotation during ion bombardment by Zalar in 1985 [1.25], in order to avoid sputtering-induced microroughening in polycrystalline materials (see Sect. 7.1.9). More recently, low-energy ion guns with high current densities even at 100 eV energy have become available (see Sect. 2.4) which strongly reduce the limitation of depth resolution by energy-dependent atomic mixing.

The first commercial Auger electron spectrometers became available in 1969. This year marks the beginning of the application of Auger electron spectroscopy to surface and interface analysis of solids (Fig. 1.1), followed by a rapid development

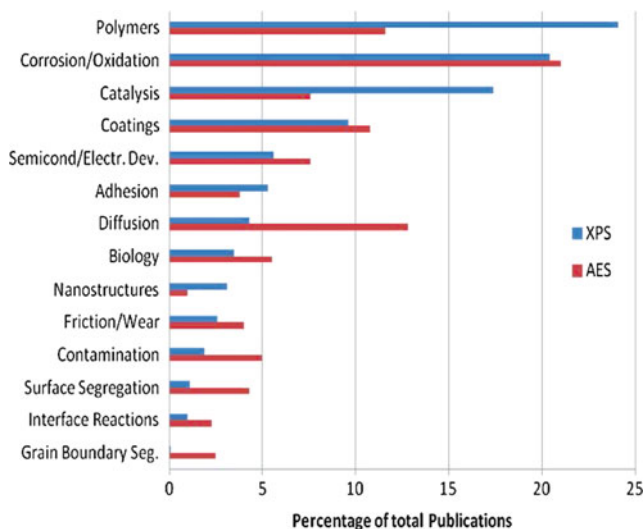


Fig. 1.2 Percentage of total publications referring to XPS (total of 122700) or AES (total of 27200) for the main topics in Table 1.1 (Courtesy of W. Marx and M. Noah, MPI Stuttgart)

of AES to one of the most popular and widespread method for surface analysis, particularly enhanced by the development of microelectronic industries. After 1985, XPS has become far more popular as a tool for materials research, as seen in Fig. 1.1. However, AES still has its appropriate applications, particularly when high spatial resolution is of advantage, as in surface and grain boundary segregation studies and in topics related to depth profiling, such as diffusion and interfacial reactions. This fact can be seen in Fig. 1.2, which shows the percentage of total publications referring to XPS or AES for different typical research fields. Although the interpretation of Fig. 1.2 is rather complicated, the relative comparison within XPS or AES gives an indication of the preferred research fields of each technique.

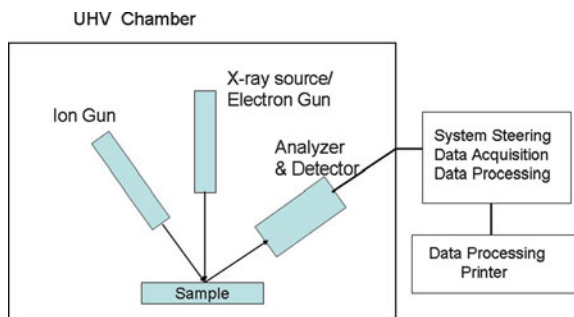
1.2 Outline of Electron Spectroscopy

Chemical analysis of solid materials with electron spectroscopy is based on energy analysis of secondary electrons that are emitted as a result of excitation by photons, electrons, ions, or neutrals. Main features of the techniques are:

1. Detection of all elements except hydrogen and helium
2. Detection of chemical bonding states
3. Information depth in the nanometer region

The reason for the surface specificity of electron spectroscopy is the small information depth of typically some nanometers (see Sect. 4.2.2) that is determined by the inelastic mean free path of electrons between typically 40 and 2500 eV.

Fig. 1.3 Components of a typical AES or XPS instrument



The most important methods that are employed in commercial surface analytical instruments are X-ray-induced photoelectron spectroscopy (XPS), often used in replacement of the term “electron spectroscopy for chemical analysis” (ESCA), and Auger electron spectroscopy (AES).

The basic components of a typical AES or XPS instrument are schematically shown in Fig. 1.3 and explained in more detail in Chap. 2. Common to both surface analysis methods is an ultrahigh vacuum (UHV)-based stainless steel chamber containing the sample stage, electron energy analyzer and detection system, an electron gun for AES, or an X-ray source (with or without monochromator) for XPS, and an ion gun for sample cleaning and for depth profiling. Frequently there are additional devices like a sample fracture stage (see Sects. 4.4.3 and 9.1.4), or an attached sample preparation chamber (see chap. 8, Fig. 8.1). Outside the UHV system are consoles with the electronics supply systems and the computer with the data acquisition and processing software.

While qualitative analysis (Chap. 3) is fairly easy, for example, by comparison with tabulated electron level energies and handbook spectra, quantitative analysis (Chap. 4) is more complicated. Peak area analysis in XPS (see Sect. 4.1.1) is generally more accurate than Auger peak-to-peak height in AES (Sect. 4.1.2). Relative elemental sensitivity factors have to be transformed into relative matrix sensitivity factors by matrix correction factors to improve the accuracy of quantitative analysis (Sects. 4.3.2 and 4.4.2). The latter can only be performed with reliability by taking into account the in-depth distribution of composition (Chap. 7), as exemplified in atomic monolayer structures within the information depth (Sects. 4.3.3 and 4.4.3).

Optimization of measured signal intensities with respect to incidence and emission angles and surface roughness (Chap. 5) is often necessary to obtain an optimum signal-to-noise ratio (Chap. 6) that determines detection limit and uncertainty. In practical surface and interface analysis (Chap. 8), sample properties, sample preparation, and artifacts caused by various beam effects determine the analytical strategy. Some typical applications (Chap. 9) illustrate the main topics in AES and XPS analysis (Table 1.1). Finally, an outlook on related techniques is presented in Chap. 10.

AES and XPS are comparable in their surface sensitivity because the small attenuation length of the Auger- and photoelectrons generally restricts the chemical information to the first few atomic layers. Therefore, both techniques are principally

not appropriate for bulk analysis. If surface contamination layers are carefully removed, for example, by argon ion sputtering, the composition of the sample surface may deviate from the bulk composition due to segregation or preferential sputtering effects (see Sect. 7.1). Since the surface of a sample is steadily reacting with the ambient gas atmosphere, constancy of the surface composition with time may hardly be achieved. To reduce this effect, AES and XPS are generally performed in a vacuum chamber at residual gas pressure of reactive gases below 10^{-7} Pa ($\approx 10^{-9}$ Torr) (see Sect. 2.1). A gas admission facility for noble gases, usually argon, and an ion gun are necessary for surface cleaning (see Sect. 8.3) and for in-depth profiling (see Sect. 7.1). Furthermore, a residual gas analyzer is useful for deciding whether a detected component originates from adsorption or from the bulk of a sample.

1.2.1 Outline of X-Ray Photoelectron Spectroscopy (XPS)

In XPS, the surface of a sample is irradiated with photons of characteristic energy (usually $\text{MgK}\alpha$ radiation) (Fig. 1.2) (Sect. 3.2). These photons directly interact with core electrons of the sample atoms. As a result, ionized states are created, and a photoelectron is emitted with a kinetic energy given approximately by the difference between the photon energy and the binding energy. The measured photoelectron spectrum is therefore a direct indication of the binding energies of the different atomic electron levels and is often directly calibrated in eV of binding energy: The lower the kinetic energy, the higher the binding energy (see Sect. 3.2.1). Because usually the kinetic energy is plotted on the x-axis with increasing energy to the right, the binding energy increases from right to left. The inelastic mean free path of the photoelectrons [1.26, 1.27] is determined by the probability to suffer an energy loss, and the attenuation length (taking into account inelastic and elastic scattering) [1.28] is determined by the probability to be received by the electron energy analyzer (see Sect. 4.2.2). In both cases, kinetic energy and matrix determine and limit the information depth to the nanometer region. Like AES, this fact makes XPS analysis surface specific. In contrast to AES, there are no primary electrons; therefore, the background is usually much smaller, and peaks are readily measured in the direct spectrum.

1.2.2 Outline of Auger Electron Spectroscopy (AES)

In a typical AES experiment, the sample is irradiated with a focused beam of primary electrons of sufficiently high energy (1–20 keV) from the electron gun. The primary electrons penetrate the sample up to a range of the order of 0.1–1 μm , depending on their energy. As a result, different electron orbitals of the target atoms are ionized within the excitation depth, and subsequently, electrons from other shells

can fill up the ionized states. The energy released by this process either results in a photon (X-ray emission) or is transmitted to another electron in an outer level that is emitted from the atom as a so-called Auger electron. Auger electrons possess characteristic energies which are well defined by the involved electron levels of the analyzed element. This characteristic energy can only be detected if the electrons emitted by each excited atom leave the surface without inelastic scattering in the solid. Their inelastic mean free path [1.26, 1.27] or more precisely their attenuation length (including inelastic and elastic scattering) [1.28] is strongly dependent on the Auger electron energy and typically is between 0.3 and 3 nm [1.26–1.28]. For the same kinetic energy, the attenuation lengths of AES and XPS are practically equal, and the surface specificity of both techniques is a direct result of its small value, corresponding to an information depth of a few monolayers from the surface (see Sect. 4.2.2).

Auger electrons are superimposed on a large and smoothly varying background consisting of inelastically scattered primary and secondary electrons. Because of this fact, Auger spectra are usually presented in the differentiated mode. The detected energies of the main Auger peaks (conventionally of the negative peak extension in the derivative mode) are usually given as Auger energies (see Sect. 3.3.3). The newer literature generally refers to the peak maximum in the normal, direct mode. Depending on the peak width, the peak energy is about 2–5 eV lower than the derivative's maximum negative extension (see Sect. 3.3.3). The area under the peak in the normal spectrum, after background removal, is approximately proportional to the number of atoms in a volume given by the primary beam diameter and the information depth (see Sect. 4.4.2). This is also valid for the Auger peak-to-peak height in the differentiated spectra, if the Auger peak shape is constant with varying Auger intensity (see Sect. 4.1.2).

1.3 State of the Art and Future Development

High-resolution scanning Auger spectrometers are characterized by field-emission electron gun for spatial resolution around 10 nm at 10 nA beam current, with energy analyzers of cylindrical mirror or concentric hemispheres type with parallel detection of a certain energy range. The capability of the latter with respect to higher energy resolution seems to favor the concentric hemispheres analyzer in present and future instruments.

Among a large number of other surface analysis methods (Chap. 10), AES and XPS have become most important because of their diverse application possibilities and highly developed commercial instruments. Already about 20 years ago, the number of AES and XPS instruments worldwide was estimated to be about 1500 [1.2].

XPS is more popular in chemistry and chemical applications, whereas the foremost feature of AES is its highly focused electron beam that allows spatially resolved investigations similar to scanning electron microscopy and is therefore

often called scanning Auger microscopy (SAM) [1.23, 2.14]. Field-emission-gun-equipped SAM instruments achieve a spatial resolution of typically 10 nm. A new instrument using the ZEISS Gemini Electron gun achieves an ultimate spatial resolution of 5 nm (Omicron NanoSAM), and 3 nm will be probably achieved in the near future.

High spatial resolution too is the main feature of modern XPS equipment. As a consequence, imaging XPS and XPS microscopy are available with typical spatial resolution of 3–15 μm , and new developed instruments attain 150-nm spatial resolution (see Fig. 2.17). The detectors are channel plates or multichanneltron detectors to ensure partial parallel detection of a spectrum. An interesting instrument design covers the angular emission between 20° and 80° by a special entrance lens system and angle-resolved detection, that is, it operates intrinsically as angle-resolved XPS (Thermo Scientific).

For both AES and XPS instruments, the hardware seems to be in a fairly mature state, although some development will go on considering improved lateral resolution. Future development seems to be mainly focused on software, particularly with respect to computerized routines for fast data acquisition and processing, sample drift compensation, and toward fully automated operation through expert systems [1.29, 1.30].

References

- 1.1. E.D. Hondros, M.P. Seah, S. Hofmann, P. Lejček, Interfacial and Surface Microchemistry, in *Physical Metallurgy*, 4th edn., ed. by R.W. Cahn, P. Haasen (Elsevier, Amsterdam, 1996), pp. 1201–1289
- 1.2. D. Briggs, M.P. Seah (eds.), *Practical Surface Analysis Vol. 1 (AES and XPS)*, 2nd edn. (Wiley, Chichester, 1990)
- 1.3. H. Hertz, Ann. Phys. U. Chem. (Wied. Ann.) **31**, 421 (1887)
- 1.4. W. Hallwachs, Ann. Phys. **33**, 301 (1888)
- 1.5. P. Lenard, M. Wolf, Ann. Phys. U. Chem. **37**, 443 (1889)
- 1.6. P. Lenard, Ann. Phys. **8**, 149 (1902)
- 1.7. A. Einstein, Ann. Phys. **17**, 132 (1905)
- 1.8. E. Rutherford, Philos. Mag. **28**, 305 (1914)
- 1.9. E. Rutherford, H. Robinson, W.F. Rawlinson, Philos. Mag. **18**, 281 (1914)
- 1.10. H.R. Robinson, Proc. R. Soc. A **104**, 455 (1923)
- 1.11. H.R. Robinson, C.R. Young, Philos. Mag. **10**, 71 (1930)
- 1.12. R.G. Steinhardt, E.J. Serfass, Anal. Chem. **23**, 1585 (1951)
- 1.13. K. Siegbahn, C.N. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bermark, S.E. Karlsson, *ESCA: Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy* (Almqvist & Wiksells, Uppsala, 1967)
- 1.14. L. Kövér, Surf. Interface Anal. **39**, 958 (2007)
- 1.15. P. Auger, Ann. Phys. (Paris) **6**, 183 (1926)
- 1.16. O.H. Duparc, Int J. Materials Research **100**, 1162 (2009)
- 1.17. P. Auger, Surf. Sci. **48**, 1 (1975)
- 1.18. J.J. Lander, Phys. Rev. **91**, 1382 (1953)
- 1.19. L.A. Harris, J. Appl. Phys. **39**, 1419 (1968)
- 1.20. L.A. Harris, J. Appl. Phys. **39**, 1428 (1968)

- 1.21. R.E. Weber, W.T. Peria, J. Appl. Phys. **38**, 4355 (1967)
- 1.22. P.W. Palmberg, G.K. Bohn, J.C. Tracy, Appl. Phys. Lett. **15**, 254 (1969)
- 1.23. N. MacDonald, Appl. Phys. Lett. **16**, 76 (1970)
- 1.24. P.W. Palmberg, H.L. Marcus, Trans. Am. Soc. Met. **62**, 1016 (1969)
- 1.25. A. Zalar, Thin Solid Films **124**, 223 (1985)
- 1.26. C.J. Powell, Surf. Sci. **49**, 29 (1974)
- 1.27. M.P. Seah, W.A. Dench, Surf. Interface Anal. **1**, 2 (1979)
- 1.28. A. Jablonski, C.J. Powell, Surf. Sci. Rep. **47**, 33 (2003)
- 1.29. J.E. Castle, Surf. Interface Anal. **33**, 196 (2002)
- 1.30. M. Mohai, Surf. Interface Anal. **38**, 640 (2006)

Chapter 2

Instrumentation

The general arrangement of the elements of any surface analysis instrument (here electron spectrometer) is shown in Fig. 1.2. Figure 2.1a shows a cross section of a typical XPS instrument and Fig. 2.1b that of a typical AES spectrometer. The main parts are (1) the specimen on a sample holder with x – y – z movement stage, (2) an excitation source (X-ray source for XPS, electron gun for AES), (3) the electron energy analyzer with detector, and (4) an auxiliary ion gun. Whereas these elements are mounted within a vacuum chamber, the detection and steering electronics are placed outside in the laboratory room.

Let us first turn briefly to the instrument's vacuum system.

2.1 Vacuum System

The SI unit of the pressure is Pascal, Pa [N/m^2], traceably defined in the metric system. However, at least two other outdated units can still be found on instruments' readout and in publications: mbar and Torr. Therefore, the relations between them should be kept in mind:

$$1 \text{ Pa} = 1 \times 10^{-2} \text{ mbar} = 0.75 \times 10^{-2} \text{ Torr}; \quad 1 \text{ Torr} = 133.3 \text{ Pa} = 1.333 \text{ mbar}.$$

In the following, we will generally use the SI unit Pa, and Torr or mbar only as an exception.

According to the kinetic theory of gases, the pressure defines the mean free path L_{coll} between two molecular collisions as

$$L_{\text{coll}} = \frac{kT}{1.414p\sigma_{\text{coll}}} \quad (2.1)$$

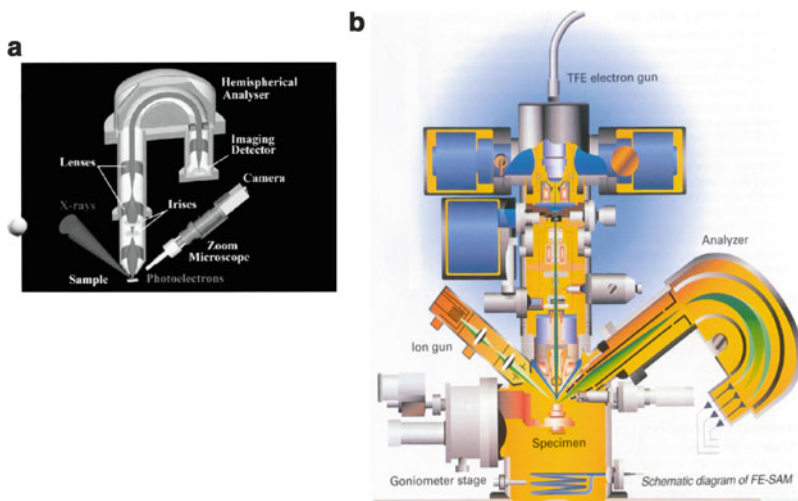


Fig. 2.1 Schematic cross section of typical XPS and AES-SAM instruments, (a) VG ESCALAB 250i with concentric hemispheres analyzer (CHA) (Courtesy of Thermo Scientific company) and (b) JAMP 7830F with high-resolution field emission (FE) electron gun (10 nm), and CHA. *Upper part:* additional ion pumps for FE-gun (Courtesy of JEOL company)

Table 2.1 Vacuum characteristics: typical pressure and pressure ranges and mean free path for nitrogen molecules

Vacuum notations	Pressure	Pressure	Mean free path	Maximum Contamination	Pressure
	$p(\text{Pa})$	$p(\text{mbar})$	$L_{\text{coll}}(\text{m})$	$t_m(\text{s/ML})$	$p(\text{Torr})$
Atmosphere	101300	1013	1×10^{-7}	1×10^{-9}	760
Coarse	133	1.33	1×10^{-4}	1×10^{-6}	1
Fine (medium)	0.133	1.33×10^{-3}	0.1	1×10^{-3}	1×10^{-3}
High (HV)	1.33×10^{-4}	1.33×10^{-6}	100	1	1×10^{-6}
Ultrahigh (UHV)	1.33×10^{-8}	1.33×10^{-10}	1×10^6	1×10^4	1×10^{-10}

Note that for hydrogen, the mean free path is about 1.5 times higher, and for argon, about 0.6 times lower than for nitrogen. Maximum contamination layer buildup in seconds necessary for one monolayer is t_m (s/ML) (Expression 2.3)

where $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$ is the Boltzmann constant, $T(\text{K})$ is the absolute temperature, p (Pa) is the pressure, and $\sigma_{\text{coll}} (\text{m}^2)$ is the cross section for collision (about $d^2\pi/4$ with d_m the molecular diameter). After (2.1), the values obtained for nitrogen gas at 300 K ($d_m(\text{N}_2) = 0.3 \text{ nm}$) are shown in Table 2.1.

According to the pressure, vacuum is named coarse or rough (10^2 to 1 Pa or 1 to 10^{-2} Torr), fine or medium (1 to 10^{-3} Pa or 10^{-2} to 10^{-5} Torr), high ((HV) 10^{-3} to 10^{-6} Pa or 10^{-5} to 10^{-8} Torr), and ultrahigh ((UHV) 10^{-6} to 10^{-9} Pa or 10^{-8} to 10^{-11} Torr). Below 10^{-9} Pa (10^{-11} Torr), the term “extreme high vacuum (EHV)” is used.

2.1.1 Basic Pressure Requirements

There are two basic conditions for the need of vacuum in electron spectroscopy:

- (1) To avoid electron scattering on gas molecules in the path from sample to analyzer
- (2) To avoid attenuation and distortion of the spectra by surface contamination

Condition (1) is already met by a vacuum of about 10^{-2} Pa ($\sim 10^{-4}$ Torr) (“high vacuum,” HV) [2.1, 2.2], as seen from Table 2.1. Therefore, in older AES equipment with simple non-differentially pumped ion guns (see Sect. 2.4), argon backfilling at 7×10^{-3} Pa (5×10^{-5} Torr) is used to carry out sputter depth profiling. As a rule of thumb, the mean free path, L_{coll} , for air at 20 °C is $L_{\text{coll}}(\text{cm}) = 0.01/p$ (Torr). For 5×10^{-5} Torr, L_{coll} is about 2 m and therefore sufficient to meet the above condition (1).

Condition (2), however, requires that adsorption from the residual gas atmosphere does not generate an intolerable amount of contamination on the surface. The key to that requirement is the monolayer formation time, t_m . When every molecule striking a surface will remain there (sticking coefficient = 1), then the time to build up a monolayer (about 10^{15} atoms/cm²) is given by

$$t_m = \frac{4}{Nvd_m^2}, \quad (2.2)$$

where N is the density of the gas (molecules/cm³), v the molecular velocity, and d_m the molecular diameter [2.1, 2.2]. Through the gas density, the monolayer formation time is inversely proportional to the pressure (see Table 2.1). For a highly reactive gas with sticking coefficient = 1 (e.g., oxygen on a clean transition metal surface), the monolayer formation time is about

$$t_m(\text{s}) = 1.7 \times 10^{-6}/p(\text{Torr}). \quad (2.3)$$

In the pressure range of 10^{-6} Torr ($\approx 10^{-4}$ Pa, high vacuum), one monolayer is built up in about one second, which is intolerable in surface analysis because a contamination monolayer reduces the signal of the underlying surface, depending on its energy, by typically 10–50% (see Sects. 4.3.3 and 4.4.3). Furthermore, a species reacting with the surface will influence the peak shape by chemical bonding. For pressures in the lower 10^{-7} Pa range (pressures below 10^{-6} Pa are generally called ultrahigh vacuum (UHV)), the monolayer formation time according to (2.3) increases to 20 min, a typical spectrum measurement time. To keep the contamination below 10% of a monolayer, partial pressures of highly reactive gases (like CO, O₂, H₂O) should be kept at least one or two orders of magnitude lower (i.e., less than 10^{-8} Pa) to ensure negligible contamination within the measurement time. The monolayer formation time increases inversely with the sticking coefficient, which varies, according to the specific reactivity of gas and surface, from 1 (e.g., CO on Ta) to zero (noble gases (e.g., Ar) on any surface, N₂ on most oxides). Usually, the total base pressure in modern UHV equipment is typically at or below 5×10^{-8} Pa (3×10^{-10} Torr).

Figure 2.2 shows two typical compositions of the residual gas atmosphere of an UHV chamber, before (Fig. 2.2a) and after (Fig. 2.2b) bake out, represented by the mass spectra obtained with an attached quadrupole mass filter. As seen in

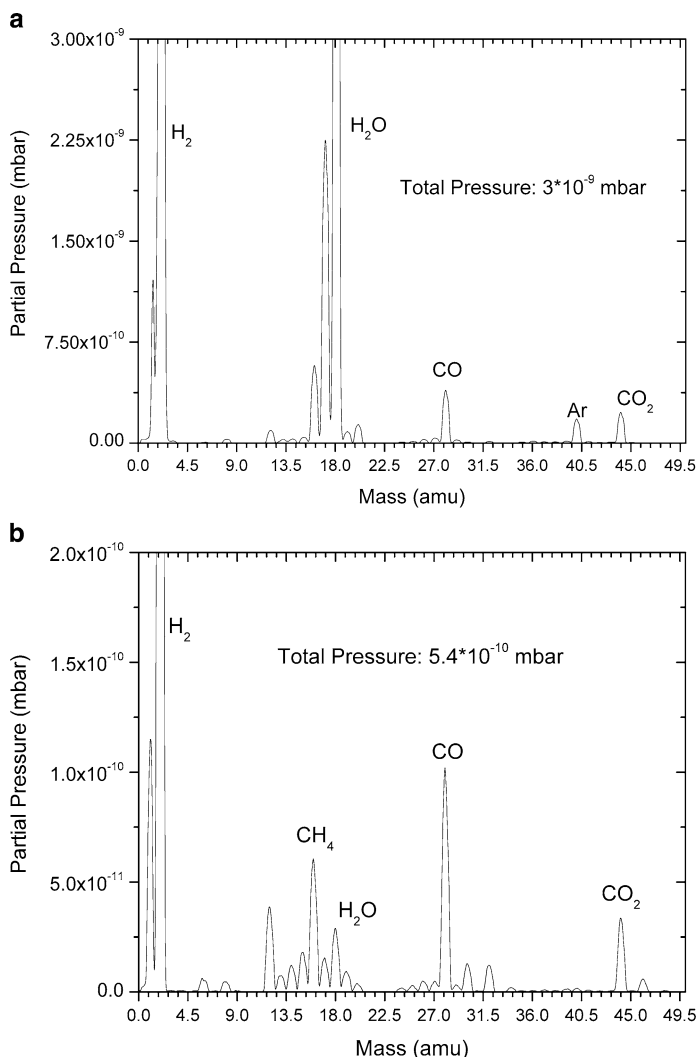


Fig. 2.2 Typical mass spectrum of (a) residual gas in an UHV chamber before bakeout, showing partial pressure (linear) in mbar as a function of atomic mass units (amu). Besides hydrogen, water is the most prominent peak, followed by CO and CO_2 . The Ar peak is caused by previous sputtering with Ar gas; and (b) the residual gas atmosphere (“Restgas”) of an UHV chamber after bakeout (with pressure scale reduced by one order of magnitude). The most preponderant peak is that of hydrogen, followed by CO (about one order of magnitude lower), CH_4 , CO_2 , and H_2O , the peak of which is more than two orders of magnitudes lower than in Fig. 2.2a (Note that in both figures, partial pressure is not exactly calibrated with respect to total pressure)

Fig. 2.2a, the most prominent peak – besides that of hydrogen – is that of water at mass 18; almost one order of magnitude lower are the peaks of CO, CO₂, and Ar. The latter originates from previous sputtering with Ar gas. The peak at mass 16 amu is most probably CH₄ with some oxygen. The latter and most of the other peaks are mainly crack products of H₂O, CH₄, and CO₂, for example, C at mass 12 amu, or doubly ionized CH₄ and argon at mass 8 and 20 amu, respectively. Water can be most effectively removed by a bakeout at > 150 °C for several hours, as seen in Fig. 2.2b. Here, at a much reduced total pressure, hydrogen is by far the most prominent peak, followed by CO and CO₂. The water peak (18 amu) is very small, more than two orders of magnitude lower than in Fig. 2.1a. With the exception of H (1 amu) and CO (28 amu), all remaining components are in the lower 10⁻¹¹ mbar region. There are at least two reasons for the typically high hydrogen peak in UHV residual gas spectra: H₂ has the lowest pumping speed due to its low mass and therefore high thermal velocity, and it can slip through small leaks and can even permeate metallic chamber walls.

2.1.2 Attainment and Maintenance of Ultrahigh Vacuum (UHV)

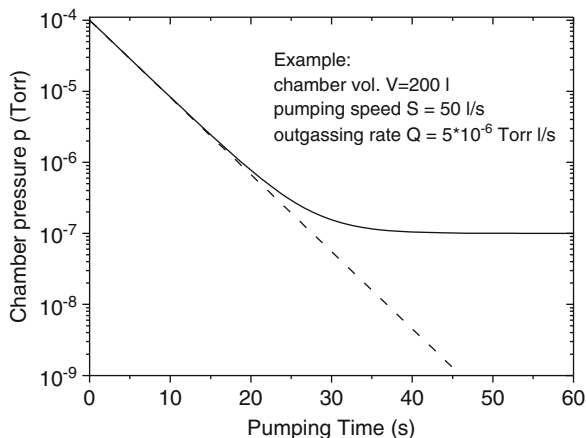
Because AES and XPS require UHV environment for proper operation, every instrument has a base UHV system that is now standard equipment. Nevertheless, for the operator, it is important to understand the basic principles of attaining and maintaining UHV.

Any UHV system is equipped with one or more pumps that are capable of attaining UHV. Generally, after getting the pressure down to about 10⁻³ Pa with a suitable roughing pump (forepump) (e.g., sorption or oil-free rotating element), an ion pump and/or a turbomolecular pump is started to get the pressure down to the UHV regime. During pump down from atmospheric pressure, several gas flow regimes are subsequently passed. After some pressure reduction, the laminar flow regime, where the mean free path is very small against the chamber dimensions, is passed. At about 10⁻¹ Pa (≈ 10⁻³ Torr), we enter gradually the regime of molecular flow, where the interaction of gas molecules is negligible and the mean free path becomes comparable to the dimensions of the vacuum chamber. That means, the gas molecules fly from wall to wall in a random manner. Like in diffusion, they move from higher density (i.e., higher pressure) to lower density (i.e., lower pressure), and the latter is maintained by effective pumps. The basic equation for pump down is

$$V \frac{dp}{dt} = -Sp \quad (2.4a)$$

where p (Pa) is the gas pressure, V (m³) is the (constant) volume of the chamber, S (m³/s) is the pumping speed, and t is the pumping time. Equation 2.4a has the simple solution

Fig. 2.3 Typical pressure–time relation for pump down of the analysis chamber with (solid line) and without outgassing load (dashed line), according to (2.4) and (2.5). The starting pressure $p_0 = 10^{-4}$ Torr ($= 1.3 \cdot 10^{-2}$ Pa) is obtained with roughing pumps



$$p = p_0 \exp\left(-\frac{S}{V}t\right), \quad (2.4b)$$

that is schematically drawn as a full line in Fig. 2.3 [2.2]. The pressure will decrease exponentially with time, and eventually, UHV would be reached. However, in the lower pressure regimes, there are always gas sources that counterbalance pumping. They add a positive term, Q , to the right hand side of (2.4a), which then reads

$$V \frac{dp}{dt} = -Sp + Q. \quad (2.5)$$

The term Q is called the outgassing rate that is only slightly time dependent and practically constant at room temperature. It is seen from the modified expression (2.5), that the pump down practically stops at a pressure where $Sp = Q$. This is shown by the dashed line in Fig. 2.3. Usually, with an ion or turbomolecular pump of nominal 200–400 l/s pumping speed, the bulk of the chamber gas can be pumped away in a few minutes (in reality, a great deal of the nominal pumping speed is lost by the connection between pump and equipment in the chamber). After that, the pumping speed is counterbalanced by outgassing of the inner walls of the chamber, which determines the end pressure that can be attained without baking the system. This pressure is often in the high-vacuum regime (10^{-4} to 10^{-5} Pa). Outgassing has to be reduced by several orders of magnitude to attain UHV (note that increasing the pumping speed by a factor of 10 would only reduce the pressure by a factor of 10 [i.e., 10^{-5} to 10^{-6} Pa, still not UHV]).

Outgassing stems from different sources. The most important are (1) evaporation of species from wrongly or improperly treated materials inside the vacuum chamber, (2) desorption from species adsorbed on the inner walls, (3) diffusion of volatile species from the wall material (e.g., from grain boundaries and other defects), and (4) permeation of gases through the chamber walls (hydrogen and helium).

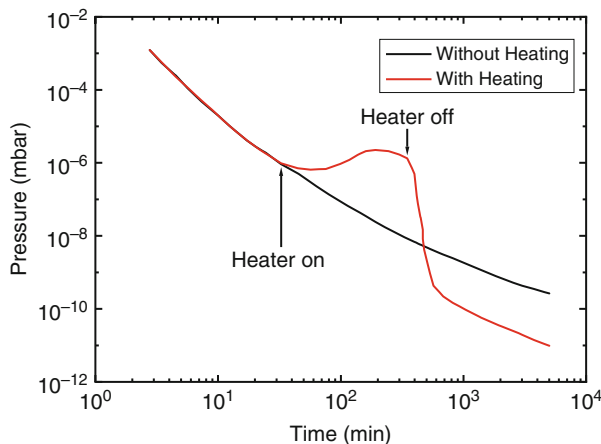


Fig. 2.4 Effect of baking of the vacuum system on the residual gas pressure (Adapted from H.G. Tompkins [2.2])

Effective reduction of the outgassing rate is usually achieved by increasing the temperature of the whole spectrometer to 150–200 °C for a few hours. During this baking of the system, the desorption and diffusion rates are increased, and the desorbed gas is pumped away. Desorption sites are depleted, and, after return to room temperature, the outgassing rate has dropped to a value ensuring the attainment of UHV, as schematically shown in Fig. 2.4 [2.2]. Outgassing rates (in Torr l s⁻¹ m⁻²) of unbaked and baked metals, for ceramics, glass, and elastomers, are given by O’Hanlon [2.1]. Often, the volume of a chamber is of less importance for the outgassing rate than the total area of particular components contained in the chamber.

The different sources of residual gas in the vacuum chamber can be distinguished by the time dependence of gas release and subsequent pumping. Whereas the original gas volume is decreasing exponentially after (2.4b), desorption from inner surfaces follows a t^{-1} law, and diffusion will decrease inversely proportional to the square root of time, and finally, permeation adds a constant flux to the residual gas [2.2]. Note that a slight leak acts like permeation.

Materials that decompose during bakeout or produce volatile species cannot be tolerated in the UHV chamber. Therefore, materials such as brass (where Zn is the volatile species) and most elastomers cannot be used, with possible exceptions such as Viton or PTFE (“bakeable” up to 150 °C). Instead of rubber O-rings that are customary down to the HV regime (10⁻⁴ Pa), generally, flanges with knife-edge profiles that cut into flat gaskets rings made of soft copper are used as UHV-compatible sealing for flange connections. UHV components are, because of strength and oxidation-resistant requirements, usually fabricated of stainless steel [2.1], the outgassing behavior of which is described in detail in Ref. [2.3].

To protect the sample surface from carbon contamination by adsorption of hydrocarbons that are cracked by the electron beam, an oil-free vacuum system is necessary. Therefore, ion pumps or turbomolecular pumps are most frequently used.

To control the residual gas composition, a quadrupole mass analyzer is indispensable. An ion gun (see Sect. 2.4) with suitable gas inlet device for surface cleaning and depth profiling (see Sect. 7.1) is generally attached to the system.

A typical UHV system for surface analysis consists of the main chamber with the sample stage, electron gun or X-ray source, ion gun (see Fig. 1.2), and other auxiliary equipment, that is directly connected to the ion or turbomolecular pumping unit (see Fig. 8.1). An UHV gate valve connects the main chamber to the sample introduction chamber, which can be opened to the atmosphere. After evacuation of the introduction chamber with roughing pumps to 10^{-2} Pa or below, the sample is transferred by a rod with a fork or a rack and pinion system to the sample stage in the main chamber. Because of the more than 100 times smaller volume of the introduction chamber as compared to the main chamber, the load of the pumps and the pressure rise in the main system is reduced by that volume ratio.

Air leaks of the UHV system are most readily detected by appearance of the oxygen peak at 32 atomic mass units in a partial pressure measurement, for example, with a quadrupole mass filter. Observing the increase in the peak at mass 4 while spraying different system locations with He gas helps to locate the leak. For more details on leak detection, see, for example, Ref. [2.1].

2.2 X-Ray Source

2.2.1 Conventional X-Ray Source

The most common X-ray sources used in XPS are equipped with Mg or Al anodes, often as a twin anode for alternative use. The characteristic Mg K_{α} radiation at 1253.6 eV and the Al K_{α} radiation at 1486.6 eV possess sufficiently high energies for core level excitation as well as a sufficiently low line width (below 1 eV) to yield XPS spectra with fairly good resolution. Figure 2.5 shows a schematic drawing of an XPS equipment with conventional X-ray source [2.4].

A thin Al foil (of about $2\text{ }\mu\text{m}$ thickness) is placed at the exit of the X-rays to shield the sample from stray electrons, from contamination, and from the heat from the anode. Higher energy Bremsstrahlung is also produced. For efficient irradiation, usual sources are operated from 500 W to 1 kW power, at 5–15 keV anode voltage. Therefore, efficient water cooling of the X-ray source is necessary, and the core of the tube consists of a copper rod, with a thin evaporated Mg and/or Al film (of about $10\text{ }\mu\text{m}$ thickness) at the end. Insufficient cooling may cause interdiffusion of Mg and Al, and evaporation. If the active anode layer becomes too thin, the CuL_{α} radiation is additionally excited (929.7 eV) and “ghost spectra” may be seen.

Fig. 2.5 Conventional X-ray source for an XPS instrument (Reproduced from M.A. Kelly, with permission of Elsevier B.V.)

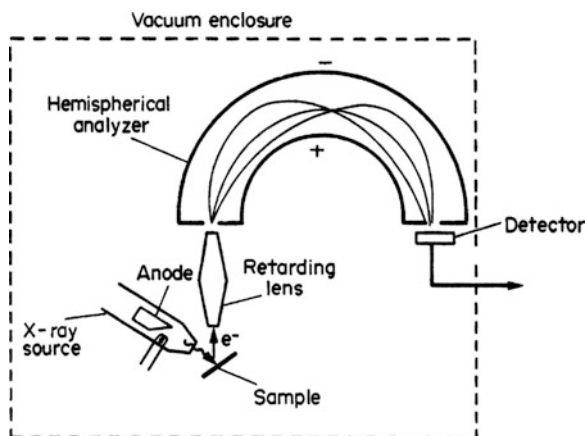


Table 2.2 X-ray satellite energies and intensities for Mg and Al sources

K lines		$\alpha_{1,2}$	α_3	α_4	α_5	α_6	β
Mg	Rel. intensity (%)	100	8.0	4.1	0.55	0.45	0.5
	Energy displacement (eV)	0	8.4	10.2	17.5	20.0	48.5
Al	Rel. intensity (%)	100	6.4	3.2	0.4	0.3	0.55
	Energy displacement (eV)	0	9.8	11.8	20.1	23.4	69.7

The X-ray source produces a main emission line together with minor lines at higher binding energy (see Fig. 2.6) [2.5]. The K_{α} line of the usual Mg and Al sources consists, besides the main unresolved doublet peak $K_{\alpha 1,2}$, of further satellite peaks and K_{β} (see Table 2.2). Whereas the $K_{\alpha 5,6}$ and K_{β} lines are negligible, the $K_{\alpha 3,4}$ lines possess together about 10% intensity of the main line and are about 10 eV shifted to lower binding energy. These satellites, together with the Bremsstrahlung background, distort the spectra (see Fig. 2.6a), the resolution of which is limited to the $K_{\alpha 1,2}$ line width of Mg or Al (0.7 and 0.85 eV, respectively). Most frequently, the Mg K_{α} line is used for systems without monochromator. In case of overlap of Auger peaks with XPS peaks, the use of Al K_{α} can be useful, because the kinetic energy of the XPS peaks shifts with the X-ray excitation energy whereas that of the Auger peaks does not.

2.2.2 Monochromatic X-Ray Source

A better energy resolution and removal of the Bremsstrahlung background and of the satellite peaks is achieved using a monochromator which selects a narrow line from the natural emission as shown in Fig. 2.6b. The principle experimental arrangement is shown schematically in Fig. 2.7 [2.6]. Source, monochromator crystal, and sample are placed on the circumference of a Rowland sphere of typically 0.5 m diameter. Usually, a bent quartz crystal (or several pieces) in combination with an Al anode is

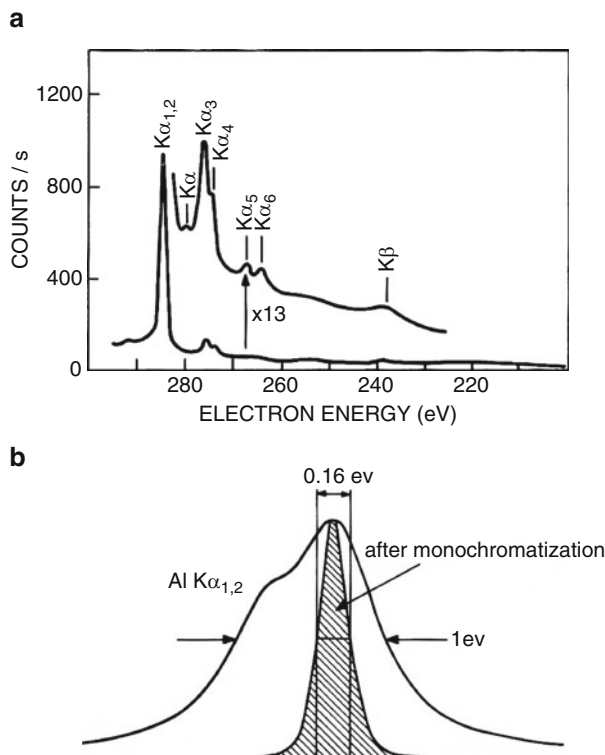


Fig. 2.6 (a) Satellites of the low binding energy side of a C1s spectrum (binding energy not calibrated) excited with Al K radiation without monochromator. (b) Action of a monochromator crystal on the Al $K\alpha_{1,2}$ radiation. The shadowed region is the excitation line shape with $\text{FWHM} = 0.16 \text{ eV}$ which puts a limit to the experimental resolution (see Sect. 3.2.7.3) (Reproduced from M. Cardona and L. Ley [2.5]. Copyright by Springer Verlag)

used for convenient Bragg law dispersion and for focusing the X-rays to the sample surface. Selecting the $K\alpha_1$ component of less than 0.4 eV line width, for a typical dispersion of 1.6 mm eV^{-1} this means that the irradiated area in the dispersion plane is only 0.6 mm , and careful adjustment is crucial for optimum operation. Of course, the photon flux is much reduced compared to a normal X-ray source. In part, this can be compensated by increasing the emission brightness using a fine-focused electron beam for the excitation. This quite naturally leads to small-spot XPS and to XPS scanning microscopy (see Sect. 2.2.3, Fig. 2.8).

2.2.3 Small-Spot X-Ray Source and Scanning XPS Microscopy

While conventional XPS usually analyzes an area of several square mm (e.g., $10 \times 2 \text{ mm}^2$), the typical analyzed area of high spatial resolution XPS is of the order of

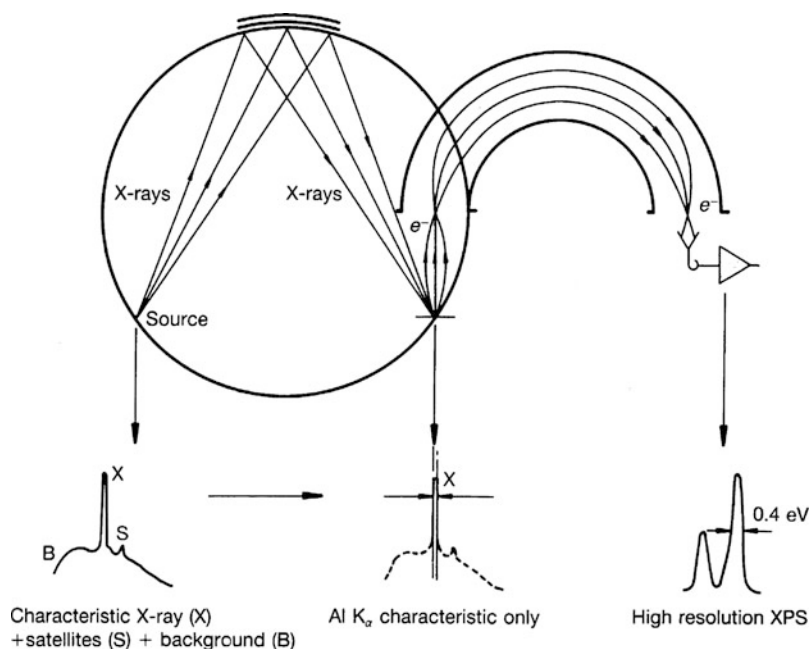


Fig. 2.7 Monochromatic X-ray source. For details see text (Reproduced from J.C. Rivière [2.6], with permission of Oxford University Press)

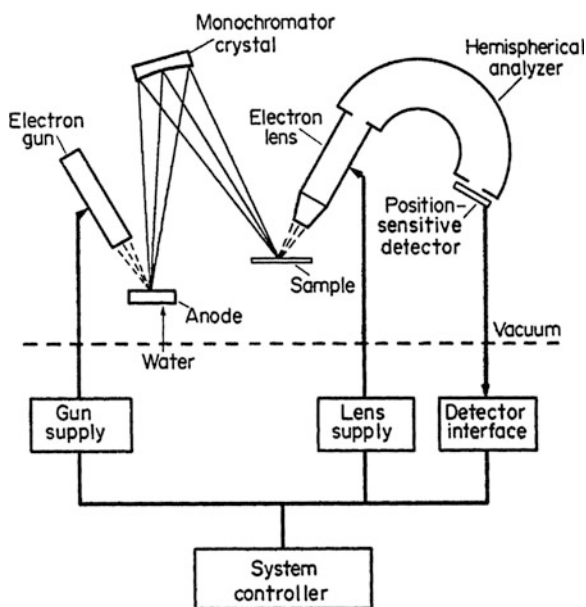


Fig. 2.8 Schematic diagram of a small-spot XPS with raster imaging capability (Reproduced from M.A. Kelly, with permission of Elsevier B.V.)

100 μm and below [2.7]. The easiest way to high-resolution XPS is using a small slit in the aperture of the analyzer, which is transferred through the lens system to the sample surface. However, the reduced analyzed area will result in a considerable loss of transmission and therefore in an intolerable intensity loss. A better way is to decrease the analyzed area by excitation of the sample with a fine-focused photon beam. This can be done by creating a small X-ray source using a focused electron beam impinging on the anode and imaging the generated X-rays through a bent monochromator crystal to the sample surface (see Fig. 2.8).

By mechanically moving the sample with a stepper motor, an areal distribution of elemental composition can be obtained. More elegant, quick, and precise is scanning of the focused electron beam. Spatial resolution is determined by the primary electron beam diameter and by the aberration of the elliptically bent mirror crystal. One of the popular instruments using this principle is the PHI Quantum 2000 and its successor, the Quantera, which has a scanned, focused, and monochromatic X-ray beam of $< 10 \mu\text{m}$ diameter. Advantages of this method are a high small-spot X-ray intensity enabling high-speed full-spectral analysis, as well as preset multipoint analysis and line scans. Other instruments using basically the same principle are the JEOL 9000 series, and the Thermo VG Scientific Theta Probe and Sigma Probe small-spot XPS. The latter instruments produce analysis spots of 10–400 μm in diameter. Maps and line scan test measurements showed a comparable resolution (80–20%) of about 20 μm . Today, spatial resolution in imaging XPS instruments is of the order of 1–3 μm . Submicron resolutions has been obtained with the NanoESCA instrument of Omicron in combination with synchrotron excitation [2.8] (see Sect. 2.5.4).

Because imaging techniques use the analyzer system as an imaging device to obtain a spatially resolved image of the sample surface with photoelectrons of a selected energy, they are considered in Sect. 2.5.4.

2.2.4 Synchrotron X-Ray Source

Powerful synchrotron electron accelerators have become an efficient photon source for all kinds of X-ray applications, notably photoelectron studies. According to electrodynamics, this is because any acceleration of a charged particle, whether linear or radial, causes the emission of light. The upper limit of the synchrotron X-ray energy depends on the amount of acceleration and, therefore, on the magnetic field strength for beam deflection and the final energy of the electrons. Several beam lines at the circumference provide access to the emitted radiation. Undulators serve to tune the photon energy to selected values [2.9–2.13].

There are two main features that make Synchrotron XPS very attractive as compared to conventional X-ray sources: (a) the extremely high brightness of the excitation and (b) the tunable photon energy. The high brightness (more than three orders of magnitude higher than conventional sources) allows application of extremely high energy resolution that is precluded in conventional XPS because

of the trade-off between resolution and transmission. The high photon flux also enhances photoelectron diffraction measurements (see Sect. 3.2.8). By tuning the photon energy, the kinetic energy and in turn the information depth of the photoelectrons can be varied (see Sect. 7.2.2, Depth Profiling). For example, the photon energy can be selected to result in the photoelectrons of interest having a kinetic energy near 50 eV, the energy for which the attenuation length (see Sect. 4.2.2) is at the minimum of about 1–2 monolayers.

2.3 Electron Gun

Any ionizing radiation causes Auger-electron emission, because an Auger transition is possible after an atom is ionized in an inner shell. X-ray excited Auger electrons (XAES) are detected in general XPS analysis too (see Fig. 3.2a) (note that the term electron spectroscopy for chemical analysis (ESCA) includes both XPS and X-ray-excited AES (XAES)). Heavy particle bombardment has also been used to excite Auger electrons [2.14]. In general, the term AES is used for electron-excited Auger electron spectroscopy. Electron guns have the advantages of easy construction and maintenance, high beam intensity, and capability of focusing and x - y deflection. The latter points are the main objectives of the development of scanning Auger microscopy (SAM) [2.15]. High spatial resolution below 10 nm [2.16] is obtained by instruments with a field emission cathode and an elaborate electron beam column (see Fig. 2.1b). Because a focused electron beam of high energy impinging on a metal surface creates characteristic X-rays, it is often used as a point source for spatially resolved XPS (see Sect. 2.2.4, Fig. 2.8).

Electron sources for AES are either based on thermionic emission or field emission. According to the Richardson equation for thermionic emission, a sufficiently high temperature is needed to efficiently overcome the work function threshold. Generally, tungsten (or tungsten–iridium) filaments are used as emitters. They are the cheapest filaments, but their use is limited to low-spatial-resolution spectrometers ($> 1\ \mu\text{m}$) because of their rather limited brightness. For spatial resolution in the submicron region, filaments with lanthanum hexaboride single-crystal emitters are used [2.17]. The highest spatial resolution for a given beam current is obtained with field emitters. For the latter, fine needles with typically 50 nm radius are used to obtain the high field strength necessary to overcome the work function barrier by the tunnel effect. Field emission sources have a high brightness that ensures high current density and spatial resolution. Because the emitted current strongly depends on adsorption from the residual gas (“flicker noise”), field emitters have to be used in UHV, and the cathode space is equipped with an attached ion pump. Even in UHV, the current for “cold” field emitters varies and is prone to an increased shot noise. Therefore, thermal Schottky field emitters are generally used, that consist of W(100) doped with Zr, and are operated above 1000 °C. [2.18]. The total current is usually below 50 nA, but with modern design of the emitter built within the first stage condenser lens, probe currents up to

500 nA can be obtained. At low currents (1 nA) and high voltage (25 keV), a spatial resolution below 5 nm can be achieved. With the novel concept of the Zeiss Gemini electron column, an SEM spatial resolution of 1.2 nm at 20 keV has been achieved [2.19–2.21].

For application in AES surface analysis, the two most important electron gun characteristics are:

1. High beam current for high sensitivity (limited by spatial resolution and sample damage)
2. Low beam diameter for high spatial resolution (limited by beam current).

For a given brightness of the electron source, the primary beam current I_p varies approximately with the beam diameter d_B in quadrature (for constant aperture angle), since [2.2]

$$I_p = \frac{\pi d_B^2}{4} j_p(\beta_B, \alpha_p), \quad (2.6)$$

where $j_p(\beta_B, \alpha_p)$ is the primary current density, given by the source brightness, β_B , and the aperture angle, α_p .

For a given beam diameter, high current density and therefore high brightness of the electron source is essential to get I_p high enough for a sufficiently high signal-to-noise level (see Sect. 6.2.5). Field emission cathodes provide the lowest beam diameter at currents useful for AES (> 1 nA). The beam diameter determines the analyzed spot size (however, see backscattering influence, Sect. 5.2.3). For small beam diameter, d_B has to be corrected by an additional term depending on the spherical aberration of the lens system [2.19]. Figure 2.9 shows the relation between beam diameter and beam current according to (2.6) for typical LaB₆ and W(Zr) field emitter electron guns [2.23]. Optimum spot size is achieved by respective focusing lenses settings. With a reduced beam current (e.g., with a small externally operated diaphragm in the beam) the sharpness of the secondary image of a sample while zooming in a certain object is a useful measure of the attainment of a small beam

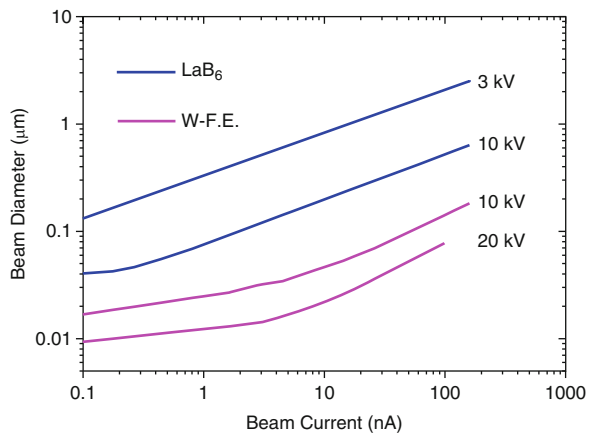


Fig. 2.9 High-resolution AES: electron beam diameter as a function of the beam current for a LaB₆ cathode (blue lines, 3 and 10 kV beam voltage, PE SAM 600) and for a W thermal field emitter cathode (red lines, 10 and 20 kV beam voltage, PE SAM 670) (After Ref. [2.23])

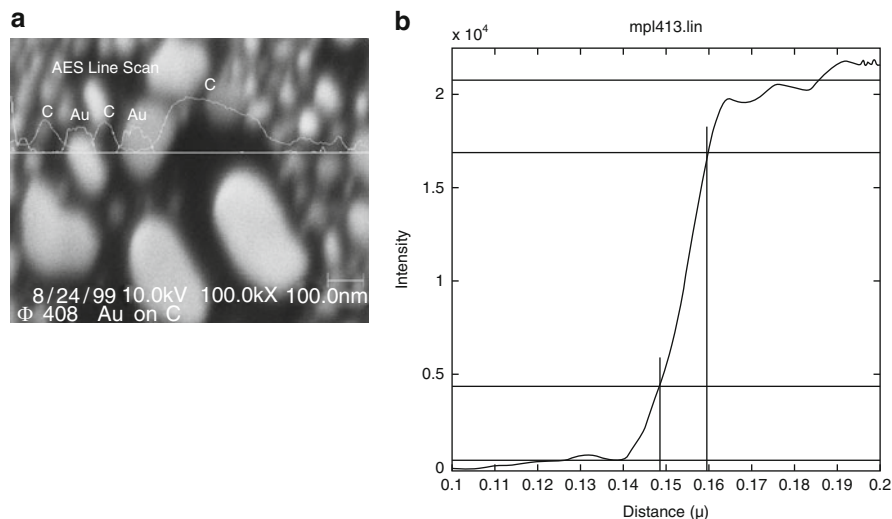


Fig. 2.10 High-resolution line scan of the intensity of Auger peaks on a gold-on-graphite spatial resolution test sample, acquired with a PHI 680 instrument at 10 kV, 1 nA. **(a)** Au (69 eV) and C (272 eV) Auger peaks; **(b)** Au (69 eV) Auger peak intensity at a gold particle edge, magnified from **(a)**. The 20–80% resolution is determined to 11 nm

diameter. Measurement can be done with a line scan at a sharp edge (e.g., on a gold particles on carbon sample) and defining the full width at half maximum (FWHM) of the beam by 20–80% increase of the intensity at the Au edge (taking 16–84% gives about 15% larger values). Note that the maximum beam current density in the center is about twice the value of j_p if a Gaussian intensity distribution across the diameter is assumed.

Figure 2.10a shows an AES line scan at high resolution (10 keV, 1 nA) for a Au-on-C resolution test sample. The peak-to-background intensity of the $N(E)$ Auger peaks of Au and of C is plotted across the line shown in the secondary electron detection (SED) image acquired with a PHI 680 Auger Microprobe. Figure 2.9b depicts the Au line scan for the edge of an Au particle, with the 20–80% width (= FWHM) of 11 nm. This is a conservative value because the boundary of the particle is not linear and the thickness may not increase from zero to a plateau in an exact step. Therefore, the resolution under the given conditions for AES is better than 10 nm, at present a typical value for AES microprobes. However, the primary beam at the sample is surrounded by a “halo” of backscattering-induced Auger electrons that tend to blur the ideal resolution [2.23] (see Sect. 5.2.1.1, Fig. 5.24). At high energy, backscattering may even cause Auger signals from areas far outside the electron impingement spot (see Sect. 5.2.3.1, Fig. 5.47). In general, spatial resolution is better with higher primary energy and in the SED mode because of lower beam current (see (2.6), Fig. 2.9).

The total electron beam current can either be measured by a Faraday cup or more conveniently by the current absorbed in the target. During the measurement, the target has to be at a slightly positive potential (typically +50 eV) with respect to the ground in order to avoid secondary emission of low-energy electrons. Note that the initial emission current is usually higher than the current impinging on the sample. Wehnelt cylinder and condenser lens settings determine the beam current. Standard beam current for useful signal-to-noise ratio is 10 nA (see Sect. 6.2.5).

The primary electron beam energy can usually be varied from 0.5 to 30 keV, with typical operation voltages of 5 or 10 keV in modern scanning AES spectrometers with high spatial resolution. The primary beam energy is essential for quantification, because the relative intensity of AES peaks changes with the beam voltage as does the backscattering yield. The energy spread of the gun is typically less than 0.5 eV and is not particularly important in AES. (However, for optimum focusing and for applications such as high-resolution reflection electron energy loss spectrometry (REELS), a negligible energy spread is desirable.)

The role of primary electron energy and of current density in quantitative and applied AES is discussed in Sects. 4.4, 6.2, 6.3, 8.5, 8.6.

2.4 Ion Gun

In contrast to SIMS and ISS, the ion gun in AES and XPS is not the primary excitation source. However, it is necessary for sample cleaning and above all for sputter depth profiling (see Sect. 7.1), where excitation of Auger electrons by ion bombardment can be a distortional side effect (see Sect. 7.1.4). Usually, ion guns for AES/XPS are rather simple in construction. Any ion gun consists of an ion formation chamber and an accelerating electrode, and in most cases, a beam-focusing electrostatic lens and deflection plates for x - y rastering of the ion beam are provided. Basically, there are several types of ion guns depending on the way of ion generation: plasma discharge with cold cathode (Penning), duoplasmatron and broad beam (Kaufmann type) guns, electron impact (accelerated electrons from hot filament), field ionization, and field evaporation (cesium and liquid metal guns, only used in SIMS).

Cold cathode ion guns are most simple in construction [2.24]. Using an external magnet, a discharge is created, and positive ions are extracted and focused with an electrostatic lens, resulting in a static spot size of up to 10 mm diameter. Therefore, guns of this type are often used for sample cleaning. Because of there usually insufficient beam homogeneity and the relatively large amount of neutrals in the beam, they are not recommended for depth profiling.

Kaufmann ion sources [2.25] are designed to create a beam with moderate energy (500–3000 eV), with high current density (1 mA/cm²), and with homogeneous distribution over a wide area (several cm). These properties are usually obtained by a special distribution of electric and magnetic fields in the formation chamber.

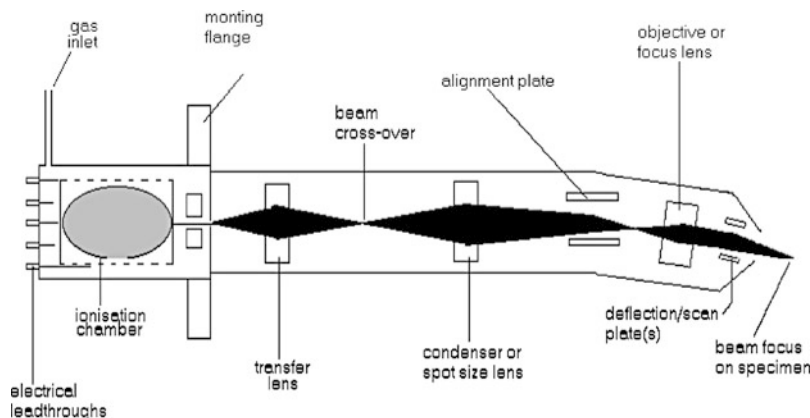


Fig. 2.11 Schematic view of a typical ion gun for sputter depth profiling with electron impact ionization chamber, electron-optical system with deflection/scanning plates to bent the ion beam in order to avoid neutrals impinging on the analyzed spot (courtesy of C. Blomfield, KRATOS Analytical Ltd.)

Because of the above specifications, these ion sources have recently become popular in depth profiling of thicker layers.

In duoplasmatron ion sources [2.26], a magnetically constricted arc generates a high density plasma from which the ion beam is extracted. The advantage of the duoplasmatron source is its relatively high current density and the use of aggressive gases (oxygen, nitrogen) without any restrictions. Therefore, it is often used in SIMS ion guns. However, the typical voltage is between 1–10 keV, relatively high for high-resolution depth profiling [2.27].

In sputter depth profiling, an electron impact ionization gun operated with continuous Argon gas inlet is most frequently used [2.28]. A heated filament produces electrons that are accelerated by a grid at typically about 100 eV positive potential to the cathode. A gas pressure of about 10^{-1} to 10^{-3} Pa ensures an effective electron impact ionization of the gas atoms. The ions are extracted from the formation chamber by an acceleration electrode with a hole that injects the ions in a focusing lens system. This system guides the ion beam through the x – y deflection plates (see Fig. 2.11). A negative voltage of typically between 0.5 and 5 keV is applied to the grid, with the accelerating electrode at ground potential. The ion beam current is increasing with the electron emission current in the ion formation chamber and with the gas pressure there. The sputtering gas, usually argon, is supplied from a high purity (6N) flask through a needle valve to the ion formation chamber, and another flange after the acceleration electrode is used to extract the gas (by a turbomolecular pump) on its way through the lens system to the analysis chamber from the system, to ensure a much reduced load of sputtering gas in the main chamber. By this kind of “differential pumping,” the Argon pressure is reduced by several orders of magnitude, for example, from 10^{-1} Pa (ionization chamber) to 10^{-6} Pa in the main chamber. This is particularly important when

ion pumps are used to evacuate the main chamber. The ion beam can be focused from several mm down to $100\text{ }\mu\text{m}$ or less in diameter, with a Gaussian intensity distribution [2.29]. Only with an electron beam adjusted in the center, a fairly well-resolved AES depth profile can be obtained. Improved equipment uses rastering of a fine-focused beam in x – y directions (Fig. 2.11). In that way, a rectangular sputtered spot (usually diamond shaped, because of nonnormal impingement of the ion beam) of up to $10 \times 10\text{ mm}^2$ can be obtained. This is particularly necessary for depth profiling with a conventional large area XPS system. Electron impact ion guns provide a focused ion beam with low-energy spread. However, a disadvantage of ion guns based on electron impact ionization is the remarkable amount of reneutralized Ar^+ ions with high energy in the beam that are not deflected but capable of eroding the target surface. Therefore, an additional sputtered spot is created, and after a certain sputtering time, the depth in that spot becomes remarkably larger than that of the adjacent area covered by the x – y -rastered beam. If the analyzed spot extends across both areas, a superposition of analyzed signals in both depths occurs and a deterioration of the depth resolution (proportional to the sputtered depth) results (see Sect. 7.1.4).

As a remedy for additional sputtering with neutral species formed during traveling in the optical column, two electrodes establishing a static field for slight beam bending are applied, as shown in Fig. 2.11. This electric field moves the center of the rastered area (where the analyzed spot has to be adjusted) away from the zero field spot of the neutrals, thus helping to improve depth resolution (see Sect. 7.1.4).

A rather useful modification for high-resolution depth profiling is an ion gun with a floating potential optical system by which the ions can be decelerated and then again accelerated to a higher potential. This technique avoids the huge drop in ion beam current when the extractor voltage is below 1000 eV with the simple version of the gun. With the acceleration–deceleration gun, a much higher current is possible even for 50 eV primary ion energy that is desirable in high-resolution depth profiling (see Sect. 7.1.6). Figure 2.11 shows the dependence of the ion current on the ion energy for a conventional electron impact ion gun and one with a decelerating lens system.

Ion guns operating with a beam of an ionized cluster of many atoms (e.g., SF_6 [2.30]) instead of a single atom, are particularly useful in high-resolution depth profiling because the energy at the surface is distributed to the atoms, thus decreasing the impact energy per atom and therefore the atomic mixing length, an important parameter in depth profiling (see Sect. 7.1.8). Elaborate ion guns supplying high energy cluster primary ions such as Au_n , Bi_nC_{60} have been developed especially for SIMS on organic materials [2.31, 2.32]. ToF-SIMS results by Sun et al. [2.33] showed optimal depth resolution of 5 nm with Ni/Cr reference bombarded with 10 keV C_{60}^+ cluster ions. The latter and particularly Ar_n^+ clusters of $n = 500$ to 1000 Ar atoms [2.34, 2.35] are promising alternatives for high-resolution AES and XPS sputter depth profiling.

2.5 Electron Energy Analyzer

The most important part of an electron spectrometer is the electron energy analyzer. In commercial electron spectroscopic instruments, only electrostatic analyzers are used. Three different types are most common: the retarding field analyzer (RFA), the concentric hemispherical analyzer (CHA) or hemispherical analyzer (HSA), and the cylindrical mirror analyzer (CMA). Whereas the RFA is a high-pass filter that cuts off all electrons below certain energy, the CHA and the CMA are deflection analyzers that operate like band-pass filters, that is, they open a window for only a small energy band around a given energy. Therefore, they intrinsically have a better signal-to-noise figure and higher sensitivity than the RFA, leaving the latter only for very special applications (e.g., AES in LEED systems). The most simple RFA, which was first successfully applied in the work of Franck and Hertz on the detection of ionization potentials in 1925, is that of placing a retarding potential on a grid before the detector. Weber and Peria [2.36], and Taylor [2.37] developed the technique to get the differentiated spectrum with a four-grid low-energy electron diffraction (LEED) device by using the second harmonic of the modulation frequency for electronic differentiation. Today, LEED systems are rarely used for AES because of the much higher noise and therefore less sensitivity of the retarding field analyzers as compared to electrostatic deflection analyzers discussed below.

At present, practically, all commercial photo- and Auger-electron spectrometers are equipped with a concentric hemispherical analyzer (CHA) (sometimes also called concentric spherical sector analyzer (CSSA) or hemispherical sector analyzer (HSA)) or a cylindrical mirror analyzer (CMA). Less frequently used are some special analyzers combining retarding field grid systems with those analyzers such as the double-pass CMA [2.38], the Staib analyzer [2.39] or the spherical mirror analyzer (SMA) (see Fig. 3.14). A brief outline of the fundamental principles of the electrostatic detection methods for the two main types of analyzers, CMA and CHA, is given in the following (see Refs. [2.6, 2.22, 2.40, 2.41]). Being only of historical interest, the retarding field analyzer (RFA) is not considered here. Whereas the CMA has become most prominent in AES instruments, XPS is almost exclusively performed with CHA type analyzers. A spherical equivalent of the CMA is the spherical mirror analyzer (SMA) which is mainly used for imaging (see Fig. 3.14).

The functional properties of the various types of spectrometers are usually characterized in terms of:

1. Total geometrical transmission, T_A , that is the fraction of emitted monoenergetic electrons in half-space (2π) which pass the detector slit.
2. Acceptance angle $\Delta\Omega/2\pi$ (point source).
3. Acceptance area, A (extended source).
4. Overall luminosity (étendue) $L_A = T_A A$ [2.6].
5. Energy resolution $R_E = \Delta E/E \times 100$ (%), where ΔE is the full width at half maximum intensity (FWHM) of the measured peak of a monoenergetic electron emission line (with approximately zero energy width) and E the energy value of this line.

6. Energy filtering quality (or electron-optical quality) which is given by the ratio of transmission to resolution, T_A/R_E . This figure determines the maximum gain or signal-to-noise ratio (see Chap. 6) and is therefore characterizing the instrumental sensitivity.

2.5.1 The Cylindrical Mirror Analyzer (CMA)

The first commercial CMA was introduced in 1996 by Palmberg et al. [2.42] for AES with high detection sensitivity. The properties of the CMA are described in detail by Sar-El [2.43]. The principle is depicted in Fig. 2.13 [2.6]. The CMA basically consists of two exactly concentric cylinders with radius r_1 and r_2 . The inner cylinder (r_1), usually at the ground potential, has two radial apertures with grids. The outer cylinder (r_2) is at a negative potential for electron deflection. A part of the electrons that are emitted from the sample enter the space between the two cylinders through the entrance aperture of the inner cylinder. Only those electrons arrive at the exit slit which possess a small energy window ΔE around the pass energy E_0 , shown by the broken lines in Fig. 2.12, and are detected by a channel electron multiplier in point F on the axis.

The field between the cylinders is given by $\ln(r_2/r_1)$, resulting in the focusing condition [2.43]

$$E_0 = \frac{eVK_0}{\ln(r_2/r_1)} \quad (2.7)$$

Optimized, second-order focusing conditions are obtained for the special case where $K_0 = 1.31$, the entrance angle $\alpha_e = 42.3^\circ$, and the distance L between S and F is given by $L = 6.130r_1$ [2.40]. As a compromise between energy resolution and transmission, the typical aperture half-angle $\Delta\alpha_e = \pm 6^\circ$. It can be shown that the minimum width of the electron paths is off axis in front of the focus F .

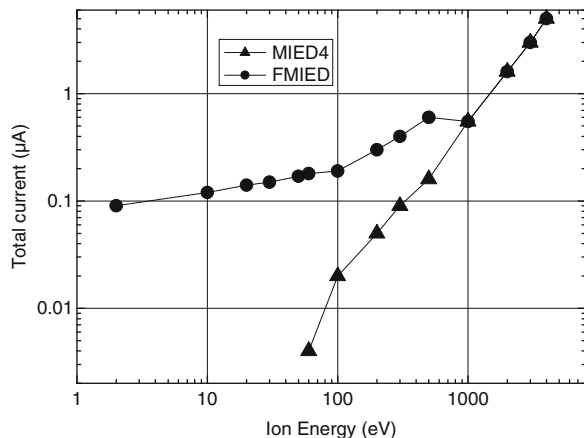


Fig. 2.12 Low-energy ion gun with relatively high current using floating potential for acceleration and deceleration (FMIED), in comparison to normal field acceleration gun (MIED4) (Courtesy of JEOL Ltd.)

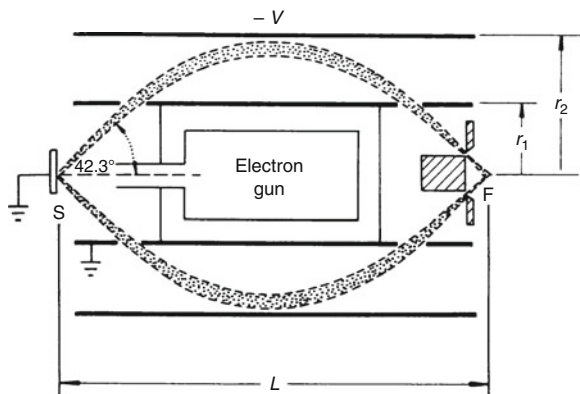


Fig. 2.13 Schematic cross section of a cylindrical mirror analyzer (CMA) with concentric electron gun and two coaxial cylinders with radii r_1 and r_2 . Electrons with energy E_0 emitted from the sample S with an azimuthal angle (with rotational symmetry) of $42.3^\circ (\pm \Delta\alpha_e)$, the aperture half-angle) enter the space between both cylinders and are focused in F . An adjustable slit improves the resolution. The inner cylinder has ground potential, whereas the outer cylinder is at the negative potential $-V$. The relation between V , r_1 , and r_2 is given in (2.7) (Reproduced from J.C. Riviere [2.6], with permission of Oxford University Press)

The geometrical analyzer transmission T_A , defined as the fraction of the half-space cut out by the ring with opening angle α_e and ring width $2\Delta\alpha_e$, is represented by

$$T_A = 2\Delta\alpha_e \sin \alpha_e = 1.35\Delta\alpha_e. \quad (2.8)$$

With $\alpha_e = 42.3^\circ$, the relation between energy resolution and transmission is

$$\frac{\Delta E}{E} = 2.255 T_A^3. \quad (2.9)$$

A typical CMA has an aperture half-angle of $\Delta\alpha_e = 6^\circ$, and therefore a resolution of $\Delta E/E = 0.6\%$ and a transmission of $T_A = 14\%$. By decreasing $\Delta\alpha_e$, the resolution is improved but transmission is reduced. For example, half the aperture angle, $\Delta\alpha_e = 3^\circ$, gives a resolution below 0.1% , but the transmission is reduced to 7% .

Special CMAs are equipped with a mechanically adjustable ring slit at the crossover position as indicated in Fig. 2.13. By variation of the slit width w_s , the energy resolution can be varied and is given by [2.43]

$$\frac{\Delta E}{E} = 0.18 \frac{w_s}{r_1} + 1.38(\Delta\alpha_e)^3. \quad (2.10)$$

Any aberration of the path of the electrons through the CMA has to be avoided. Therefore, the two apertures are covered with a fine mesh to ensure no distortion of the inner field by the sample. Furthermore, the equipotential areas have to be

concentric cylinders, which mean both ends of the analyzer have to be terminated as if the analyzer would stretch out to infinity. For example, this can be attained by a prolongation beyond the sample area and a special concentric opening at the ends (as theoretically determined by Varga et al. [2.44] and practically used in the metrological CMA of Goto et al. [2.45, 2.46]).

In commercial CMAs, a purely radial field component is provided by a termination with an evaporated semiconductor resistance layer of constant resistivity between the inner and outer cylinder on both ends, which forces the equipotential areas at the ends to the same locations as in the free space between the cylinders. This even enables a conical shape of the analyzer front end that allows more useful space in front of the analyzer.

In practice, some malfunction (poor resolution, double peaks) may occur if the resistivity of the layer of the first termination becomes inhomogeneous through contamination, for example, by evaporation or sputter deposition after many months of sputter depth profiling. Because of the meshes over the slits have a finite transmission, and are usually interrupted by solid bridges for mechanical reasons, the transmission of a CMA is always less than the above calculated ideal values. In addition, nonconducting material sputter deposited on the entrance mesh may lead to charging which in turn causes distortion of the electric field and hence a loss in resolution.

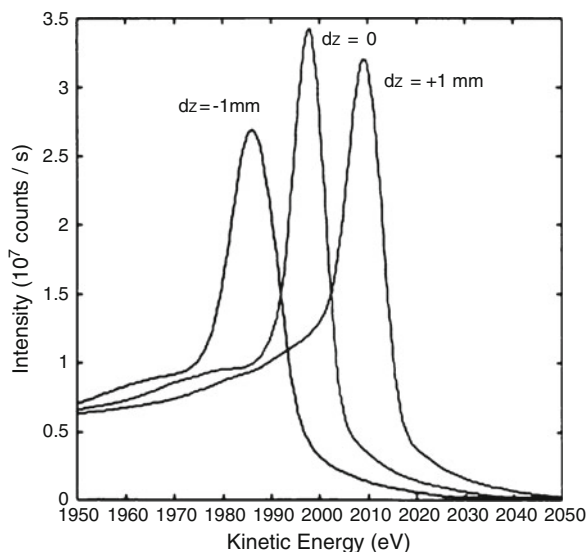
According to (2.8), the transmission T_A of the CMA is independent of the energy, and after (2.9), $\Delta E/E$ is constant; hence, the energy window for transmitted electrons, ΔE , is proportional to $\Delta E = \text{const.} \times E$. The count rate in the spectrum for any energy E is given by $N(E)$. Therefore, the transmitted electron intensity is $\Delta E \times N(E)$, and the measured intensity $I(E)$ (in counts per second, cps) is given by

$$I(E) \propto \Delta E \times N(E) = (\Delta E/E)E \times N(E) = R_E \times E \times N(E) \quad (2.11)$$

where ΔE is the width of the energy window, that is the resolved energy called (absolute) energy resolution, and $R_E = \Delta E/E$ is the relative energy resolution of the analyzer, usually given in percentage ($R_E(\%) = 100 \times \Delta E/E$). This principal operation of the CMA can be achieved by the CHA when the retarding lens is set to work in the “constant retard ratio” (CRR) mode (see below).

The main disadvantage of the CMA is its sensitivity to axial movement Δx_a of the sample away from the focal point, resulting in decreased signal intensity and a shift of the measured peak energy, ΔE_s , which is proportional to E according to $\Delta E_s/\Delta x_a = k_{sh}E$ [2.47]. For a typical value of the inner cylinder radius, r_1 , of 15 mm, $k_{sh} = 0.012 \text{ mm}^{-1}$, that is, the energy shift is about 12 eV at 1000 eV and 1 mm sample movement [2.47]. For a CMA with about twice the size, as for the PHI 680, $k_{sh} = 0.0063 \text{ mm}^{-1}$. Figure 2.14 shows the result for a PHI 680 instrument. The shift of the elastic peak energy at 2000 eV is 12.5 eV/mm, corresponding to 5.7 eV/mm for the Cu (914 eV) peak but negligible shift (0.37 eV/mm) for the Cu (60 eV) peak. As seen in Fig. 2.14, the optimum analysis spot is easy to find by monitoring the intensity and energy of the elastic peak at 2000 eV while moving

Fig. 2.14 Variation of elastic peak energy (2000 eV), intensity (counts/s), and resolution (peak width) by changing the axial distance from the focal point of the CMA ($dz = 0$) measured with a PHI 680 instrument



the sample in the direction of the analyzer axis. Besides a rather limited energy resolution (typically around 0.5%), the CMA has a small acceptance area, that is, a low luminosity (étendue, the product of transmission and acceptance area), and, therefore, it is not suitable for XPS. By putting two CMA together, with the exit aperture of the first being the entrance aperture of the second CMA, Palmberg [2.38] achieved an improved luminosity and high resolution using spherical grids before the first entrance aperture. This double-pass CMA analyzer (DP-CMA), schematically shown in Fig. 2.15, can be used for AES and for XPS in two adequate modes [2.48]. For XPS, the analyzer operates at a selected pass energy to which the electrons are retarded by the entrance mesh. In the AES mode, the grids are grounded as is the inner cylinder, and operation is analogous to a single-pass CMA. A special feature, namely, a drum with a slit in the second analyzer, allows the selection of a specific part of the electrons at the circumference of the circular cross section of the electron path and therefore the selection of a specific emission angle. Thus, angle-resolved XPS and AES (see Sect. 7.2.1) are enabled without the necessity of moving the sample. Today, the DP-CMA has been replaced by electron analyzers of CHA type with specially designed input lens for parallel detection of angular resolved electron emission (see below and Sect. 5.1.2).

2.5.2 The Concentric Hemispherical Analyzer (CHA)

The concentric hemispherical analyzer (CHA) (also called concentric spherical sector analyzer or hemispherical analyzer (HSA)) was first exclusively used by XPS

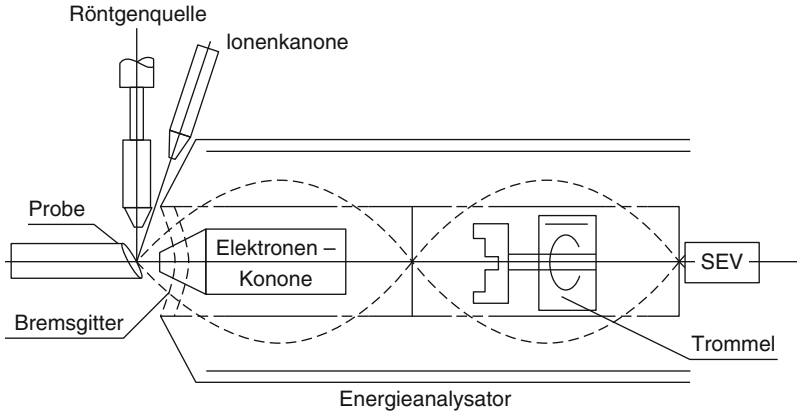


Fig. 2.15 Sketch of a double-pass CMA (DP-CMA), with entrance grids, concentric electron gun in first CMA, drum device with narrow (6°) and wide (12°) slits, and additional X-ray source (Adapted from S. Hofmann and J.M. Sanz [2.48])

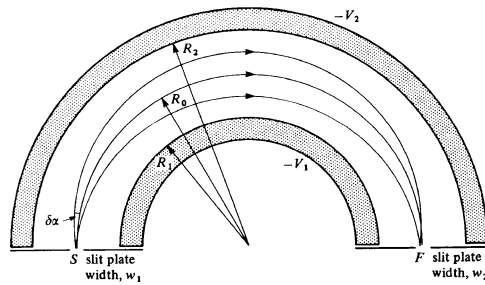


Fig. 2.16 Schematic cross section of a concentric hemispherical analyzer (CHA), with R_1 and R_2 the radii of the concentric hemispheres at potentials $-V_1$ and $-V_2$, respectively ($|V_2| > |V_1|$), R_0 the radius of the median equipotential surface, source S in entrance slit width w_1 and focus F in the exit slit w_2 , and entrance half-angle $\delta\alpha$ of the electrons (Reproduced with permission of Cambridge University Press from M.P. Seah [2.40]. Crown Copyright 1985)

because of its superior energy resolution and areal transmission (étendue, area $\times$ transmission). It is now increasingly used for AES too.

The CHA consists of two concentric hemispheres with radius R_1 and R_2 , as schematically depicted in Fig. 2.16. The outer sphere is put on a negative potential $-V$ against the inner hemisphere, and the mean radius $R_0 = (R_1 + R_2)/2$ describes an equipotential plane that connects entrance and exit slits of widths w_1 and w_2 . For an electron with energy E_0 traveling from entrance to exit, the condition

$$e(V_2 - V_1) = e\Delta V = E_0 \left(\frac{R_2}{R_1} - \frac{R_1}{R_2} \right) = \frac{1}{k_s} E_0 \quad (2.12)$$

has to be fulfilled [2.2]. The electron energy E_0 is directly proportional to the applied potential difference ΔV , $E_0 = k_s e \Delta V$, with the spectrometer constant k_s given by the radii in (2.12). For optimum point source conditions, the entrance slit width (w_1) is effectively zero and the relative energy resolution is given by [2.22, 2.41]

$$\frac{\Delta E}{E} = \frac{w}{2R_0} + \frac{1}{4}(\Delta\alpha_e)^2 \quad (2.13)$$

where w is the exit slit width and $\Delta\alpha_e$ is the aperture half-angle analogous to the CMA (Sect. 2.5.1). Equation (2.13) denotes the basic spectrometer resolution. For a typical geometry (slit width $w = 3$ mm and $R_0 = 150$ mm), $\Delta E/E = 2\%$. This is insufficient for most applications. Because of this fact and because the sample cannot be placed in the entrance slit, concentric hemispherical analyzers have an input lens that defines the analyzed area (Figs. 2.1 and 2.5).

As a useful compromise between large transmission (high $\Delta\alpha_e$) and high resolution (low $\Delta\alpha_e$), $\Delta\alpha_e \approx w/(2R_0)$ is generally chosen which gives

$$\frac{\Delta E}{E} = 0.63 \frac{w}{R_0}. \quad (2.14a)$$

Neglecting higher-order terms, the geometrical transmission T_A is given by [2.22].

$$T_A = 2 [1 - \cos(\Delta\alpha_e)]. \quad (2.14b)$$

For a typical value of $\Delta\alpha_e = \pm 6^\circ$, $T_A \approx 1\%$, which is considerably lower than that for the CMA (see (2.8)), although some improvement is possible by a higher aperture angle in the direction perpendicular to the dispersion plane [2.40].

The dependence between transmission, resolution, and étendue on various operation modes of the lens is given in detail by Seah [2.40].

The main purpose of the input lens is retardation of the electrons to reduce their energy before they enter the analyzer. This reduced (and constant) energy is called the pass energy. Because $\Delta E/E = \text{const.}$, a lower pass energy E means a lower absolute energy resolution ΔE . In the above example with $\Delta E/E = 2\%$, a pass energy of 100 eV gives an energy resolution of 2 eV, sufficient for survey scans. A pass energy of 10 eV or lower with $\Delta E = 0.2$ eV is adequate for high-resolution small energy range scans. Note that the resolution discussed is the spectrometer resolution, irrespective of the natural line width (see Fig. 2.7 and Sect. 3.2.7). An input lens with a very high acceptance angle of 85° is used in the Thetaprobe instrument of Thermo VG Company to enable angle-resolved measurement in combination with a position-sensitive detector which gives count rates for selected emission-angle regions. Thus, angle-resolved XPS is possible without tilting the sample (see Sect. 4.3.2.6).

CHA spectrometers can be operated in two different modes, the constant or fixed retard ratio (CRR or FRR) mode, where $\Delta E/E = \text{const.}$, or the constant or fixed analyzer transmission (CAT or FAT) mode, where $\Delta E = \text{const.}$ Whereas the FRR ($\Delta E/E = \text{const.}$) mode is generally used in AES, in XPS, the FAT mode is exclusively used in XPS.

Advantages and disadvantages of the CMA and the CHA are summarized in the following by a comparison of the principles and operation of both devices.

- (a) *Transmission.* A high transmission is the prerequisite of high detection sensitivity (see Chap. 6). Because of the full 2π acceptance cone of the CMA, the geometrical point source transmission is usually higher (typically about 14%, see Sect. 2.5.1) than for the CHA, for which it is typically of the order of 1% (see (2.14b) [2.22]). Consequently, CMA systems for AES under otherwise similar conditions have a higher count rate and, therefore, a higher sensitivity (lower detection limit) than CHA systems (see Sect. 6.2.6, Table 6.1). However, multichannel detector systems (see Sect. 2.5.3) increase the count rate and make the performance of a CHA in AES comparable to a single detector CMA (modern AES instruments use multichannel detection with CMA too). In XPS, the usually larger source requires a larger area transmission or luminosity (étendue), which is the product of transmission and source area. Therefore, the CHA is better suited for XPS with respect to transmission and acceptance area, which is relatively small for the CMA and less well defined.
- (b) *Energy resolution.* The relative energy resolution of the CMA primarily depends on the acceptance angle. A typical figure is $R = \Delta E/E = 0.5\%$ for most commercial instruments. The CHA is much more flexible in operation because the entrance lens generally enables a much better energy resolution (about 0.05% in the CRR mode) than the CMA. This is one of the main reasons why the CHA is increasingly used for AES too.
- (c) *Positional sensitivity and operation space.* The dependence of the signal intensity and measured electron energy on the position of the sample with respect to the distance to the analyzer is much less for the CHA (less than 0.5 eV/mm/1000 eV for the JEOL 7830F) than for the CMA (6.3 eV/mm/1000 eV for the PHI 680, Fig. 2.13). The entrance lens system of the CHA provides a larger distance to the sample and therefore a wider space for additional instrumentation and sample manipulation (e.g., 25 mm for PHI 680 and 50 mm for JEOL 7830F).

The deflection properties of all electrostatic spectrometers used in AES and XPS are charge and energy dependent but mass independent. Therefore, they can be used in ion spectroscopic techniques as well, such as ion scattering spectrometry (ISS) [2.49].

2.5.3 Multichannel Detection

Both the CMA and the CHA are energy dispersive systems that can be used to simultaneously detect electrons arriving at different locations in the dispersion plane, as already indicated in Fig. 2.1b and shown in more detail in Fig. 2.17. Therefore, parallel multichannel detection of a certain energy range (usually about 10% of the pass energy) is enabled, as realized in commercial instruments in a

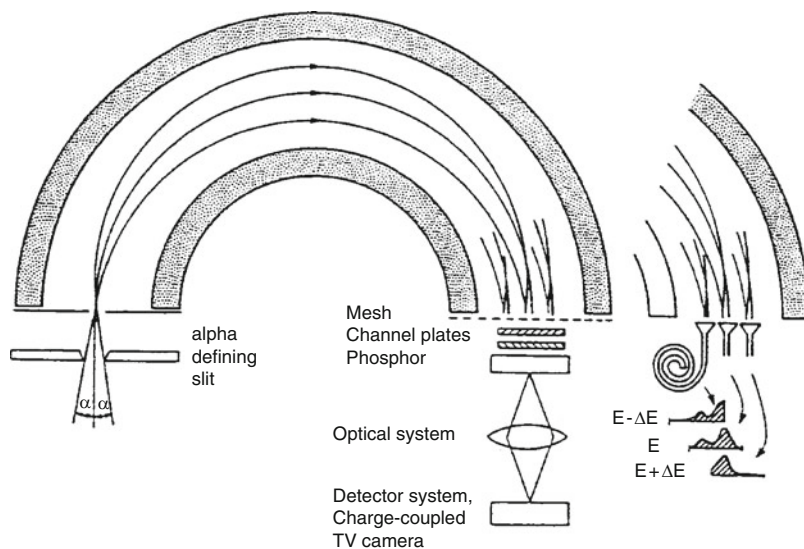


Fig. 2.17 Schematic multichannel output systems for CHA: channel plates with position-sensitive detection (*left*) and several channeltrons (*right*) (Reproduced with permission of Cambridge University Press from M.P. Seah [2.40]. Crown Copyright 1985)

variety of ways, for example, by using a channel plate for amplifying the electron current and a resistive plate as a position-sensitive detector or by using discrete channeltrons at the exit slit. Using N_c channels for detection, the measurement time for a given signal-to-noise ratio is reduced by a factor of $1/N_c^{1/2}$ (see Sect. 6.2.8).

2.5.4 Imaging XPS

In contrast to scanning techniques, imaging techniques use the analyzer system as a device to obtain a spatially resolved image of the sample surface with photoelectrons of a specific energy (chemical maps). Typical instruments of this category are the Scienta 300 and its successor, Scienta 4000, the VG Scientific ESCASCOPE and ESCALab 220i, and the Kratos AXIS Ultra. The Scienta 300 uses a position-sensitive detector parallel to the nondispersive plane at the output of the analyzer while detecting the energy on the other axis. In that way, an energy versus position map is obtained with a spatial resolution of $25\text{ }\mu\text{m}$ ($9\text{ }\mu\text{m}$ for Scienta 4000). In the VG Scientific ESCASCOPE instrument, two lenses, one at the entrance and the other at the exit of the analyzer, establish a Fourier transform optical system. Analysis of features smaller than $5\text{ }\mu\text{m}$ have been demonstrated and full spectral analysis for a $15\text{ }\mu\text{m}$ diameter area [2.50]. ESCALAB 220i specifies a spatial resolution of $3\text{ }\mu\text{m}$.

A high-performance imaging XPS system is offered by the Kratos AXIS Ultra system [2.51] that uses an additional spherical mirror analyzer (SMA) consisting

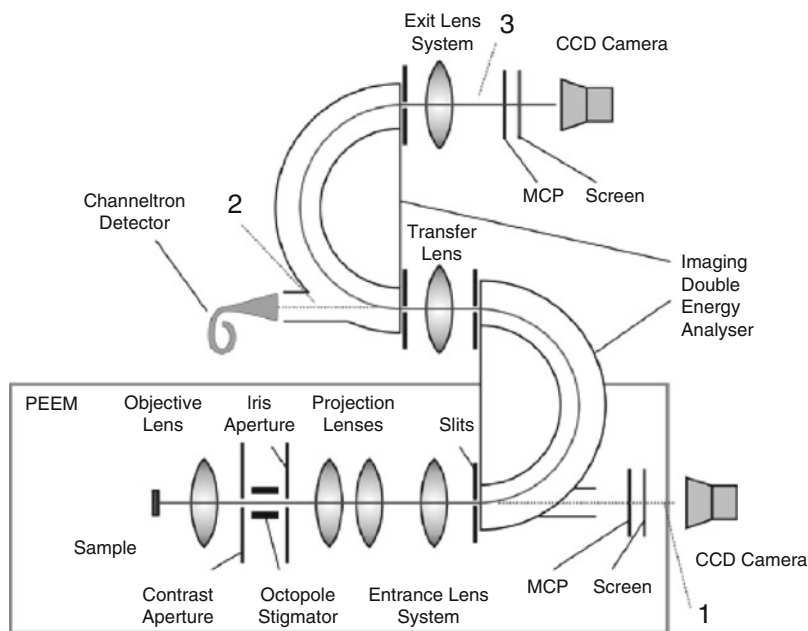


Fig. 2.18 Schematic layout of the NanoESCA (Company Omicron) instrument. Three possible operation modes are indicated: (1) photoelectron emission microscopy (PEEM) mode, (2) selected area spectroscopy, (3) energy-filtered ESCA imaging (Reproduced from M. Escher et al. [2.8], with permission of IOP publishing Ltd.)

of two concentric hemispheres and a delay-line detector system which records position-sensitive spectra. The principle is as follows: Owing to the ideally radial field in the space between the inner mesh hemisphere and the outer one at negative potential, the SMA provides perfect focusing for monoenergetic electrons in the equator plane for every source point lying symmetrically to the radial center. Therefore, a two-dimensional image of the object is generated in the exit plane with zero spherical aberration and with no first-order energy dispersion at image position. However, there are two locations where there is no first-order radial dependence of the trajectory on position in image (crossover points), but there is maximum energy dispersion on the second location. Using a baffle with an aperture within the mirror field selects a small energy range. By stacking up a number of images at different energies, a spectrum can be obtained for every pixel in the image. Thus, elemental and chemical state as well as multipoint analyses are provided. Reported spatial resolution is below $15\ \mu\text{m}$.

The newly developed NanoESCA instrument of Omicron Company uses two CHA in series, thus correcting for the main spherical aberration term by the asymmetry of the tandem configuration. The principle is shown in Fig. 2.18 [2.8]. Three operation modes are possible: direct imaging with nonenergy-filtered photoelectron emission microscopy (PEEM) (1), selected area XPS with the first

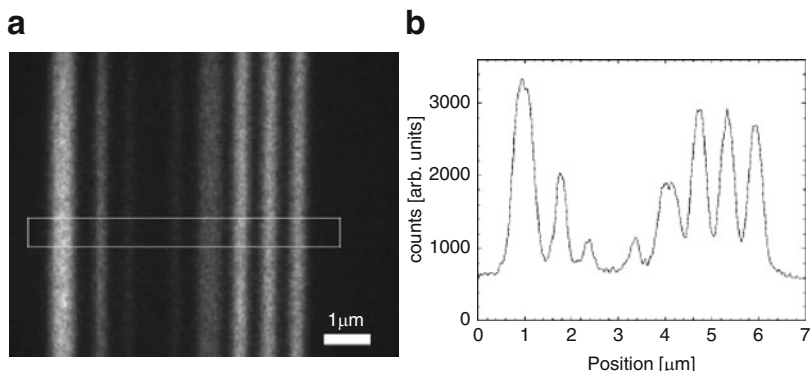


Fig. 2.19 (a) Energy-filtered image of the Al 2p peak intensity at a GaAs/Al(0.65)Ga(0.35)As heterostructure [2.52] excited with synchrotron radiation ($h\nu = 120$ eV, 1000 photons $\text{mm}^{-2} \text{s}^{-1}$), obtained with a NanoESCA (Omicron) instrument; (b) Line scan (intensity profile) of the area indicated in (a). The first three layers (at *left*) are 500, 150, and 50 nm wide, and the last three layers (*right*) are 300 nm wide separated by 300 nm spaces. A lateral resolution (20–80%) of about 150 nm can be determined applying edge measurement for the first and multilayer resolution determination for the last three layers (see Sect. 7.1.3) (Reproduced from M. Escher et al. [2.8], with permission of IOP Publishing Ltd.)

CHA only (2), and energy-filtered XPS imaging (3). Using excitation with high-brightness synchrotron radiation, an edge resolution (20–80%) of about 150 nm was obtained in the latter mode, as demonstrated in Fig. 2.19 [2.8].

Test measurements on different instruments have shown that XPS images can be routinely obtained with a spatial resolution below 20 μm . Today's useful resolution seems to be more like 10 μm , with a tendency to 1 μm and below. Development toward the 10 nm region is proceeding, but the interplay between high spatial resolution and low count rate (and therefore high acquisition times) sets a practical limit. Careful test measurements are indispensable to reasonably judge the useful resolution of a given instrument.

2.6 Software

Software for instrument steering, control, and data acquisition is distinguished from software for data processing and manipulation. Whereas the latter can be changed and extended by the analyst, the former is an integral part of the instrumentation. We cannot go into detail here, but the reader is recommended to carefully test the provided software for instrument operation that is important when making a decision about acquisition of an instrument. Although a good data processing software is of great value, it is less important when compared to the software for instrument operation. So-called expert systems [2.53,2.54] have been developed that use the numerous experimental experience compiled in current literature to guide the operator in finding the optimum instrumental setup for the problem under study.

References

- 2.1. J.F. O'Hanlon, *A User's Guide to Vacuum Technology*, 2nd edn. (Wiley, New York, 1989)
- 2.2. H.G. Tompkins, *The Fundamentals of Vacuum Technology*, 2nd edn. (AVS Monograph Series M-6, American Vacuum Society, New York, 1991)
- 2.3. V. Nemanic, T. Bogataj, *Vacuum* **50**, 431 (1998)
- 2.4. M.A. Kelly, ESCA, in *Concise Encyclopedia of Materials Characterization*, ed. by R.W. Cahn, E. Lifshin (Pergamon Press, Oxford, 1993), pp. 139–144
- 2.5. M. Cardona, L. Ley, Introduction, in *Photoemission in Solids I*, ed. by M. Cardona, L. Ley (Springer, Berlin/Heidelberg/New York, 1978), pp. 1–285
- 2.6. J.C. Rivière *Surface Analytical Techniques* (Clarendon Press, Oxford 1990)
- 2.7. J. Kritzek, K. Berresheim, G. Panzner, *Fres. Z. Anal. Chem.* **329**, 139 (1987)
- 2.8. M. Escher, N. Weber, M. Merkel, C. Ziethen, P. Bernhard, G. Schoenhense, S. Schmidt, F. Forster, F. Reinert, B. Kroemker, D. Funnemann, *J. Phys. Condens. Matter* **17**, 1329 (2005)
- 2.9. T.A. Carlson, *Surf. Interface Anal.* **4**, 125 (1982)
- 2.10. V. Schmidt, *Electron Spectrometry of Atoms Using Synchrotron Radiation* (Cambridge Scientific Press, Cambridge, 1997)
- 2.11. G. Paolucci, *J. Phys. Condens. Matter* **13**, 11293 (2001)
- 2.12. H.W. Nesbitt, M. Scaini, H. Hoechst, G.M. Bancroft, A.G. Schaufuss, R. Szargan, *Am. Miner.* **85**, 850 (2000)
- 2.13. K. Sato, Y. Nishimura, M. Imamura, N. Matsubayashi, H. Shimada, *Anal. Sci.* **17**(Suppl.), i1062 (2001)
- 2.14. K.O. Groeneveld, R. Mann, W. Meckbach, R. Spohr, *Vacuum* **25**, 9 (1975)
- 2.15. N.C. MacDonald, G.E. Riach, R.L. Gerlach, *Res. Dev.* **27**, 8 (1976)
- 2.16. J.A. Venables, A.P. Janssen, C.J. Harland, B.A. Joyce, *Philos. Mag.* **34**, 495 (1976)
- 2.17. J.D. Verhoeven, E.D. Gibson, *J. Phys. E Sci. Instrum.* **9**, 65 (1976)
- 2.18. S.C. Lee, Y. Irokawa, M. Inoue, R. Shimizu, *Surf. Sci.* **365**, 429 (1996)
- 2.19. H. Jaksch, J.P. Martin, *Fres. J. Anal. Chem.* **353**, 378 (1995)
- 2.20. K. Shimizu, T. Mitani, *New Horizons of Applied Scanning Electron Microscopy* (Springer, Berlin/Heidelberg, 2010)
- 2.21. H. Iwai, *J. Surf. Anal.* **16**, 114 (2009)
- 2.22. M. Kudo, AES Instrumentation and Performance, in *Practical Surface Analysis Vol. 1 (AES and XPS)*, 2nd edn., ed. by D. Briggs, M.P. Seah. (Wiley, Chichester, 1990), pp. 145–166
- 2.23. S. Hofmann, *Microchim. Acta* **114/115**, 21 (1994)
- 2.24. K. Yoshida, T. Yamada, *Jpn. J. Appl. Phys.* **18**, 201 (1978)
- 2.25. H.R. Kaufman, *J. Vac. Sci. Technol.* **15**, 272 (1978)
- 2.26. C.D. Coath, J.V.P. Long, *Rev. Sci. Instrum.* **66**, 1018 (1995)
- 2.27. A. Zalar, E.W. Seibt, P. Panjan, *Appl. Surf. Sci.* **101**, 92 (1996)
- 2.28. J.M.B. Bakker, *J. Phys. E Sci. Instrum.* **6**, 457 (1973)
- 2.29. J.B. Malherbe, J.M. Sanz, S. Hofmann, *Surf. Interface Anal.* **3**, 235 (1981)
- 2.30. S. Hofmann, A. Rar, *Jpn. J. Appl. Phys.* **37**, L785 (1998)
- 2.31. R. Hill, P.W.M. Blenkinsopp, *Appl. Surf. Sci.* **231–232**, 936 (2004)
- 2.32. F. Kollmer, *Appl. Surf. Sci.* **231–232**, 153 (2004)
- 2.33. S. Sun, C. Szakal, T. Roll, P. Mazarov, A. Wucher, N. Winograd, *Surf. Interface Anal.* **36**, 1367 (2004)
- 2.34. J.L.S. Lee, S. Ninomiya, J. Matsuo, I.S. Gilmore, M.P. Seah, A.G. Shard, *Anal. Chem.* **82**, 98 (2010)
- 2.35. S. Ninomiya, K. Ichiki, H. Yamada, Y. Nakata, T. Seki, T. Aoki, J. Matsuo, *Surf. Interface Anal.* **43**, 221 (2011)
- 2.36. R.E. Weber, W.T. Peria, *J. Appl. Phys.* **38**, 4355 (1967)
- 2.37. N.J. Taylor, *J. Vac. Sci. Technol.* **6**, 241 (1969)
- 2.38. P.W. Palmberg, *J. Vac. Sci. Technol.* **12**, 379 (1975)

- 2.39. P. Staib, U. Dinklage, J. Phys. E Sci. Instrum. **10**, 914 (1977)
- 2.40. M.P. Seah, Electron and Ion Energy Analysis, in *Methods of Surface Analysis*, ed. by J.M. Walls (Cambridge University Press, Cambridge, 1985), pp. 57–86
- 2.41. J.C. Riviere, Instrumentation, in *Practical Surface Analysis Vol. 1 (AES and XPS)*, 2nd edn., ed. by D. Briggs, M.P. Seah (Wiley, Chichester, 1990), pp. 19–83
- 2.42. P.W. Palmberg, G.K. Bohn, J.C. Tracy, Appl. Phys. Lett. **15**, 254 (1969)
- 2.43. H. Sar-El, Rev. Sci. Instrum. **38**, 1210 (1967)
- 2.44. D. Varga, A. Kover, L. Redler, Nucl. Instrum. Phys. Res. A **238**, 393 (1985)
- 2.45. K. Goto, H. Iwata, Y. Sakai, J. Vac. Soc. Jpn. **31**, 906 (1988)
- 2.46. K. Goto, N.N. Rahman, Y.Z. Jiang, Y. Asano, R. Shimizu, Surf. Interface Anal. **33**, 245 (2002)
- 2.47. E.N. Sickafus, D.M. Holloway, Surf. Sci. **51**, 131 (1975)
- 2.48. S. Hofmann, J.M. Sanz, Fres. Z. Anal. Chem. **314**, 215 (1983)
- 2.49. G.B. Hoflund, D.M. Minahan, J. Catal. **126**, 48 (1996)
- 2.50. P. Coxon, J. Krizek, M. Humpherson, I.R.M. Wardell, J. Electron Spectrosc. **52**, 821 (1990)
- 2.51. U. Vohrer, C. Blomfield, S. Page, A. Roberts, Appl. Surf. Sci. **252**, 61 (2005)
- 2.52. Sample BAM-L002, *Nanoscale Strip Pattern for Length Calibration and Testing of Lateral Resolution* (Bundesanstalt fuer Materialforschung (BAM), Berlin, 2003)
- 2.53. J.E. Castle, M.A. Baker, J. Electron Spectrosc. **105**, 245 (1999)
- 2.54. J.E. Castle, C.J. Powell, Surf. Interface Anal. **36**, 225 (2004)

Chapter 3

Qualitative Analysis (Principle and Spectral Interpretation)

3.1 Introduction: Notation of Atomic Electron Levels

Electron spectroscopy is based on the element-specific binding energy of electrons in the atomic shell and their determination by electron spectrometers.

The notation of the electrons involved is standardized but different in XPS and AES. Whereas the spectroscopic notation is used in XPS, the X-ray notation is used in AES [3.1–3.3]. Table 3.1 gives a survey of the electron notations. The principal quantum numbers 1, 2, 3, 4, ... are equivalent to K, L, M, N, ... shells, the angular momentum 0, 1, 2, 3, ... is denoted by s, p, d, f, and the total angular momentum is given by the absolute value of the sum of angular and spin momentum ($j = |\vec{l} + \vec{s}|$ in the so-called j - j coupling; for the total angular momentum L–S coupling (Russell-Saunders coupling) and for intermediate coupling, see, e.g., [3.2, 3.3]). A photoelectron can be attributed to one electron level (nl_j), for example, $3p_{3/2}$. In contrast, an Auger transition involves three electron levels and is therefore notified as, for example, by $KL_{2,3}L_{2,3}$, where the subscripts are often omitted, and by KVV if the valence band is involved (see Sect. 3.3).

The kinetic energy of an emitted electron is measured by the electron spectrometer. This value is characteristic for the binding energies of the involved energy levels. However, the respective connection is different for AES and XPS, as outlined in the following.

3.2 Qualitative XPS

3.2.1 Principle of XPS Analysis

Photoelectron emission can be imagined as a simple three-stage process: (1) X-rays interact with the electrons in the atomic shell and photoelectrons (and Auger electrons) are generated, (2) part of these electrons move through the solid to the

Table 3.1 Electron shell levels in spectroscopic (XPS) and X-ray (AES) notation based on principal quantum number, n ; orbital angular momentum, l ; spin angular momentum, s ; and total angular momentum, j

Quantum numbers				Spectroscopic notation (XPS)	X-ray notation (AES)
n	l	s	j		
1	0	$+1/2, -1/2$	$1/2$	$1s_{1/2}$	K
2	0	$+1/2, -1/2$	$1/2$	$2s_{1/2}$	L_1
2	1	$-1/2$	$1/2$	$2p_{1/2}$	L_2
2	1	$+1/2$	$3/2$	$2p_{3/2}$	L_3
3	0	$+1/2, -1/2$	$1/2$	$3s_{1/2}$	M_1
3	1	$-1/2$	$1/2$	$3p_{1/2}$	M_2
3	1	$+1/2$	$3/2$	$3p_{3/2}$	M_3
3	2	$-1/2$	$3/2$	$3d_{3/2}$	M_4
3	2	$+1/2$	$5/2$	$3d_{5/2}$	M_5
					etc.

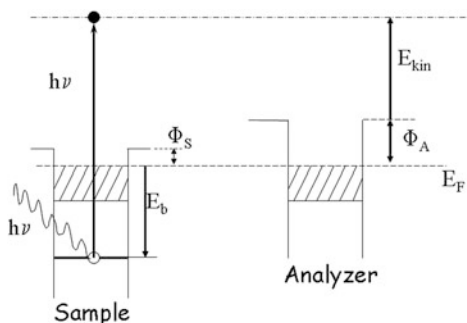


Fig. 3.1 Schematic explanation of relevant energy terms in XPS of solid surfaces. An X-ray with energy, $h\nu$, generated a vacancy in a core electron level with binding energy, E_b . The emitted photoelectron has to overcome the work function of the sample, Φ_S , and the energy measured by the analyzer with reference to the Fermi Energy E_F is the emitted energy diminished by the difference between the analyzer work function Φ_A and Φ_S

surface and are subject to various scattering processes (those which are inelastically scattered creating the background), and (3) electrons reaching the surface are emitted in the vacuum (after surmounting the work function threshold). The kinetic energy of a photoelectron is schematically derived from the energy level scheme shown in Fig. 3.1. An X-ray with characteristic energy $h\nu$ transfers its energy to a core electron with binding energy E_b (with reference to the Fermi level, E_F). The kinetic energy of that electron in vacuum is given by $h\nu - E_b - \Phi_S$, where Φ_S is the work function of the sample. With Φ_A the work function of the analyzer, according to Fig. 3.1, the kinetic energy E_{kin} measured by the analyzer is given by $E_{kin} = h\nu - E_b - \Phi_S - (\Phi_A - \Phi_S) = h\nu - E_b - \Phi_A$, that is,

$$E_b = h\nu - E_{kin} - \Phi_A \quad (3.1)$$

Equation 3.1 is fundamental for qualitative XPS. Because the sample work function cancels, the photoelectron energy is known and the analyzer work function is constant, the kinetic energy determines the binding energy and vice versa. Usually, the analyzer work function (about 4–5 eV) is empirically found by setting the energy scale to zero at the Fermi edge of reference samples, for example, Ag or Ni [3.4, 3.5]. After energy calibration, Φ_A in (3.1) becomes zero, and E_b and E_{kin} are directly related through $E_{kin} = h\nu - E_b$. As indicated in Fig. 3.1, (3.1) is only valid for conductive samples where the Fermi energy level is equal for sample and analyzer. For insulators or in case of charging, the Fermi level is not well defined, and the energy scale may shift (see Sect. 8.5.1, charging of insulators).

Two different types of X-ray sources are generally used: Mg K_α ($h\nu = 1253.6$ eV, linewidth 0.70 eV) and Al K_α ($h\nu = 1486.6$ eV, linewidth 0.85 eV) (see Sect. 2.2).

3.2.2 Photoelectron Spectra: Elemental Identification

XPS spectra are usually given by intensity (counts per second) as a function of the binding energy. Because binding energy and kinetic energy have a different sign, the binding energy scale is plotted with increasing energy from right to left, somehow strange as compared to usual coordinates. Besides photoelectron core level and valence band peaks, spectra contain Auger electron peaks (X-ray-induced Auger electron spectra, often called XAES) (see Fig. 3.2) and may further contain satellite peaks and energy loss peaks (see Sect. 3.2.6). Photoelectron spectra of the elements are compiled in handbooks [3.6–3.9], generally provided by the instrument manufacturers, and in Internet databases [3.10, 3.11]. A collection of further databases is found in Ref. [3.12].

An example of a wide scan XPS (survey) spectrum is shown in Fig. 3.2, where the photoelectron peaks of magnesium (Mg 1s, 2s, 2p) and the KLL Auger peaks are indicated. Figure 3.3 shows the narrow scan (individual scan) of the Mg 2s peak which reveals the satellite plasmon structure. Valence band spectra can also be observed, as demonstrated in Fig. 3.4. Setting the 50% value of the Fermi edge to binding energy zero adjusts the energy scale with reference to the Fermi level. A comparison with handbook and database spectra [3.6–3.9, 3.11] simplifies elemental analysis, even when some charging occurs (see Sect. 8.5.1).

Using simple X-ray sources without monochromator (Mg/Al) (see Sect. 2.2), the main peak ($K\alpha_{1,2}$) is accompanied by satellite peaks caused by X-ray satellite lines such as $K\alpha_{3,4}$, etc. [3.13] (see Fig. 2.6). The relative intensity of the preponderant $K\alpha_{3,4}$ peak is about 10% of the main peak intensity, and its shift is about 10 eV to lower binding energy (see Table 2.2) for exact energies and intensities. Because their energy and intensity relative to the main peak is well known, the source satellite peaks can easily be subtracted from the total spectrum. Most modern instruments work with monochromatic X-rays where this kind of satellites does not exist (see Sect. 2.2.2).

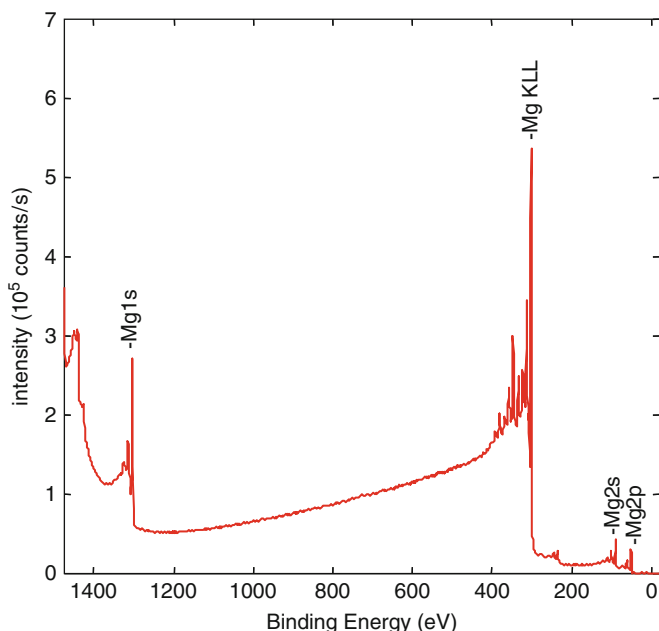


Fig. 3.2 Survey XPS spectrum of a sputter-cleaned Mg surface in the CRR mode (constant retarding ratio, $\Delta E/E = \text{const.}$, see Sect. 2.5.2). Besides the Mg 1s, Mg 2s and Mg 2p photoelectron peaks, the high-intensity Mg $\text{KL}_{23}\text{L}_{23}$ Auger electron peak is also recognized. The small feature at binding energy 242 and 244 eV is the $2p_{3/2,1/2}$ doublet of Ar implanted during sputter cleaning (see Sect. 8.3.2.1). The Auger parameter (see Sect. 3.2.4) is given by the energy difference between the Mg $\text{KL}_{23}\text{L}_{23}$ and the Mg 1s peaks, (see Sect. 3.2.4)

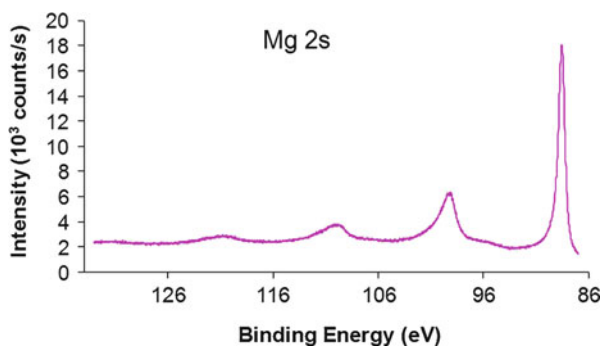


Fig. 3.3 Split scan or individual scan (detail scan) of the Mg 2s peak (constant analyzer energy (CAE) mode, $\Delta E = \text{const.}$, see Sect. 2.5.2). Besides the most intense Mg 2s peak, bulk plasmon peaks with a multiple of about 12 eV kinetic energy loss from the photoelectron main peak are recognized until the third harmonic. A small hump on the right side of the first bulk plasmon loss indicates the surface plasmon energy loss which is by a factor of $1/\sqrt{2}$ lower than that of the bulk plasmon (see Sect. 3.2.6)

Fig. 3.4 High-resolution (10 eV pass energy) valence band spectrum of Ag. The binding energy scale is not calibrated

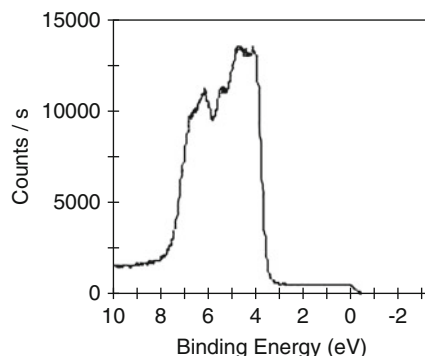


Table 3.2 Spin-orbit splitting intensities

Subshell	j values	Intensity ratio (peak areas)
s	1/2	–
p	1/2, 3/2	1:2
d	3/2, 5/2	2:3
f	5/2, 7/2	3:4

While inelastic scattering causes the increased but smoothly varying background on the high binding energy (= low kinetic energy) side of the main elemental peak, frequently, plasmon excitation loss peaks are observed above the background. They are caused by discrete losses due to collective electron oscillations in the valence band [3.14–3.17] and are typically of the order of 10–20 eV. As an example, Fig. 3.3 shows plasmon peaks in the Mg 2s spectrum, where even the second and third harmonics can be observed. (At the first plasmon peak, a slight hump indicates the surface plasmon of which the loss energy is about $1/\sqrt{2}$ times that of the – usually more intense – bulk plasmon [3.14].)

A doublet peak structure is observed for electron transitions from levels with total angular momentum higher than s, that is, for p, d, f. Whereas all s peaks ($l = 0$) are singlets, all other levels are doublets with slightly different energies. Because the unpaired electron left after photoemission has either a parallel or an antiparallel orientation to the orbital momentum (spin-orbit coupling), there is an energy difference. The energy separation of the two adjacent peaks of the same orbit (same n , l) increases with atomic number and decreases for the same n with higher l values. For example, the binding energy of the $2p_{1/2}$ and $2p_{3/2}$ is practically the same for magnesium ($E_b = 50$ eV), whereas for silicon it is $E_b(2p_{3/2}) = 99$ eV, $E_b(2p_{1/2}) = 100$ eV. The relative intensities of the doublet peaks are given by the ratio of their degeneracy ($2j + 1$), as compiled in Table 3.2. Particularly for overlapping doublet peaks in different bonding states, peak decomposition in components appears more complicated. However, the known and fixed relation between doublet peak intensities facilitates decomposition as demonstrated in Fig. 3.5 for the Ta $4f_{5/2,7/2}$ doublet in different valence states.

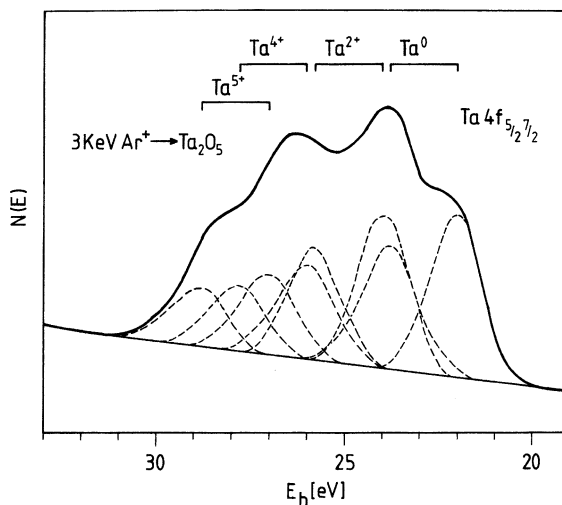


Fig. 3.5 Decomposition of the Ta $4f_{5/2,7/2}$ doublet peak structure measured at a Ta_2O_5 sample after bombardment with 3 keV Ar^+ ions. The chemical shift of the four doublets indicated is about 1 eV per valence, the doublet distance is 1.8 eV and constant, the peak width is 1.6 eV, and the area ratio of $(5/2)/(7/2)$ after Table 3.2 is 3:4. These facts are helpful for the trial-and-error peak fitting procedure with Gaussians (*dashed lines*) because of the low analyzer resolution (see Sect. 3.1.7) (From S. Hofmann and J.M. Sanz [3.20])

3.2.3 Chemical Shift of Photoelectron Peak Energy

Any change in the bonding state of an atom gives rise to changes in the observed spectral characteristics: binding energy, peak width and shape, valence band changes, and sometimes bonding satellites. The change in core electron binding energies, the “chemical shift,” was the major driving force in developing XPS and is indeed its major application today.

Chemical bonding in a compound usually causes a change of the binding energy as compared to bonding in the pure element which is called “chemical shift” (Fig. 3.5). Ignoring final-state effects, the chemical shift can be explained by the effective charge potential change on an atom [3.13–3.18]. For example, when an atom is bonded to another one with higher electronegativity, a charge transfer to the latter occurs and the effective charge of the former becomes positive, thus increasing the binding energy. Vice versa, the binding energy of the atom with higher electronegativity is decreased. Therefore, metal oxides typically show a shift of the metal XPS peaks to higher binding energies, with increasing shift with the valence state of the metal atom, as shown in Fig. 3.5. For many oxides, there exists a direct relation between the formation enthalpy and chemical shift. The full theory of chemical shift includes screening and relaxation effects for which the reader is referred to Refs. [3.13–3.18].

In practice, references to standard spectra of compounds are used to interpret measured chemical shifts. Tabulated values from the literature are often helpful

(e.g., handbooks [3.6, 3.7] and databases [3.10–3.12]). Frequently, two different bonding states are observed in one spectrum, but with a chemical shift smaller than the peak width. In that case, a careful decomposition of the measured peak is necessary to disclose the energy and intensity of each component (see Fig. 3.5). If two spectra with the same element in different binding states are compared, special care has to be taken to avoid even small charging effects which may obscure absolute binding energies. In this case, using the Auger parameter is helpful (see Sect. 3.2.4).

For nonconducting samples, surface charging occurs which tends to shift the energy of the peaks. For low level charging, reference to a standard spectrum, usually of adventitious carbon ($E_b = 285 \pm 0.2$ eV), can be used. For experimental charge compensation methods, see Chap. 8. For very thin films on metals or semiconductors with different Fermi levels, (p/n interfaces), local charges (band bending) will have a direct influence on the XPS peak energy. While this effect compensates in the Auger parameter, electronic screening by the metal substrate may influence the total polarization and therefore the Auger parameter [3.19] (see below).

3.2.4 Auger Parameter

A convenient means to avoid the effect of charging on the identification of a chemical bond is the so-called Auger parameter [3.86]. Additionally measured in a survey spectrum (see Fig. 3.2) are Auger spectra, which often show a larger chemical shift than photoelectron spectra. The Auger parameter, α_{AP} , is defined as the difference in kinetic energy between the most prominent Auger and photoelectron peaks of the same element recorded in the same spectrum [3.21]

$$\alpha_{AP} = E_k(W, X, Y) - E_k(W), \quad (3.2)$$

where $E_k(W, X, Y)$ is the kinetic energy of the Auger transition involving the core energy levels W, X, and Y and $E_k(W)$ is the kinetic energy of the photoelectron from core level W (which can also be a different core level). The Auger parameter defined by (3.2) is independent of static charging and of work function energy but depends on the X-ray energy. Therefore, the so-called modified Auger parameter, α'_{AP} , is generally used which is given by α plus the excitation energy $h\nu$ [3.22, 3.23]

$$\alpha'_{AP} = \alpha_{AP} + h\nu = h\nu + E_k(W, X, Y) - E_k(W) = E_k(W, X, Y) + E_b(W) \quad (3.3)$$

As seen from the difference in (3.2), the analyzer work function Φ_A cancels because it is the same for Auger- and photoelectrons, and for similar reason, charging potentials also cancel. The advantages of the (modified) Auger parameter are:

1. For a given chemical state, there is a well-defined and fixed energy difference between a given Auger peak energy and a given photoelectron peak energy.

2. No charge correction is necessary for the measurement of the photoelectron and Auger peaks (see Sect. 8.5.1.1).
3. No work function correction is necessary, and Fermi and vacuum levels can equally be applied.
4. A shift in the extra-atomic relaxation energy (i.e., polarization energy shift) can be determined even in cases where there is no chemical shift of the photoelectron energy [3.19, 3.24, 3.25].

The main difference in chemical shift of the photoelectron binding energy and that of the Auger electron kinetic energy is given by the difference in the final-state extra-atomic relaxation energy. The latter, in a core Auger transition, is a one core hole state for the photoelectron and an (additional) two core hole state for the Auger electron. Thus, the energy shift between two different binding states for the photoelectron, $\Delta E_b(W)$, and for the kinetic energy of the Auger electron, $\Delta E_k(W, X, Y)$, in the simplest approximation is given by [3.23, 3.26–3.28]

$$\Delta E_b(W) = \Delta V_i - \Delta R_{ea}, \quad (3.4)$$

$$\Delta E_k(W, X, Y) = -(\Delta V_i - 3\Delta R_{ea}), \quad (3.5)$$

where ΔV_i reflects the initial-stage charge distribution and ΔR_{ea} reflects the final-state extra-atomic relaxation energy. The latter represents the electronic response of the molecular environment of the atom to the creation of the core hole. Keeping in mind that the kinetic energy changes oppositely to the binding energy the shift in the Auger parameter according to (3.3) is given by the sum of (3.4) and (3.5),

$$\alpha'_{AP} = E_k(W, X, Y) + E_b(W) = 2\Delta R_{ea} \quad (3.6)$$

The shift in the Auger parameter after (3.6) provides a simple and direct measurement of the shifts in the extra-atomic relaxation energy (polarization energy) and also of ΔV_i . As pointed out by Thomas [3.27] and by Riviere et al. [3.28], (3.4)–(3.6) are strictly valid only if the chemical shifts of the different core levels involved in the core ionization and the Auger processes are equal. Frequently this is not the case, and the proportional relation has to be replaced by a linear relation between the shifts with slope $\neq 1$ [3.28].

A two-dimensional representation of the modified Auger parameter is the so-called Wagner plot, in which the most prominent Auger peak energy is plotted against the photoelectron peak energy of the same element [3.6, 3.23]. As shown in the Wagner plot for silicon compounds in Fig. 3.6, parallel straight lines with gradient 1 denote the Auger parameter of an element in the respective compound. Because the Auger parameter approximately represents the relaxation energy, compounds with higher relaxation energy lie in the upper part of the Wagner plot. For constant valence electron number in the final state, the relaxation energy will depend essentially on the dipole polarizability of the nearest neighbor ligands of the core-ionized atom [3.24, 3.25]. Thus, information about the local electronic structure can be obtained by XPS. An example was presented by Jeurgens et al. [3.19] who demonstrated that the transition from amorphous to crystalline Al_2O_3

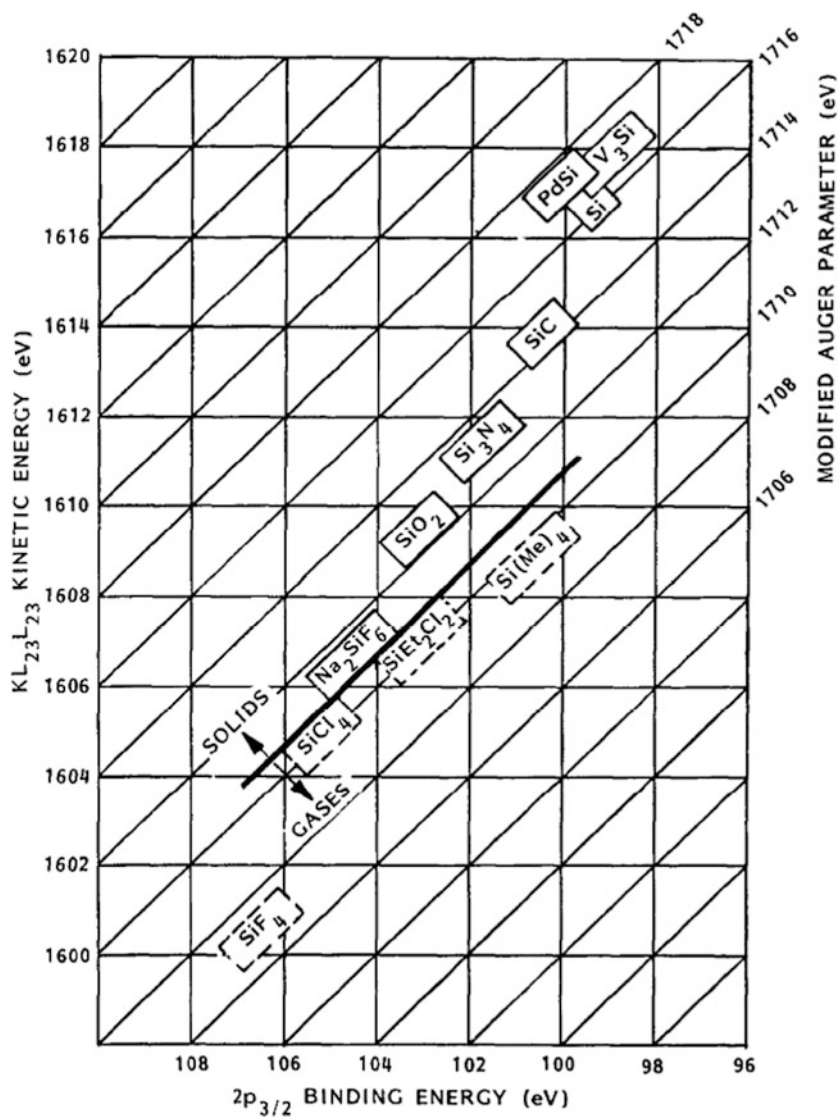


Fig. 3.6 Wagner plot for silicon. The Si $KL_{2,3}L_{2,3}$ Auger peak energy is plotted against the Si $2p_{3/2}$ photoelectron binding energy for the compounds indicated (Reproduced from C.D. Wagner and A. Joshi [3.23], with permission of Elsevier B.V.)

is accompanied by a shift of the difference in the respective Auger parameters of Al and O which can be measured in the same spectrum. This was attributed to a decrease of the polarization energy of oxygen from 0.4 to 0.1 eV.

3.2.5 Valence Band Spectra

Valence band spectra represent a convoluted picture of the electron density of states, given by the band structure of solids (see Fig. 3.4). Therefore, they can be used to distinguish between different structures of materials. For example, TiO_2 shows different valence band spectra in its rutile and anatase structures [3.7]. Valence band XPS studies on TiN and $(\text{Ti,Al})\text{N}$ hard coatings have shown that the degree of metal-ligand bonding can be correlated with the stoichiometry and with mechanical properties of the coating [3.29] (Sect. 9.1.1). Although the information gained is most often rather complex, valence band spectroscopy has a yet to be exploited potential for detailed surface chemistry studies.

3.2.6 Satellite Peaks

Besides the photoelectron and Auger electron peaks, so-called satellite peaks can occur in the spectrum because of:

- (1) Satellite peaks without monochromator
 - (2) Plasmon loss peaks
 - (3) Shake-up, shake-off, and multiplet splitting
- (1) *Satellite peaks without monochromator*: Satellite peaks from non-monochromatic Mg and Al sources are well known and can be easily subtracted from any spectrum (see Table 2.2 and Fig. 2.6). They do not appear when monochromatic X-ray sources are used.
 - (2) *Plasmon Loss Peaks* (see Figs. 3.3 and 3.7): Bulk and surface plasmon peaks are of extrinsic plasmons which have their origin in collective oscillations of an electron gas excited by interactions with electrons of sufficient kinetic energy. The bulk or volume plasmon frequency, $h\nu_p$, in metals is given by the electron density, n_e , in the valence band, $h\nu_p \propto (n_e)^{1/2}$ [3.13, 3.14]. This means sensitivity to electron structure changes as in intermetallic phases [3.30] and covalent semiconductor compounds (see Sect. 9.1.5). Surface plasmon peaks arise from two-dimensional oscillations in surface layers. Their intensity is usually below that of the volume plasmon, and their frequency is lower by about the square root of 2. The order of magnitude of the bulk plasmon is typically 10–30 eV, with higher harmonics ($2h\nu_p$, $3h\nu_p$) having strongly decreasing intensities (see Fig. 3.2).

Whereas the extrinsic plasmons arise after photoelectron emission and therefore are part of the background, intrinsic plasmons are excited by interaction of the emitted electron with the core hole. They lead to a loss of emission intensity already at the spot of electron emission, and, therefore, they are not included in the derivation of the inelastic mean free path. As a consequence, they diminish the Scofield ionization cross section (see Sect. 4.3.3) which has to be corrected by an element (and matrix)

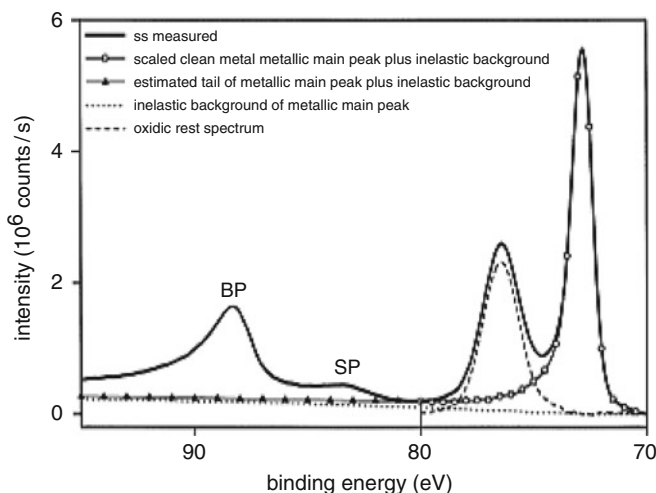
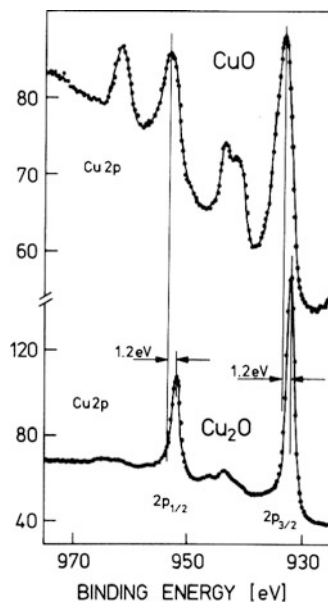


Fig. 3.7 Al 2p spectrum of oxidized Al, showing the core level peak for metal and oxide as well as the first (extrinsic) peaks for bulk (BP) and surface (SP) plasmon associated with the metal peak. After subtraction of the “universal” Tougaard background (see Sect. 4.1.1), the metal peak is fitted by a Doniach–Sunjic (D–S) line shape (actually two D–S lines for the nonresolved $2p_{1/2}$ and $2p_{3/2}$ spin doublet (see Sect. 3.2.2)) convoluted with a Gaussian with tail cutoff at 80 eV binding energy. The dashed peak is the remaining (symmetric) oxide peak (Reproduced from L.P.H. Jeurgens et al. [3.31], with permission of Elsevier B.V.)

specific amount. Usually, this amount is given by a correction term (in percentage of the total primary peak intensity) for the respective elements and compounds. The contribution is particularly high for the elements Si, Mg, and Al [3.14]. For example, in Al, the intrinsic bulk plasmon contribution is 14% and that of the intrinsic surface plasmon is 2% of the Al 2p peak, as determined by Jeurgens et al. [3.31]. Because intrinsic losses almost vanish when Al is in an Al_2O_3 bonding state, comparison of the relative peak area changes of the 2p peak areas of Al and Al^{3+} for different oxide layer thickness of oxidized discs reveals the amount of intrinsic contributions [3.29] (for details, see Sect. 4.3.3). Consequently, for a correct quantitative evaluation of oxide layer thickness on metals, either the different sensitivity factors (i.e., corrected Scofield cross sections) have to be used for metal and oxide peaks, or the respective intrinsic plasmon contributions have to be added to the metallic XPS peak intensity. The same holds for determination of attenuation length values by the layer thickness method.

- (3) *Shake-up, shake-off, and multiplet splitting* [3.3, 3.13, 3.14, 3.18]: Rearrangement of the electrons after photoemission often results in an excited state a few eV above the ground state. The photoelectron suffers a loss in kinetic energy of this magnitude that gives rise to a peak at a few eV to the higher binding energy side of the main peak. In inorganic systems, these satellite peaks can be quite strong, particularly for transition metals and rare earth metals with unpaired electrons in the 3d or 4f shells. A well-known

Fig. 3.8 XPS spectra of the Cu $2p_{1/2,3/2}$ core levels in Cu_2O . The CuO spectrum shows strong shake-up satellites at about 10 eV higher binding energies (Reproduced from S. Hüfner [3.13]. Copyright by Springer Verlag 1979)



example is the Cu 2p peak that shows a strong shake-up satellite in the two valence state (CuO) but an almost negligible one in the monovalent state, that is, Cu_2O (see Fig. 3.8). Interaction of photoelectrons with valence band electron may cause shake-off features. Photoelectrons in metals with high electron density near the Fermi edge may suffer energy losses by excitations in empty states above the Fermi edge. Therefore, instead of discrete losses, a tail on the low kinetic energy (i.e., high binding energy) side of the core level peak is generated, resulting in the typical asymmetric peak shape of many metals (e.g., Al, Pt) as shown in Sect. 3.2.7 (Doniach–Sunjic line shape).

If there is a net spin of an atom due to unpaired electrons in either the valence band or shallow core levels, an exchange interaction can occur during an s-electron emission because the remaining s-electron is also unpaired, giving rise to a doublet of the s-peak (multiplet splitting [3.3, 3.14, 3.18, 3.34]). For example, some transition metal ions (Mn^{2+} , Cr^{3+} , Fe^{3+}) show multiplet splitting for the 3s-peak [3.6].

3.2.7 XPS Line Shapes

3.2.7.1 Gaussian-Lorentzian Line Shape

The basic line shape of the photoemission process is given by the Lorentzian function [3.14, 3.35] (see Fig. 3.8). The natural line width ΔE_0 is determined by the lifetime of the core hole state left by photoemission (lifetime broadening) and can be estimated by the uncertainty principle as

$$\Delta E_0 = \frac{h}{\tau} = \frac{4.1 \times 10^{-15}}{\tau} \quad (3.7)$$

with Planck constant h in eV s and lifetime τ in seconds. For example, a typical lifetime of about 10^{-14} s corresponds to a line width of 0.4 eV as found for the $\text{Ag}3d_{5/2}$ peak.

In crystalline materials, atomic vibrations impose a small Gaussian broadening which is temperature dependent [3.18]. In addition, a Gaussian broadening is caused by the analyzer. This instrumental broadening function is directly given by the resolution of the analyzer [3.36] (see Sect. 2.5.2). Thus, usually the line shape of an XPS peak is well represented by a combination of both line shape types using a mixed Gaussian–Lorentzian function or, physically more correct, using convolution of a Lorentzian with a Gaussian (Voigt function) [3.36, 3.37]. Empirical tail functions can be added to take care of asymmetric lines which are caused by loss processes (see Sect. 3.2.6) (see Table 3.3).

3.2.7.2 Doniach–Sunjic Line Shape

In contrast to the symmetric Lorentzian (natural or atomic) line shape, the XPS line in conductors is asymmetric around the peak energy and typically skewed with a tail to higher binding energy which is caused by many-body interactions of the photoelectron with free electrons at the Fermi edge as shown by Doniach and Sunjic [3.38]. The Doniach–Sunjic (D–S) line shape is given by

$$I_{\text{DS}}(E) = \frac{(1 - \alpha_{\text{DS}}) \cos \left\{ \pi \alpha / 2 + (1 - \alpha_{\text{DS}}) \arctan \left[(E_{\text{b}}^0 - E) / (\Delta E_0 / 2) \right] \right\}}{\left[(E_{\text{b}}^0 - E)^2 + (\Delta E_0 / 2)^2 \right]^{(1 - \alpha_{\text{DS}}) / 2}} \quad (3.8)$$

where E_{b}^0 is the binding energy of the respective subshell core level, ΔE_0 is the FWHM of the natural (Lorentzian) line, and α_{DS} the characteristic asymmetry factor ($0 \leq \alpha_{\text{DS}} \leq 0.5$) [3.39] which is determined by the phase shift for scattering of conduction electrons from the hole potential and is largest for s-type screening (e.g., 0.20 for Na, 0.13 for Mg, and 0.12 for Al) [3.39]. For $\alpha_{\text{DS}} = 0.1$ and 0.2, (3.8) is plotted in Fig. 3.9 together with the natural Lorentzian line for which $\alpha_{\text{DS}} = 0$, and a Gaussian with the same FWHM ($= 0.8$ eV). The exact shape of the D–S curve depends on the transition probability for excitation of energy E which is proportional to the average density of states of electrons and holes around the Fermi edge, $A(E)$ [3.40] (Fig. 3.10a). According to Wertheim and coworkers [3.39, 3.40], the line shape depends on $A(E)$ and changes gradually from the basic Lorentzian (no interaction) to the D–S function (maximum interaction, constant $A(E)$), as depicted in Fig. 3.10b for different density of state distributions. From Fig. 3.10, it is obvious that changes of electron densities in the valence band, for example, by alloy formation, have an influence on the D–S function [3.41]. Appropriate line shapes for fitting experimental peaks are summarized in Table 3.3.

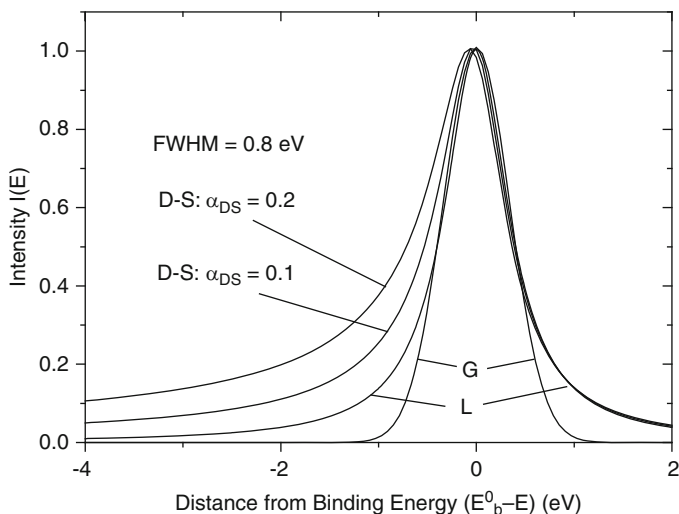


Fig. 3.9 Lorentz (L), Gauss (G), and Doniach–Sunjić (D–S) functions for line shape peak fitting in XPS after (3.8), normalized to maximum intensity = 1 and FWHM = 0.8 eV. The D–S function is plotted for different asymmetry parameters $\alpha_{DS} = 0.1$ and 0.2 (3.3b). For $\alpha_{DS} = 0$, the D–S function is identical to the Lorentz function (L). While the original line shapes are Lorentzian (e.g., insulators) or D–S type (metals), they have always to be convoluted by the Gaussian (G) given by the analyzer resolution. Note the influence of α_{DS} on the FWHM of the line, and the small but measurable shift to higher binding energy with increasing α_{DS}

Usually, α_{DS} is found empirically by fitting the experimental XPS metal peak with a Gaussian convolution of the appropriate D–S function. A typical result is shown in Fig. 3.7 for the Al 2p metal peak [3.32]. The oxide Al 2p peak is fitted with a symmetrical, mixed Lorentz–Gaussian function.

3.2.7.3 Line Fitting and Peak Width

Correct peak shapes are essential for quantitative evaluation of overlapping spectra, for example, Al 2p in Al and Al oxide (Fig. 3.7). A survey is given in Table 3.3. For many metals, assuming a symmetric peak for peak fitting gives erroneous results [3.42]. Modern instrumental software has capabilities for using asymmetric peak shapes, either theoretical or empirical. Of course peak fitting can only be done correctly after background subtraction has been performed (see Sect. 4.1.1). The accuracy of decomposition of overlapping peak components depends on the peak width, usually given by the full width at half maximum (FWHM), ΔE , which is a convolution of several contributions which (in Gaussian approximation) add up in quadrature as

$$\Delta E = (\Delta E_0^2 + \Delta E_{is}^2 + \Delta E_p^2 + \Delta E_{WA}^2)^{1/2} \quad (3.9)$$

where ΔE_0 is the natural line width of the core level, ΔE_{is} denotes further screening effects from phonon and local configuration interactions, ΔE_p is given by the line

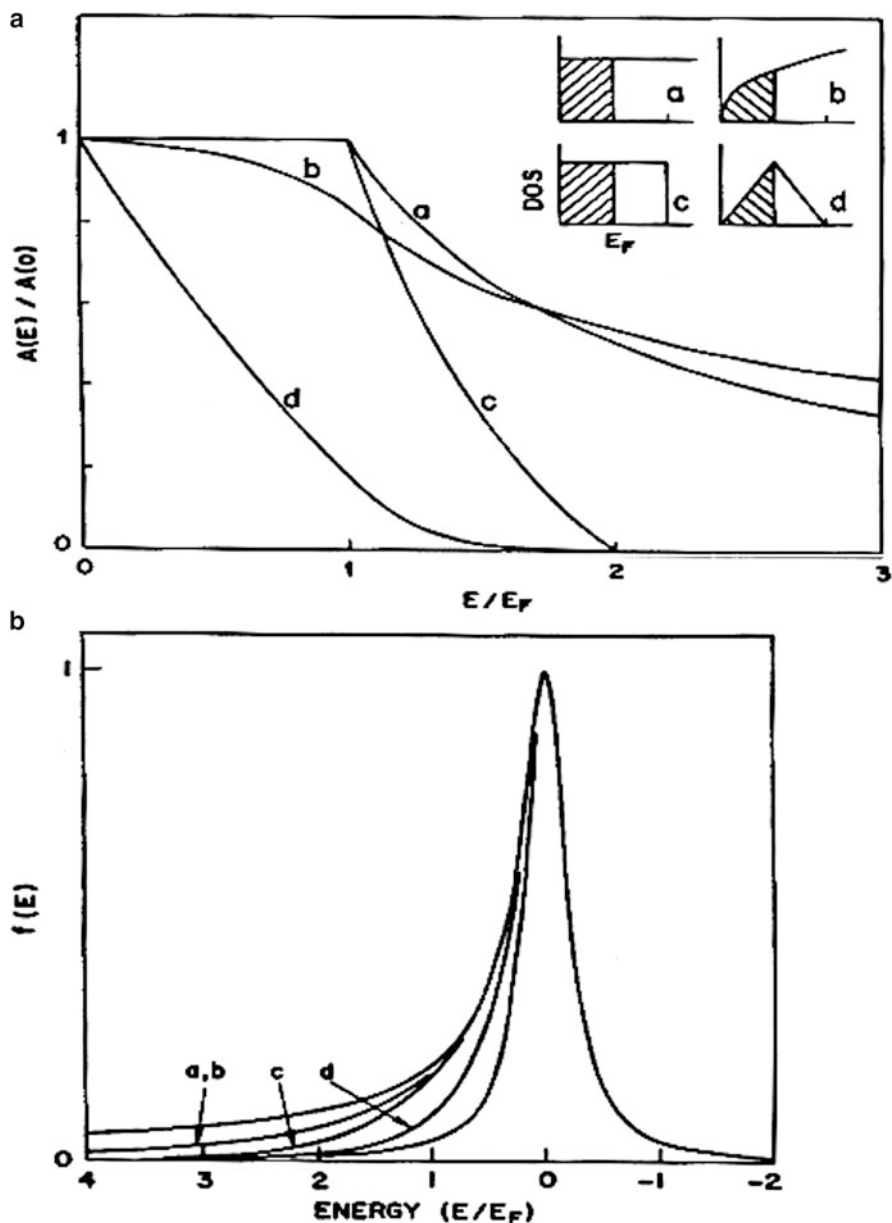


Fig. 3.10 Effect of the density of states on the photoemission line shape of a metal. (a) The relative average electron-hole pair excitation function $A(E)/A(0)$ is shown, for the occupied and empty electron states depicted in the inset of (a) (a, b, c, d). (b) Line shapes corresponding to the density of states given in (a). All calculated line shapes are between the outer Doniach–Sunjic (D–S) function ((3.3b), $\alpha_{DS} = 0.2$) and the inner Lorentzian function (FWHM = 0.4 eV). Note that a cutoff energy on the *left* side is imposed by the width of the conduction band as clearly seen for cases c, d [3.41]. This cutoff can also be arbitrarily introduced to overcome the infinity value of the integral over the D–S function (Fig. 3.9) (Reproduced from G.K. Wertheim and P.H. Citrin [3.39]. Copyright by Springer Verlag 1978)

Table 3.3 Survey of practical XPS line shapes and peak fitting

	Insulators, semiconductors, and metals with low electron state densities around the Fermi level	Metals with high electron state density around the Fermi level	Any photoelectron peak
Basic (natural) line shape	Lorentzian	Doniach–Sunjic (D-S)	Polynomial fit of measured line shape of reference
Modified, experimentally measured line shape for decomposition of overlapping peaks	(a) Mixed Lorentzian–Gaussian (b) Gaussian convolution of Lorentzian (c) Tail function added	Gaussian convolution of D-S line	Fit of measured reference line shape to overlapping peaks

width of the excitation source (see Sect. 2.2.1), and ΔE_{WA} is the analyzer resolution (see Sect. 6.2.2). Whereas ΔE_{p} and ΔE_{WA} are given by the instrument and its settings, ΔE_0 and ΔE_{is} are determined by the nature of the transition and by the atomic environment. According to the uncertainty principle, the natural line width is inversely proportional to the lifetime of the ionic state after photoemission (see (3.7)). Narrow lines such as Ag 3d_{5/2} ($\Delta E_0 = 0.35$ eV) are often used for testing the analyzer resolution. Lines of metals in oxide bonds are usually broader because of an increased term ΔE_{is} [3.18] (see Fig. 3.7). If the latter and ΔE_{WA} are preponderant, a simple fitting by Gaussian peaks is of sufficient accuracy, as demonstrated in Fig. 3.5. For spin doublet peaks, the relative intensities (= peak areas) are useful for correct peak decomposition (see Table 3.2).

3.2.8 Emission Angle Effects

3.2.8.1 Amorphous Materials

Crystalline effects can be ignored for amorphous and also for polycrystalline samples, if the crystallite size is much smaller than the analyzed area. Provided the instrument's analyzer-source geometry is set to the “magic angle” of 54.7 (see Sect. 4.3.1), the photoelectron emission is isotropic. Therefore, a decrease of the signal intensity by a cosine law with the emission angle (with respect to the normal to the sample surface) is observed [3.43] (see Sects. 4.3.2 and 5.1.1). However, the relative intensity of a species in the very first surface layers compared to the intensity from deeper layers (“bulk”) increases with the emission angle. Thus, a quick qualitative check of surface layer species is possible by comparison of the relative intensities at two different emission angles. Angle-resolved XPS is the basis of quantitative layer structure analysis within a depth range of about three times the electron attenuation length (Sects. 4.3.3 and 7.2.1).

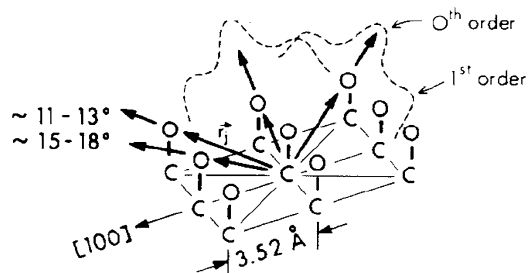


Fig. 3.11 Schematic illustration of the intermolecular scattering of C1s photoelectrons in $c(2 \times 2)$ CO on Ni(001) (Reproduced from P.J. Orders et al. [3.48], with permission of Elsevier B.V.)

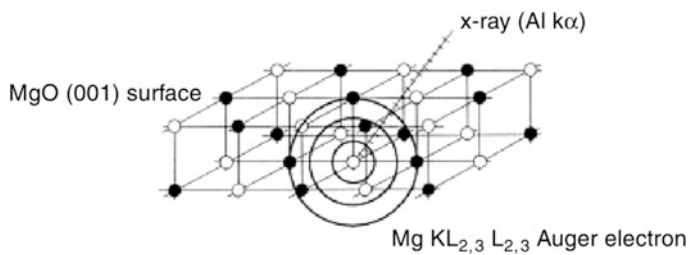
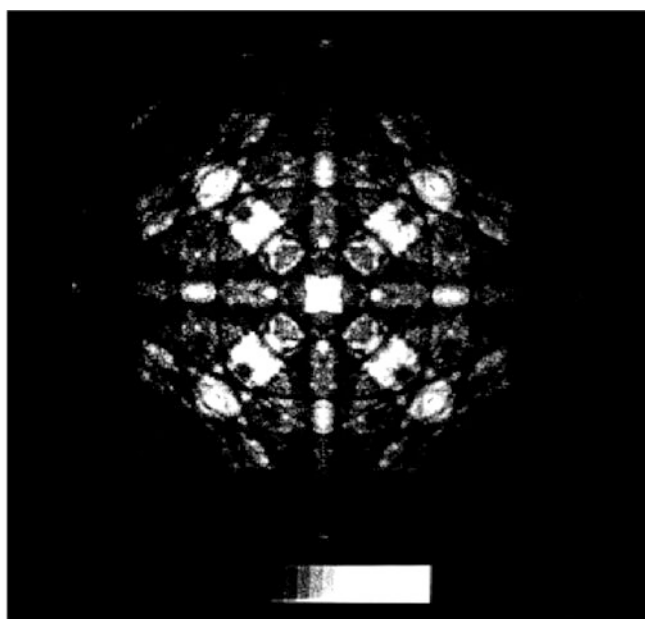
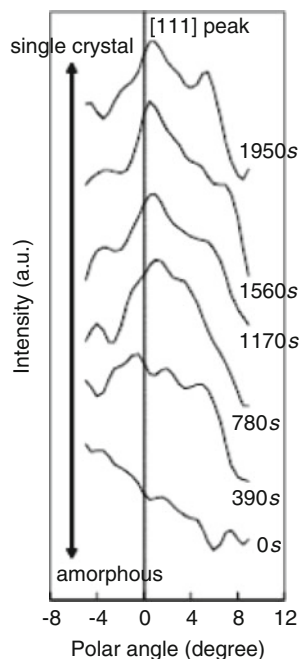


Fig. 3.12 XPD on MgO (011) surface, showing schematically the scattering process and the full solid angle diffraction pattern of the Mg KLL X-ray-excited Auger electrons (1182 eV) (Reproduced from Y. Nihei [3.46], with permission of J. Wiley & Sons Ltd.)

Fig. 3.13 Polar scan of Si2p XPD pattern from a previously amorphized Si(111) surface as a function of annealing time at 1030 K (Reproduced from Y. Kisaka et al. [3.51], with permission of J. Wiley & Sons Ltd.)



3.2.8.2 Single Crystals

In single crystals, the general angular dependence of the intensity of photoelectrons and Auger electrons is modified by lattice orientation dependent scattering and diffraction effects, [3.43–3.50] which can be used to study the structure of the first few atomic layers. These short-range structural probes, called X-ray photoelectron diffraction (XPD) and Auger electron diffraction (AED), are particularly useful to disclose surface adsorbate structures [3.48]. Figure 3.11 schematically shows the occurrence of forward scattering for the C1s emission at O atoms in the C–O (2×2) ordered structure of CO adsorbed on (001) Ni [3.48]. Single scattering cluster theory is usually applied to compare theoretical predictions with measured data, but multiple scattering gives more realistic patterns [3.49,3.50] (see Fig. 3.11). Medium-range patterns obtained by observation of crystalline surfaces can be characterized by superposition with Kikuchi-like lines from electron channeling as shown in Fig. 3.12 for the MgO (001) surface by Nihei [3.46]. Using XPD, El Kazzi et al. [3.47] studied in detail γ -Al₂O₃ films grown on Si(111). Besides structural symmetry of crystal surfaces and structural analysis of adsorbed molecules, chemical state and spin-resolved structural analyses are possible by XPD and AED. While XPD can principally be observed with conventional XPS equipment, high-resolution and dynamic measurements require more sophisticated instrumentation [3.46]. This was demonstrated by Kisaka et al. [3.51] by the time dependence of recrystallization of amorphous Si (previously generated by argon bombardment of Si(111)) at elevated temperatures, as shown in Fig. 3.13. The increase of the crystalline pattern from

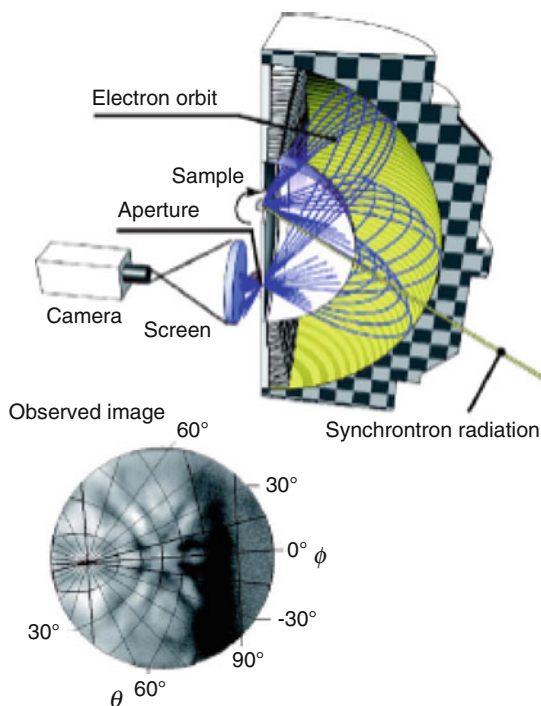


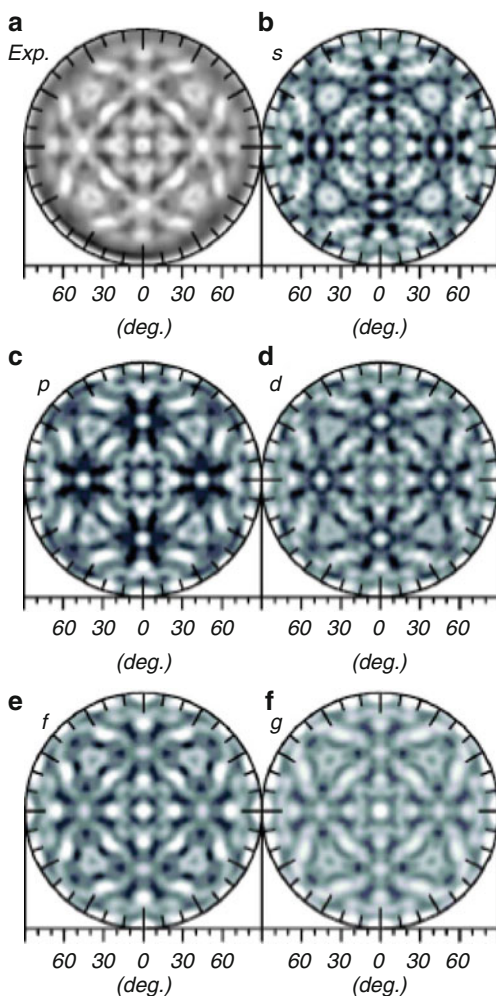
Fig. 3.14 Schematic view of the experimental setup and the two-dimensional display-type analyzer. Circularly polarized synchrotron radiation is impinging on the sample. The electrons emitted from the sample are focused to the aperture by the electric field in the spherical mirror analyzer (SMA). The electron that has passed the aperture is projected to the screen, and the angular distribution is observed directly on the screen. When the measured image is divided by the transmission function of the analyzer, a clear angular distribution image is obtained as shown in the figure (From T. Matsushita et al. [3.54], reproduced with permission of the American Physical Society)

Si(111) below the amorphous layer enabled determination of the thickness decrease of the latter with time according to the usual quantitative surface layer analysis (see Sect. 4.3.3).

Photoelectron holography should be possible since Fourier transformation of the angular distribution pattern should reconstruct an image of the atomic structure of the surface [3.52]. However, the highly anisotropic character of electron scattering causes problems that are supposed to be overcome by taking the difference of two holograms in the so-called differential photoelectron holography [3.53]. Figure 3.14 shows how a hologram of a single crystalline Cu surface is obtained with synchrotron radiation-excited Cu L_3 VV peak [3.54]. The results shown in Fig. 3.15 can be transformed in real space atomic arrangements [3.54].

A survey and more details on XPD and AED are found in Refs. [3.44, 3.46, 3.52, 3.54, 3.55].

Fig. 3.15 (a) The observed L_3VV Auger electron hologram of Cu (001) with 914 eV kinetic energy. (b–f) show simulated multiple-scattering patterns for emitted waves of s, p, d, f, and g angular momenta for a spherical cluster of 241 atoms. Angular resolution is set to 3° (From T. Matsushita et al. [3.54], reproduced with permission of the American Physical Society)



3.2.8.3 Quantitative Aspects

Because quantitative XPS (and AES) usually neglects any crystalline effects in angular dependence, it is strictly speaking only correct for amorphous systems (attenuation length values are calculated under these conditions, see Sect. 4.2.2). For large area analysis of polycrystalline surfaces, orientation effects are averaged out. A similar effect takes place for analyzers with high acceptance angle, as for cylindrical mirror analyzers (or four-grid LEED devices in AES) or for instruments like the Thetaprobe (see Sect. 2.5.2). However, the usual concentric hemispheres analyzer within 6° acceptance angle is sensitive to emission-angle-dependent effects on single crystalline surfaces that can add up to 40% in the worst case [3.56]. In such a case, two or more measurements at different angles (corrected for the amorphous material emission angle dependence, see Sect. 4.3.2) should be averaged in order to ensure an average intensity value.

3.3 Qualitative AES

3.3.1 Principle of AES Analysis

Auger electron emission is imagined as a three-stage process which involves three electron levels [3.1, 3.23.57–3.60]. If an atom is ionized by electron impact, the resulting vacancy in a core electron shell will be filled by an electron from a higher level. The excess energy will either cause emission of a characteristic X-ray (e.g., analyze in the electron microprobe) or emission of another electron, the Auger electron, named after Pierre Victor Auger (see Chap. 1), which leaves the atom with a characteristic energy. The energy scheme for Auger excitation, emission, and measurement is shown in Fig. 3.16. The kinetic energy E_{kin} of the emitted electron is equal to the measured Auger electron energy, E_{WXY} , and is given by the difference between the binding energies of electron levels W, X, Y,

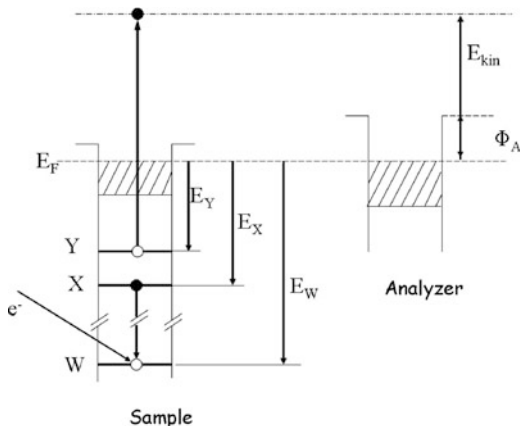
$$E_{\text{WXY}} = E_{\text{W}} - E_{\text{X}} - E_{\text{Y}} - \Phi_{\text{A}}, \quad (3.10)$$

where the analyzer work function Φ_{A} is a small correction as in XPS measurement. By calibration of the analyzer using the elastic peak (with well-defined energy, usually at 2000 eV), Φ_{A} is removed from (3.10). Reference samples for which standard kinetic energies of Auger electrons are available (e.g., direct spectra with reference to the Fermi level: Cu $M_{2,3}VV$: 62 eV, Cu L_3VV : 919 eV [3.4, 3.5]) help to establish a correct energy scale (see Sect. 8.4.1). Equation 3.10 neglects the ionization and relaxation effects which accompany any Auger transition. In principle, E_{W} and E_{X} are the binding energies for the singly ionized atom, and E_{Y} is that of the doubly ionized state, because finally two electrons have left the atom. It is obvious that, because of the more complicated Auger transition involving three electrons and the respective relaxation and screening effects, the exact final energy is difficult to predict. However, an empirical rule has been found useful which basically shifts the energy levels by one ionization state and therefore starts from the ground state (nonionized, corresponding to atomic number Z) for E_{W} . For E_{X} and E_{Y} , an average binding energy between the ground state (Z) and the singly ionized state ($Z + 1$), that is, $E_{\text{X}} = [E_{\text{X}}(Z) + E_{\text{X}}(Z + 1)]/2$ and $E_{\text{Y}} = [E_{\text{Y}}(Z) + E_{\text{Y}}(Z + 1)]/2$, is assumed. With this approximation, the Auger electron energy is described by [3.61].

$$E_{\text{WXY}}(Z) = E_{\text{W}}(Z) - [E_{\text{X}}(Z) + E_{\text{X}}(Z + 1) + E_{\text{Y}}(Z) + E_{\text{Y}}(Z + 1)]/2 \quad (3.11)$$

This energy can be determined from X-ray tables of electron energies E_{W} , E_{X} , E_{Y} [3.62] with a typical accuracy of a few electron volts [3.60, 3.61]. As an example, all the possible Auger transitions for sulfur calculated with (3.11) are shown in Table 3.4. The energy of the main Auger peak of sulfur at 149 eV corresponds to the $L_3M_{2,3}M_{2,3}$ transition (the energy difference between the levels M_2 and M_3 is negligibly small) given by

Fig. 3.16 Schematic energy diagram for Auger electron excitation, emission, and measurement, involving the three electron levels W , X , Y with binding energies E_W , E_X , E_Y , Fermi energy E_F , kinetic (vacuum) energy E_{kin} , and analyzer work function Φ_A . The hatched areas indicate the valence band



$$E_{L_3M_{2,3}M_{2,3}}(Z) = E_{L_3}(Z) - [E_{M_{2,3}}(Z) + E_{M_{2,3}}(Z + 1)] \quad (3.12)$$

Since at least two electrons in the L shell are required for the Auger process depicted in Fig. 3.16, H and He give no Auger signal, as well as atomic Li. However, in metallic lithium, the L shell will broaden to the valence band which contains many electrons and an LVV Auger transition is possible (V usually denotes the valence band).

The width of the Auger lines is limited by the transition time, which is typically of the order of 10^{-15} s. Due to the uncertainty principle, E_{WXY} is of the order of a few eV (see (3.7)). Valence band transitions of the type WVX will cause an enlarged line width of about twice the valence band energy width. The so-called Coster–Kronig transition of the type WWX [3.18, 3.64] gives a significant line broadening due to its small transition time (10^{-16} s). The possible Auger electron energies can be calculated from (3.11) from all energetically possible transitions using tables of electron energies [3.65] because there are less stringent selection rules as there are for X-ray transitions. A useful catalog of calculated Auger transition based on (3.11) has been given by Coghlan and Clausing [3.63]. An example for sulfur is shown in Table 3.3 [3.63]. Modern handbooks and databases [3.8–3.11] give AES energies of the elements more accurately.

3.3.2 Auger Spectra and Elemental Identification

The bewildering number of Auger transitions, already for the example of sulfur ($Z = 16$) listed in Table 3.4, shows one of the difficulties in identification of Auger spectra. Fortunately, most of these lines are too weak to be detected. To give an estimation of the expected relative intensity, Coghlan and Clausing [3.63] used the product of the number of electrons in the three levels involved in the transition, normalized to a maximum value of 100 for the largest product of a given element.

Table 3.4 Calculated Auger energies for sulfur ($Z = 16$) using (3.11) and the normalized term multiplicities as a measure of expected relative intensity (From Ref. [3.63])

Orbital	Population		Z energy (eV)	(Z + 1) energy (eV)
K	2		2462.0	2823.0
L ₁	2		229.0	270.0
L ₂	2		165.0	202.0
L ₃	4		164.0	200.0
M ₁	2		16.0	18.0
M ₂₃	4		8.0	7.0
Vacancy level	Interaction levels		Auger energy (eV)	Norm multiplicity
L ₁	L ₂	M ₁	28.5	12
L ₁	L ₃	M ₂₃	30.0	25
L ₁	L ₂	M ₁	38.0	25
L ₁	L ₃	M ₂₃	39.5	50
L ₃	M ₁	M ₁	130.0	25
L ₂	M ₁	M ₁	131.0	12
L ₃	M ₁	M ₂₃	139.5	50
L ₂	M ₁	M ₂₃	140.5	25
L ₃	M ₂₃	M ₂₃	149.0	100
L ₂	M ₂₃	M ₂₃	150.0	50
L ₁	M ₁	M ₁	195.0	12
L ₁	M ₁	M ₂₃	204.5	25
L ₁	M ₂₃	M ₂₃	214.0	50
K	L ₁	L ₁	1573.0	12
K	L ₁	L ₂	2039.0	12
K	L ₁	L ₃	2040.5	25
K	L ₂	L ₂	2105.0	12
K	L ₂	L ₃	2106.5	25
K	L ₃	L ₃	2109.0	50
K	L ₁	M ₁	2205.5	12
K	L ₁	M ₂₃	2215.0	25
K	L ₂	M ₁	2271.5	12
K	L ₃	M ₁	2273.0	25
K	L ₂	M ₂₃	2281.0	25
K	L ₃	M ₂₃	2282.5	50
K	M ₁	M ₁	2438.0	12
K	M ₁	M ₂₃	2447.5	25
K	M ₂₃	M ₂₃	2457.0	50

This number, called the “normalized multiplicity,” gives a crude but helpful means to identify the most prominent Auger transitions in experimental analysis. Since the relative intensities depend on peak width, ionization cross section, and fluorescence probability, they may deviate from calculations based on first principles [3.60], and a direct identification of the species in a multielement specimen by using only tabulated energies is rather difficult. In addition to the element specific main peak energy, the intensity of neighboring peaks gives a pattern which is characteristic of

a specified “family” of transitions (KLL, LMM, and MNN) (see Fig. 3.16). Both features are a fairly reliable guide for qualitative analysis. Standard “fingerprint” spectra of the elements, compiled in handbooks and databases [3.8,3.9,3.11], enable a reliable identification of the elements present in the surface region of a sample.

The Auger process is dominant for kinetic energies below 2,000 eV with more than 90% and decreases strongly for higher energies where the fluorescence yield is becoming larger. Therefore, the most prominent Auger peaks are the KLL transitions for elements with atomic number from $Z = 3$ to 14, the LMM transitions for elements $Z = 14$ –40, and MNN transitions for the heavier elements. A diagram of the principal Auger transitions observed from the elements is shown in Fig. 3.17 [3.8].

Frequently, the line shape is influenced by plasmon losses on the lower kinetic energy side (see Sect. 3.2.7). Bulk spectra and those of monolayer coverage of the same element may be different because of the missing bulk plasmon for the monolayer, as demonstrated for Sn [3.59, 3.65]. In contrast to XPS, there is no intrinsic plasmon loss (associated with the photoelectron) in Auger electron emission. Ionization loss features can be observed, usually with rather low intensity, at an energy given by the difference between the primary beam energy and the binding energy [3.66]. In contrast to Auger peaks, the energy of ionization losses changes with changing the primary beam energy. A schematic picture of the features seen in the total spectrum of secondary electron besides Auger peaks is shown in Fig. 3.18 [3.67].

3.3.3 Direct and Derivative Spectra

Today, practically all AES instruments are operating in the digital (pulse counting) mode which directly yields the intensity (counts per second), N , as a function of the kinetic energy E , ($N(E)$ (direct mode, see Fig. 3.19a). Frequently, the first derivative of the direct spectra, $d(N(E))/dE$, is measured (usually in analog equipment) or obtained from $N(E)$ data by mathematical algorithms (see Sect. 4.1.2). Figure 3.19b shows the characteristic structure of the derivative Cu peak intensities. For constant relative analyzer resolution (usually 0.5–0.6%), the absolute intensity increases with the kinetic energy and corresponds to $E(N(E))$, and the derivative is $d[E(N(E))/dE]$. Although the use of derivative spectra has historical reasons (because in analog equipment with retarding grids, the derivative spectrum is directly obtained by detection of the second harmonic of the modulation frequency by a lock in amplifier, see, e.g., Ref. [3.59]), the derivative notation is still used today. Besides better comparison with older data, differentiation provides an apparent “automatic” background subtraction, and the intensity is directly measured as the Auger peak-to-peak height (APPH, see Fig. 4.1b). (Further details are given in Sect. 4.1.2.) Because of the difficulty to find the zero value in the derivative mode which corresponds to the maximum value in $N(E)$, the negative maximum signal extension has been defined as the Auger energy, which is 1–5 eV higher than the

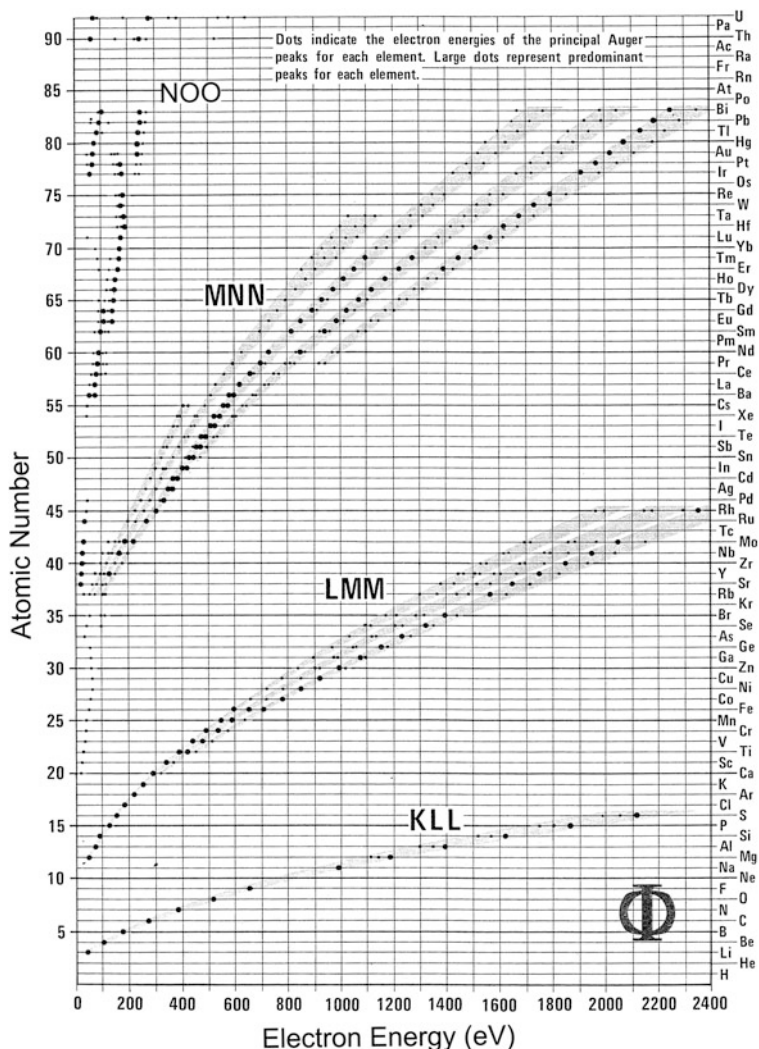


Fig. 3.17 Kinetic energies of the principal Auger electron peaks for the elements, showing the “family” of KLL, LMM, MNN and NOO transitions (Adapted from K.D. Childs et al. [3.9], Handbook of AES, Physical Electronics Inc., 1995)

“true” peak energy in the direct spectrum and depends on instrumental parameters (in the strongest $LM_{2,3}M_{2,3}$, peak energy in the direct spectrum is 914 eV, and in the derivative mode, Fig. 3.19b, the negative excursion is at 916 eV, as referenced to the vacuum level). This is sometimes confusing. Today, instrument calibration procedures exist for AES peaks with reference energies of Cu, Al, and Au in the direct and derivative mode [3.5, 3.68] (see Sect. 8.4.1).

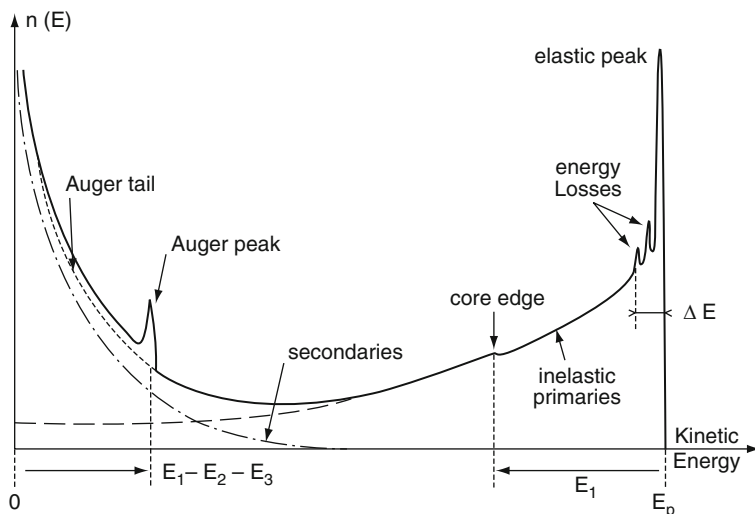


Fig. 3.18 Schematic view of the different components of the total secondary electron spectrum observed with an AES instrument. Plasmon energy losses (ΔE , shown for elastic peak E_p), an ionization loss (core edge, E_1), and an Auger peak are shown together with the three main parts of the background, consisting of the “Auger tail,” of the “true” secondary electrons, and of the inelastically scattered primary electrons (From J.P. Langeron [3.67], with permission of J. Wiley & Sons, Ltd.)

3.3.4 Recognition and Influence of Chemical Bonding

Chemical effects in AES are frequently observed not only by peak energy shift but also by line shape changes. Owing to the dominating influence of screening and relaxation effects of the final two hole state in AES, chemical shifts of Auger energies are often relatively high as compared to XPS [3.18, 3.70]. A comparison of chemical shifts for the atoms Al, Si, Ca, Ti, Fe, Co, As, Ag, and Pb in 64 compounds is shown in Fig. 3.20 [3.70].

The linear correlation indicates the higher energy shifts in AES (on average by a factor of 1.2). Plasmon energy changes, and in particular, valence band transitions additionally change the shape of the Auger peaks. A well-known example is shown in Fig. 3.21 [3.59] for the carbon C KVV transition in carbon monoxide and in chromium carbide. An example of a cross-transition between oxygen and metal levels causing an energy shift of 15 eV is shown in Fig. 3.22 for the Al LVV spectrum [3.59]. Line shape analysis of valence band transitions can reveal the electronic structure of the latter [3.70–3.73]. For practical analysis, compilations of Auger chemical shifts and line shapes in various compounds are useful [3.6–3.12].

Peak overlapping is frequently encountered in multielement analysis. There are several means for a remedy, such as (1) selecting a nonoverlapping peak in element spectra with several peaks, (2) peak subtraction in comparison with reference

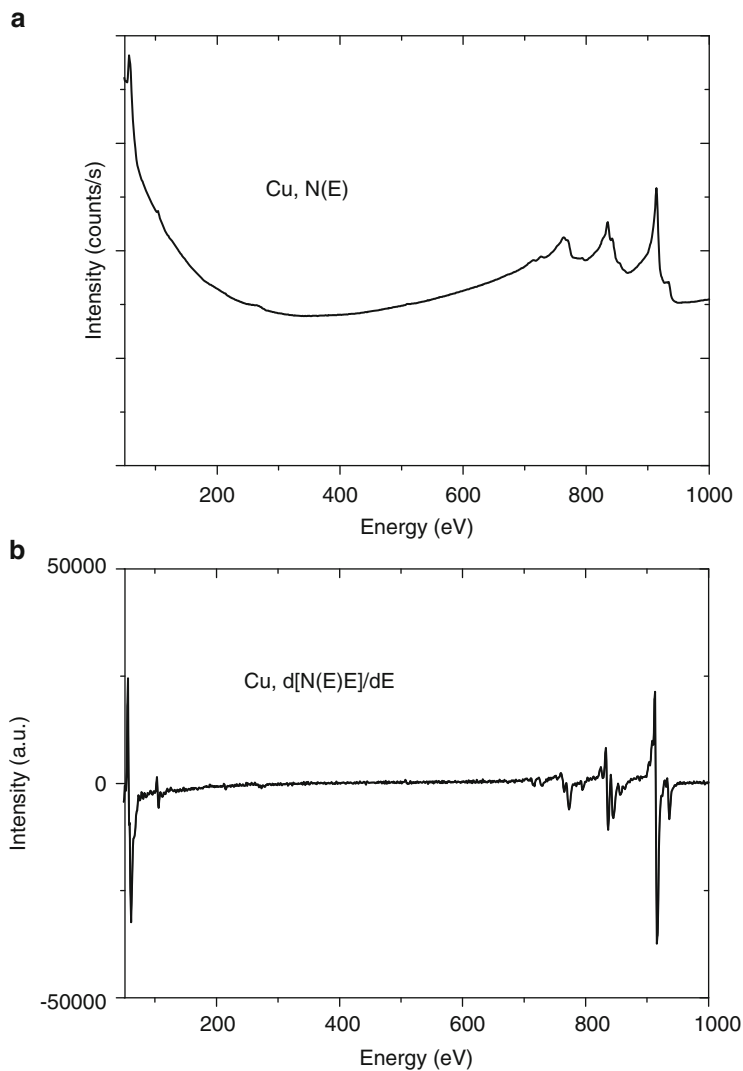


Fig. 3.19 (a) Auger spectrum of Cu in the direct N(E) mode, showing the most prominent Auger peaks $M_{2,3}VV$ at 58 eV and L_3VV at 914 eV (referenced to vacuum level). (b) Derivative spectrum obtained by differentiation of spectrum in (a). The negative excursions of the strongest Cu peaks, $M_{2,3}VV$ and L_3VV , are at 60 eV and at 916 eV, respectively

sample, and (3) linear least square fitting or factor analysis for a sequence of spectra (see Sects. 4.1.4 and 9.3).

Chemical effects in AES are a great problem in quantitative analysis using derivative spectra because the APPH is very sensitive to any change in the line shape. A remedy is to blur the fine features by worsening the analyzer resolution,

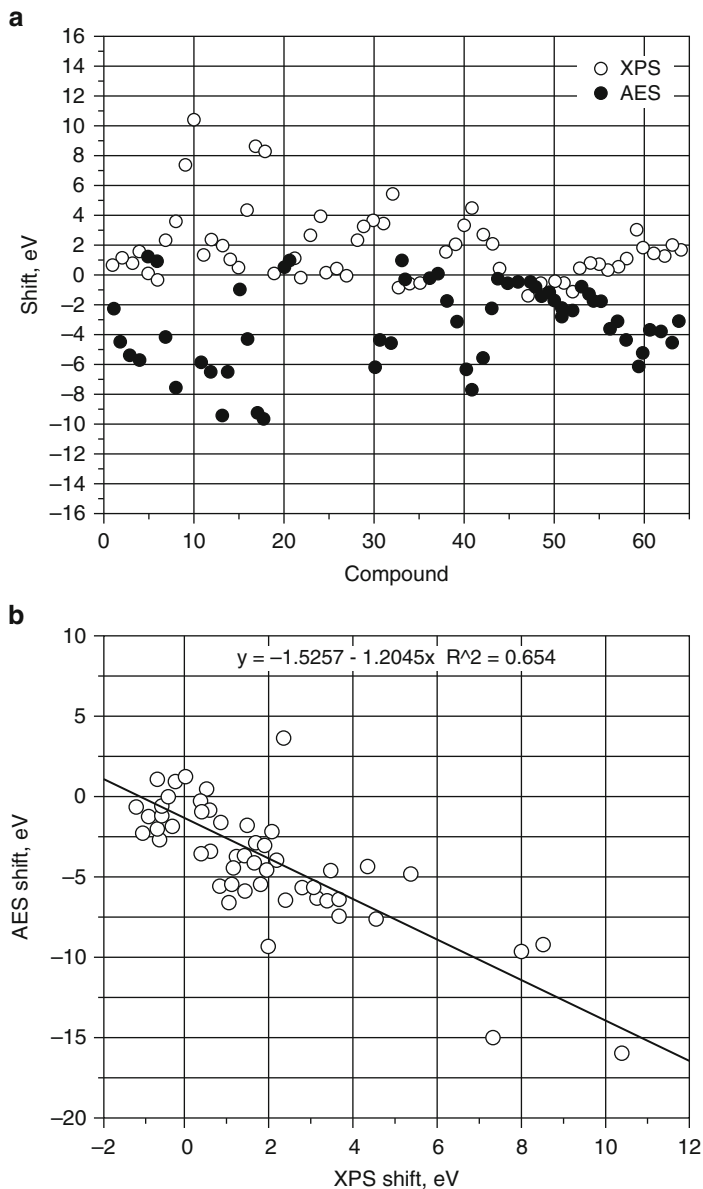


Fig. 3.20 (a) Plot of chemical shifts in AES and XPS for 64 compounds numbered on the horizontal axis. The vertical axis shows the chemical shifts in AES and XPS. (b) Plot of AES chemical shifts versus XPS chemical shifts for the compounds in (a). The coordinates of each circular dot are the values of AES and XPS chemical shifts of corresponding compounds (Reproduced from T. Sekine et al. [3.69], with permission of Elsevier B.V.)

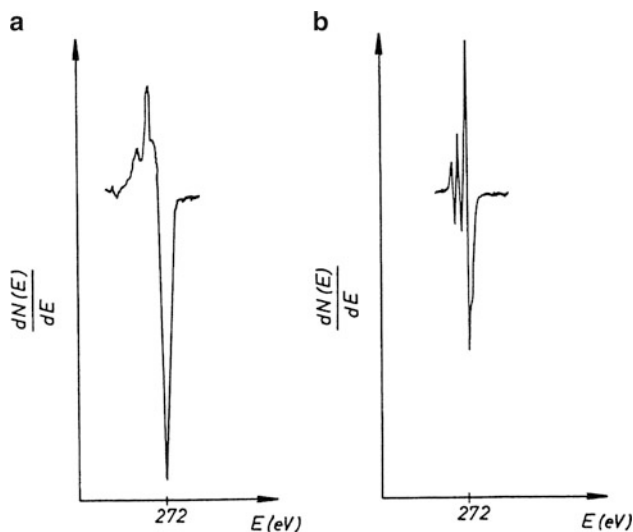


Fig. 3.21 Typical AES spectra of the carbon C KVV Auger peak in (a) contamination (CH_x , CO) layer and in (b) carbide (here CoC_3) bond (Reproduced from S. Hofmann [3.59])

for example, by “overmodulation” or increased smoothing and differentiation (see Sect. 4.1.2) [3.33], or by using factor analysis for quantification (see Fig. 9.17).

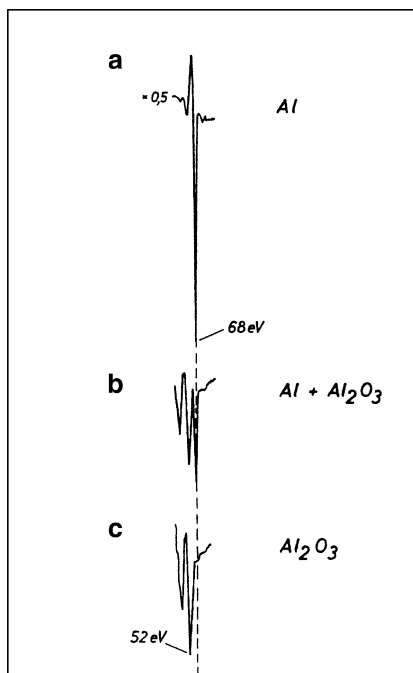
Working with the peak area of direct spectra after an appropriate background subtraction (see Sect. 4.1) basically avoids the influence of changes in chemistry to elemental quantification. Decomposition of the measured peak by comparison with standard spectra will disclose the amount of different species and will increase the information about the sample. Because of the complexity of Auger spectra, peak decomposition is less frequently applied than principal component analysis (or linear least square fitting of standard spectra) which can be very powerful in quantitative analysis of different bonding states [3.74] (see Sects. 4.1.4.9.3). Information about the chemistry of a sample is often distorted by electron beam effects such as electron-stimulated desorption (and deposition), beam heating, and charging. These effects are considered in Sect. 8.6.

3.3.5 Electron Backscattering, Channeling, and Diffraction

3.3.5.1 Backscattering

Electron backscattering is responsible for the shape of the background observed in survey spectra and for the excitation of Auger electrons in addition to that of the incoming primary electrons (see Fig. 3.18). Therefore, the effect of electron backscattering is a major topic in quantitative Auger electron spectroscopy (see

Fig. 3.22 Derivative spectra of the Al $L_{2,3}$ VV peak in (a) pure Al, (b) mixture of Al and Al_2O_3 , and (c) pure Al_2O_3 (Reproduced from S. Hofmann [3.59])



Sects. 4.4.1 and 5.2.1) [3.75] and depth profiling (see Sect. 7.1.8). Elastically backscattered electrons with exactly the energy of the primary beam provide a means for energy calibration and sample adjustment, as well as for additional information such as crystallographic orientation and topography [3.76] and of chemical composition [3.77]. Loss features of the elastic peak provide information about the inelastic mean free path of the electrons [3.78] in elastic peak electron spectroscopy (EPES) [3.79–3.81].

3.3.5.2 Channeling and Diffraction

The contrast frequently observed between different grains on a clean polycrystalline metallic sample surface in a secondary electron image can be attributed to the channeling effect of primary electrons [3.49, 3.66, 3.82]. Electrons in a channeling direction penetrate deeper into the crystal and cause less surface excitations than those having nonchanneling directions. Therefore, this effect is also recognized when Auger line intensities are observed on different crystals [3.66]. Elastic peak detection while rocking the primary beam produces characteristic, Kikuchi-like channeling patterns which are also observed in Auger peak measurements but with less intensity [3.83]. Calculations based on cluster multiple-scattering theory can explain the typical channeling patterns in directionally resolved elastic peak electron spectroscopy (DEPES) with high intensities in close packed directions as shown in

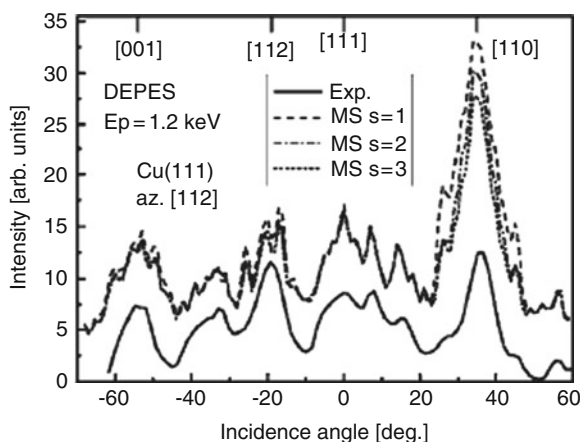


Fig. 3.23 Experimental directional elastic peak electron spectrometry (DEPES) for Cu(111) at $E_p = 1.2$ keV and theoretical calculations obtained with the use of multiple-scattering approach for scattering orders $s = 1, 2$, and 3 (Reproduced from I. Morawski and M. Nowicki [3.49], with permission of the American Physical Society)

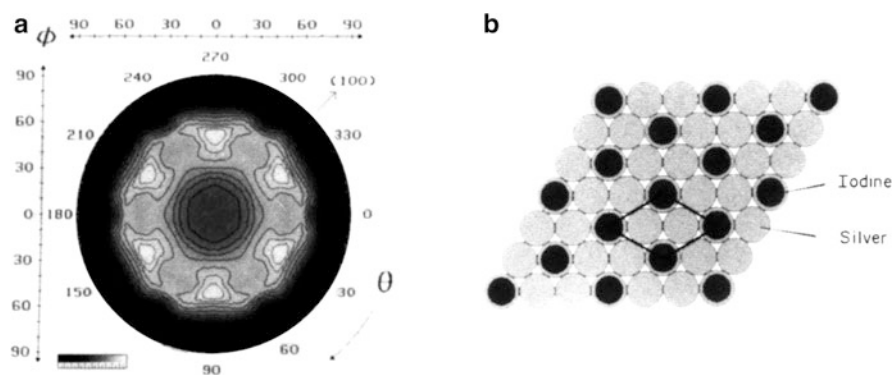


Fig. 3.24 (a) Angular distribution Auger microscopy (ADAM) image of the Ag (355 eV) peak of a monolayer of Ag atoms on a Pt (111) surface, with an overlayer of iodine atoms, in polar (Φ) and azimuthal (θ) coordinates. Bright regions denote strong Auger signal. The hexagonal array of silhouettes in the Ag signal intensity caused by the iodine atoms with the structure shown in (b) (Reproduced from D.G. Frank and A.T. Hubbard [3.84], with permission of Elsevier B.V.)

Fig. 3.23 [3.49]. Low-energy Auger electron diffraction (AED) patterns are element specific [3.50]. Therefore, AED is a probe of the short-range order of specified atoms at the surface similar to XPD (see Sect. 3.2.8). An example is shown in Fig. 3.24, where the structure of an iodine overlayer on an Ag monolayer is disclosed by angular distribution Auger microscopy (ADAM) [3.84]. The measured image in Fig. 3.24a is reproduced by simulations starting with the structure in Fig. 3.24b.

3.3.5.3 Quantitative Aspects

Crystalline orientation is expected to have a nonnegligible effect on quantitative AES. However, the theory of quantitative AES considers samples as effectively amorphous (see Sect. 4.2.2). This can only be justified if the surface layer is truly amorphous (e.g., sputter-cleaned single crystals) or if the crystallite size is much smaller as the analyzed area. Normalization of the peak to the background intensity can provide a means to get a first-order effect correction of the backscattering contribution, for example, in a line scan or a depth profile (see Sect. 7.1.8.4, Fig. 7.28). In general, crystalline orientation effects are expected to be smaller for CMA as compared to CHA analyzers because the former averages over the whole acceptance cone (azimut) angle 2π (see Sect. 2.5.1 and Fig. 5.4). Another way is to correct for the intensity differences by taking the ratio between signal intensity and background intensity in the direct mode. In many cases, taking the average over the intensities obtained in several measurements will yield representative values for quantification (e.g., in segregation measurements [3.85]).

References

- 3.1. J.F. Watts, J. Wolstenholme, *An Introduction to Surface Analysis by XPS and AES* (Wiley, Chichester, 2003)
- 3.2. M. Thompson, M.D. Baker, A. Christie, J.F. Tyson, *Auger Electron Spectroscopy* (Wiley, New York, 1985)
- 3.3. D. Briggs, J.C. Rivière, Spectral Interpretation, in *Practical Surface Analysis Vol. 1 (AES and XPS)*, 2nd edn., ed. by D. Briggs, M.P. Seah (Wiley, Chichester, 1990), pp. 85–141
- 3.4. M.P. Seah, I.S. Gilmore, S.J. Spencer, *Surf. Interface Anal.* **26**, 617 (1998)
- 3.5. M.P. Seah, Instrument Calibration for AES and XPS, in *Surface Analysis by Auger and Photoelectron Spectroscopy*, ed. by D. Briggs, J.T. Grant (IM Publications, Chichester, 2003), pp. 167–189
- 3.6. J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy* (Perkin–Elmer Corp., Physical Electronics Division, Eden Prairie, 1992)
- 3.7. N. Ikeo, Y. Iijima, N. Niimura, M. Sigematsu, T. Tazawa, S. Matsumoto, K. Kojima, Y. Nagasawa, *Handbook of X-ray Photoelectron Spectroscopy* (JEOL, Akishima, 1991)
- 3.8. T. Sekine, Y. Nagasawa, M. Kudo, Y. Sakai, A.S. Parker, J.D. Geller, A. Mogami, K. Hirata, *Handbook of Auger Electron Spectroscopy* (JEOL, Tokyo, 1982)
- 3.9. K.D. Childs, B.A. Carlson, L.A. LaVanier, J.F. Moulder, D.F. Paul, W.F. Stickle, D.G. Watson, *Handbook of Auger Electron Spectroscopy*, 3rd edn. (Physical Electronics Inc., Eden Prairie, 1995)
- 3.10. C.D. Wagner, A.V. Naumkin, A. Kraut-Vass, J.W. Allison, C.J. Powell, J.R. Rumble, NIST X-Ray Photoelectron Spectroscopy Database, SRD 20, Version 3.5 (National Institute of Standards and Technology, Gaithersburg, 2008), <http://srdata.nist.gov/xps/>
- 3.11. Common Data Processing System (COMPRO). www.sasj.gr.jp/COMPRO/index.html
- 3.12. J.T. Grant, Databases, in *Surface Analysis by Auger and Photoelectron Spectroscopy*, ed. by D. Briggs, J.T. Grant (IM Publications, Chichester, 2003), pp. 869–873
- 3.13. S. Hüfner, Unfilled InnerShells: Transition Metals and Compounds, in *Photoemission in Solids II*, ed. by L. Ley, M. Cardona (Springer, Berlin-Heidelberg-New York, 1979), pp. 173–216

- 3.14. S. Hüfner, *Photoelectron Spectroscopy*, 3rd edn. (Springer, Berlin, 2003)
- 3.15. A. Rosencwaig, G.K. Wertheim, *J. Electron Spectrosc. Relat. Phenom.* **1**, 493 (1973)
- 3.16. K. Siegbahn, C.N. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bermark, S.E. Karlsson, *ESCA: Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy* (Almqvist and Wiksells, Uppsala, 1967)
- 3.17. U. Gelius, *Phys. Scr.* **9**, 133 (1974)
- 3.18. L. Kövér, Chemical Effects in XPS, in *Surface Analysis by Auger and Photoelectron Spectroscopy*, ed. by D. Briggs, J.T. Grant (IM Publications, Chichester, 2003), pp. 421–464
- 3.19. L.P.H. Jeurgens, F. Reichel, S. Frank, G. Richter, E.J. Mittemeijer, *Surf. Interface Anal.* **40**, 259 (2008)
- 3.20. S. Hofmann, J.M. Sanz, *Fres. Z. Anal. Chem.* **314**, 215 (1983)
- 3.21. C.D. Wagner, *Anal. Chem.* **44**, 967 (1972)
- 3.22. S.W. Gaarenstrom, N. Winograd, *J. Chem. Phys.* **67**, 3500 (1977)
- 3.23. C.D. Wagner, A. Joshi, *J. Electron Spectrosc. Relat. Phenom.* **47**, 283 (1988)
- 3.24. G. Moretti, *J. Electron Spectrosc. Relat. Phenom.* **95**, 95 (1998)
- 3.25. R.H. West, J.E. Castle, *Surf. Interface Anal.* **4**, 86 (1982)
- 3.26. G. Moretti, *Surf. Interface Anal.* **17**, 352 (1991)
- 3.27. T.D. Thomas, *J. Electron Spectrosc. Relat. Phenom.* **20**, 117 (1980)
- 3.28. J.C. Rivière, J.A.A. Crossley, G. Moretti, *Surf. Interface Anal.* **14**, 257 (1989)
- 3.29. I.leR. Strydom, S. Hofmann, *Vacuum* **41**, 1619 (1990)
- 3.30. M.-L. Abel, P. Tsakiroopoulos, J.F. Watts, J.A.D. Matthew, *Surf. Interface Anal.* **34**, 775 (2002)
- 3.31. L.P.H. Jeurgens, W.G. Sloof, C.G. Borsboom, F.D. Tichelaar, E.J. Mittemeijer, *Appl. Surf. Sci.* **161**, 139 (2000)
- 3.32. L.P.H. Jeurgens, W.G. Sloof, C.G. Borsboom, F.D. Tichelaar, E.J. Mittemeijer, *Appl. Surf. Sci.* **144–145**, 11 (1999)
- 3.33. W. Pamler, *Surf. Interface Anal.* **13**, 55 (1988)
- 3.34. D. Briggs, V.A. Gibson, *Chem. Phys. Lett.* **25**, 493 (1974)
- 3.35. G.K. Wertheim, *Phys. Rev. B* **25**, 1987 (1982)
- 3.36. P.M.A. Sherwood, Data Analysis in XPS and AES, in *Practical Surface Analysis Vol. 1 (AES and XPS)*, 2nd edn., ed. by D. Briggs, M.P. Seah (Wiley, Chichester, 1990), pp. 555–586
- 3.37. N. Fairley, XPS Lineshapes and Curve Fitting, in *Surface Analysis by Auger and Photoelectron Spectroscopy*, ed. by D. Briggs, J.T. Grant (IM Publications, Chichester, 2003), pp. 421–464
- 3.38. S. Doniach, M. Sunjic, *J. Phys. C* **3**, 285 (1970)
- 3.39. G.K. Wertheim, P.H. Citrin, Fermi Surface Excitations in X-Ray Photoemission Line Shapes from Metals, in *Photoemission in Solids I*, ed. by M. Cardona, L. Ley (Springer, Berlin/Heidelberg, 1978), pp. 197–236
- 3.40. G.K. Wertheim, L.R. Walker, *J. Phys. F. Metal Phys.* **6**, 2297 (1976)
- 3.41. G.K. Wertheim, S. Hüfner, *J. Inorg. Nucl. Chem.* **38**, 1701 (1976)
- 3.42. I. Olefjord, H.J. Mathieu, P. Marcus, *Surf. Interface Anal.* **15**, 681 (1990)
- 3.43. C.S. Fadley, *Prog. Surf. Sci.* **16**, 275 (1984)
- 3.44. C.S. Fadley, *Nucl. Instrum. Methods Phys. Res. A* **601**, 8 (2009)
- 3.45. G. Grenet, Y. Jugnet, S. Holmberg, H.C. Poon, Tran Minh Duc, *Surf. Interface Anal.* **34**, 367 (2003)
- 3.46. Y. Nihei, *Surf. Interface Anal.* **35**, 45 (2003)
- 3.47. M. El Kazzi, G. Grenet, C. Merckling, G. Saint-Girons, C. Botella, O. Marty, G. Hollinger, *Phys. Rev. B* **79**, 195312 (2009)
- 3.48. P.J. Orders, S. Kono, C.S. Fadley, R. Trehan, J.T. Lloyd, *Surf. Sci.* **119**, 371 (1982)
- 3.49. I. Morawski, M. Nowicki, *Phys. Rev. B* **75**, 155412 (2007)
- 3.50. A. Chasse, L. Niebergall, Yu. Kucherenko, *Surf. Sci.* **501**, 244 (2002)
- 3.51. Y. Kisaka, A. Hashimoto, A. Suzuki, S. Miyasaka, M. Nojima, M. Owari, Y. Nihei, *Surf. Interface Anal.* **40**, 1646 (2008)

- 3.52. J. Osterwalder, Structural Effects in XPS and AES: Diffraction, in *Surface Analysis by Auger and Photoelectron Spectroscopy*, ed. by D. Briggs, J.T. Grant (IM Publications, Chichester, 2003), pp. 557–585
- 3.53. S. Omori, Y. Nihei, E. Rotenberg, J.D. Denlinger, S.D. Kevan, B.P. Tonner, M.A. Van Hove, C.S. Fadley, *Phys. Rev. Lett.* **88**(55), 504 (2002)
- 3.54. T. Matsushita, F. Zhun Guo, F. Matsui, Y. Kato, H. Daimon, *Phys. Rev.* **75**, 085419 (2007)
- 3.55. S.A. Chambers, *Surf. Sci. Rep.* **16**, 261 (1992)
- 3.56. L. Kubler, F. Lutz, J.L. Bischoff, D. Bolmont, *Surf. Sci.* **251/252**, 305 (1991)
- 3.57. J.C. Vickerman (ed.), *Surface Analysis* (Wiley, Chichester, 1997)
- 3.58. J.M. Walls, *Methods of Surface Analysis* (Cambridge University Press, Cambridge, 1989)
- 3.59. S. Hofmann, Auger Electron Spectroscopy, in *Wilson and Wilson's Comprehensive Analytical Chemistry*, vol. IX, ed. by G. Svehla (Elsevier, Amsterdam, 1979), pp. 89–172
- 3.60. D. Chattarji, *The Theory of Auger Transitions* (Academic, London, 1976)
- 3.61. M.F. Chung, L.H. Jenkins, *Surf. Sci.* **22**, 479 (1970)
- 3.62. J.A. Bearden, A.F. Burr, *Rev. Mod. Phys.* **39**, 125 (1967)
- 3.63. W.A. Coghlan, R.E. Clausing, *USAEC Rep. ORNL-TM-3676* (U.S. Dept. of Commerce, Springfield, 1971)
- 3.64. D. Coster, R.L. Kronig, *Physica* **2**, 13 (1935)
- 3.65. J. Erlewein, Ph.D. thesis, University of Stuttgart, Stuttgart, 1977
- 3.66. H.E. Bishop, J.C. Riviere, *Appl. Phys. Lett.* **16**, 21 (1970)
- 3.67. J.P. Langeron, *Surf. Interface Anal.* **14**, 381 (1989)
- 3.68. G.C. Smith, M.P. Seah, *Surf. Interface Anal.* **16**, 144 (1990)
- 3.69. T. Sekine, N. Ikeo, Y. Nagasawa, *Appl. Surf. Sci.* **100/101**, 30 (1996)
- 3.70. D.E. Ramaker, *Crit. Rev. Solid State Mater. Sci.* **17**, 211 (1991)
- 3.71. D.E. Ramaker, *J. Electron Spectrosc. Relat. Phenom.* **66**, 269 (1994)
- 3.72. D.E. Ramaker, Chemical Information from Auger Lineshapes, in *Surface Analysis by Auger and Photoelectron Spectroscopy*, ed. by D. Briggs, J.T. Grant (IM Publications, Chichester, 2003), pp. 465–500
- 3.73. A.P. Dementjev, K.I. Maslakova, A.V. Naumkin, *Appl. Surf. Sci.* **245**, 128 (2005)
- 3.74. S. Hofmann, J. Steffen, *Surf. Interface Anal.* **14**, 59 (1989)
- 3.75. Z.-J. Ding, R. Shimizu, Electron Backscattering and Channeling, in *Surface Analysis by Auger and Photoelectron Spectroscopy*, ed. by D. Briggs, J.T. Grant (IM Publications, Chichester, 2003), pp. 587–618
- 3.76. M. Prutton, I.R. Barkshire, M.M. El Gomati, J.C. Greenwood, P.G. Kenny, H. Roberts, *Surf. Interface Anal.* **18**, 295 (1992)
- 3.77. D.J. Szostak, H. Thomas, *Surf. Interface Anal.* **1**, 312 (1988)
- 3.78. F. Yubero, S. Tougaard, E. Elizalde, J.M. Sanz, *Surf. Interface Anal.* **20**, 719 (1993)
- 3.79. G. Gergely, *Surf. Interface Anal.* **3**, 201 (1981)
- 3.80. F. Yubero, S. Tougaard, *Phys. Rev. B* **46**, 2486 (1992)
- 3.81. G.G. Fuentes, E. Elizalde, F. Yubero, J.M. Sanz, *Surf. Interface Anal.* **33**, 230 (2002)
- 3.82. B. Akamatsu, P. Henoc, F. Maurice, C. Le Gressus, K. Raouadi, T. Sekine, T. Sakai, *Surf. Interface Anal.* **15**, 7 (1990)
- 3.83. Y. Sakai, A. Mogami, *J. Vac. Sci. Technol. A* **5**, 1222 (1987)
- 3.84. D.G. Frank, A.T. Hubbard, Auger Microscopy, Angular Distribution, in *Concise Encyclopedia of Materials Characterization*, ed. by R.W. Cahn, E. Lifshin (Pergamon Press, Oxford, 1993), pp. 34–41
- 3.85. P. Lejček, A. Rar, S. Hofmann, *Surf. Interface Anal.* **34**, 375 (2002)
- 3.86. C.J. Powell, *J. Electron Spectrosc. Relat. Phenom.* **185**, 1 (2012)

Chapter 4

Quantitative Analysis (Data Evaluation)

AES and XPS are quantitative analytical tools. The basis of their quantification is the determination of the intensity of a characteristic signal from a measured spectrum. Mainly depending on the tolerable uncertainty in the respective analytical task, the signal intensity is obtained by application of more or less elaborate procedures to the raw data, as outlined in the next paragraph (Sect. 4.1). Section 4.2 presents the basic tools for quantification such as relative sensitivity factors and electron attenuation length in electron spectroscopies. As shown in Sect. 4.3 for XPS and in Sect. 4.4 for AES, quantification of intensities in terms of atomic concentrations is only possible by knowledge of the in-depth distribution of composition, with the limiting cases of homogeneous distribution and of thin atomic layer(s) on a substrate.

4.1 Measurement and Determination of Intensities

In any spectrum – whether in AES or in XPS – the intensity of a measured peak (P) is sitting on a background intensity (B) that has to be subtracted to give the signal intensity (P–B). For direct, “normal” spectra (usually given by $N(E)$ in XPS and $E \times N(E)$ in AES (with a CMA or with a CHA and fixed retard ratio), with E the kinetic energy of N counted electrons), the most simple procedure is to take the peak intensity (or height) (= counts at peak maximum) and subtract the background intensity (= counts measured at higher energy minimum in the vicinity of the peak), as shown in Fig. 4.1. Since in the normal mode, counts per second are measured for an energy window ΔE (i.e., $N(E)/\Delta E$), for $\Delta E = \text{const.}$ (usually in XPS), the intensity is proportional to $N(E)$. For constant retard factor ($\Delta E/E = \text{const.}$, usually in AES), the intensity is proportional to $(E \times N(E))$. For a wide energy range, the instrumental transmission function has to be taken additionally into account (see Sect. 2.5)

In AES, still most popular is the use of Auger peak-to-peak height (APPH) in the differentiated spectra ($d[N(E) \times E]/dE$) as a measure of the intensity (Fig. 4.2)

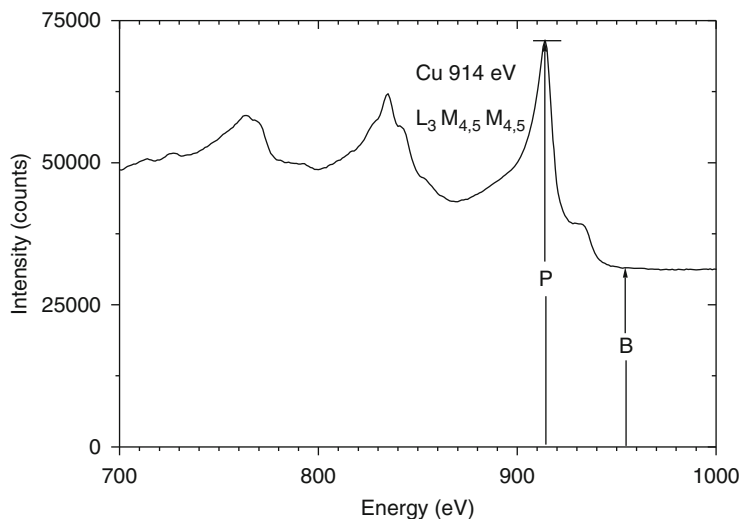


Fig. 4.1 L_3VV Auger peak of pure Cu in the direct “ $N(E)$ ” mode acquired with constant retardation factor ($\Delta E/E = \text{const.}$; hence, intensity is proportional to $(E \times N(E))$). P and B are measures of the peak and background counts, respectively

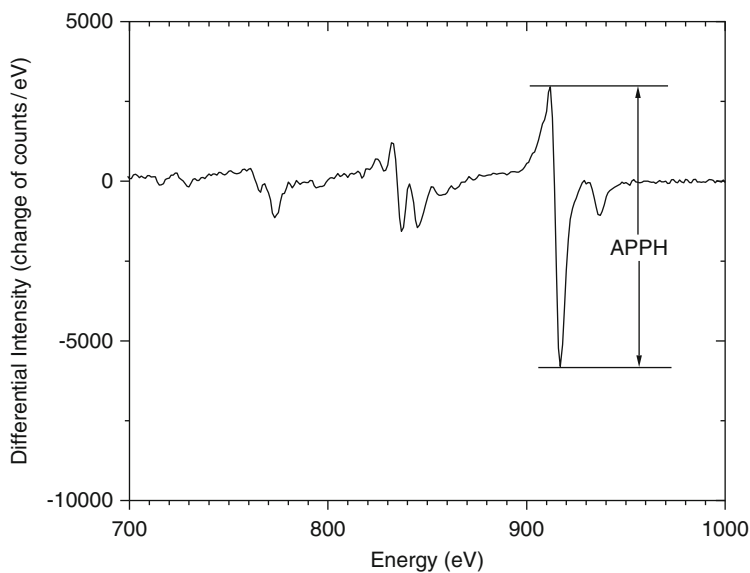
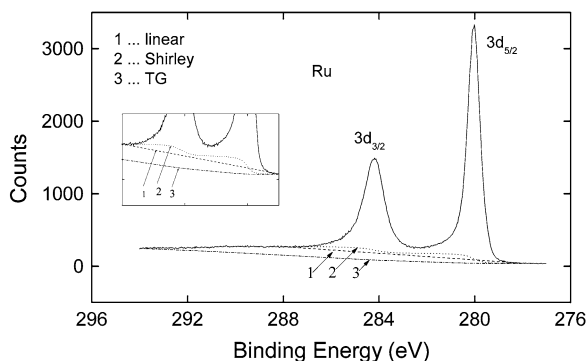


Fig. 4.2 Cu L_3VV Auger spectrum as in Fig. 4.1 but shown in derivative (“differential”) mode. A measure of the $L_3M_{4,5}M_{4,5}$ main peak intensity is the Auger peak-to-peak height (APPH) with negative excursion at 917 eV, i.e., at the maximum negative slope of the $N(E)$ peak in Fig. 4.1

Fig. 4.3 Example of the three generally applied methods to find the background under measured spectra, shown for the Ru $3d_{5/2,3/2}$ peak doublet (TG = Tougaard background)



(see Sect. 4.1.2). However, application of the (P-B) or of the APPH intensity for quantification (e.g., in combination with (4.4)) can only be recommended if the peak shape stays constant (i.e., negligible change in chemical bonding, Chap. 3) and if spectrometer resolution (Chap. 6) is the same as for the elemental standard.

A resolution-independent method of determination of the peak intensity is taking the sum of the count rate of small energy intervals or channels $\Delta E(t)$ over the total energy range of the peak (= peak area). However, the total count rate for each energy channel contains a background count rate which has to be subtracted from the measured count rate to obtain the true peak intensity. Thus, the peak shape diminished by the background shape under the peak in the same energy interval is the physically defined intensity that is necessary for accurate quantification (Fig. 4.3). Because the background intensity under the peak cannot be measured, an appropriate model description for the background is required to enable correct background subtraction.

4.1.1 Background Subtraction

Three types of background models are generally used [4.1–4.3]:

- (a) Linear background
- (b) Integral or Shirley background
- (c) Tougaard background

In addition, a kind of “automatic” background subtraction, common in AES, is provided by application of differentiation (see Sect. 4.1.2) that eliminates a linearly varying background. Another method is provided by principal component analysis (see Chaps. 7 and 8), where a part of the background with constant pattern can be treated as a principal spectral component.

The three generally applied methods are illustrated for the Ru $3d_{3/2,5/2}$ spin doublet spectra shown in Fig. 4.3:

- (a) *Linear background*: The straight line between the two endpoints of the peak is physically unrealistic but simple and therefore most convenient (Fig. 4.3) [4.1–4.3]. However, it is clear that the physics of background generation is more complicated and that the choice of the endpoint at lower kinetic energy (= higher binding energy) is not well defined. Therefore, the expected error is larger than for the more refined methods. However, the error is tolerable if the background is relatively small compared to the peak, as in case of XPS signals of surface layers with high kinetic energy.
- (b) *Integral or Shirley background*: In XPS (and in AES), the background at the lower energy side of a peak is usually higher than at the higher kinetic energy side. Assuming that this difference mainly stems from inelastically scattered photoelectrons of which the measured ones are those who survived at the surface without being inelastically scattered, the background at a given kinetic energy in the peak spectrum should be proportional to the total number of (signal) electrons above this energy. Therefore, in the Shirley model [4.4, 4.5], the peak spectrum is decomposed in N channels between the peak limiting high kinetic energy and low kinetic energy, which correspond to the lowest binding energy $E_{B,\min}$ and the highest $E_{B,\max}$, respectively. The background intensity B_{i+1} in each channel $i + 1$ in the Shirley model is given by a fraction k_s of the signal intensity $(I_i - B_i)$ in the previous channel,

$$B_{i+1} = k_s \sum_{i=0}^{i_{\max}} (I_i - B_i), \quad (4.1)$$

where $i = 0$ corresponds to $E_{B,\min}$ and $i = i_{\max}$ corresponds to $E_{B,\max}$. Per definition, $P_0 = B_0$ for $E_B = E_{B,\min}$. The constant “Shirley factor” k_s is determined by the condition that at $E_{B,\max}$, $I(E_{B,\max}) = B(E_{B,\max})$. The Shirley background subtraction gives best results if the background on the high binding energy side is horizontal with energy, and usually has a tendency to too low peak areas for further increasing background [4.6]. For both methods, the linear (a) and integral (b) background, the result strongly depends on an appropriate choice of the low- and high-energy endpoints.

- (c) *Tougaard background*: The Tougaard background model [4.7–4.9] has a firm physical base because it takes into account the initial energy distribution function and inelastic electron scattering. The Tougaard background is usually given by

$$B_i = \int_{E^k}^{E_{\max}^k} \frac{B(E' - E)}{[C + (E' - E)^2]^2} I(E') dE', \quad (4.2)$$

where $E_{\max}^k$ is the high kinetic energy endpoint where the background is equal to the measured intensity, and B and C are fitting parameters. It was found [4.1, 4.8] that a value of $B = 681.2 \text{ eV}^2$ and of $C = 355.0 \text{ eV}^2$ gives good results for 59

elements. For more details, including experimental determination of the background from reflected electron energy loss spectra (REELS), the reader is referred to the paper by Seah et al. [4.10] and references therein. Most instrument manufacturers offer Tougaard software for background subtraction. The Tougaard background is physically realistic but requires a large energy range extending some 50 eV to the higher binding energy side to get the data needed for a reasonable fit. Because of this complication and because of its dependence on the in-depth elemental distribution, the Tougaard background is less frequently used in practical applications, where the Shirley approach seems to be sufficiently accurate [4.11].

It is obvious that prior to any background subtraction satellite lines such as $K\alpha_{3,4}$ for nonmonochromatic X-rays or ghost lines as well as plasmon loss peaks (see Sect. 3.2.6) should be identified and subtracted from the spectra if they overlap with an elemental peak. Special data acquisition and/or processing methods can be considered as “automatic” background subtraction methods, such as the use of derivative or differentiated (“differential”) spectra in AES (Sect. 4.1.2) and principal component or target factor analysis in AES and XPS (Sect. 4.1.4). Because the Tougaard background intensity and shape depend on the depth of origin of the signal emitter, it can be used as a means of nondestructive depth profiling (see Sect. 7.2.3).

A thorough round-robin study of the uncertainties encountered when applying the three above methods to quantify different simulated XPS spectra by Powell and Conny [4.11]. The results showed that the narrow integration limits in linear and Shirley background subtractions lead to peak intensities that are much smaller than the total peak intensities. Nevertheless, such measurements can yield good consistency for quantitative measurements except when there is a change in the peak line shape or the fraction of intensity in intrinsic (shake-up) excitations due to change of chemical state. Fits to all of the peaks associated with an elemental line (i.e., the main peak together with other structures due to inelastic scattering) can give intensity for the main peak close to the total peak intensity except for that fraction due to intrinsic excitations; the latter fraction is typically included with the intensity of an inelastic peak (Sect. 3.2.6).

4.1.2 Differential (Derivative) Spectra (APPH in AES)

In principle, the above three methods of background subtraction can be applied to direct AES spectra. However, the electron background intensities in AES are much larger than in XPS because of two additional sources: (1) inelastic scattering of the primary electrons and (2) the secondary electron emission at lower energies. These effects can, in principle, be corrected for, and useful approximate formulas can be found, for example, in [4.12]. At present, there seems to be no generally accepted procedure for optimum background subtraction in practical AES. Because in typical AES spectra background intensities exceed by far signal intensities, it is clear that uncertainties after background subtraction are higher as compared to XPS. This is one of the reasons that quantification using derivative spectra is still widespread

in use, despite the disadvantage of its sensitivity to chemical bond influence (see, e.g., Fig. 3.21). Differentiation of a bell-shaped peak results in a curve with both a positive and a negative peak. The distance between these two peak amplitudes, the so-called Auger peak-to-peak height (APPH), is taken as a measure of the elemental intensity. It can be shown that the APPH is proportional to the peak area if the peak shape does not change with intensity. Another reason for the popularity of APPH is elimination of the linear component in the background. Since the background at higher energies increases almost linearly with the energy, the differential spectrum shows a nearly horizontal line at energies >100 eV, with superposition of the typical double peaks with low- and high-energy extensions (cf. Fig. 4.2).

Because many Auger peaks have a broad low-energy shoulder, which is sensitive to background changes, frequently the background-to-peak extension (on the high kinetic energy side) is used to describe the signal intensity for quantification [4.13–4.15]. (Of course, sensitivity factors have to be changed accordingly.)

In older, analog equipment, the slow, time proportional increase of the analyzer voltage is modulated by a small, high-frequency modulation voltage followed by output detection at that frequency with a lock-in amplifier which directly gives the derivative spectrum [4.2, 4.15]. The modulation voltage determines the observed intensity. A plot of the intensity in terms of peak area approximated by $I_{\max} \times W$ (with $I_{\max}$ the negative peak extension and W the peak width) versus the ratio of modulation voltage (V) to peak width (W) is shown in Fig. 4.4 [4.15]. For low modulation amplitudes, the dependence is linear. Therefore, this is the appropriate region for a proportional gain in intensity with no change in peak width, i.e., $V/W \leq 0.5$. Above that value, the curve begins to deviate from linearity and approaches maximum intensity around $V/W = 2$. Above $V/W > 3$, the intensity

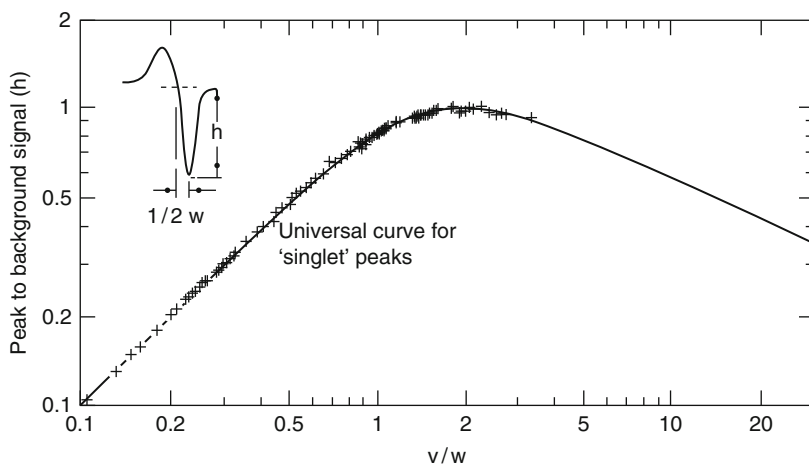


Fig. 4.4 Differential peak intensity (here peak-to-background, see *inset*) as a function of the normalized modulation voltage V/W with V , the modulation voltage amplitude and W , the peak width (Reproduced from M.P. Seah and M.T. Antony [4.15], with permission of Elsevier B.V. Crown Copyright 1983)

decreases. This is the region of “overmodulation,” with severe loss of resolution and intensity. A similar behavior is observed by changing the analyzer resolution [4.2].

In contrast, pulse counting digital instruments acquire direct spectra in counts per seconds (for constant energy interval), as shown for Cu in Figs. 4.1 and 3.19a. Usually, direct spectra are converted to derivative spectra by Savitzky–Golay cubic N -point differentiation with N between 3 and 25 (most common is 5-point differentiation) (see Fig. 3.19b). For other differentiation and smoothing algorithms and their comparison, see Seah et al. [4.1, 4.12, 4.15, 4.16].

Figure 4.4 demonstrates how Auger peak-to-peak heights depend on the resolution and/or the differentiation method used. It is obvious that with higher point smoothing and differentiation (corresponding to overmodulation in analog equipment), peaks are apparently broadened and therefore are less sensitive to possible APPH changes caused by chemical bonding influence, as shown by Pamler [4.17] for quantification of TiN with respect to Ti. Because the effect of broadening depends on shape and peak width, the relative APPH may change with derivative smoothing. Thus, the ratio of APPH (Cu 917 eV)/APPH(Cu 61 eV) changes from 0.97 in Fig. 3.19b (5-point S-G differentiation) to 1.36 when using 25-point S-G differentiation, with an according influence on relative elemental sensitivity factors of both peaks (see Sect. 4.3.2).

4.1.3 *Decomposition of Overlapping Peaks*

Frequently, a measured peak consists of contributions of two different elements, or of the same element in different bonding or valence states, such as metal and metal oxide. Depending on the energy separation and on the analyzer resolution, multiplet splitting (e.g., $2p_{1/2}$, $2p_{3/2}$) can either be treated as one peak or as two peaks with constant and known energy difference and intensity ratio (see Table 3.2). Figure 3.8 shows an example of the measured XPS $2p_{3/2}$ peak of Al when both metallic and oxide states are present, together with its decomposition to the contributions of both states. Usually, XPS peaks are characterized by a Gaussian/Lorentzian fit of the peak shape, and the respective contributions are provided with the instruments software (see Sect. 3.1.7). While most instrument manufacturers include software for peak decomposition, the traditional and still very useful way to look for peak components is peak synthesis. By assuming peak width and location of several peaks and their Gauss/Lorentz ratio, the convoluted spectra can be approximated. The residue after subtraction from measured spectra can be minimized by repeated trial and error, which is done automatically by the usual software. Overlapping peaks in derivative spectra (AES) can be separated by factor analysis.

4.1.4 *Factor Analysis and Principal Component Analysis*

General chemometric methods based on mathematical algorithms of pattern recognition have become popular because of their ability to decompose an array of

many complicated spectra into meaningful spectral components. These methods, notably factor analysis and principal component analysis, together with spectral synthesis and linear least squares fitting, have shown their usefulness in quantitative analysis for typical areas such as chemical mapping, depth profiling (Figs. 7.3–7.5), oxidation (Fig. 9.6, Figs. 9.14 and 9.17), implantation (Fig. 9.12), and background subtraction [4.18]. Therefore, a summary of these chemometric methods will be presented in Sect. 9.3.

4.2 Quantification Using Intensities

Careful determination of elemental intensities is the basis of any quantification. Having determined the intensity for all measurable elemental peaks in a sample, we can find its composition, usually given in atomic percent (“atomic fraction”) or mole fraction of the elements. There are principally three ways to quantify measured intensities: (a) elemental relative sensitivity factors (E-RSFs) derived from pure element standard intensities, (b) using basic physical equations with appropriate materials and instrumental parameters, and (c) a combination of both, with correction for matrix effects and for elemental in-depth distribution. Whereas (b) is rarely applied in practice because the necessary instrumental parameters are not accurately known and (a) is easy and therefore most frequently used but has high uncertainty, (c) is an appropriate way applied in practical surface analysis.

4.2.1 Quantification Principles Using Elemental Relative Sensitivity Factors (E-RSFs)

The most simple, purely empirical approach to quantification is comparison of the signal intensity, I_A , of an element A in a sample of unknown composition with the signal intensity, I_A^0 ,¹ of an elemental reference sample of pure A (with a clean, smooth surface; for roughness influence, see Chap. 5). The ratio of both intensities is then taken as a measure of the mole fraction X_A of element A in the analyzed sample, i.e.,

$$X_A = \frac{I_A}{I_A^0}. \quad (4.3)$$

Equation 4.3 ignores any matrix effect (see Sect. 4.3.2) and assumes homogeneous elemental concentrations. It is only valid if measurements of I_A and I_A^0 are performed with exactly identical conditions (e.g., photon flux in XPS, or beam

¹Frequently, the notation I_A^∞ is used (to indicate infinite sample thickness) [4.1, 4.2] instead of I_A^0 used here (with the superscript 0 denoting any standard reference quantity in chemistry as recommended by IUPAC [4.19]).

current and voltage in AES, as well as excitation and emission angle and analyzer settings). Because of the necessity of identical excitation strength, (4.3) is practically restricted to samples with spatial or in-depth distribution where a region of pure A can be used as an internal standard (see Fig. 7.34a). In a multielement sample, the ratio of the atomic concentration (or mole fraction) of elements A and B follows from (4.3) as

$$\frac{X_A}{X_B} = \frac{I_A/I_A^0}{I_B/I_B^0} = \frac{I_A/S_A}{I_B/S_B} = \frac{I_A}{I_B} S_{B,A}, \quad (4.4)$$

where X_A , X_B , I_A , I_B and I_A^0 , I_B^0 are the mole fractions, the measured intensities, and the 100% standard intensities of elements A and B, respectively, $I_A^0 = S_A$, $I_B^0 = S_B$ are the absolute elemental sensitivity factors, and $S_{B,A} = S_B/S_A$ is the *elemental relative sensitivity factor* (E-RSF, often simply called RSF) of A relative to B. For a binary system, $X_B = 1 - X_A$ and (4.4) can be solved for absolute mole fractions X_A , X_B . If matrix effects are ignored, (4.4) is still valid in systems with additional components $C, D, \dots$. The elemental standard intensities I_A^0 , I_B^0 , etc., have to be measured under the same experimental conditions as the analyzed sample intensities. In contrast, their ratio, i.e., the elemental relative sensitivity factor $S_{B,A}$ in (4.4), is independent of the excitation intensity (photon flux or beam current). The method of quantification by relative elemental sensitivity factors is most commonly used in AES and XPS because of its simplicity. The idea is that – at least for a specific instrument and with constant instrument parameters – every pure element sample shows up with certain intensity I_i^0 . When measuring a sample of unknown composition the same peak with intensity I_i , the ratio I_i/I_i^0 is thought to be equal to the mole fraction of element i , X_i . If all elements n in the specimen are measured by one specific peak each, the sum of all relative peak heights (or peak areas) or molar fractions X_j with $j = 1 \dots n$ should add up to unity, $\sum X_j = 1$ [4.20]. This means

$$X_i = \frac{I_i/I_i^0}{\sum_{j=1}^n (I_j/I_j^0)} = \frac{I_i/S_i}{\sum_{j=1}^n (I_j/S_j)}. \quad (4.5)$$

Expression (4.5), introduced by Palmberg [4.20], is only valid if *all* elements in a sample are detected, each by one selected peak. This may cause problems when hydrogen is a major component. However, (4.3) and (4.4) are still correct if pure element standards (I_A^0 , I_B^0) are measured under identical experimental conditions.

As an example of the application of (4.5), let us consider a specimen consisting of three elements (1,2,3). The relative concentration X_i of each element (in atomic fraction) is given by

$$X_1 = \frac{I_1/I_1^0}{\left(\frac{I_1}{I_1^0} + \frac{I_2}{I_2^0} + \frac{I_3}{I_3^0}\right)} = \frac{I_1/S_1}{\left(\frac{I_1}{S_1} + \frac{I_2}{S_2} + \frac{I_3}{S_3}\right)} = \frac{I_1}{\left(I_1 + \frac{S_1}{S_2} I_2 + \frac{S_1}{S_3} I_3\right)}, \quad (4.6a)$$

$$X_2 = \frac{I_2/I_2^0}{\left(\frac{I_1}{I_1^0} + \frac{I_2}{I_2^0} + \frac{I_3}{I_3^0}\right)} = \frac{I_2/S_2}{\left(\frac{I_1}{S_1} + \frac{I_2}{S_2} + \frac{I_3}{S_3}\right)}, \quad (4.6b)$$

$$X_3 = \frac{I_3/I_3^0}{\left(\frac{I_1}{I_1^0} + \frac{I_2}{I_2^0} + \frac{I_3}{I_3^0}\right)} = \frac{I_3/S_3}{\left(\frac{I_1}{S_1} + \frac{I_2}{S_2} + \frac{I_3}{S_3}\right)} \quad (4.6c)$$

with the elemental standard intensities I_1^0 , I_2^0 , I_3^0 and the relative elemental sensitivity factors S_1 , S_2 , S_3 , with $S_i = I_i^0/I_{\text{std}}^0$ (with I_{std}^0 the standard reference intensity of a chosen element (std)). For example, if element 1 is chosen as reference element, $S_1 = I_1^0/I_1^0 = 1$, $S_1/S_2 = I_1^0/I_2^0$, and $S_1/S_3 = I_1^0/I_3^0$, as shown in (4.6a). Values for the elemental standard intensities are sometimes provided in handbooks (e.g., in mm length of Auger peak-to-peak heights [4.21]). Note that in contrast to peak area measurements, for intensity measurements by peak height in direct mode or by Auger peak-to-peak height (APPH) in differential mode, the instrumental resolution for the sample measurement has to be the same as that used for the standard measurement (see Sect. 4.1.2). As seen from (4.6a) to (4.6c), only the relative elemental intensities I_1^0/I_2^0 , I_1^0/I_3^0 are required. Generally, these different ratios are given with respect to one standard element peak intensity (usually Ag ($M_5N_{4.5}N_{4.5}$) for AES, C 1s or F 1s for XPS), and the elemental relative sensitivity factors are given as E-RSF (for element i) = $S_i = I_i^0/I_{\text{Ag}}^0$ for AES and $I_i^0/I_{\text{Cl s}}^0$ or $I_i^0/I_{\text{F s}}^0$ for XPS. These RSFs are often tabulated by the instrument suppliers or in handbooks [4.21–4.24] and have been critically discussed by Seah [4.25]. It is important to keep in mind that the conditions of excitation (primary electron energy, incidence angle) and of analysis (e.g., analyzer resolution (in case of peak height in the $N(E)$ mode or APPH in the derivative mode), emission angle, and transmission as a function of energy) are decisive for the accuracy of quantification by RSFs [4.40]. The simple quantification procedure with (4.5) can only give reasonable values if the sample is homogeneous in depth as well as in lateral dimension, i.e., in the analyzed volume. Equation 4.5 provides a quick, semiquantitative result of the concentrations of the detected elements. However, with the exception of special cases, it has to be corrected because of inevitable matrix effects discussed below, even for a single phase with homogeneous composition.

The most accurate way of quantification is based on the analysis of a standard material of known composition (i.e., known relative sensitivity factors) that should be close to that of the sample with unknown composition under identical measurement conditions and then apply (4.5). In general, this is rarely the case, and it is easier to measure pure elements with identical experimental conditions (i.e., I_1^0 , I_2^0 , I_3^0 , etc., in (4.6)). It is recommended to use one's own elemental standards and measure their intensity under exactly the same instrumental conditions as those used to analyze the sample (a convenient arrangement of some 50 elements for AES is commercially available [4.26]). When an improved accuracy is required, matrix effects have to be taken into account, and the elemental relative

sensitivity factors (E-RSFs) have to be corrected to yield matrix relative sensitivity factors (M-RSFs). To get an idea how to perform matrix effect corrections, we have first to consider the physics behind the relative sensitivity factors, as disclosed by consideration of the basic quantitative equations in Sect. 4.3.2. A guide for the use of relative sensitivity factors for quantitative analysis of homogeneous materials (including matrix effect corrections) is given in Ref. [4.27].

4.2.2 Key Parameters: Inelastic Mean Free Path (IMFP) and Effective Attenuation Length (EAL)

An exact quantitative analysis by AES or XPS requires a unique relation between a measured Auger- or photoelectron intensity (count rate or current) and an elemental concentration. Since the first basic equations were established by Palmberg 1972 [4.20] for quantitative AES and by Fadley 1974 [4.28] for quantitative XPS, many authors have used variations or extensions of these equations. The principle of quantification is similar for AES and XPS, but different excitation and electron generation mechanisms have to be taken into account.

The fundamental approach of Jablonski and Powell [4.29] is based on the assumption that the sample is either amorphous or sufficiently polycrystalline that diffraction or channeling effects can be ignored. The latter effects can be important in AES if a narrow primary beam is incident on a single grain (see Sect. 3.3.5). Keeping in mind this limitation, the totally emitted intensity I_{em} of Auger- or photoelectrons for a homogeneous, amorphous solid can be rigorously described by an integral over depth z , of the product of the (appropriately normalized) excitation depth distribution function (EXDDF), $\Phi(z, E_i, E_p, \alpha)$, and the emission depth distribution function (EDDF), $\Psi(z, E_{P,A}, \theta)$,

$$I_{\text{em}} = K \int_0^{\infty} \Phi(z, E_i, E_p, \alpha) \Psi(z, E_{P,A}, \theta) dz, \quad (4.7)$$

where α is the incidence angle of the photons or electrons, E_p their primary energy, E_i , the ionization potential, $E_{P,A}$, the kinetic energy of the generated Auger- (A) or photoelectrons (P), θ their emission angle and K a constant.² (For visualization of the respective angles with respect to the sample, see Figs. 4.12 and 4.13.) Although extensive Monte Carlo calculations of both functions have been made [4.29, 4.30], in practice, analytical expressions of the functions Φ and Ψ are generally used. Whereas the excitation depth distribution function, Φ , can be shown to be depth independent for most practical purposes (except for grazing incidence XPS and

²Unfortunately, notations of incidence and emission angles (α, θ) are opposite in the work of Jablonski and Powell [4.29] and of Seah [4.1, 4.2], which we have adopted here.

AES, see Sects. 5.1.3 and 5.2.1), the emission depth distribution function is strongly depth dependent. In fact, its confinement to a small region in nanometer dimensions is the cause of surface sensitivity of both AES and XPS. For most practical applications, (4.7) is usually written in the approximate form (see Sect. 4.3),

$$I_{\text{em}} = K_{\Phi} \int_0^{\infty} N_A(z) \exp \left[-\frac{z}{\lambda_{m,E(A)} \cos \theta} \right] dz, \quad (4.8)$$

where K_{Φ} stands for $K_{\Phi}(z, E_i, E_p, \alpha)$, and $\Psi(z, E_{p,A}, \theta)$ is expressed by the term under the integral, where $N_A(z)$ is the atomic concentration of element A at depth z , and $\lambda_{m,E(A)}$ is the (effective) attenuation length of the Auger- or photoelectrons of a specific line of element A, characterized by its kinetic energy $E(A)$, and m denotes the matrix, i.e., the atomic surroundings of A. For both techniques, XPS and AES, the basic parameter is the effective attenuation length (EAL). $\lambda_{m,E(A)}$, given by the inelastic mean free path (IMFP) combined with a correction term that takes into account the additional elastic scattering of the respective photo- or Auger electrons (see, e.g., [4.16,4.29]). It should be kept in mind that scattering cross sections locally depend on matrix composition $N_{m,z}$, on the depth of origin below the surface, and on the emission angle. Therefore, the parameter $z/\lambda_{m,E(A)}$ is an average value of the integral

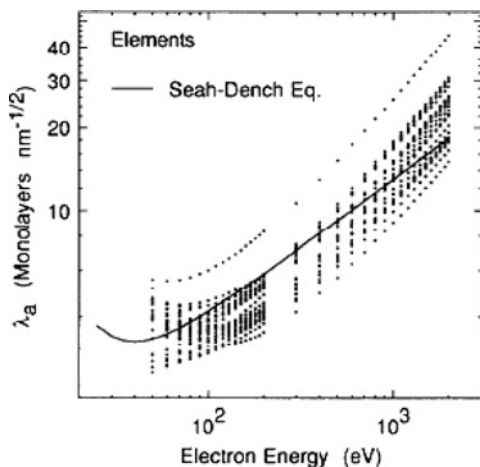
$$z/\lambda_{m,E(A)} = \int_0^z [1/\lambda_{E(A)}(N_{m,z}z, \theta)] dz'. \quad (4.9)$$

Usually, the thickness and emission angle dependences (at least for $\theta < 60^\circ$, see below) are relatively small and negligible, and the matrix dependence can be considered by a stepwise change $\lambda_{m,E(A)}$ with depth z (see Sect. 4.3.3). Therefore, for a given, constant matrix composition, $\lambda_{m,E(A)}$ can be assumed to be constant in (4.8). However, as pointed out by Chen [4.31], for very thin layers and at high emission angles ($\theta > 60^\circ$), additional surface excitations decrease the inelastic mean free path and therefore the attenuation length (see next paragraph, Fig. 4.5).

Because of its principal importance in quantitative AES and XPS, we will first summarize the most important features of the attenuation length for the practical analyst. For more detailed information, the reader is referred to reviews by Jablonski and Powell [4.29, 4.33–4.35].

Electrons of typically a few hundreds eV energy cannot travel very far in solids without suffering energy losses. Therefore, XPS and AES are surface sensitive techniques. Although the incident X-rays – or high-energy electrons – penetrate the sample up to relatively large depths, the depth from which the generated photo- or Auger electrons can escape from the sample surface without energy loss is usually less than a few nanometers. In analogy with the Lambert–Beer law in optics for transmission of light through matter, the probability of transmission is described by an exponential decay with traveling length z (4.8), with a characteristic decay length given by the attenuation length (AL, or effective attenuation length, EAL,

Fig. 4.5 Comparison of the Seah–Dench equation (4.10) (in monolayers and divided by $a^{1/2}$) with the IMFP results for 27 elements after TPP–2M (4.12). Note that the exponent of the energy dependence of $1/2$ (Seah–Dench) is too small as compared to the exponent of $3/4$ corresponding to the TPP–2M equation for the IMFP (Reproduced from C. J. Powell [4.32], with permission of Elsevier B V.)



see below). The attenuation length, λ , which determines the surface sensitivity of XPS and AES, is thought to consist of at least two contributions, inelastic and elastic scattering. Inelastic scattering is described by the inelastic mean free path (IMFP) (denoted in the following by the symbol λ_{in}). The IMFP is defined as the mean distance an electron travels before engaging in an interaction in which it experiences an energy loss.

The inelastic mean free path, λ_{in} , is a complex quantity that one would expect to depend on the nature of the solid sample. However, using an extensive database, Seah and Dench [4.36] compiled a “universal curve” of $\lambda(SD)$ as a function of the electron energy in a benchmark paper published 1979. The authors considered $\lambda(SD)$ to be the inelastic mean free path (IMFP), but actually it corresponds to the attenuation length (see below) since that is the quantity to be experimentally determined. Because of its simplicity, the Seah and Dench relation was used as a popular database in quantitative AES for many years. Although outdated, we present here the Seah and Dench formula because of useful comparison with older work (in particular for corrections of absolute layer thicknesses, see Sects. 4.3.3 and 4.4.3). According to Seah and Dench, values for the IMFP of elements are given by the expression [4.36]

$$\lambda(SD)(nm) = \frac{538a}{E^2} + 0.41a^{3/2}E^{1/2}, \quad (4.10)$$

where a is the mean atomic distance (“monolayer thickness”) in nanometers and E is the kinetic energy in eV. The first term can be ignored for $E > 100$ eV, resulting in a proportionality with $E^{1/2}$. The parameter a is calculated from

$$a = \left(\frac{M}{\rho N_{Av0}} \right)^{1/3}, \quad (4.11)$$

where a is in m when M is the atomic mass in kg, ρ the density in kg/m³ and N_{Av0} Avogadro’s number for 1 kmol, 6.02×10^{26} kmol^{−1}.

Today, there is general agreement that there is no universal curve for IMFP. However, $\lambda(SD)$ values for most elements are of the right order of magnitude but may deviate by up to about 50% (in particular at high energies) as compared to present theoretical values from the NIST database [4.37] (see Table 4.1 and Figs. 4.5 and 4.6). (For inorganic and organic compounds, the deviation may even be larger.) In all cases, the exponent 0.5 of the energy dependence of $\lambda(SD)$ is too low as compared to 0.75 for the NIST values [4.32] (see Fig. 4.5).

4.2.2.1 The TPP–2M Equation for IMFP

Today, the so-called TPP–2M equation (the second modification of respective publications by Tanuma, Powell, and Penn) is generally accepted for quantitative prediction of IMFP values in amorphous solids. According to Tanuma et al. [4.38], IMFP values for electron energies between 10 and 2000 eV for any material are fitted to a modified Bethe equation for inelastic electron scattering in matter, which is given by the TPP–2M equation

$$\lambda_{\text{in}} = \frac{E}{E_p^2 [\beta \ln(\gamma E) - (C/E) + (D/E^2)]}, \quad (4.12)$$

where E is the electron energy in eV, $E_p = 28.8(N_v \rho / M)^{1/2}$ is the free electron plasmon energy in eV, N_v is the number of valence electrons per atom, M is the atomic mass in g mol/cm³, and ρ is the density in g/cm³. Numerical values of the parameters β , γ , C , and D are obtained by fitting (4.12) to the computed IMFPs for each material.

Tanuma et al. [4.38] derived the following empirical expressions for β , γ , C , and D :

$$\beta = -0.10 + 0.944 / \left(E_p^2 + E_g^2 \right)^{1/2} + 0.069 \rho^{0.1}, \quad (4.13a)$$

$$\gamma = 0.191 / \sqrt{\rho}, \quad (4.13b)$$

$$C = 1.97 - 0.91U, \quad (4.13c)$$

$$D = 53.4 - 20.8U, \quad (4.13d)$$

with

$$U = N_v \rho / M = E_p^2 / 829.4, \quad (4.13e)$$

where E_g is the bandgap energy (in eV) for a nonconducting material.

IMFPs can be estimated from TPP–2M (4.12) for elements [4.41], inorganic [4.41] and organic [4.38] compounds with an uncertainty of typically 10% [4.43]. As an example, Fig. 4.5 shows the energy dependence of the IMFP for several elements (C, Fe, Ta, Bi) calculated with (4.12) and (4.13a)–(4.13e). Necessary values of β , γ , C , and D can also be found in [4.38, 4.41]. It is clear that there is

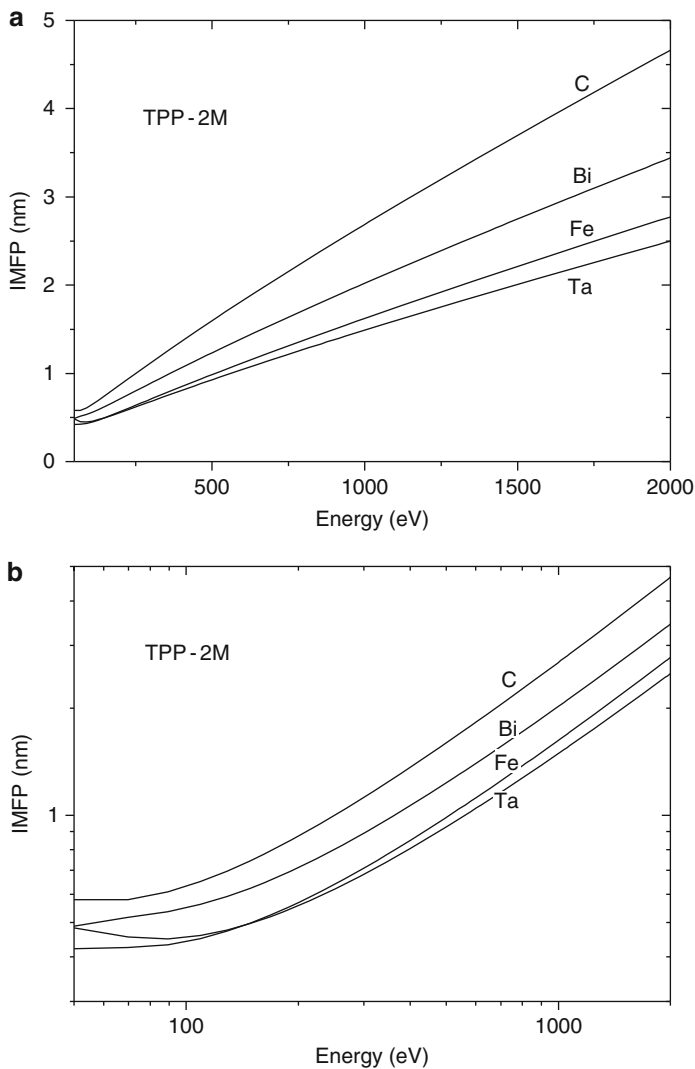


Fig. 4.6 Inelastic mean free path λ_{in} (IMFP) as a function of the kinetic electron energy: (a) C, Fe, Ta, and Bi between 50 and 2000 eV calculated with TPP-2M (4.12) and parameters given in [4.38]; (b) as (a) but on double logarithmic scale to illustrate the exponent function with $m = 0.75 \pm 0.02$ for energy > 200 eV (cf. (4.19))

no “universal curve,” but the double logarithmic scale in Fig. 4.5 demonstrates that the energy dependence for these elements above $E = 200$ eV is well represented by a proportionality to E^m with exponent $m = 0.75 \pm 0.02$. This important fact will be used later (Sect. 4.3.2) to calculate ratios of attenuation length values.

New calculations of the IMFP for 41 elemental solids are reported and discussed by Tanuma et al. [4.44], showing improved agreement with experimental data.

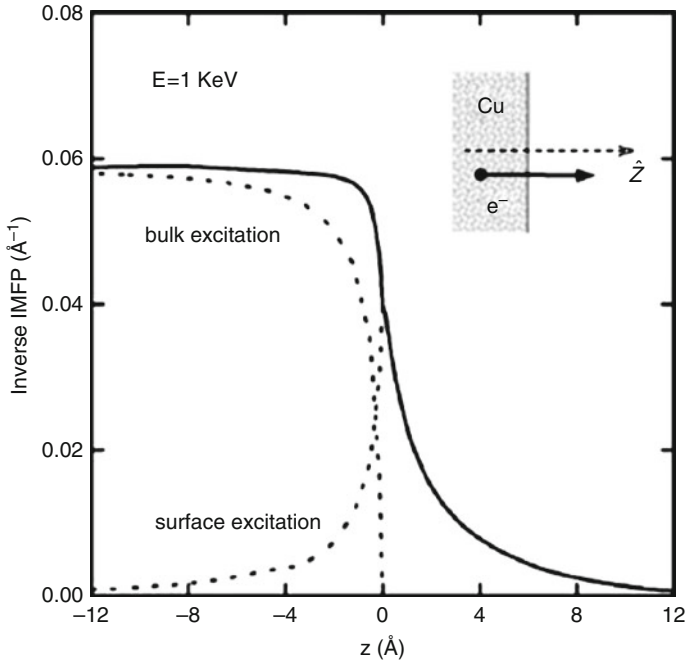


Fig. 4.7 Position dependence of the calculated inverse IMFP for bulk and surface excitations and their superposition (*solid line*) in the vicinity of the surface at $z=0$ (Reproduced from Y. F. Chen [4.46], with permission of Elsevier B.V.)

4.2.2.2 Correction of IMFP for Surface Excitations (SEP Parameter)

The IMFP described by (4.12) is derived for infinitely extended bulk solids. When electrons from the bulk are crossing a surface, surface excitations have to be taken into account. Whereas the IMFP is characterized by bulk excitations, surface excitations are characterized by the surface excitation parameter (SEP) which is given by the mean number of surface plasmons excited by an electron crossing the surface [4.31 4.45–4.47]. The cross sections for both contributions (proportional to the inverse inelastic mean free path) are described by the dielectric function of the solid. As shown by Chen and Kwei [4.46], both contributions can be separated and (at least in a first order approximation [4.48]), as schematically shown for 1 keV electrons in Cu as a function of the distance to the planar surface in Fig. 4.7 [4.45]. This material- and energy-dependent surface “Begrenzungs-Effekt” is confirmed by theoretical studies of Werner [4.49], Salma et al. [4.50], and Pauly and Tougaard [4.51]. Since the surface excitation is inversely proportional to both the velocity of

the electron (i.e., proportional to $E^{-1/2}$) and the distance to the surface (proportional to $(\cos \theta)^{-1}$), Chen [4.45] derived for the surface excitation parameter (SEP) for metals and semiconductors,

$$P_s(E, \theta) = \frac{a_{\text{Ch}}}{\sqrt{E_p} \cos \theta}, \quad (4.14)$$

where E is the kinetic energy in eV, a_{Ch} is a material-dependent fitting parameter with dimension $(\text{eV})^{1/2}$, and θ is the emission angle. For the free electron gas, $a_{\text{Ch}} = 2.9 (\text{eV})^{1/2}$ [4.45]. The semiempirical Oswald–Werner equation [4.52] is rather similar but shows a weaker dependence on emission angle and energy:

$$P_s(E, \theta) = \frac{1}{a_w \sqrt{E_p} \cos \theta + 1}. \quad (4.14a)$$

Here, $a_w (\text{eV})^{-1/2}$ is a different material-dependent fitting parameter.

With the surface excitation parameter given by (4.14) and (4.14a), the probability for an electron traversing the solid surface without suffering energy losses by generating surface plasmons is proportional to

$$f_s = \exp[-P_s(E, \theta)]. \quad (4.15)$$

To correct the bulk IMFP for surface excitations, the general equation used for quantitative XPS, (4.12), has to be multiplied by the factor f_s given by (4.15). Using (4.14) and (4.14a), both the energy and emission angle dependencies of the surface excitation factor f_s are shown for Ag in Figs. 4.8 and 4.9, respectively.

Because of considerable uncertainties of both theoretical estimation of a_{Ch} and a_w and experimental measurements, calculated values of f_s and $P_s(E, \theta)$ generally deviate from those determined experimentally [4.53]. The main techniques to study surface excitations are elastic peak electron spectroscopy (EPES) [4.53–4.55] and reflection electron energy loss spectroscopy (REELS) [4.56, 4.57], as recently reviewed by Nagatomi and Tanuma [4.58]. While the theoretical energy dependence of the SEP parameter was qualitatively confirmed by REELS experiments [4.56], the strong angular dependence at high emission angles as seen for the SEP correction factor f_s in Fig. 4.9 was not verified experimentally [4.49]. The surface excitation correction for the IMFP(TPP–2M) values strongly depends on the material and on the energy. Tanuma et al. [4.54] report an average root-mean-square difference between IMFP(TPP–2M) and IMFP(EPES) of 10.7% for energies from 100 to 5000 eV for 13 elements, with Ta and W showing the largest difference of 26%. Because of the effect of surface excitations is most pronounced for very thin layers and high emission angles [4.162], this fact may compensate for the increase of EAL calculated for these cases [4.37] (see Fig. 4.10) and thus explain the experimentally found independence of both parameters (see Sect. 7.2.1).

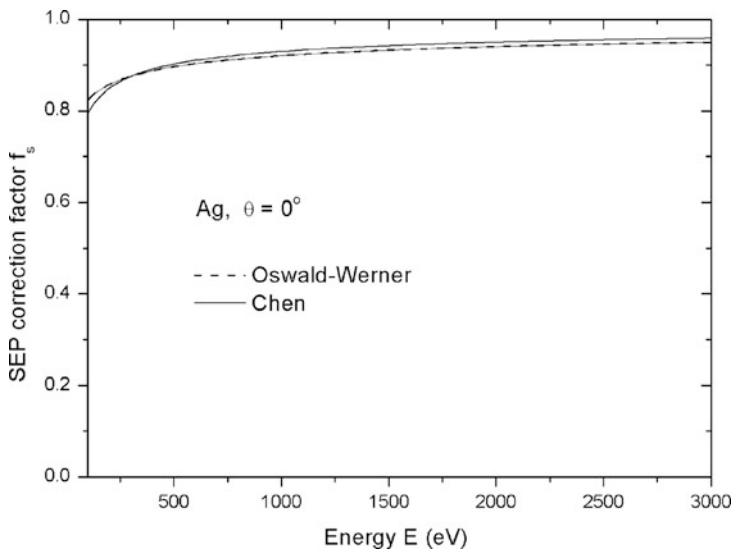


Fig. 4.8 Energy dependence of the SEP correction factor f_s for Ag with (4.15), using (4.14) (solid line: Chen, $a_{\text{Ch}} = 2.3 \text{ eV}^{1/2}$) [4.45] and (4.14a) (dashed line: Oswald-Werner, $a_{\text{W}} = 0.32 \text{ eV}^{-1/2}$) [4.53]

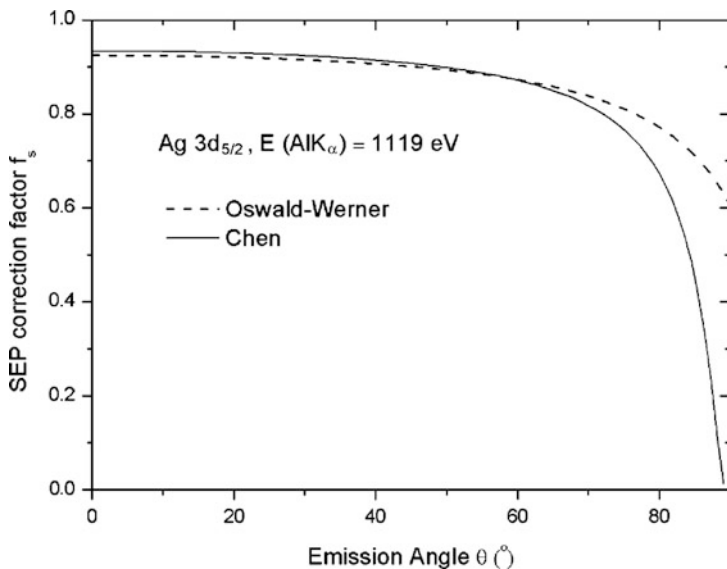


Fig. 4.9 Emission angle dependence of the SEP correction factor, f_s , calculated for Ag $3d_{5/2}$ peak (for AlK_α source $E = 1119 \text{ eV}$), with (4.13c) using (4.13a) (solid line: Chen, $a_{\text{Ch}} = 2.3 \text{ eV}^{1/2}$) [4.45] and (4.13b) (dashed line: Oswald-Werner, $a_{\text{W}} = 0.32 \text{ eV}^{-1/2}$) [4.53]

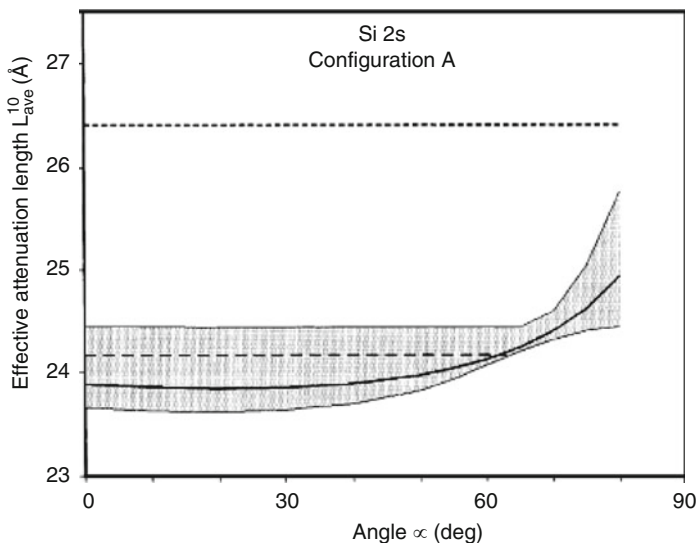


Fig. 4.10 The average practical EAL (effective attenuation length) of Si 2s (at 1300 eV) in Si as a function of the emission angle α ($=\theta$ in our usage) (solid line) as compared to the CS2 predictive formula (4.15) shown as long dashed line. The shaded region gives the range of practical EAL values for film thicknesses between zero and a maximum film thickness (for thickness independence). The short dashed line gives the IMFP after (4.12) (dashes are short or long) (Reproduced from A. Jablonski and C.J. Powell [4.33], with permission of Elsevier B.V.)

4.2.2.3 The Effective Attenuation Length (EAL)

The inelastic mean free path (IMFP, (4.12)) ignores elastic scattering. Until about 20 years ago, the influence of elastic scattering on the attenuation of the measured intensity was neglected, and only inelastic scattering was considered. All measurements, however (e.g., overlayer measurements), yield the attenuation length (AL) (or better the effective attenuation length, EAL (including dependence on overlayer thickness and emission angle, see below)). Therefore, the semiempirical formula of Seah and Dench of 1979, that is still used today by some researchers, is not giving IMFP (as it claims) but AL values.

In general, the dependence of signal intensities on film thickness will not be exactly exponential. In XPS, the effects of elastic scattering are particularly pronounced because the photoionization process is anisotropic. Fortunately, for practical purposes, the dependence of the attenuation length on film thickness is exponential with a fairly good approximation [4.33]. In any case, inelastic and elastic scattering have to be considered together, and the resulting λ is the effective attenuation length (EAL) (see the definitions below). Owing to additional elastic scattering of the electrons, their total path length before emission from the solid increases. Since this fact increases the inelastic scattering probability, the resulting traveled distance from the surface is less than without elastic scattering. Without elastic scattering, IMFP and EAL would be equal. When starting from IMFP values,

Table 4.1 Comparison of different attenuation length values for some elements at $E = 1500$ eV, obtained from different sources: (1) $\lambda_{\text{in}} = \text{IMFP}(\text{TPP-2M})$, (4.12); (2) $\lambda = \lambda_{\text{in}} \times Q(0)$, (4.20); (3) $\lambda = \lambda(\text{EAL})$, (average practical EAL from [4.37]); (4) $\lambda = \lambda(\text{CS2})$, (4.17); (5) $\lambda = \lambda(\text{PJ})$, (4.29); (6) $\lambda = \lambda_{\text{in}}(\lambda/\lambda_{\text{in}})$, (4.16); (7) $\lambda = \lambda(\text{SD})$, (4.10)

	C	Al	Si	Fe	Cu	Ta	Bi
λ_{in} (nm)	3.70	2.70	3.37	2.21	2.20	2.00	2.75
$\lambda_{\text{in}}Q(0)$ (nm)	3.66	2.66	3.31	2.11	2.09	1.87	2.60
$\lambda(\text{EAL})$ (nm)	3.59	2.56	3.18	1.92	1.88	1.61	2.30
$\lambda(\text{CS2})$ (nm)	2.96	2.91	3.09	1.83	1.75	1.50	1.97
	3.31 ^a						
$\lambda(\text{PJ})$ (nm)	3.55	2.53	3.11	1.85	1.79	1.52	2.19
$\lambda(\lambda_{\text{in}}(\lambda/\lambda_{\text{in}}))$ (nm)	3.44	2.64	3.01	1.88	1.86	1.53	2.03
$\lambda(\text{SD})$ (nm)	1.50	2.04	2.25	1.72	1.73	2.14	3.01
λ_{in} (Dev) (%)	+1	+2	+2	+5	+5	+7	+6
$\lambda(\text{EAL})$ (Dev) (%)	−2	−4	−4	−10	−10	−14	−12
$\lambda(\text{CS2})$ (Dev) (%)	−19	+9	−7	−13	−16	−20	−32
	−10						
$\lambda(\text{PJ})$ (Dev) (%)	−3	−5	−6	−12	−14	−19	−16
$\lambda(\lambda_{\text{in}}(\lambda/\lambda_{\text{in}}))$ (Dev) (%)	−6	0	−9	−11	−11	−18	−22
$\lambda(\text{SD})$ (Dev) (%)	−59	−23	−32	−18	−17	+14	+16
$\lambda = 2.33$ nm (Dev)	−36	−12	−30	+10	+11	+25	−10

Relative deviations of the respective λ values from $\lambda = \lambda_{\text{in}} \times Q(0)$ are given in % of the latter value. (According to Tanuma et al. [4.38], IMFP values from EPES show RMS deviations of the order of 10%)

^aThis value is from NIST database (1) [4.37]. According to CS2 equation, this would mean $a = 0.223$ and $\rho/M = 0.1498 \text{ mol cm}^{-3}$ in (4.18)

a separate term is needed describing elastic scattering influence, to get the EAL needed for quantitative AES and XPS. According to Jablonski [4.39] (cf. [4.2]), the EAL, λ , can be approximately obtained from the IMFP, λ_{in} , by multiplication with the ratio

$$\frac{\lambda}{\lambda_{\text{in}}} = (1 - 0.028\sqrt{Z}) [0.501 + 0.068 \ln(E)]. \quad (4.16)$$

According to (4.16), the ratio $\lambda/\lambda_{\text{in}}$ decreases with atomic number Z and increases with kinetic electron energy E (in eV). From today's point of view, (4.16) is a rather crude approximation and ignores emission angle dependence. Therefore, it should be replaced by the more exact parameter $\lambda/\lambda_{\text{in}} = Q(\theta)$, as shown below (cf. (4.20)).

The difference between EAL (λ) and IMFP (λ_{in}) can be up to about 30% ($\lambda/\lambda_{\text{in}} = 0.7$). On average, the difference is more like 15–20%.

In the past, EAL values (λ) were often obtained by multiplying λ_{in} with $\lambda/\lambda_{\text{in}}$. At present, most reliable data for EALs of elements and compounds are given in the NIST database [4.36], where (4.18) is recommended for quantification purpose (see Table 4.1).

Exact definitions of the relevant terms after ASTM and ISO can be found in [4.1, 4.33] and in ISO 18115 [4.60], with thorough discussion given by Jablonski and Powell [4.33, 4.61]. The most important definitions are given here:

EDDF, emission depth distribution function (for a measured signal of particles or radiation): probability that the particle or radiation leaving the surface in a specified

state and in a given direction, originated from a specified depth measured normally from the surface into the material (cf. (4.7)).

EFDL, emission function decay length: negative reciprocal slope of the logarithm of the EDDF at a specified depth.

AEFDL, average emission function decay length: negative reciprocal slope of the logarithm of a specified exponential approximation to the EDDF over a specified range of depths, as determined by a straight line fit to the EDDF plotted on a logarithmic scale versus depth on a linear scale.

IMFP, inelastic mean free path: average distance that an electron with a given energy travels between successive inelastic collisions.

AL, attenuation length: quantity l in the expression x/l for the fraction of a parallel beam of specified particles or radiation removed in passing through a thin layer x of a substance in the limit as x approaches 0, where x is measured in the direction of the beam. (Notes: (1) The intensity or number of particles in the beam decays as $\exp(-x/l)$ with the distance x ; (2) for electrons in solids, the behavior only approximates an exponential decay due to the effects of elastic scattering. Where this approximation is valid, the term EAL is used.) [4.33].

EAL (effective attenuation length) is defined as the average emission function decay length when the emission depth distribution function (EDDF) is sufficiently close to exponential for a given application. The local EAL varies with depth and depends on the film thickness. An average value, the practical EAL can be taken as the attenuation length (AL) defined by a Lambert–Beer law with $I/I_0 = \text{const} \times \exp(-z/\lambda(\text{AL}))$. According to Jablonski and Powell [4.33], if there is no likelihood of confusion, the term EAL can be further abbreviated to “AL.”

Further refined definitions include the practical EAL, derived with the assumption that the EDDF is exponential over a specified depth range, resulting in a constant EAL over this range. The average (practical) EAL (L_{ave}^{10}) is the arithmetic average of the EAL over a larger overlayer thickness corresponding to the attenuation of the substrate signal to 10% of its original value without an overlayer. (A corresponding definition holds for marker layer experiments [4.33].)

The usual definition of the AL is based on a parallel beam of radiation in a material and not for the case of AES or XPS, where emission within a small solid angle corresponding to the analyzer acceptance angle has to be considered. Furthermore, due to elastic scattering, the signal intensities are generally attenuated nonexponentially. Because the EDDF is not necessarily exponential and generally varies with depth or thickness of an overlayer, it is necessary to define an “effective” AL, or EAL, in terms of the local negative slope of the EDDF of the signal electrons when plotted on a logarithmic scale as a function of depth on a linear scale [4.62]. The “practical” EAL introduced by Jablonski and Powell is valid as an exponential approximation over a specified depth range, and an average practical EAL (often denoted L_{ave}^{10}) for a range of an overlayer-film thickness for which the substrate signal varies between 10% and 100% of its maximum value [4.33].

An important note for the practical analyst is given by Jablonski and Powell [4.33]: “...We also note that terms such as ‘local EAL,’ ‘practical EAL,’ and ‘average practical EAL’ are rather unwieldy and inconvenient for routine use.

We have used these expressions here (i.e., [4.33]) to ensure clarity in the descriptions of the terms and the related numerical results. After a first use of one of these terms in a review paper (where the full description is given), we suggest that ‘local AL,’ ‘practical AL,’ or ‘average AL’ be used subsequently together with suitable acronyms (e.g., LAL, PAL, or AAL). If there is no likelihood of confusion, these terms can be further abbreviated to ‘AL.’ In practice, we use the “average practical EAL” that means a constant value with an exponential attenuation relation. In the following, we will also use the term “AL” as sufficiently clear for practical purposes.

For the measurement of overlayer-film thickness by XPS, the practical EALs do not vary significantly with overlayer-film thickness for emission angles in the range $0 < \alpha < 65^\circ$ [4.62]. It is therefore convenient to compute average practical EALs that can be applied in XPS or AR-XPS experiments for a useful range of overlayer thickness over the same range of emission angles. These “average practical EALs” can be used as the “lambda parameter” in equations that were developed based on the assumption that elastic scattering was negligible. For other cases, calculations should be made of the local or practical EALs for the particular measurement and specimen conditions of interest to determine the extent of EAL variations for those conditions; the NIST EAL database should be used [4.37].

In the following, in order to keep continuity and direct relation to past work, we will use this “lambda parameter,” the practical EAL, or simply AL, for practical surface analysis, if not otherwise mentioned. As recommended in NIST EAL database [4.37], for quantification purposes, we use λ as an abbreviation for $\lambda = Q \times \lambda_{\text{in}}$, where Q is the elastic scattering correction factor described in the next paragraph (see Table 4.1, values in boldface).

A practical approach that allows a simple calculation of the practical EAL or AL (in nm) known as CS2 has been proposed by Cumpson and Seah [4.43],

$$\lambda_{\text{AL}} = 0.316a^{3/2} \left\{ \frac{E}{Z^{0.45} [\ln(E/27) + 3]} + 4 \right\} (\text{nm}), \quad (4.17)$$

where E is the kinetic energy in eV and Z is the atomic number. The parameter a is the average atomic distance (in nm) given by

$$a (\text{nm}) = 10^9 \left(\frac{M}{\rho n_M N_{\text{Avo}}} \right)^{1/3}, \quad (4.18)$$

where M is the mole mass in kg/kmol, ρ is the density in kg/m³, n_M is the number of atoms in the molecule, and N_{av} ($6.02 \times 10^{26} \text{ kmol}^{-1}$) is Avogadro’s number. Equations 4.17 and 4.18 were found to fit the average EALs (computed by IMFP from TPP–2M and correction for inelastic scattering) with an average standard deviation of 6% at energies of 200 eV and 1 keV [4.43]. Equation 4.17 is valid up to an emission angle of about 60–70° with respect to the normal to the sample surface. For the practical analyst, the advantage of (4.17) and (4.18) is that only three easy to find parameters are necessary to calculate a value of the attenuation length. For Si 2s, Fig. 4.10 shows a comparison of (4.17) with the average practical EAL as a

function of the emission angle after [4.38]. For further comparison, Table 4.1 shows IMFP and AL values for several elements, giving an idea of more or less typical deviations of different approaches. The measured ALs can be described by a simple exponent dependence on energy [4.38],

$$\lambda_{\text{AL}} = k_{\text{AL}} E^m, \quad (4.19)$$

where λ_{AL} is the AL in nm, E is the energy in keV, and k_{AL} and m are numerical parameters. According to Tanuma et al. [4.38], for 500–2000 eV, this relation is valid with k_{AL} ranging from 1.1 to 1.5 nm and an average value of $m = 0.75$ for elements (cf. Fig. 4.6b) and inorganic compounds, and of $m = 0.79$ for organic compounds (see also Ref. [4.161]). Equation 4.19 only gives a rough estimation as long as the factor k_{AL} is not exactly known. For example, k_{AL} varies between 1.2 and 2.6 for the elements in Table 4.1, with a mean value of $\lambda_{\text{mean}} = 2.33$ nm at 1.5 keV. As expected, on average, the deviations from (4.20) shown in Table 4.1 are largest for the outdated Seah and Dench value, $\lambda(\text{SD})$, followed by $\lambda(\text{CS2})$. Because the value of Q is near unity for high energy, the deviation from λ_{in} at 1500 eV is relatively small (see Fig. 4.12a). The elastic scattering correction for the attenuation length is a complicated function of atomic number, energy, and emission angle and is considered in the following paragraph.

4.2.2.4 Elastic Scattering Correction Factor and Emission Angle Dependence

In contrast to inelastic scattering, the elastic scattering contribution shows a nonexponential behavior with depth and a peculiar dependence on the angle of emission. Therefore, it has become customary to treat both parts separately and to represent the attenuation length λ by a product of the IMFP, λ_{in} and an “elastic scattering correction factor” Q [4.1, 4.59, 4.160]. Because of the generally anisotropic photoelectron emission in XPS, the elastic scattering correction factor has to be multiplied by an additional term that takes into account the effect of elastic scattering on the asymmetry of photoelectron emission (see Sect. 4.3.1 and Fig. 4.11). The parameter Q depends on the emission angle θ and on the material.

For AES (and for XPS in the “magic angle” configuration, see Sect. 4.3.1), we may write [4.33, 4.63]

$$\lambda = \lambda_{\text{in}} Q(\theta, \omega) \quad (4.20)$$

with

$$Q(\theta, \omega) = (1 - \omega)^{1/2} H(\cos \theta, \omega), \quad (4.21)$$

where $H(\cos \theta, \omega)$ is the Chandrasekar function (see, e.g., [4.33, 4.159] and Refs. given therein) which is approximately represented by [4.59]

$$H(\cos \theta, \omega) = \frac{1 + 1.9078}{1 + 1.9078 \cos \theta (1 - \omega)^{1/2}}, \quad (4.22)$$

depending on the so-called single scattering albedo ω [4.33] defined by

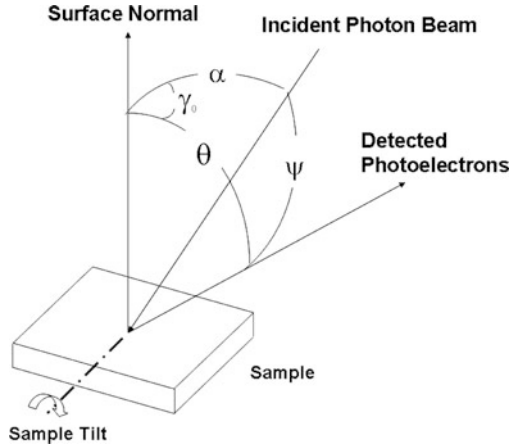


Fig. 4.11 Visualization of the general geometry for XPS instruments showing the angular relations: α is the incidence angle of photons to the normal to the sample surface, θ is the angle of emission of the photoelectrons to the normal to the sample surface, ψ is the angle between the direction of the incident photons and the detected electrons, and γ_0 is the angle between the plane of surface normal-incident beam and the plane of surface normal-photoelectron emission. Sample tilt axis is in the surface plane and perpendicular to the plane between surface normal and emission of detected photoelectrons

$$\omega = \frac{1}{1 + \frac{\lambda_{tr}}{\lambda_{in}}} \quad (4.23)$$

with the inelastic mean free path λ_{in} and the transport mean free path λ_{tr} . Calculations of λ_{tr} are given by Jablonski [4.59]. Because λ_{tr} is tedious to calculate, tables are available, and databases such as [4.37] provide values for λ_{tr} . The transport mean free path, λ_{tr} , increases more strongly with energy than λ_{in} . Thus, ω decreases after (4.23), and $Q(\omega)$ increases with energy after (4.21), as shown for Al as an example in Fig. 4.12a.

Useful approximations for the exact Monte Carlo calculations of $Q_{A,x}$ are provided by Jablonski and Powell [4.61] and by Seah and Gilmore [4.64]. These authors give the following expression for the dependence of Q on the emission angle θ :

$$Q(\theta) = (0.863 + 0.308 \cos \theta - 0.171 \cos^2 \theta) Q(0) \quad (4.24)$$

with

$$Q(0) = (1 - \omega)^{0.5} (1 + 0.412\omega) \text{ for } \omega < 0.245 \quad (4.25a)$$

and

$$Q(0) = (1 - \omega)^{0.5} \left[0.091 + 0.923 \left(\frac{1 + 1.908}{1 + 1.908(1 - \omega)^{1/2}} \right) \right] \quad (4.25b)$$

for $\omega \geq 0.245$.

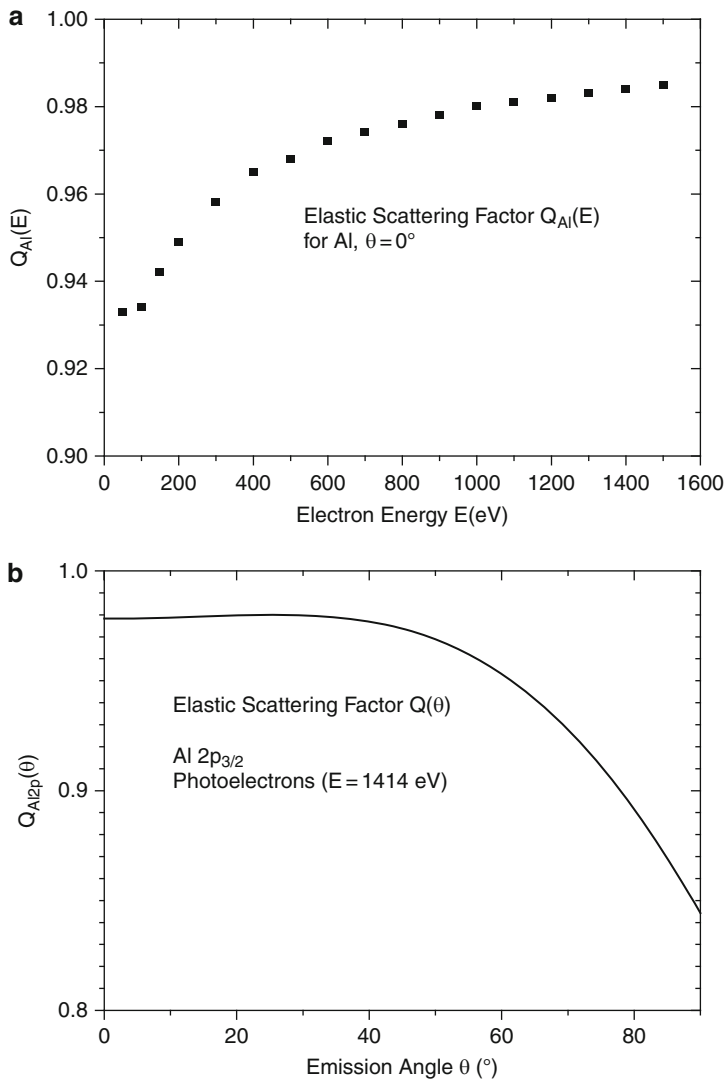


Fig. 4.12 (a) Energy dependence of the elastic scattering correction factor for Al, $Q_{Al}(E)$ for $\theta = 0^\circ$, according to $\lambda_{tr}(E)/\lambda_{in}(E)$ [4.59] and (4.23) in (4.22). $Q_{Al}(E)$ (Data are from Ref. [4.43]). (b) Emission angle dependence of the elastic scattering correction factor for Al 2p, Q_{Al2p} , after (4.24)

As an example, the emission angle dependence of the elastic scattering correction factor Q after (4.24) is shown for Al 2p in Fig. 4.12b. From this example, it is obvious that the emission angle dependence is only significant for emission angles $\theta > 60^\circ$. At $\theta = 60^\circ$, the deviation from $Q(0)$ is -3% , as compared to -10% at $\theta = 80^\circ$.

Whereas (4.12), (4.17), (4.19), and (4.20) are generally valid for both AES and XPS, if the latter is used in the “magic angle” geometry, for which the asymmetry factor is unity. This means the angle between X-ray incidence and photoelectron emission (see Fig. 4.12) should ideally be $\psi = 57.4^\circ$. This is a weak condition because, according to Jablonski and Powell [4.61], the ratio $\lambda/\lambda_{\text{in}}$ given by (4.20) only changes by about 2% for ψ between 40° and 70° (ψ between 49° and 60° is realized in many instruments [4.65]).

Equation 4.20 is strictly valid for gases. In solids, the EAL changes with the effective asymmetry factor which is an additional parameter in XPS. Therefore, this influence is discussed in Sect. 4.3.1.

4.2.2.5 Mean Escape Depth

According to ISO 18115 [4.60], the mean escape depth (MED) is defined as average depth normal to the surface from which the specified particles or radiations escape as defined by

$$\text{MED} = \int_0^\infty z \Psi(z, \theta) dz \bigg/ \int_0^\infty \Psi(z, \theta) dz, \quad (4.26)$$

where $\Psi(z, \theta)$ is the emission depth distribution function for depth, z , from the surface into the material and for angle of emission, θ , with respect to the surface normal [4.34].

Let us first ignore elastic scattering. The inelastic mean free path (IMFP) within the sample only depends on the electron energy and on the material but is completely independent of the emission angle. In general, emission is not in direction of the normal to the sample surface (the emission angle θ (see Figs. 4.12 and 4.13) is not zero). As seen in Fig. 4.12, for any emission angle, the mean depth of emission below the surface in the direction normal to the surface (usually the z -coordinate), called mean escape depth (MED), is simply given by the IMFP multiplied by the cosine of the emission angle (see Fig. 4.15)

$$\lambda_{\text{MED}}(\text{IMFP}) = \lambda_{\text{in}} \cos \theta, \quad (4.27)$$

where λ_{in} denotes the IMFP and θ is the emission angle to the normal to the surface. Equation 4.27 shows that the surface sensitivity of AES and XPS strongly increases with the emission angle.

Equation 4.27 is exactly valid only when elastic scattering is neglected. However, elastic scattering generally restricts the validity of (4.27). As discussed in detail by Jablonski and Powell [4.33, 4.34], the effective attenuation length (EAL) takes elastic scattering into account but – in contrast to the IMFP – depends itself on the emission angle. Therefore, a refined definition of the mean escape depth (MED) is necessary involving details of the emission depth distribution function (EDDF) that depends on depth z and on the emission angle θ [4.34] (see (4.26)). In general, with

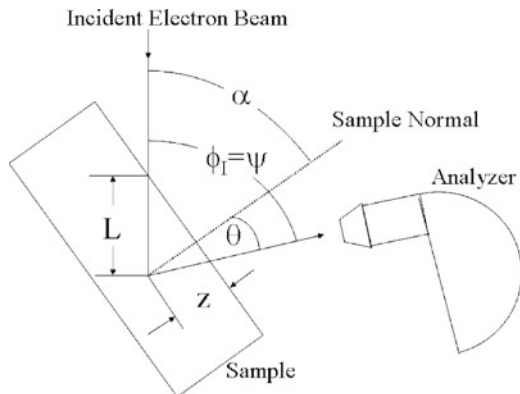


Fig. 4.13 Schematic view of the geometrical relations of incident electron (AES) or photon (XPS) beam, sample and analyzer (CHA), showing – with respect to the normal to the sample surface – the beam incidence angle, α , and electron emission angle θ . In contrast to Fig. 4.12, all angles are in one plane. The angle between electron beam and electron emission angle in direction to the analyzer is ψ ($=\phi_1$, denoting an angle normally fixed for a specific instrument). L is a measure for the travel length of the incident beam in the sample and z the depth (perpendicular to the surface plane) from which an analyzed electron is emitted

increasing θ , the (effective) attenuation length λ_{AL} surpasses λ_{MED} (see Fig. 4.10). For most practical applications, the MED can be assumed to be

$$\lambda_{MED} = \lambda_{EAL} \cos \theta \text{ (for } \theta < 65^\circ \text{)}. \quad (4.28)$$

Straight cosine dependence follows from the simplified assumption of a straight line for the emitted electron (see Figs. 4.12 and 4.13), and therefore, it is often called straight line assumption (SLA) [4.43]. It is interesting to note that many researchers have used (4.28) with great success up to emission angles of about 80° [4.67–4.70].

For emission angles $\theta < 60^\circ$, Powell and Jablonski [4.71] found an empirical relation for the average practical AL:

$$\lambda_{AL} = \lambda_{in}(1 - A\omega), \quad (4.29)$$

where the term $(1 - A\omega)$ is an elastic scattering correction term with the parameter $A = 0.7$ which slightly depends on θ ($A = 0.713$ and 0.685 for $\theta = 0$ and 45° , respectively), and the so-called single scattering albedo ω which is defined above (4.23). Deviations of (4.29) from (4.20) are given in Table 4.1. Based on newer data for λ_{in} [4.44], Powell and Jablonski [4.34, 4.93] give a constant value of $A = 0.735$ with an average deviation of 0.61%.

For most AES and XPS measurements, ω is between 0.05 and 0.45. Therefore, the elastic scattering correction factor $(1 - A\omega)$ is between 0.96 and 0.68. Thus, the mean electron escape depth for isotropic emission (AES) is given by

$$\lambda_{\text{MED}} = \lambda_{\text{in}}(1 - A\omega) \cos \theta. \quad (4.30)$$

In the following, we adopt (4.28) and write simply λ for the value of the attenuation length $\lambda_{\text{EAL}} = \lambda$, or, more appropriate for layer structure quantification, expression (4.20),³ and get

$$\lambda_{\text{MED}} = \lambda \cos \theta = \lambda^e. \quad (4.31)$$

In the following, we write $\lambda^e = \lambda_{\text{MED}}$. In typical AES measurements with a CMA with its axis normal to the sample surface, $\alpha_e(\text{CMA}) = 42.3^\circ$ corresponds to θ , and therefore $\lambda^e = 0.74\lambda$ applies (see Fig. 2.12) (for measurements with sample tilt, see Chap. 5). Today, AES measurements are often performed with a CHA, where angle-dependent AES (AR-AES) measurements are less restricted as compared to those with a CMA (see Chaps. 5 and 7).

4.2.2.6 Information Depth

The information depth is a measure of the depth from the surface within which useful information is obtained. According to ISO 18115 [4.60], the information depth can be identified with the sample thickness from which a specified percentage (e.g., 95% or 99%) of the detected signal originates. For an exponential depth distribution function, the latter percentages mean an information depth definition of 3λ or 5λ , respectively [4.60], for emission in direction of the normal to the sample surface (note that the information depth parameter in the MRI model (Sect. 7.1.8) is given by the mean escape depth λ^e (4.31)).

The attenuation length is of fundamental importance for both AES and XPS. However, because there are basic differences in the excitation and emission processes, the quantification for both techniques is treated separately.

4.3 Quantitative XPS

4.3.1 Fundamental Quantities for XPS

In a solid with the density of atoms of element A, N_A , the total intensity, $I_{A,i}$, originating from the core level subshell i ($i = 1s, 2p_{1/2}$, etc.) of an element A, is proportional to the exciting X-ray intensity of energy $h\nu$, $I_{h\nu}$, to the integral of the spatial distribution of excitation and emission, according to (4.7). For constant excitation function, assumed in (4.8), the total emission of photoelectrons in a small solid angle $\Delta\Omega$ (e.g., given by the analyzer acceptance angle) can be expressed by [4.2, 4.72]

³In earlier publications (e.g., Ref. [4.67, 4.151, 4.154]), the experimentally relevant $\lambda_{\text{MED}} = \lambda$ was frequently used as short form of $\lambda^0 \cos \theta$ with the attenuation length λ^0 .

$$I_{A,i,\text{em}} = \frac{\Delta\Omega}{4\pi} \int_0^\infty I_{h\nu}(\alpha, z) \sigma_{A,i} W_{A,i}(\beta_{A,i}, \psi) N_A(z) \exp\left[-\frac{z}{\lambda_{m,E(A,i)} \cos \theta}\right] dz, \quad (4.32)$$

where z is the in-depth distance from the surface (perpendicular to the surface), α is the incidence angle of the X-ray beam, $\sigma_{A,i}$ is the total ionization cross section of all electrons in subshell i for photons of energy $h\nu$, and $W(\beta_{A,i}, \psi)$ ⁴ is the angular asymmetry factor (after Reilmann et al. [4.66]) of that level at an angle ψ between the direction of X-ray and analyzer axis, $\lambda_{m,E(A,i)}$ is the “effective attenuation length” (EAL) of the photoelectrons of A in matrix m with kinetic energy $E(h\nu) - E(A, i)$ (see Sect. 4.2.2), and θ is the emission angle of the detected photoelectrons. Figure 4.12 gives a schematic illustration of the geometrical relations with the three angles in (4.32) for XPS. Usually, the incident beam and the emitted electrons lie in a plane with the surface normal and a sample tilt changes both angles in a complementary way (see also Fig. 4.13). Let us first consider the two main parameters specific for XPS, the photoionization cross section and the asymmetry factor. Expression (4.32), like all fundamental equations for quantitative analysis (e.g., 4.7), is based on the assumption that the sample is amorphous or sufficiently fine-grained polycrystalline to avoid diffraction effects (see Sects. 3.2.8 and 3.3.5).

4.3.1.1 Photoionization Cross Section

Using transition matrix elements with electrons in the initial and final states treated as moving in the same Hartree–Slater potential, photoionization cross sections for complete atomic subshells have been calculated by Scofield [4.73] and tabulated for Mg K_α and Al K_α X-ray excitation energies for all elements. Figure 4.14 shows the relative cross sections for Al K_α referred to C 1s for the most intense subshell signals of the elements [4.2]. These data are thought to be fairly exact and are the basis of relative elemental sensitivity factors (RSFs) given by Wagner [4.74] (see Sect. 4.3.2). For nonseparated doublets (e.g., Al $2p_{1/2,3/2}$), the subshell cross sections have to be added. Scofield cross sections do not contain screening effects that cause intrinsic plasmon losses (see Sect. 3.2.6). The Wagner RSFs are based on experimental measurements, not the calculated Scofield cross sections.

⁴Note that it has become customary to express the product $\sigma_{A,i} W(\beta_{A,i}, \psi)$ by the differential cross section $d\sigma_{A,i}/d\Omega = (1/4\pi)\sigma_{A,i} W(\beta_{A,i}, \psi)$ [4.29]. Furthermore, in solids $\beta_{A,i}$ has to be replaced by the modified parameter $\beta_{A,i,\text{eff}}$ (see Sect. 4.3.1.2).

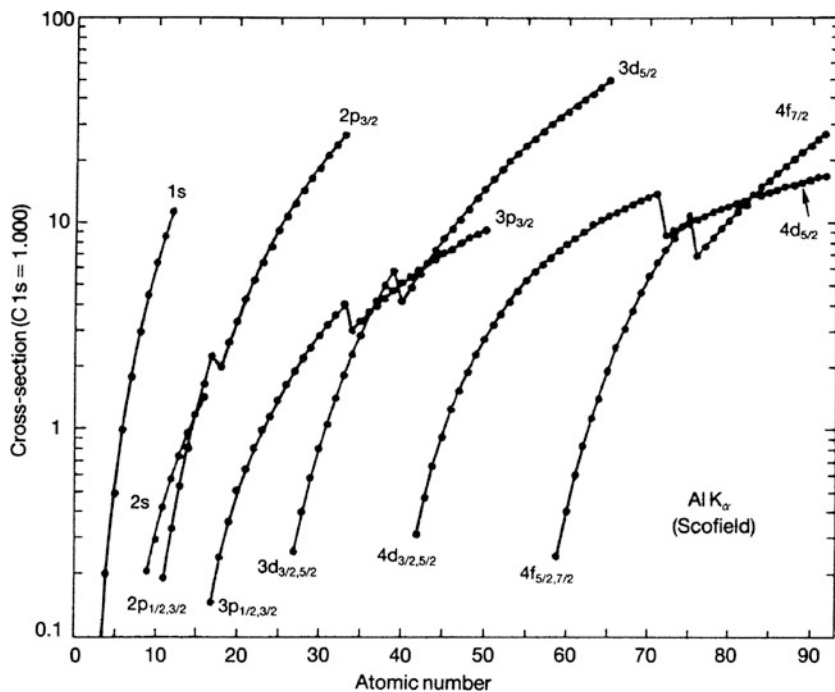


Fig. 4.14 Relative cross sections $\sigma_{A,i}/\sigma_{C1s}$ for Al K_{α} radiation after Scofield [4.73] (Reproduced with permission of J. Wiley & Sons, Ltd. from M.P. Seah [4.2]. Crown Copyright 1990.)

4.3.1.2 Asymmetry Factor in XPS

In contrast to the isotropic emission in AES, the angular asymmetry factor, $W_{A,i}(\psi)$, is typical for XPS and describes the angular intensity distribution of the photoelectrons from atoms or molecules excited by unpolarized X-rays, given by [4.66]

$$W_{A,i}(\beta_{A,i}, \psi) = 1 + \frac{1}{2}\beta_{A,i} \left(\frac{3}{2} \sin^2 \psi - 1 \right) = 1 + \beta_{A,i} \frac{1}{4} (1 - 3 \cos^2 \psi), \quad (4.33)$$

where the asymmetry parameter $\beta_{A,i}$ is a constant for a given subshell i of a given element A and X-ray photon, and ψ is the angle between photon incidence from the X-ray source and photoelectron emission to the detector (see Fig. 4.12). The asymmetry parameter, $\beta_{A,i}$, is ≤ 2 and depends on the angular momentum number l , i.e., the type of the subshell, and on the kinetic energy of the emitted photoelectrons (and therefore on the X-ray source). Only for s-levels ($l = 0$) $\beta_{A,i} = \text{const.} = 2$. Values of $\beta_{A,i}$ are tabulated in the literature [4.66, 4.75]. An example of (4.33) for Al 2p is given in Fig. 4.15 (dashed line).

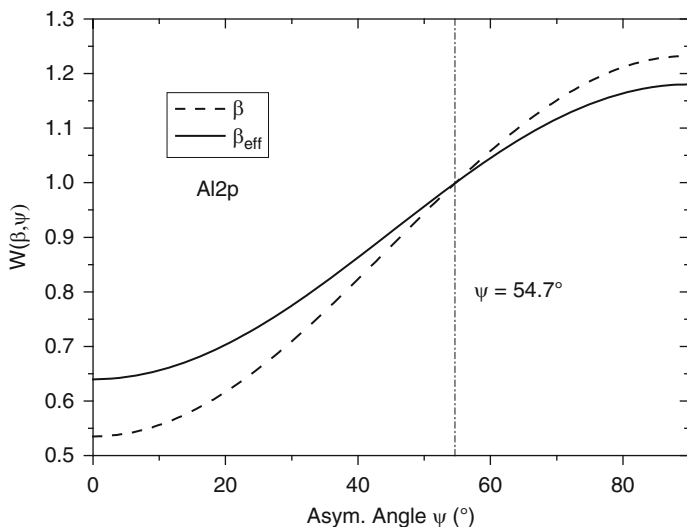


Fig. 4.15 Dependence of the asymmetry factor $W(\beta, \psi)$ on the angle ψ between the X-ray incidence and the photoelectron direction (see Fig. 4.12), for β (gases) and for β replaced by β_{eff} (solids) for Al2p photoelectrons excited with AlK α X-rays, after (4.33), (4.35), and (4.36), with $\beta(\text{Al } 2p) = 0.93$ [4.66]. The dash-dotted line indicates the “magic angle,” $\psi = 54.7^\circ$, for which $W(\beta, \psi) = 1$

It is evident from the general quantification equation (4.32) that for a meaningful intercomparison of peak intensities in XPS, the angle ψ between X-ray excitation and photoelectron emission has to be taken into account (see Fig. 4.12). The asymmetry parameter can only be neglected when $W(\beta_{\text{A},i}, \psi) = 1$, i.e., the term in parenthesis of (4.33) is zero, ($1.5 \sin^2 \psi = 1$). The result is $\psi = 54.74^\circ$, which is often called the “magic angle” (Fig. 4.15). Most of the commercial spectrometers operate at that angle. Usually, ψ is constant when angle-resolved measurements are performed by tilting the sample (see AR-XPS, Sect. 7.2.1). Care has to be taken when using instruments that detect photoelectrons at various emission angles, either by a slit in a shadowing drum that can be rotated [4.67] (Double-pass CMA, see Sect. 2.5.1, Fig. 2.15) or by an electronic aperture (e.g., Thetaprobe, see example in Sect. 4.3.2.6), because then ψ changes with the emission angle.

Equation 4.33 is strictly only valid for gas phase analysis. In solids, elastic scattering reduces β to an effective asymmetry parameter β_{eff} that is slightly smaller than β because of the directionally randomizing action of elastic scattering. Therefore, β_{eff} has an influence on λ . The ratio β_{eff}/β is typically between 0.4 and 0.9 [4.76]. A database for β_{eff} is given in [4.77].

Equation 4.20 is the basic equation for the attenuation length for AES and for XPS with $\psi = 54.7^\circ$. For XPS instruments with $\psi \neq 54.7^\circ$, (4.20) has to be extended by an angular asymmetry term correction $W(\beta_{\text{eff}}, \psi)/W(\beta, \psi)$, which gives for the attenuation length $\lambda_{\text{AL}}(\text{XPS})$ [4.33],

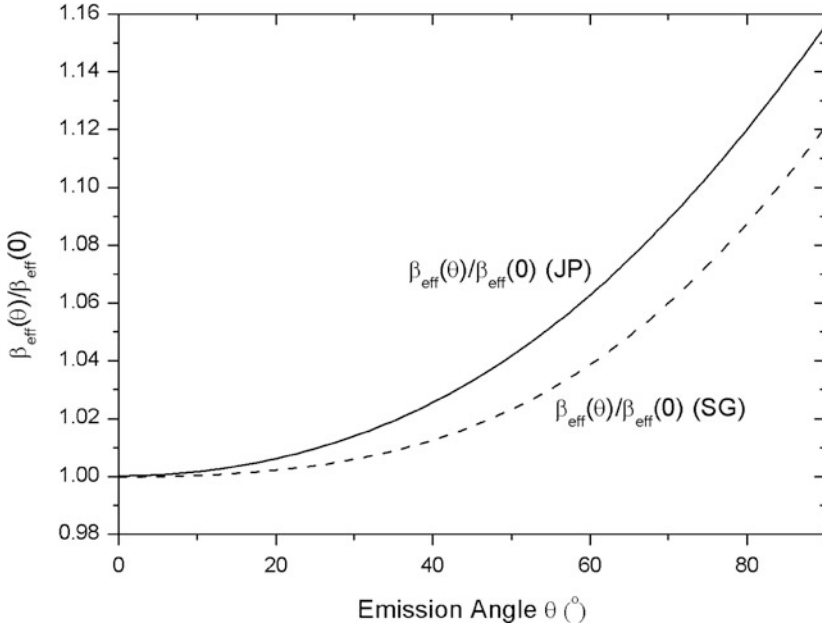


Fig. 4.16 Dependence of $\beta_{\text{eff}}(\theta)/\beta_{\text{eff}}(0)$ on the emission angle θ , after (4.38a) (SG, dashed line) [4.64] and (4.38b) (JP, solid line) [4.33]

$$\lambda_{\text{AL}}(\text{XPS}) = \lambda_{\text{in}} Q(\theta, \omega) \frac{W(\beta_{\text{eff}}, \psi)}{W(\beta, \psi)}. \quad (4.34)$$

Conceptually, $W(\beta, \psi)$ represents the anisotropy of the photoemission cross section, which is an atomic parameter, whereas $W(\beta_{\text{eff}}, \psi)$ includes the effect of elastic scattering of a solid (because β_{eff} depends on the emission angle, see (4.38) below). Therefore, the ratio usually gives a small anisotropic emission correction ($< 6\%$ for $40^\circ < \psi < 70^\circ$, see Fig. 4.16). Equation 4.34 means that, in general, the attenuation length for XPS is slightly different from that for AES. Only for $\psi = 54.7^\circ$, the asymmetry correction term $W(\beta_{\text{eff}}, \psi)/W(\beta, \psi)$ is equal to unity, and $\lambda_{\text{AL}}(\text{AES}) = \lambda_{\text{AL}}(\text{XPS})$. If not otherwise stated, we will refer in the following to $\psi = 54.7^\circ$.

For simplified notation, we use $W(\beta_{\text{eff}}, \psi)$ instead of $W(\beta_{\text{eff}, A, i}, \psi)$ (4.33), keeping in mind that W and β_{eff} always are for a specified subshell i of an element A . With an effective value β_{eff} which takes into account the elastic scattering effect, we write for the asymmetry factor in solids,

$$W(\beta_{\text{eff}}, \psi) = 1 + \frac{\beta_{\text{eff}}}{2} \left(\frac{3}{2} \sin^2 \psi - 1 \right) = 1 - \frac{\beta_{\text{eff}}}{4} (3 \cos^2 \psi - 1). \quad (4.35)$$

Note that the factor $1/4\pi$ usually introduced here [4.33] is considered later in the analyzer acceptance angle $\Delta\Omega/4\pi$.

After Seah and Gilmore [4.64], for zero emission angle, the relation between β and β_{eff} is approximately given by

$$\beta_{\text{eff}}(0) = 0.876 [1 - \omega(0.995 - 0.0777 \ln Z)] \beta, \quad (4.36)$$

where Z is the (average) atomic number. Note that β_{eff} is always lower than β . According to (4.33) and (4.36), the influence of β_{eff} on the ψ dependence of the asymmetry factor $W(\beta, \psi)$ as compared to β is shown in Fig. 4.16 for Al 2p.

Another expression for (4.36) is given by Jablonski and Powell [4.33] in which β_{eff}/β is described by ω and Q :

$$\beta_{\text{eff}}(0) = \frac{1 - \omega}{Q} \beta. \quad (4.37)$$

The dependence of the parameter β_{eff} on the emission angle θ is given by Seah and Gilmore (SG) [4.63, 4.64] as

$$\beta_{\text{eff}}(\theta) = (1.121 - 0.208 \cos \theta + 0.0868 \cos^2 \theta) \beta_{\text{eff}}(0), \quad (4.38a)$$

and by Jablonski and Powell (JP) [4.33] as

$$\beta_{\text{eff}}(\theta) = \frac{0.053087 \cos^2 \theta - 0.18662 \cos \theta + 0.99076}{0.857} \beta_{\text{eff}}(0). \quad (4.38b)$$

The dependence of the ratio $\beta_{\text{eff}}(\theta)/\beta_{\text{eff}}(0)$ on the emission angle after (4.38a) and (4.38b) is given in Fig. 4.17. An example of the above approach to quantitative XPS with variation of the angle ψ using the Thetaprobe instrument is shown in Sect. 4.3.2, where (4.37) and (4.38b) show better agreement with experimental data than (4.36) and (4.38a) (see Fig. 4.16).

The fundamental relations and parameters in XPS outlined in Sect. 4.3.1 can be applied to quantitative analysis of homogeneous material (Sect. 4.3.2) and of thin layers (Sect. 4.3.3).

4.3.2 Quantitative XPS Analysis of Homogeneous Material

With the exception of grazing incidence, the depth dependence of I_{hv} in (4.32) can be ignored, leaving only the integral over depth z of the depth-dependent terms. However, the solution of the remaining integral requires knowledge of the in-depth composition of the sample:

$$I_{A,\text{em}} = \sigma_A W_A(\beta_{\text{eff}}, \psi) I_{\text{hv}}(\alpha) \frac{\Delta\Omega}{4\pi} \int_0^\infty N_A(z) \exp\left[-\frac{z}{\lambda_{m,E(A)} \cos \theta}\right] dz. \quad (4.39)$$

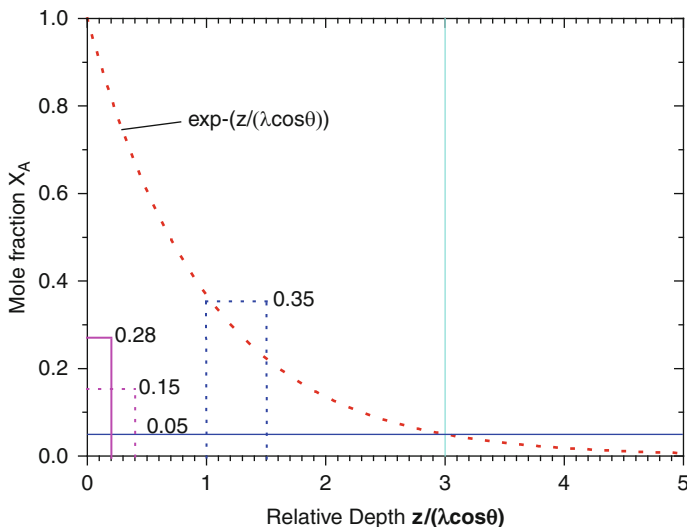


Fig. 4.17 Example of five different in-depth distributions of element A which (according to (4.39) with $N_A/N_m^0 = X_A$) result in the same relative XPS or AES intensity $I_A/I_A(N_A = 1) = I_A/I_A^0 = 0.05$. Red dotted line: probability of transmitted signal intensity as a function of relative depth $z/(\lambda \cos \theta)$, referred to escape depth $\lambda^e = \lambda \cos \theta$, with λ the attenuation length assumed independent of composition. Blue dotted lines: 35 at% concentration in a layer of $0.5(\lambda \cos \theta)$ thickness, $z = 1(\lambda \cos \theta)$ beneath the surface. Further equivalent in-depth distributions shown are: surface layers of $0.4(\lambda \cos \theta)$ thickness with 15 at% concentration (magenta dotted lines), and of $0.2(\lambda \cos \theta)$ thickness with 28 at% concentration (magenta full lines), a homogeneous composition of 5 at% extending from the surface to infinity (i.e., $> 5(\lambda \cos \theta)$) (blue full line), and a substrate of pure A below an overlayer of $3(\lambda \cos \theta)$ (cyan full line). Calculations of intensities obtained for typical layer structures are presented in Sect. 4.3.3

Equation 4.39 introduces a simplified notation, used in the following, by omitting subscript i (4.32). Let us keep in mind that the subscript A in σ_A , W_A , $\lambda_{m,E(A)}$ always refers to a measured signal of a core level of element A and subshell i (e.g., Cu 2p_{3/2}).

The solution of the integral in (4.39) requires knowledge of the in-depth composition of the sample. Because (4.39) gives the intensity as a function of the integral over the product of the in-depth composition $N_A(z)$ and the attenuation length, a variety of in-depth distributions will produce exactly the same signal intensity, as shown in Fig. 4.17 for composition-independent $\lambda_{m,E(A)}$. (It is important to keep in mind that the attenuation length is composition dependent as shown, e.g., in layer structure analysis, Sect. 4.3.3.) Figure 4.17 demonstrates that a meaningful quantification of the photoelectron or Auger-electron intensities requires knowledge of the in-depth distribution of composition (see Sect. 4.3.3 and Chap. 7). In contrast to the intensity, the background contains information about the in-depth distribution (see Chap. 7). The solution of the integral in (4.39) is straightforward for two limiting cases, (a) a homogeneous composition to a depth much larger

than the information depth and (b) a thin overlayer (typically a monolayer) on a homogeneous substrate. The first case is considered in detail in the following and the second case in Sects. 4.3.3 (XPS) and 4.4.3 (AES).

4.3.2.1 Basic Equations and Analyzed Intensity

For $N_A(z) = \text{const.}$ (homogeneous sample), the integral in (4.39) can be solved. Assuming that the generation of photoelectrons per unit length is constant at any point along $L = z/\cos\alpha$ (see Fig. 4.13), the intensity at any point at depth z from the surface varies with $dz/\cos\alpha$ in (4.39), whereas $I_{h\nu}$ per unit length is independent on α and z . Integrating (4.39) from $z = 0$ to $z = \infty$, the total, emitted signal intensity is obtained as

$$I_{A,\text{em}} = \sigma_A W_A(\beta_{\text{eff}}, \psi) \frac{I_{h\nu}}{\cos\alpha} \frac{\Delta\Omega}{4\pi} N_A \lambda_{m(A),E(A)} \cos\theta. \quad (4.40)$$

Equation 4.40 gives the total emitted intensity into the small solid angle $\Delta\Omega$ and a small analyzed area (see Fig. 5.1b). The analyzed fraction of this intensity is given by the analyzer transfer characteristic (intensity–energy response function, IERF [4.1]) or analyzer efficiency, $G(E_A)$. By multiplying (4.40) with $G(E_A)$, we get the detected intensity:

$$I_A = \sigma_A W_A(\beta_{\text{eff}}, \psi) G(E_A) \frac{I_{h\nu}}{\cos\alpha} N_A \lambda_{m,E(A)} \cos\theta. \quad (4.41)$$

For constant excitation intensity and angle- and depth-independent N_A , the intensity decreases with $\cos\theta$. For constant θ and an elemental sample, $\lambda_{m,E(A)} = \lambda_{A,E(A)}$, $N_A = N_A^0$ and $I_A = I_A^0$ where I_A^0 is the standard elemental intensity or absolute sensitivity defined in Sect. 4.2.1. Note that all equations containing the measured elemental intensity I_A^0 are for a given emission angle θ .

Expression (4.41) is the basic equation for quantification. The spectrometer terms contained in $G(E_A)$ are the analyzer transmission function or spectrometer function, $T(E)$, and the detector efficiency $D(E)$ together with the geometrical transmission $\Delta\Omega/(4\pi)$ [4.2], where $\Delta\Omega$ is the spatial aperture angle (note that the latter can be altered by electron optical focus changes). A better characteristic of the overall transmission is the “étendue,” i.e., the product of aperture angle and analyzed area (see Sect. 2.5). For analyzers operating in the constant $\Delta E/E$ mode, the acceptance angle is constant, and therefore, the total transmission is proportional to ΔE . In effect, this means the intensity in (4.4.1) is proportional to E , because

$$G(E_A) = T(E)D(E) = \frac{\Delta\Omega}{4\pi} \left(\frac{\Delta E}{E} \right) ED(E). \quad (4.42)$$

Equation 4.42 is valid for small spot XPS and AES instruments where the analyzed area exceeds the irradiated area. When using broad source of nonmonochromated

X-rays, the transmission function has to be replaced by the etendue [4.78, 4.79]. Unfortunately, the detector efficiency $D(E)$ is not only energy dependent, but it may change with age of the detector (Ref. [4.2], p.180). The detector function variation with energy can be determined by comparison with standard spectra taken by a metrological analyzer with a Faraday cup instead of a multiplier [4.65, 4.80–4.82].

Spectrometers operating in the constant ΔE mode, as usually in XPS, the electron optics that have to retard the high-energy electrons to the constant pass energy follow the Helmholtz–Lagrange equation which gives

$$G(E) \propto \frac{1}{E}. \quad (4.43)$$

Many spectrometers follow approximately the $1/E$ dependence [4.65]. For low kinetic energies, deviations to lower exponents until zero are found [4.2]. An advantage of constant pass energy is that the detector term $D(E)$ is constant for different photoelectron energies.

The exact spectrometer function can be determined by comparison of measurements of pure Cu, Ag, and Au spectra with standard spectra after Seah [4.65, 4.82]. An excellent description of the behavior of the spectrometer function (etendue) is given in Ref. [4.2].

The basic equation (4.41) contains the factors necessary to connect the “true” measured intensity, I_A , with the concentration of atoms of A, N_A . Values for the cross section σ_A of each subshell i relative to carbon C 1s for Al K_α and Mg K_α are given by Scofield [4.73] (see Fig. 4.14) and the asymmetry parameter by Reilmann et al. [4.66]. Most commercial instruments are constructed with the angle between the X-ray beam and the analyzer optical axis equal to the “magic angle” of $\psi = 54.7^\circ$; hence, $W(\beta_{\text{eff}}, \psi) = 1$ after (4.33). The attenuation length (EAL), $\lambda_{A,E(A)}$, can be taken from NIST database [4.37]. However, because the instrumental parameters and the absolute photon flux are hard to determine, it is customary to quantify the composition of a sample on a relative basis, for example, by using relative elemental sensitivity factors introduced in Sect. 4.2.1. Equation 4.41 gives insight about the physical basis and is useful for the derivation of matrix correction factors.

4.3.2.2 Elemental and Matrix Relative Sensitivity Factors (E-RSFs and M-RSFs)

As pointed out in Sect. 4.2.1, relative elemental sensitivity factors are empirically defined by measurements of the intensity of pure element standards with the same instrument and the same experimental conditions, and their ratio according to (4.4). In general, this ratio is given by choosing a particular elemental intensity, in XPS usually the fluorine F 1s line [4.22, 4.74] (or the C 1s line from graphite [4.2] (Fig. 4.14)), measured under the same condition as any other element, as a common reference. The physical meaning of relative elemental sensitivity factors is

seen by using (4.41) for a pure element sample A and standard pure element *Std*, and taking the ratio. The excitation and explicit angular terms cancel, and we obtain

$$\frac{I_A^0}{I_{\text{Std}}^0} = \frac{\sigma_A G(E_A) \lambda_{A,E(A)} N_A^0}{\sigma_{\text{Std}} G(E_{\text{Std}}) \lambda_{\text{Std},E(\text{Std})} N_{\text{Std}}^0} = S_{A,\text{Std}} = S_A. \quad (4.44)$$

Equation 4.44 defines the elemental relative sensitivity factor (E-RSF), $S_{A\text{Std}} = S_A$ for element A with respect to standard reference element *Std*. While the latter can be any element, fluorine F 1s was chosen by Wagner [4.22], with N_A^0 and N_F^0 the atomic densities of A and F (in atoms/m³) (Wagner [4.23, 4.74] uses solid stoichiometric fluorine compounds as standards). Note we have simplified (4.41) by assuming an instrument with the “magic angle” of $\gamma = 57.4^\circ$ between X-ray beam and analyzer axis, therefore $W(\beta_{\text{eff}}, \psi) = 1$ in (4.33) and (4.41). If $\psi \neq 57.4^\circ$, all cross section values σ have to be multiplied with the asymmetry factor of the respective subshell, and their ratio only cancels for the same subshell. With the F 1s intensity as standard reference and $\sigma_{\text{A}}^{\text{rel}} = \sigma_A / \sigma_F$, we get from (4.44)

$$\frac{I_A^0}{I_F^0} = S_A = \frac{\sigma_{\text{A},F}^{\text{rel}} G(E_A) \lambda_{A,E(A)} N_A^0}{G(E_F) \lambda_{F,E(F)} N_F^0}. \quad (4.45)$$

Equation 4.45 defines the (elemental) relative sensitivity factor (E-RSF), S_A , of a specific atomic level A_i of element A related to the atomic level F_{1s}, with the relative excitation cross section of A compared to F 1s, $\sigma_{\text{A},F}^{\text{rel}}$. Tables of $\sigma_{\text{A},F}^{\text{rel}}$ for elemental subshells have been provided by Scofield [4.73] (see Fig. 4.14). For many instruments, the factor $G(E_i)$ is proportional to E^{-1} [4.1, 4.65], and the energy dependence of the attenuation length λ for elements can be approximated by $E^{0.75}$ after (4.19) [4.38]. Together this gives a dependence of $E^{0.25}$. Introducing the density dependence of the attenuation length proportional to $N^{-1/2}$ ($\lambda \propto a^{3/2}$, see (4.17) [4.43]) and neglecting the dependence of λ on the atomic number, the elemental relative sensitivity factor is given by

$$\frac{I_A^0}{I_F^0} = S_A \approx \sigma_{\text{A},F}^{\text{rel}} \left(\frac{E_A}{E_{\text{F 1s}}} \right)^{-0.25} \left(\frac{N_A^0}{N_F^0} \right). \quad (4.46)$$

In view of the weak dependence on molar density, N , and its relatively small variations within metallic elements, the latter is frequently ignored, which gives [4.25]

$$\frac{I_A^0}{I_F^0} = S_A = \sigma_{\text{A},F}^{\text{rel}} \left(\frac{E_A}{E_{\text{F 1s}}} \right)^{-0.25}. \quad (4.47)$$

Because of the weak dependence on the kinetic energy after (4.47) (about 15% maximum deviation for binding energies between 0 and 1000 eV), the relative sensitivity factors are approximately given by the relative Scofield cross sections $\sigma_{\text{A},F}^{\text{rel}}$ (for Mg K_α or Al K_α excitation, see Fig. 4.14). Assuming proportionality

of λ to $E^{0.66}$ (resulting in $(E_A/E_{F1s})^{-0.34}$) in (4.47), Wagner et al. [4.22, 4.74] derived RSF's related to fluorine $I_{F1s}^0 = 1$, given in a popular handbook [4.22]. Comparison of empirical data obtained with different instruments with theoretical data on the basis of (4.47) (with $(E_A/E_{F1s})^{-0.34}$) shows agreement within typically 10% deviation [4.74]. The data of Wagner et al. [4.74] are reproduced in Appendix 6, p. 635, of Ref. [4.2].

Although the approximate relation (4.47) for relative elemental sensitivity factors shows no matrix dependence, the exact relation (4.45) is clearly matrix dependent. Indeed, a popular handbook [4.23] uses the relative matrix density factor as in (4.46) for definition of an “atomic sensitivity factor” (ASF) [4.83]. To elucidate the necessity of matrix correction terms, let us briefly consider a binary system with components A, B. According to (4.45), the ratio of the concentration (particles per volume), N_A/N_B , is given by

$$\frac{N_A}{N_B} = \frac{I_A/S_A}{I_B/S_B} = \frac{I_A/(\sigma_A G(E_A)\lambda_{A,E(A)}N_A^0)}{I_B/(\sigma_B G(E_B)\lambda_{B,E(B)}N_B^0)} \propto \frac{(\rho_A/M_A)X_A}{(\rho_B/M_B)X_B}, \quad (4.48)$$

because after (4.18), $N_i = X_i/a_i^3 = (\rho_i/M_i)N_{\text{avo}}X_i$, with density ρ_i , and molar mass M_i , and Avogadro's number, N_{avo} , cancels in the ratio.

Equation 4.48 is only correct if the molar density cancels, $(\rho_A/M_A) = (\rho_B/M_B)$. Actually, this is true because both species of atoms are in the same, common matrix m with molar mass M_m and density ρ_m . This new matrix molar density generally is neither the elemental molar density ρ_A/M_A nor ρ_B/M_B . Thus, it is clear that correct relative elemental sensitivity factors do not give exact results when applied to compounds or alloys. In addition to density correction, a correction of the attenuation length is necessary because of its dependence on the average atomic number, as seen in the following section. (In AES, in addition, a matrix-dependent backscattering factor has to be introduced.) Correctly, (4.48) is represented by

$$\frac{X_A}{X_B} = \frac{I_{A,m}/(\sigma_A G(E_A)\lambda_{m,E(A)}N_m^0)}{I_{B,m}/(\sigma_B G(E_B)\lambda_{m,E(B)}N_m^0)} = \frac{N_A}{N_B} = \frac{I_{A,m}}{I_{B,m}} \frac{\sigma_B G(E_B)\lambda_{m,E(B)}}{\sigma_A G(E_A)\lambda_{m,E(A)}}. \quad (4.49)$$

In (4.49), the Scofield cross sections, σ_A and σ_B , can be taken from the literature [4.73]. The ratio of the spectrometer function or intensity–energy response function (IERF), $G(E_B)/G(E_A)$, frequently is unknown but can be separately determined as described in [4.65, 4.82]. If E_A is close to E_B , as for the metal and the shifted oxide peak of the same element, $G(E_B)/G(E_A) = 1$. The only really matrix-dependent term is the ratio of the attenuation lengths, $\lambda_{m,E(B)}/\lambda_{m,E(A)}$. For several compounds, the respective attenuation length (EAL) values can be found in Ref. [4.37], and newly calculated IMFP values for 41 elemental solids in Ref. [4.44].

With (4.49), a matrix-dependent (binary) relative sensitivity factor (M-RSF), $S_{A,B}^m$, can be defined as

$$\frac{S_{A,m}}{S_{B,m}} = \frac{\sigma_A G(E_A)\lambda_{m,E(A)}}{\sigma_B G(E_B)\lambda_{m,E(B)}} = S_{A,B}^m. \quad (4.50a)$$

Comparing (4.50a) with (4.44) and (4.48), the elemental and matrix relative sensitivity factors are related by

$$\frac{S_{A,m}}{S_{B,m}} = \frac{S_A \lambda_{B,E(B)} N_B^0 \lambda_{m,E(A)}}{S_B \lambda_{A,E(A)} N_A^0 \lambda_{m,E(B)}} = S_{A,B} \frac{1}{F_{A,B}^m} = S_{A,B}^m \quad (4.50b)$$

with the (relative) matrix correction factor $F_{A,B}^m$ given by

$$F_{A,B}^m = \frac{\lambda_{A,E(A)} N_A^0 \lambda_{m,E(B)}}{\lambda_{B,E(B)} N_B^0 \lambda_{m,E(A)}} = \frac{1}{F_{B,A}^m}. \quad (4.50c)$$

Equation 4.50c corresponds to (5.14) (p. 208 in Ref. [4.2]), when the backscattering terms for AES are ignored.

Because matrix m is the same for both EALs, above $E \cong 200$ eV, we may replace the ratio by $\lambda_{m,E(B)}/\lambda_{m,E(A)} = [E(B)/E(A)]^{0.75}$ (see (4.19)) and get from (4.49)

$$\frac{X_A}{X_B} = \frac{I_{A,m} \sigma_B G(E_B)}{I_{B,m} \sigma_A G(E_A)} \left[\frac{E(B)}{E(A)} \right]^{0.75}, \quad (4.50d)$$

and from (4.50c),

$$F_{A,B}^m = \frac{\lambda_{A,E(A)} N_A^0}{\lambda_{B,E(B)} N_B^0} \left(\frac{E(B)}{E(A)} \right)^{0.75} = \frac{1}{F_{B,A}^m}. \quad (4.50e)$$

4.3.2.3 Quantification Including Matrix Effects

Usually, the analyst is not interested in pure element samples but in multielement samples. Of course, an element in a certain matrix with other elements is expected to have values of the attenuation length, λ , and of the atomic density, N , that are different from those of the pure element. For simplicity, let us consider a binary system with elements A and B. If necessary, the equations can easily be expanded to multielement systems, as shown by (4.5) and (4.6a)–(4.6c). A guideline for the use of sensitivity factors for quantitative analysis for homogeneous samples is given in Refs. [4.27, 4.83].

Taking (4.41) for the intensity of A in matrix m , $I_{A,m}$, to the intensity of pure elemental A, I_A^0 , the ionization cross section, the photoelectron energy, and the spectrometer function $G(E_A)$ are independent of composition, and they cancel in the ratio. In analogy to (4.44), we may write

$$\frac{I_{A,m}}{I_A^0} = \frac{\lambda_{A,m,E(A)} N_m}{\lambda_{A,E(A)} N_A^0} X_A = \frac{S_{A,m}}{S_A} X_A, \quad (4.51)$$

where S_A is the relative elemental sensitivity factor, as defined above, and $S_{A,m}$ denotes the matrix relative sensitivity factor for element A in matrix m . Therefore,

the mole fraction of A in matrix m , X_A , is given by

$$X_A = \frac{I_{A,m}}{I_A^0} \frac{\lambda_{A,E(A)} (N_A^0)}{\lambda_{A,m,E(A)} (N_m)} = \frac{I_{A,m}}{I_A^0} \frac{S_A}{S_{A,m}} = \frac{I_{A,m}}{I_A^0} F_{A,m}. \quad (4.52)$$

The matrix correction factor, $F_{A,m}$, for A in matrix m is defined by (4.49) [4.2] as

$$F_{A,m} = \frac{S_A}{S_{A,m}} = \frac{I_A^0}{I_{A,m}^0}. \quad (4.53a)$$

In analogy, we can define the matrix correction factor, $F_{B,m}$, for B in matrix m :

$$F_{B,m} = \frac{S_B}{S_{B,m}} = \frac{I_B^0}{I_{B,m}^0}. \quad (4.53b)$$

Thus, the ratio of matrix relative sensitivity factors is given by dividing the relative elemental sensitivity factor ratio with the matrix correction factor ratio:

$$\frac{S_{A,m}}{S_{B,m}} = \frac{S_A}{S_B} \frac{F_{B,m}}{F_{A,m}}. \quad (4.54)$$

Note that in (4.53a) and (4.53b), the elemental relative sensitivity is given with respect to the standard intensities of F 1s or C 1s. In the following, we refer to C 1s, with $S_A = I_A^0 / I_{C1s}^0$, $S_B = I_B^0 / I_{C1s}^0$ (according to Ref. [4.74], $S_i(\text{C 1s}) = 4.0 \times S_i(\text{F 1s})$). These E-RSFs are either based on empirically measured intensity values (preferable performed with the same instrument under identical conditions) or they are based on relative Scofield cross section (Fig. 4.14) corrected for the energy dependencies of transmission and attenuation length, for example, after (4.45).

According to (4.52), the matrix correction factors $F_{A,m}$ and $F_{B,m}$ are given by

$$F_{A,m} = \frac{\lambda_{A,E(A)} N_A^0}{\lambda_{m,E(A)} N_m} \quad (4.55a)$$

and

$$F_{B,m} = \frac{\lambda_{B,E(B)} N_B^0}{\lambda_{m,E(B)} N_m}. \quad (4.55b)$$

The matrix correction factor is a measure of the deviation of the atomic density (given by N) and the attenuation length (λ) between matrix and elemental standard. Introducing (4.51, 4.52) in (4.5), we can now give the mole fraction of A in matrix m , $X_{A,m}$, and of B in matrix m , $X_{B,m}$, in a binary system A–B in terms of elemental sensitivity factors combined with matrix correction factors:

$$\begin{aligned} X_A &= \frac{I_{A,m} F_{A,m} / I_A^0}{(I_{A,m} F_{A,m} / I_A^0 + I_{B,m} F_{B,m} / I_B^0)} \\ &= \frac{I_{A,m} / (S_A / F_{A,m})}{I_{A,m} / (S_A / F_{A,m}) + I_{B,m} / (S_B / F_{B,m})} = \frac{I_{A,m} / S_{A,m}}{I_{A,m} / S_{A,m} + I_{B,m} / S_{B,m}} \end{aligned} \quad (4.56a)$$

with the intensity of any standard (subscript *Std*, e.g., F 1s or C 1s) $I_A^0 = S_A \times I_{Std}^0$, $I_B^0 = S_B \times I_{Std}^0$, and $S_A/F_{A,m} = S_{A,m}$, $S_B/F_{B,m} = S_{B,m}$, and in analogy to (4.56a),

$$\begin{aligned} X_B &= \frac{I_{B,m} F_{B,m} / I_B^0}{(I_{A,m} F_{A,m} / I_A^0 + I_{B,m} F_{B,m} / I_B^0)} \\ &= \frac{I_{B,m} / (S_B / F_{B,m})}{I_{A,m} / (S_A / F_{A,m}) + I_{B,m} / (S_B / F_{B,m})} = \frac{I_{B,m} / S_{B,m}}{I_{A,m} / S_{A,m} + I_{B,m} / S_{B,m}}. \end{aligned} \quad (4.56b)$$

Expressions (4.56a) and (4.56b) can further be simplified by introducing (binary) elemental relative sensitivity factors (E-RSFs), $S_{A,B} = S_A / S_B$, and matrix relative sensitivity factors (M-RSFs) $S_{A,B}^m = S_{A,m} / S_{B,m}$. Relative matrix correction factors are obtained by the ratio of (4.55a) and (4.55b), $F_{A,B}^m = F_{A,m} / F_{B,m}$. Because $S_{B,A}^m = 1 / S_{A,B}^m$ and $F_{B,A}^m = 1 / F_{A,B}^m$, it is sufficient to calculate $S_{A,B}^m$ or $F_{A,B}^m$, which are related, by

$$S_{A,B}^m = \frac{S_{A,m}}{S_{B,m}} = \frac{S_A F_{B,m}}{S_B F_{A,m}} = S_{A,B} F_{B,A}^m = \frac{S_{A,B}}{F_{A,B}^m}. \quad (4.57)$$

Introducing (4.57), we rewrite (4.55a) and (4.55b) and get

$$X_A = \frac{I_{A,m}}{I_{A,m} + \frac{I_{B,m} S_{A,B}}{F_{A,B}^m}} = \frac{I_{A,m}}{I_{A,m} + I_{B,m} S_{A,B}^m} \quad (4.58a)$$

and

$$X_B = \frac{I_{B,m}}{I_{B,m} + \frac{I_{A,m} S_{B,A}}{F_{B,A}^m}} = \frac{I_{B,m}}{I_{B,m} + I_{A,m} S_{B,A}^m}. \quad (4.58b)$$

Since the relative (binary) matrix correction factors $F_{A,B}^m$, $F_{B,A}^m$ are given by the ratio of (4.55a) with (4.55b), we obtain

$$\begin{aligned} F_{A,B}^m &= \frac{F_{A,m}}{F_{B,m}} = \frac{\lambda_{A,E(A)} N_A^0 \lambda_{m,E(B)}}{\lambda_{B,E(B)} N_B^0 \lambda_{m,E(A)}} = \frac{\lambda_{A,E(A)} (\rho_A / M_A) \lambda_{m,E(B)}}{\lambda_{B,E(B)} (\rho_B / M_B) \lambda_{m,E(A)}} = \\ &= \frac{(\rho_A / M_A) \lambda_{in,A,E(A)} Q_{A,E(A)} \lambda_{in,m,E(B)} Q_{m,E(B)}}{(\rho_B / M_B) \lambda_{in,B,E(B)} Q_{B,E(B)} \lambda_{in,m,E(A)} Q_{m,E(A)}} = \frac{1}{F_{B,A}^m}. \end{aligned} \quad (4.59)$$

According to (4.49), N_{Av0} cancels in the ratio of atomic densities, and N_A^0 can be replaced by the more practical molar density (ρ_A / M_A). In the last expression, λ is replaced by $\lambda_{in} Q$ (see (4.20)). While $\lambda_{in,i,E(i)} Q_{i,E(i)}$ for element i can directly be taken from databases [4.37], $\lambda_{in,m,E(i)} Q_{m,E(i)}$ for the matrix to be determined is unknown.

Despite the complicated energy dependence of Q , the ratio for the same matrix can be replaced by a simple exponent function as discussed below.

Note that in (4.59), the matrix density term $N_m = (M_m / \rho_m)$ ((4.55a) and (4.55b)) cancels because components A and B are in the same matrix m . However, we still

do not know the exact matrix dependence of the atomic density which is necessary to estimate the correct attenuation length $\lambda_{m,E(A)}$ and $\lambda_{m,E(B)}$. In case of small concentrations of one element (A) in a binary system A–B, we see by comparison with (4.52) that the matrix m is replaced by B, and the matrix-corrected attenuation lengths are replaced by $\lambda_{B,E(A)}$ and $\lambda_{A,E(B)}$. It is shown below that this corresponds to the ratio $\lambda_{m,E(A)}/\lambda_{m,E(B)}$ in (4.59), which is practically independent of matrix composition. Thus, for any binary system, the relative matrix correction factors given by (4.59) can be predicted using values for the attenuation lengths of the elements, for example, from the NIST database [4.37], from the product $Q\lambda_{in}$ (see Sect. 4.2), or from the CS2 equation of Cumpson and Seah [4.43], and (ρ/M) values, i.e., for atomic mass and density, for example, from periodic tables of the elements or from the *Handbook of Chemistry and Physics* [4.84].

Several models have been proposed to correct for matrix effects assuming a single, homogeneous phase. In essence, they are fairly similar, as elucidated below for binary systems. All equations can easily be extended to multielement systems, as shown in (4.4)–(4.6). An example of the ternary system (Fe–Cr–C) is shown in Sect. 4.3.2.5. Although the early models were applied to AES, the general equations given above apply equally well for XPS with the respective sensitivity factors and discarding electron backscattering. The most important approaches are:

1. Dilute alloy approximation (Hall and Morabito [4.85]) and composition dependence (Holloway [4.86])
2. Simplified correction factor (Payling [4.87])
3. Average matrix correction (Seah and Gilmore [4.88, 4.89])
4. Synopsis and resume: improved Hall–Morabito–Payling approach: Matrix-less formulation of binary matrix correction factors

1. Matrix Correction Factor for Dilute Alloys (Hall and Morabito, XPS) and Composition Dependence (Holloway)

As pointed out by Hall and Morabito [4.85] (originally for AES), for dilute systems with preponderant concentration of one element and small concentrations of the other(s), the solution is simplified by approximately taking the main element, for example, B, as the matrix m . Hence, in (4.59), for low concentrations of A in B, $\lambda_{m,E(B)} = \lambda_{B,E(B)}$ and $\lambda_{m,E(A)} = \lambda_{B,E(A)}$, and we get

$$F_{A,B}^m(H - M) = \frac{\lambda_{A,E(A)} N_A^0}{\lambda_{B,E(A)} N_B^0}, \quad (4.60a)$$

and similarly for small concentrations of B in A,

$$F_{B,A}^m(H - M) = \frac{\lambda_{B,E(B)} N_B^0}{\lambda_{A,E(B)} N_A^0}. \quad (4.60b)$$

Note that for consistency with present work, we use the matrix correction factor definition of (4.57) after Seah [4.2] which is the inverse of that of Hall–Morabito and

Holloway. In principle, the relation of the exact relative matrix correction factors in (4.59), $F_{A,B}^m = 1/F_{B,A}^m$, is no more valid for (4.60a) and (4.60b). However, in practice, this relation is still fulfilled with good accuracy because the difference is only in the λ ratios at different energies and the energy dependencies are expected to be rather similar (cf. (4.19) and Fig. 4.7). Hall and Morabito showed similar results for the two different attenuation lengths determinations after Penn [4.90] and Seah and Dench [4.36]. Using the proportionality of λ with $E^{1/2}a^{3/2} = E^{1/2}N^{-1/2}$ of the latter (according to (4.10)), the energy dependence cancels in (4.60a) and (4.60b), and the $N^{-1/2}$ term reduces the atomic density term to the square root. This results in

$$F_{A,B}^m(H - M) \approx \left(\frac{N_B^0}{N_A^0} \right)^{1/2} = \frac{1}{F_{B,A}^m(H - M)}. \quad (4.61)$$

In 4,680 elemental combinations for AES (with an added backscattering term in both the nominator and the denominator) (see Sect. 4.4.1), Hall and Morabito found a distribution around 1 and a scatter between 0.2 and 5 that means a maximum error of as much as a factor of five could result if the matrix correction factor is ignored. However, they reported a standard deviation of 0.5, indicating that typically this factor is within 1 ± 0.5 , i.e., clearly less than a factor of 2.

For selected examples, matrix-corrected sensitivity factors after (4.60a) and (4.60b) are given in Table 4.2 for comparison with other approaches.

Composition Dependence: Holloway [4.86] (and later Zagorenko and Zaporochenko [4.91]) tried to improve the dilute alloy approach of Hall and Morabito by assuming a linear dependence of the matrix attenuation lengths $\lambda_{m,E(A)}$, and $\lambda_{m,E(B)}$ in (4.59) on composition. In this approximation, the matrix-corrected attenuation length is represented by

$$\lambda_{m,E(A)} = \lambda_{B,E(A)}(1 + b_{A,A}X_A) \quad (4.62a)$$

with

$$b_{A,A} = (\lambda_{A,E(A)} - \lambda_{B,E(A)})/\lambda_{B,E(A)}. \quad (4.63a)$$

For element B, we get

$$\lambda_{m,E(B)} = \lambda_{B,E(B)}(1 + b_{B,A}X_A) \quad (4.62b)$$

with

$$b_{B,A} = (\lambda_{A,E(B)} - \lambda_{B,E(B)})/\lambda_{B,E(B)}. \quad (4.63b)$$

With (4.62b) and (4.63b) in (4.59), $F_{A,B}^{\text{rel}}$ can be written as

$$F_{A,B}^m = \frac{F_{A,m}}{F_{B,m}} = \frac{\lambda_{A,E(A)}N_A^0\lambda_{B,E(B)}(1 + b_{B,A}X_A)}{\lambda_{B,E(B)}N_B^0\lambda_{B,E(A)}(1 + b_{A,A}X_A)} = \frac{1}{F_{B,A}^m}. \quad (4.64)$$

Table 4.2 Quantification data for XPS analysis of Fe–Cr and Fe–C

Element <i>i</i>	Fe	Cr	C
(ρ/M) (mol/cm ³)	0.1411	0.1383	0.1883
<i>a</i> (nm)	0.228	0.229	0.207
<i>Z</i> (atomic number)	26	24	6
<i>E</i> (eV)(AlK α)	780 (2p _{3/2})	913 (2p _{3/2})	1202 (1s)
$\lambda_{\text{Fe},E(i)}$ (nm)(CS2)	1.11	1.25	1.54
$\lambda_{\text{Cr},E(i)}$ (nm) (CS2)	1.15	1.30	1.60
$\lambda_{\text{C},E(i)}$ (nm) (CS2)	1.75	1.98	2.47
	(1.95) ^a	(2.21) ^a	(2.76) ^a
$(\lambda_{\text{in}}Q)_{\text{Fe},E(i)}$ (nm)	1.27	1.43	1.88
$(\lambda_{\text{in}}Q)_{\text{Cr},E(i)}$ (nm)	1.30	1.47	1.83
$(\lambda_{\text{in}}Q)_{\text{C},E(i)}$ (nm)	2.19	2.47	3.07
$(\lambda_{\text{in}}Q)_{\text{av},E(i)}$ (nm)	1.83	2.06	2.56
<i>S_i</i> (E-RSF, Basis C 1s)	8.0	6.0	1.0
<i>F_{i,m}</i> / <i>F_{C,m}</i> (Payling)	0.75	0.79	1.0
<i>F_{i,m}</i> / <i>F_{C,m}</i> (H–M)	0.475	0.482	1.0
<i>F_{i,m}</i> / <i>F_{av,m}</i> (S–G)	1.130	1.142	2.61
<i>F_{i,m}</i> / <i>F_{av,C}</i> (S–G)	0.433	0.437	1.0
<i>F_{i,C}^m</i> (Syn)(CS2)	0.466	0.475	1.0
<i>S_{i,C}^m</i> (Syn)(CS2)	17.2	12.6	1.0
<i>F_{i,C}^m</i> (Syn)($\lambda_{\text{in}}Q$)	0.429	0.432	1.0
<i>S_{i,C}^m</i> (Syn)($\lambda_{\text{in}}Q$)	18.6	12.3	1.0

Values for: $\lambda_{\text{in}}Q$ are from Ref. [4.37], $S_{i,C} = S_i (= \text{E-RSF})$ data for Al K α excitation are from Wagner et al. [4.74]. Average matrix data after Refs. [4.10, 4.92]: (ρ/M) (mol cm^{−3}) = 0.0864, $a = 0.268$ nm

Abbreviations in parentheses: (CS2): expression (4.17), (Payling): (4.69), (4.70); (H–M): (4.60a, b); (S–G): (4.73a–c), (4.77), (4.78); (Syn): (4.80)–(4.82)

^aThis value is from NIST database (I) [4.37]. According to CS2 (4.17), this value would mean $a = 0.223$ nm, ρ (graphite) = 1.80 g cm^{−3}, and $\rho/M = 0.1500$ mol cm^{−3} in (4.80). We found ρ (graphite) = 2.25 g cm^{−3} [4.84]

The linear relations in (4.62b) and (4.63b) and their ratio according to (4.64) are shown as dashed lines in Fig. 4.18 for the binary system Fe–C as an example with a relatively large variation of the attenuation length.

We may improve Holloway's approach by the more correct procedure of adding up the scattering cross sections, i.e., the inverse values of the attenuation length, which gives the following matrix composition-corrected values:

$$\lambda_{m,E(A)} = \frac{1}{X_A \frac{1}{\lambda_{A,E(A)}} + X_B \frac{1}{\lambda_{B,E(A)}}} = \frac{\lambda_{B,E(A)}}{1 + X_A \left(\frac{\lambda_{B,E(A)}}{\lambda_{A,E(A)}} - 1 \right)} \quad (4.65a)$$

and

$$\lambda_{m,E(B)} = \frac{\lambda_{B,E(B)}}{1 + X_A \left(\frac{\lambda_{B,E(B)}}{\lambda_{A,E(B)}} - 1 \right)}. \quad (4.65b)$$

Then

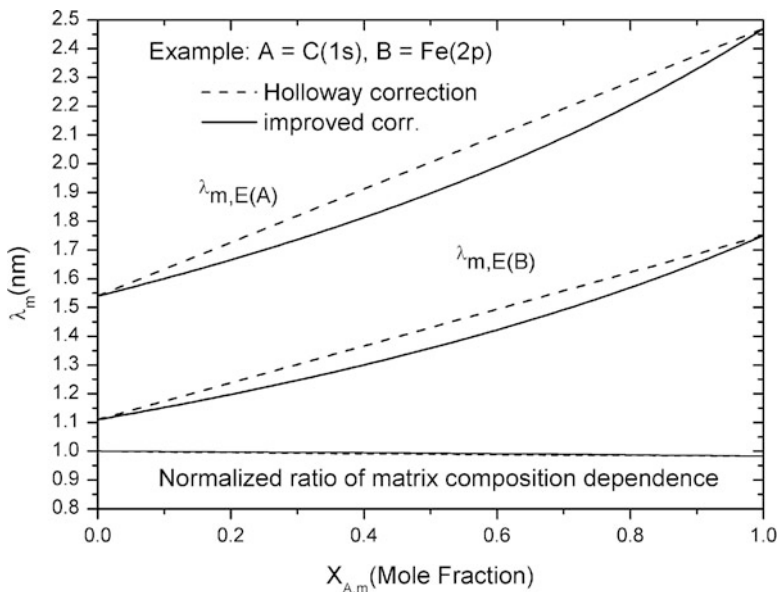


Fig. 4.18 Matrix composition dependence of the attenuation lengths $\lambda_{m,E(A)}$ and $\lambda_{m,E(B)}$ after (4.62a) and (4.62b) (Holloway correction), and (4.65a) and (4.65b) (improved correction) for the hypothetical system Fe–C (A = C, B = Fe, with corresponding λ values from Table 4.2), and their ratio normalized by $\lambda_{B,E(B)}/\lambda_{B,E(A)}$, demonstrating the composition independence of the relative matrix correction factor $F_{m,A,B}$

$$F_{A,B}^m = \frac{F_{A,m}}{F_{B,m}} = \frac{\lambda_{A,E(A)} N_A^0 \lambda_{B,E(B)} \left[1 + X_A \left(\frac{\lambda_{B,E(A)}}{\lambda_{A,E(A)}} - 1 \right) \right]}{\lambda_{B,E(B)} N_B^0 \lambda_{B,E(A)} \left[1 + X_A \left(\frac{\lambda_{B,E(B)}}{\lambda_{A,E(B)}} - 1 \right) \right]} = \frac{1}{F_{B,A}^m}. \quad (4.66)$$

Equations 4.65a and 4.65b are additionally plotted in Fig. 4.18 for Fe–C (solid lines), together with their ratio which is equivalent to the second, composition-dependent part (in parentheses) of (4.65)–(4.66). While the difference in the variation of both approaches for the absolute attenuation length values, $\lambda_{m,E(A)}$ and $\lambda_{m,E(B)}$, is 6% at maximum, the variation of the ratio of the composition-dependent part of $F_{A,B}^m$ is less than 0.5% for the whole concentration range of X_A ($= 1 - X_B$), i.e., practically constant and given by the ratio $\lambda_{B,E(A)}/\lambda_{B,E(B)}$. The reason for this result is the similarity in composition dependence of the attenuation length (see Fig. 4.18). Thus, as already noticed by Hall and Morabito [4.85], the dilute alloy approach ((4.60a) and (4.60b)) holds for nondilute alloys, too.

2. Simplified Matrix Correction Factor After Payling

As already shown by Hall and Morabito [4.85], the (nowadays outdated) attenuation length equation of Seah and Dench of 1979 [4.36] gives a scaling of λ with atomic distance, a (for $E > 50$ eV), of $\lambda \propto a^{3/2}$ (see (4.10)), hence with atomic

density as $N^{-1/2}$. Based on this fact, Payling [4.87] proposed a modification of the relative elemental sensitivity factor that is proportional to the product $(\lambda N) \propto N^{1/2}$ (see consistency with $F_{A,B}^m$ after Hall–Morabito, (4.61)). Because the density N is constant for all elements in the sample, he concluded that a matrix-corrected elemental sensitivity factor, $S_{i,m}$, can be introduced in the basic expression (4.59) that is given by

$$S_{i,m} = S_i N_i^{-1/2} \propto S_i (\rho_i / M_i)^{-1/2}, \quad (4.67)$$

where the relative elemental sensitivity factor $S_i = S_{i,Ag}$ for XPS [4.21] of element i with respect to F 1s intensity. Originally, Payling made the correction for AES with $S_i = S_{i,Ag}$ of the relative elemental sensitivity factor of element i with respect to Ag (Auger peak-to-peak heights). Because he did not consider backscattering effects, his equations apply for XPS as well as for AES. Comparison of (4.67) with (4.55a) and (4.55b) and with (4.56a) and (4.56b) shows that the matrix modified Payling relative elemental sensitivity factor, $S'_{A,B}(\text{Payl})$, means that the matrix correction factor $F_{A,m}$ is replaced by $N_A^{-1/2}$:

$$\begin{aligned} S_{A,B}^m &\approx S'_{A,B}(\text{Payl}) \\ &= \frac{S_{A,m}}{S_{B,m}} = \left(\frac{S_{A,Ag}}{S_{B,Ag}} \right) \left(\frac{N_B^0}{N_A^0} \right)^{1/2} = \left(\frac{S_{A,Ag}}{S_{B,Ag}} \right) \left(\frac{(\rho_B / M_B)}{(\rho_A / M_A)} \right)^{1/2}. \end{aligned} \quad (4.68)$$

Indeed, (4.68) means a simplification of (4.57) by setting the relative matrix correction factor for a (dilute) binary system of A in B to a density correction term which includes a simplified attenuation length correction. Hence, the relative matrix correction factor after Payling is

$$F_{A,B}^m(\text{Payl}) = \left(\frac{N_A^0}{N_B^0} \right)^{1/2} = \left(\frac{\rho_A / M_A}{\rho_B / M_B} \right)^{1/2} \quad (4.69)$$

in accordance with the simplified definition of Hall and Morabito (see (4.61)).

For AES, Payling [4.87] gives tabulated values of $S_{i,m}$ of the elements according to (4.67), with S_i relative to Ag, resulting in

$$\begin{aligned} S'_i(\text{Payl}) &= \frac{S_{i,m}}{S_{Ag,m}} = \frac{S_{i,Ag}}{S_{Ag,Ag}} \frac{1}{F_{i,Ag}^m(\text{Payl})} = S_i \left(\frac{(N_{Ag}^0)}{(N_i^0)} \right)^{1/2} \\ &= S_i \left(\frac{\rho_{Ag} / M_{Ag}}{\rho_i / M_i} \right)^{1/2} \end{aligned} \quad (4.70)$$

As an example, for carbon this gives

$$S'_C(\text{Payl}) = S_C \left(\frac{\rho_{Ag} / M_{Ag}}{\rho_C / M_C} \right)^{1/2} = 0.14 \times \left(\frac{10.5/107.9}{2.26/12.0} \right)^{1/2} = 0.10$$

with $S_C = 0.14$ from the Handbook of Davies et al. [4.21].

The modified sensitivity factors after Payling according to (4.67) and (4.68) are indeed “universal” sensitivity factors which are decreased with respect to S_i for most of the light elements, and increased or nearly unchanged for the heavier elements as compared to the elemental sensitivity factors. Note that (4.69) is equivalent to the approach of Hall and Morabito, (4.60), if the simplification $\lambda = \text{const.} \times N^{-1/2}$ is introduced. However, both simplifications ignore the dependence of the attenuation length in different matrix combinations with respect to the energy considered. Therefore, we cannot expect correct values from the approach. In general, the relative matrix correction factors after Payling point in the right direction but are relatively “mild” as compared, for example, to those of Hall and Morabito (see Table 4.3). Today, they are outdated but can easily be updated by an improved relative matrix correction factor after (4.59) with λ values, for example, from NIST database or from CS2.

3. Average Matrix Correction Factor After Seah and Gilmore

As already observed by Hall and Morabito [4.85], the relative (binary) matrix correction factors, $F^m_{A,B}$, show a much narrower distribution around unity than the usual factors related to an arbitrarily chosen matrix. With a concept similar to that and to that of Payling [4.87] but more refined, Seah and Gilmore [4.10, 4.89] reformulated the matrix correction factor approach by introducing a “weak matrix correction term” and an “average matrix.” Their basic concept is to replace the general matrix correction factor $F_{A,m}$ in (4.59), depending on the unknown matrix m , by a product of a “weak matrix correction” term, $P_{A,m}$, with an average matrix correction factor, $F_{A,av}$, based on a known, suitably chosen, fictitious “average” matrix.

For a binary system A–B, according to Seah and Gilmore [4.89], the new reference is the matrix elemental intensity $I^0_{A,av}$ (or matrix sensitivity factor) instead of the former pure element intensity I^0_A , and in analogy to (4.51), (4.52), the average matrix correction factor is given by

$$F_{A,av} = I^0_A / I^0_{A,av}. \quad (4.71)$$

With the basic definition in (4.55a) and (4.55b) and $F_{A,m}$ given by $P_{A,m} F_{A,av}$, we get

$$F_{A,m} = P_{A,m} F_{A,av} = \frac{N^0_A \lambda_{A,E(A)}}{N^0_{av} \lambda_{av,E(A)}} P_{A,m} = \frac{N^0_A \lambda_{in,A,E(A)} Q_{A,E(A)}}{N^0_{av} \lambda_{in,av,E(A)} Q_{av,E(A)}} P_{A,m}, \quad (4.72a)$$

and similarly for component B, in binary system A,B,

$$F_{B,m} = P_{B,m} F_{B,av} = \frac{N^0_B \lambda_{B,E(B)}}{N^0_{av} \lambda_{av,E(B)}} P_{B,m} = \frac{N^0_B \lambda_{in,B,E(B)} Q_{B,E(B)}}{N^0_{av} \lambda_{in,av,E(B)} Q_{av,E(B)}} P_{B,m}. \quad (4.72b)$$

The following expressions for the average matrix parameters in (4.72a) and (4.72b) are recommended by Seah et al. [4.10, 4.27, 4.89, 4.92] ($i = A, B, \dots$):

$$N_{\text{av}}^0 = 5.20 \times 10^{28} \text{ atoms} \cdot \text{m}^{-3}, \quad (4.73\text{a})$$

$$\lambda_{\text{in,av},E(i)}(\text{nm}) = \frac{0.000523E(i)^3}{48.6 - 1.76E(i) + 0.518E(i)^2(\ln E(i) - 2.61)}, \quad (4.73\text{b})$$

$$Q_{\text{av},E(i)} = 0.951 - \left(\frac{E(i) - 2,310}{10,300} \right), \quad (4.73\text{c})$$

where $E(i)$ is the kinetic energy of the relevant photoelectron energy of element i in eV.

Reformulation of (4.56a) by introducing the “weak” matrix correction factors, $P_{A,m}$ and $P_{B,m}$, with (4.71) and (4.72a) gives for the mole fraction X_A of A in matrix m :

$$X_A = \frac{P_{A,m} (I_{A,m} / I_{A,\text{av}}^0)}{[P_{A,m} (I_{A,m} / I_{A,\text{av}}^0) + P_{B,m} (I_{B,m} / I_{B,\text{av}}^0)]}. \quad (4.74)$$

The normalizing $I_{A,\text{av}}^0$ (i.e., the average matrix sensitivity factor) can be calculated using the parameters for the average matrix given by Seah and Gilmore [4.10, 4.89, 4.92]. The interdependence with the general matrix correction factors is disclosed when replacing $I_{A,\text{av}}^0$ by $I_A^0 / F_{A,\text{av}}$ and $I_{B,\text{av}}^0$ by $I_B^0 / F_{B,\text{av}}$ (4.71):

$$\begin{aligned} X_A &= \frac{I_{A,m}}{I_{A,m} + \frac{P_{B,m} I_{A,\text{av}}^0}{P_{A,m} I_{B,\text{av}}^0} I_{B,m}} = \frac{I_{A,m}}{I_{A,m} + \frac{P_{B,m} F_{B,\text{av}} I_A^0}{P_{A,m} F_{A,\text{av}} I_B^0} I_{B,m}} \\ &= \frac{I_{A,m}}{I_{A,m} + \frac{S_A P_{B,m} F_{B,\text{av}}}{S_B P_{A,m} F_{A,\text{av}}} I_{B,m}}. \end{aligned} \quad (4.75)$$

Comparison of (4.57)–(4.58) with (4.75) clearly shows that $F_{A,m}$ and $F_{B,m}$ are now replaced by the products $P_{A,m} F_{A,\text{av}}$ and $P_{B,m} F_{B,\text{av}}$, respectively, and with (4.72) and (4.73), the ratio $P_{A,m} / P_{B,m}$ follows as

$$\frac{P_{A,m}}{P_{B,m}} = \frac{F_{A,m} F_{B,\text{av}}}{F_{A,\text{av}} F_{B,m}} = \frac{\lambda_{m,E(A)} \lambda_{\text{av},E(B)}}{\lambda_{m,E(B)} \lambda_{\text{av},E(A)}}, \quad (4.76)$$

because the atomic densities cancel. It is seen that $P_{A,m} / P_{B,m} = 1$ is valid if the energy dependencies of the attenuation lengths in matrix m and the average matrix are exactly the same. The remaining average matrix relative correction factors are

$$\frac{F_{A,\text{av}}}{F_{B,\text{av}}} = \frac{N_{\text{av}}^0 \lambda_{A,E(A)} \lambda_{\text{av},E(B)}}{N_B^0 \lambda_{B,E(B)} \lambda_{\text{av},E(A)}} = \frac{N_{\text{av}}^0 \lambda_{A,E(A)} \lambda_{\text{in,av},E(B)} Q_{\text{av},E(B)}}{N_B^0 \lambda_{B,E(B)} \lambda_{\text{in,av},E(A)} Q_{\text{av},E(A)}}. \quad (4.77)$$

Comparison with (4.59) shows that the attenuation lengths for the unknown matrix m are replaced by the known (although fictitious) average matrix. Introducing (4.76) in (4.59) gives for the traditional relative matrix correction factors

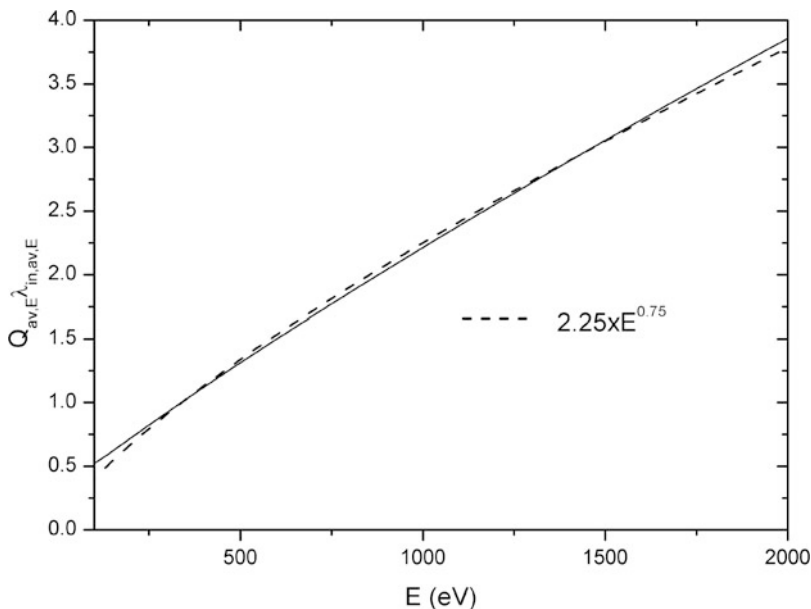


Fig. 4.19 Energy dependence of the expression $\lambda_{av,E(i)} = Q_{av,E(i)} \lambda_{in,av,E(i)}$ in (4.77) and (4.78) calculated with (4.73b) and (4.73c) as compared to the expression $2.25E(i)^{0.75}$

$$\frac{F_{A,m}}{F_{B,m}} = \frac{N_A^0 \lambda_{A,E(A)} \lambda_{m,E(B)}}{N_B^0 \lambda_{B,E(B)} \lambda_{m,E(A)}} = \frac{N_A^0 \lambda_{A,E(A)} P_{A,m} \lambda_{av,E(B)}}{N_B^0 \lambda_{B,E(B)} P_{B,m} \lambda_{av,E(A)}} \quad (4.78)$$

with the weak matrix correction term ratio assumed to be unity [4.89], we expect that $F_{A,m}/F_{B,m} = F_{A,av}/F_{B,av}$ if the energy dependencies of the attenuation length for matrix m and for the average matrix are the same, i.e.,

$$\frac{F_{A,m}}{F_{B,m}} = \text{const} \frac{\lambda_{m,E(B)}}{\lambda_{m,E(A)}} = \text{const} \frac{\lambda_{av,E(B)}}{\lambda_{av,E(A)}} = \frac{F_{A,av}}{F_{B,av}}. \quad (4.79)$$

In Fig. 4.19, the energy dependence of $\lambda_{av} = \lambda_{in,av} \times Q_{av}$ as a function of the energy E is shown and compared with $\lambda_{av} = 2.25E^{0.75}$ after (4.19). Between 200 and 2,000 eV, the deviation between both relations is less than 2%. Therefore, it is not surprising that the example of Fe–C in Table 4.3 gives nearly identical results. For $E < 200$ eV, neither (4.79) nor (4.19) is fulfilled, and the more complicated energy dependencies for λ_{in} and Q for at least an approximate matrix composition have to be determined.

Note that the ratio of the “weak” relative matrix correction factors, $P_{A,m}/P_{B,m}$, in (4.78) is about unity for $E(A)$, $E(B)$ above 200 eV, when (4.17) is valid. Comparison of (4.72) and (4.73) with (4.78) and (4.79) shows that the major variable, the atomic density, N_i , in the “general” matrix correction factor is now left in the average matrix correction factor, $F_{i,av}$, and the “weak” matrix factor

$P_{i,m}$ depends only weakly on Z and is close to unity for most elements if the average matrix is chosen properly. As shown by Seah and Gilmore, the normalized weak matrix factors, $P_{i,m}/P_m$, with P_m the average over all species i in matrix m are confined within a rather narrow distribution around unity [4.10, 4.89]. Despite the fact of the normalized weak matrix factors being practically unity, the average matrix correction factors $F_{i,av}$ which are necessary to solve (4.76) show a much larger variation [4.10, 4.89].

In conclusion, average matrix relative sensitivity factors (AM-RSFs) can be used instead of the formerly defined general matrix relative sensitivity factors (M-RSFs) which can be easily taken from existing parameters in databases [4.37, 4.84]. Values of $I_{i,av}$ for XPS and AES are given in Ref. [4.92]. Here, like in any matrix relative sensitivity factor system, the matrix reference cancels in the usual quantification equations. Therefore, the traditional references (e.g., C 1s for XPS, Ag NVV for AES) can still be used, with obviously no loss in accuracy or convenience. Indeed, the results of both approaches are practically identical (see Table 4.3). However, when considering theoretical and experimentally determined I_{av}^0 values as pointed out by Seah and Gilmore [4.27] and by Powell and Jablonski [4.93], a spectroscopic correction term has to be introduced which takes into account such phenomena as intrinsic plasmon and shake-up intensities (see Sect. 3.1.6).

4. Synopsis and Resume (Improved Hall–Morabito–Payling Approach): A “Matrix-less” Binary (Matrix) Correction Factor

The original approach by Payling [4.87], based on the Seah and Dench relation for the attenuation length (4.10), concludes with (4.67) by setting $\lambda_{A,E(A)} N_A^0$ in (4.55a) proportional to $N^{-1/2}$. Hall and Morabito [4.85] originally leave the general expression $\lambda_{A,E(A)} N_A^0$ but derive their (4.60a) and (4.60b) for low concentration alloys. However, these authors already supposed that the Holloway [4.86] extension of a linear matrix composition dependence is negligible (see Fig. 4.18). Because in the matrix the density N and the average atomic number Z are the same, it is clear that they cancel in the ratio and only the energy dependence remains (see, e.g., CS2 equation, (4.17)). Assuming that the matrix influence for emitted electrons is similar at energies $E(A)$ and $E(B)$, we may write for the matrix-dependent term in (4.59), $\lambda_{m,A}/\lambda_{m,B} = (E(A)/E(B))^{0.75}$ (see (4.19)),⁵ and get another approximation for (4.59) which is expected to be practically independent of composition and contains no other matrix-related terms (“matrix-less”):

$$\begin{aligned} F_{A,B}^m &= \frac{F_{A,m}}{F_{B,m}} = \frac{N_A^0 \lambda_{A,E(A)}}{N_B^0 \lambda_{B,E(B)}} \left(\frac{E(B)}{E(A)} \right)^{0.75} \\ &= \frac{(\rho_A/M_A) \lambda_{in,A,E(A)} Q_{A,E(A)}}{(\rho_B/M_B) \lambda_{in,B,E(B)} Q_{B,E(B)}} \left(\frac{E(B)}{E(A)} \right)^{0.75} = \frac{1}{F_{B,A}^m}. \end{aligned} \quad (4.80)$$

⁵The exponent 0.75 applies only for $E > 200$ eV, and for elements and inorganic compounds. For organic compounds, the exponent is 0.79 [4.39].

In fact, (4.80) is similar to the Hall–Morabito relation (4.60a) when $\lambda_{B,E(A)}$ is replaced by $\lambda_{B,E(B)}(E(A)/E(B))^{0.75}$. The advantage of (4.80) is that, in accordance with the above discussed proposal by Payling [4.87], for every element, a relative matrix correction factor can be precalculated with respect to an arbitrary reference instead of element B, for example, carbon (C 1s), which gives

$$\frac{F_{A,m}}{F_{C,m}} = \frac{N_A^0 \lambda_{A,E(A)}}{N_C^0 \lambda_{C,E(C)}} \left(\frac{E(C)}{E(A)} \right)^{0.75} = F_{A,C}^m. \quad (4.81)$$

With similar definition for B, the ratio $F_{A,C,m}/F_{B,C,m} = F_{A,B}^m$ is the binary relative matrix correction factor given by (4.80), which is practically independent of the actual matrix composition. Indeed, the variation of the ratio $\lambda_{C,E(C)}/\lambda_{A,E(A)}$ is found below 6% when $E(C)/E(A)$ varies by a factor of two and the atomic number Z is between 10 and 90, according to the CS2 relation (cf. (4.17)).

According to (4.53a), an improved binary matrix relative sensitivity factor $S_{A,B}^m$ (BM-RSF) is defined by

$$S_{A,B}^m = \frac{S_{A,B}}{F_{A,B}^m}. \quad (4.82)$$

4.3.2.4 Numerical Example of XPS Quantification: Fe–Cr and Fe–C

Equations 4.80 and 4.81 establish a system of new relative (elemental) matrix sensitivity factors related, for example, to carbon C 1s, because all terms in these equations are known (see Table 4.2). For example, with the values for C and Al K α source (see Table 4.2) and with $E(C)$ in eV, λ in nm and $N_i^0/N_{Av0} = (\rho_i/M_i)$ in (mol cm⁻³), we get for Fe

$$\begin{aligned} S_{Fe,m} &= \frac{S_{Fe,C}}{F_{Fe,m}} = S_{Fe} \frac{[E(Fe)]^{0.75}}{N_{Fe}^0 \lambda_{Fe,E(Fe)}} \frac{N_C^0 \lambda_{C,E(C)}}{[E(C)]^{0.75}} \\ &= S_{Fe} \frac{(\rho_C/M_C) \lambda_{C,E(C)}}{(\rho_{Fe}/M_{Fe}) \lambda_{Fe,E(Fe)}} \left(\frac{E(Fe)}{E(C)} \right)^{0.75} = 8 \frac{0.1883 \times 2.47}{0.1411 \times 1.11} \left(\frac{780}{1202} \right)^{0.75} \\ &= 8 \times 2.15 = 17.2 \end{aligned}$$

with the relative elemental sensitivity factors $S_{Fe,C} = 8$ taken from Wagner et al. [4.74]. For the attenuation lengths, CS2 values calculated after (4.17) were used here. Using the value recommended in the NIST EAL database [4.37] for quantification by replacing $\lambda_{C,E(C)}$ (CS2) by $\lambda_{in} Q$ (see Table 4.2), a slightly different value of $S_{Fe,m} = 18.3$ is obtained. This result means that the Fe 2p peak is more than two times as sensitive in a carbon matrix ($S_{Fe,m} = 18.3$ (17.2)) than it is in pure iron ($S_{Fe} = 8.0$). The corresponding value for Cr is $S_{Cr,m} = 12.3$ (12.6) (see Table 4.2). Because in a two-component Fe–Cr matrix, according to (4.63a), the term for C in

$S_{\text{Fe,C}}$ and $S_{\text{Cr,C}}$ cancels, the ratio is equal to $18.3/12.3 = 1.49$ (with CS2 values: $17.2/12.6 = 1.37$). The latter values are valid for $S_{\text{Fe,Cr},m}$ in a binary Fe–Cr system.

The approximate, composition-independent matrix correction factors given above suggest an “average” matrix as a reference that has density and attenuation length values similar to most of the other elements, such as Cr or Fe (see Table 4.2). As proposed by Seah and Gilmore [4.10, 4.89, 4.92] such a fictitious “average matrix” minimizes deviations from an average correction parameter, and together with a “weak matrix correction” term, the attenuation length ratio for the unknown matrix m in (4.59) is replaced by that of the known average matrix. However, as shown above, a completely matrix-less quantification equation is obtained when replacing both expressions by the simple expression $[E(\text{B})/E(\text{A})]^{0.75}$ (see (4.80)). Because in the Palmberg quantification formula ((4.57) and (4.58a)) only the relative matrix correction factors $F_{\text{A,B}}^m$ (4.59) or matrix relative sensitivity factors ($S_{\text{A,B}}^m$) are used, the reference values cancel, and there is no need for any matrix, even for an “average matrix” (see comparison in Table 4.2). To emphasize this fact, we may write $F_{\text{A,B}}^m = F_{\text{A,B}}^{\text{rel}}$ and $S_{\text{A,B}}^m = S_{\text{A,B}}^{\text{rel}}$ (see Sect. 4.4.2.3 (4)). The uncertainty are expected to be minimal when the most abundant element is taken as a reference for M-RSFs.

As an example, the results for two binary systems, Fe–Cr and Fe–C, for low and high concentration using different matrix correction approaches are compared in Table 4.3. It is assumed that by applying elemental relative sensitivity factors to the measured intensities, 10 at% and 50 at% Cr or C in Fe were obtained, while the correct concentrations are obtained by matrix-corrected M-RSFs.

With the exception of the original, simplified approach by Payling (that is relatively “mild”), the other three matrix correction schemes agree until the third digit, i.e., with less than 1% mutual deviation. As expected, deviations of the correct M-RSF values from E-RSF values are small (less than 2%) for Cr in Fe because of their similar densities and atomic numbers. In contrast, a much higher deviation occurs for C in Fe (90% or 9at% for 19at%, and 36% or 18at% for 68at% matrix-corrected mole fraction, respectively). The improved Hall–Morabito–Payling matrix correction proposed here has the advantage that, with the elemental data given in Table 4.2, for every element, the matrix relative sensitivity factor (M-RSF), $S_{i,m}$, can be calculated and used in the basic expression (4.57) and (4.58a), in place of the relative elemental sensitivity factor, S_i . For a binary system, the relation between the mole fraction given by the latter, $X_{\text{A,el}}$ (E-RSF) and the true, matrix-corrected mole fraction, X_{A} (M-RSF), is given by

$$X_{\text{A}} = \frac{I_{\text{A},m}/S_{\text{A}}}{\frac{I_{\text{A},m}}{S_{\text{A}}} + \frac{I_{\text{B},m}F_{\text{B},m}}{S_{\text{B}}F_{\text{A},m}}} = \frac{X_{\text{A,el}}}{X_{\text{A,el}} + \frac{1 - X_{\text{A,el}}}{F_{\text{A,B}}^m}}. \quad (4.83)$$

As an example, a plot of (4.83) for Fe–C is shown in Fig. 4.20.

Using instead of λ (CS2) (or λ (EAL)) the more exact product $Q\lambda_{\text{in}}$ (cf. (4.20)), the accuracy of $S_{\text{A,B}}^m$ will be increased. With the respective values for Fe–C in Table 4.3, we obtain $S_{\text{C,Fe}}^m = 18.3$. Because Q varies only slightly at higher

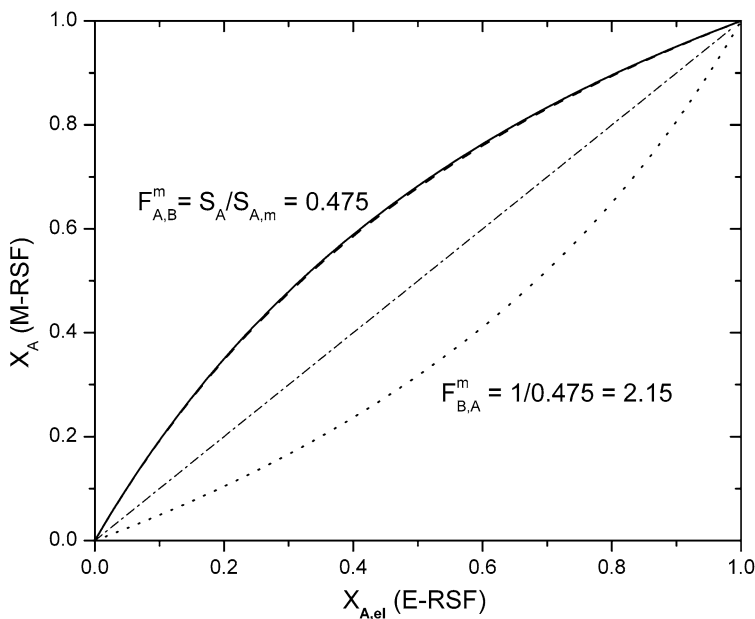


Fig. 4.20 The matrix-corrected mole fraction of A, X_A , using matrix relative sensitivity factors (M-RSFs), as a function of the mole fraction $X_{A,el}$ obtained by using elemental relative sensitivity factors (E-RSFs), for a relative matrix correction factor $F_{A,B}^m = 0.475$ after (4.83) (solid line). This value corresponds to the system Fe–C if A = C, B = Fe. The dashed line corresponds to the composition-dependent matrix correction factor after Holloway [4.86], (4.66). When X_A is replaced by X_B , the dotted line for $F_{B,A}^m = 1/0.475 = 2.15$ gives the relation between X_{Fe} (M-RSF) and $X_{Fe,el}$ (E-RSF)

energies (see Fig. 4.11) [4.93], even the ratio of the IMFP values at higher energies may be a reasonable approximation, giving $S_{C,Fe}^m = 16.3$ here. In view of the theoretical as well as experimental uncertainties, deviations of less than 10% for a correction factor appear to be tolerable.

4.3.2.5 Multielement System

The binary system approach, used above for its simplicity, can easily be extended to a multielement system (for example, by (4.5) and (4.6)), when the elemental relative sensitivity factors (E-RSFs) $S_1, S_2, \dots$ are replaced by the matrix relative sensitivity factors (M-RSFs), $S_{1,m}, S_{2,m}, \dots$, given in Table 4.3 for a few elements. The latter are obtained by dividing the E-RSFs [4.23, 4.74] with the M-RSFs, and they can be used like the E-RSFs in the original Palmberg relation (4.5). As an example, let us briefly refer to a ternary system of Fe, Cr, and C with the $S_{i,m}/S_{C,m}$ in Table 4.2. If the intensities are proportional to these factors, we will expect about the same mole fraction of each element. Choosing, for example, $I_C = 1$, $I_{Fe} = 17.2$, and $I_{Cr} = 12.6$ (usually peak areas in XPS), we get with (4.6) for

Table 4.3 Comparison of the expected XPS results for Fe–Cr and Fe–C, for normalized elemental intensities $I_A/S_A = X_A$ with S_A the E-RSF value [4.74], giving mole fractions of X_{Cr} or $X_C = 0.1$ and 0.5 without matrix correction, with results of (4.83) using different matrix correction factors (see text) with corresponding values from Table 4.2 (with AL from CS2 except last row where $Q\lambda_{in}$ values were used)

System	Fe (ca. 10 at% Cr) X_{Cr}	Fe (ca. 50 at% Cr) X_{Cr}	Fe (ca. 10 at% C) X_C	Fe (ca. 50 at% C) X_C
Elemental Relative Sensitivity Factor (E-RSF)	0.100	0.500	0.100	0.500
Paying correction	0.105	0.513	0.129	0.571
Dilute approximation (Hall–Morabito)	0.101	0.504	0.190	0.678
Average matrix correction (S–G)	0.100	0.502	0.204	0.698
Improved (Syn) (CS2)	0.103	0.508	0.193	0.682
Improved (Syn) ($\lambda_{in}Q$)	0.102	0.505	0.205	0.700

the denominator $(1/1 + 17.2/17.2 + 12.6/12.6) = 3$, and $X_C = X_{Fe} = X_{Cr} = 0.33$. If we had used the E-RSF approach with S_i/S_C , the result for the same intensities would have been for the denominator $(1/1 + 17.2/8 + 12.6/6) = 5.25$, resulting in $X_C = 0.19$, $X_{Fe} = 0.41$, and $X_{Cr} = 0.40$.

In principle, the matrix correction could be improved by using the ratio of the λ_C/λ_m values for the average atomic number of the matrix (18.67 in our example). However, according to the CS2 relation, the deviation is less than 0.1% for the matrix sensitivity factor of Fe, and therefore, it is fully negligible.

In conclusion, knowledge of E-RSFs (S_A) and (binary) matrix correction factors ($F^m_{A,B}$) yields matrix (binary) relative sensitivity factors (M-RSFs) ($S^m_{A,B}$) which can be directly used instead of E-RSFs for matrix-corrected quantification (see (4.54) and (4.55a)). Use of Handbook values for E-RSFs is expected to give only semiquantitative results because of unknown spectrometer function (intensity–energy response function, IERF) [4.1]. Measurement of elemental standard samples eliminates this problem and can be used to determine the IERF. Then, the M-RSFs can be directly derived from Scofield cross sections and appropriate density and attenuation length values. Indeed, the trend at present is to move away from matrix correction factors and instead use sensitivity factors that are adequate for the respective matrix and directly derived from its characteristic physical parameters. For example, these data are required when using quantification software such as SESSA [4.94].

All of the above equations for matrix correction factors, (4.44)–(4.83), are for instruments with an angle between the X-ray beam and analyzer equal to $\psi = 57.4^\circ$ or close to this value, i.e., for $W(\beta_{eff}, \psi)_A = 1$ (see (4.35)). For any other angle ψ , after looking up the parameter β for the respective subshell [4.75], β_{eff} is obtained

with (4.36) or (4.37), and its emission angle dependence is given by (4.38a,b). With β_{eff} , the asymmetry factor, $W(\beta_{\text{eff}}(\theta), (\psi))$, has to be calculated with (4.35) and inserted in (4.37) for quantification. When changing the emission angle θ by tilting the sample, ψ stays constant, and only β_{eff} changes slightly with θ (see (4.38a, b) and Fig. 4.16). When the emission angle is varied with a fixed sample position (as in the DP-CMA) or with the Thetaprobe instrument (see Chap. 2 and below), the change of ψ with θ has to be taken into account additionally. This fact is shown in the following example.

4.3.2.6 XPS Quantification Including Variation of the Angle Between Excitation and Emission (e.g., Thetaprobe)

A special case of quantification is encountered when detecting photoelectrons over a wide range of the emission angle without tilting the sample. The “Thetaprobe” instrument manufactured by Thermo VG (see Chap. 2) has the capability of parallel data acquisition mode for emission angles between 23 and 80°, divided in up to 96 channels. This enables recording of angle-resolved XPS (AR-XPS) data in parallel in contrast to a conventional AR-XPS setup which requires step-by-step tilting the sample and sequential data acquisition for the same purpose. However, with the Thetaprobe, the excitation-to-emission angle is varied, and therefore, quantitative consideration of the asymmetry factor variation is necessary (see Fig. 4.12). Because the elemental relative sensitivity factors are defined for $\theta = 0^\circ$, $\psi = 57.4^\circ$ (see (4.44)), the matrix relative sensitivity factors have to be modified by the asymmetry factor $W(\beta_{\text{eff}}, \psi)$ [4.1]. (Wagner et al. [4.74] discussed this fact but found no remarkable influence of ψ in their experimental data.)

To include the asymmetry term in the matrix quantification scheme, we extend (4.51) by the asymmetry terms, $W(\beta_{\text{eff}}, \psi)_{A,m}$, for element A in elemental standard and in matrix m , respectively, and get, according to (4.41),

$$\frac{I_{A,m}}{I_A^0} = \frac{\lambda_{m,E(A)} N_m^0}{\lambda_{A,E(A)} N_A^0} \frac{W(\beta_{\text{eff}}, \psi)_{A,m}}{W(\beta_{\text{eff}}, \psi)_A} X_A = \frac{S_{A,m} W(\beta_{\text{eff}}, \psi)_{A,m}}{S_A} X_A, \quad (4.84a)$$

since for standard intensities and E-RSFs $I_A^0 = S_A$, and $W(\beta_{\text{eff}}, \psi = 54.7^\circ)_A = 1$. For a binary system with components A,B, according to (4.51)–(4.59), we get from (4.84a), for the intensity ratio⁶ measured for matrix m ,

⁶In principle, the dependence of the elastic scattering correction factor Q on the emission angle has to be considered in the attenuation length $\lambda = \lambda_{\text{in}} Q(\theta, \omega)$ (4.20). Because after (4.24) the dependence of Q on θ is proportional to $Q(0, \omega)$, the angular dependence cancels in (4.84a)–(4.84c). The slight effect of the angular dependence of ω is again similar for both elements [4.68] and practically cancels in the ratio. With the matrix correction factor $F_{A,B}^m(\psi)$ inserted in (4.57), (4.58a), and (4.58b), quantification to obtain X_A , X_B can be accomplished for $\psi \neq 54.7^\circ$ with (4.50), (4.52), and (4.54).

Table 4.4 Values of the parameters used in calculating $W(\beta_{\text{eff}}, \theta)_{\text{O } 1s} / W(\beta_{\text{eff}}, \theta)_{\text{Al } 2p}$ of O 1s and Al 2p for quantitative analysis with the Thetaprobe instrument

	E(eV)	λ_{in} (nm) [4.38]	λ_{tr} (nm) [4.37]	ω [4.37]	$H(\cos \theta, \omega)$ ($\theta = 40^\circ$)	$Q_s(0)$ [4.21]	β [4.40]	β_{eff} (SG) [4.38]	β_{eff} (JP) [4.39]
O 1s	954	2.42	18.0	0.153	1.07	0.969	2.0	1.477	1.674
Al 2p	1416	3.26	9.78	0.198	1.05	0.978	0.93	0.77	0.81

For details, see text

$$\frac{I_{A,m}}{I_{B,m}} = \frac{S_{A,B} W(\beta_{\text{eff}}, \psi)_{A,m}}{F_{A,B}^m W(\beta_{\text{eff}}, \psi)_{B,m}} \frac{X_A}{X_B} = S_{A,B}^m \frac{W(\beta_{\text{eff}}, \psi)_{A,m}}{W(\beta_{\text{eff}}, \psi)_{B,m}} \frac{X_A}{X_B}. \quad (4.84b)$$

Because $S_{A,B}/F_{A,B,m} = S_{A,B}^m = \text{const.}$ (all defined for $\psi = 54.7^\circ$), we expect the measured intensity ratio $I_{A,m}/I_{B,m}$ to vary with the ratio $W_{A,m}/W_{B,m}$. For the example of Al_2O_3 , $X_A/X_B = 3/2$. With A = O, B = Al, and the measured intensity of the O 1s and Al 2p peaks, $I_{\text{O } 1s}/I_{\text{Al } 2p}$, we get

$$\frac{2}{3} \frac{I_{\text{O } 1s}}{I_{\text{Al } 2p}} = S_{\text{O } 1s, \text{Al } 2p}^m \frac{W(\beta_{\text{eff}}, \psi)_{\text{O } 1s,m}}{W(\beta_{\text{eff}}, \psi)_{\text{Al } 2p,m}}. \quad (4.84c)$$

The asymmetry factors $W_{\text{O } 1s,m}$ and $W_{\text{Al } 2p,m}$ can be calculated with (4.35) as follows. For the asymmetry term β_{eff} after (4.36) or (4.37), we first take $\beta(\text{O } 1s)$ and $\beta(\text{Al } 2p)$ from Ref. [4.75], then calculate the single scattering albedo ω with (4.23) by taking the IMFP, λ_{in} , and the transport mean free path λ_{tr} for O 1s and Al 2p from Ref. [4.37]. Using the Jablonski [4.59] approximation of the Chandrasekhar function (4.22), $(H(\cos \theta, \omega) = (1 + 1.9078 \cos \theta) / [1 + 1.9078(1 - 0.135)^{1/2} \cos \theta])$, we get an average value for an average emission angle ($\theta = 40^\circ$). With these values, compiled in Table 4.4, $W(\theta)$ can be calculated if $\psi(\theta)$ is known. There are two equations to predict β_{eff} from β , one given by Seah and Gilmore (SG) [4.64], (4.36), and another one given by Jablonski and Powell (JP) [4.33], (4.37). Both give slightly different values for β_{eff} , as shown in Table 4.4. The angular dependence according to these authors is also different, given by (4.38a) (SG) and (4.38b) (JP), as visualized in Fig. 4.21.

The asymmetry factor $W(\beta_{\text{eff}}, \psi)$, given by (4.35), depends on the angle ψ between photon beam and analyzer direction, as shown in Fig. 4.12. Changing the emission angle θ in the Thetaprobe means changing angle ψ with angles α and γ_0 fixed. The relation between θ and ψ after Fig. 4.11 is given by the trigonometric expression

$$\cos \psi = \sin \alpha \cos \gamma_0 \sin \theta + \cos \alpha \cos \theta. \quad (4.85)$$

⁷Note that (4.84b) is in accordance with (5.36), p. 226 of Ref. [4.2], and with (46), p. 362 and (61), p. 364 of Ref. [4.1], but at variance with (58), p. 363 of Ref. [4.1].

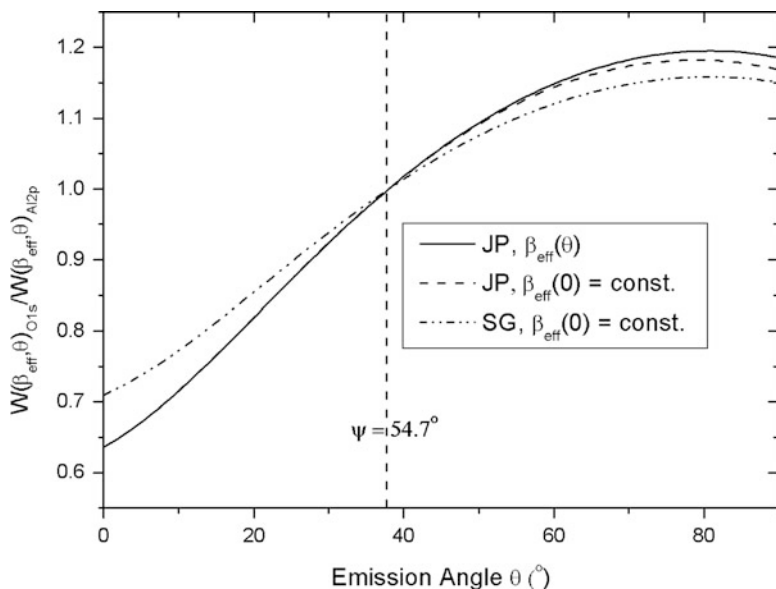


Fig. 4.21 Ratio of the asymmetry factors $W(\beta_{\text{eff}}, \theta)_{\text{O1s}} / W(\beta_{\text{eff}}, \theta)_{\text{Al2p}}$ of O 1s and Al 2p for the Thetaprobe geometry as a function of the emission angle θ , for two different approximations given by Jablonski and Powell (JP) [4.33], (4.37) and (4.38b), and by Seah and Gilmore (SG) [4.64], (4.36) and (4.38a). A better fit to experimental data by Vinodh and Jeurgens [4.69] is obtained with the JP approximation (*solid line*), even when the slight emission angle dependence of $\beta_{\text{eff}}(\theta)$ is ignored (see Fig. 4.22)

For the Thetaprobe instrument, $\alpha = \text{const.} = 30^\circ$ and $\gamma_0 = \text{const.} = 110^\circ$. Thus, $\cos \psi = 0.8660 \cos \theta - 0.1710 \sin \theta$ has to be inserted in (4.38). With the values compiled in Table 4.4, the calculated ratio $W(\beta_{\text{eff}}, \theta)_{\text{O1s}} / W(\beta_{\text{eff}}, \theta)_{\text{Al2p}}$ is presented in Fig. 4.21 for the approximations by Seah and Gilmore (SG), (4.36) and (4.38a), and by Jablonski and Powell (JP), (4.37) and (4.38b).

Fig. 4.22 shows excellent fit of the calculated ratio $W(\beta_{\text{eff}}, \theta)_{\text{O1s}} / W(\beta_{\text{eff}}, \theta)_{\text{Al2p}}$ (*solid line* in Fig. 4.21), multiplied with the factor 3.65, with experimentally determined intensity ratio $I(\text{O 1s}) / I(\text{Al 2p})$, divided by the atomic ratio 3/2 in Al_2O_3 , from Vinodh and Jeurgens [4.69] as a function of the emission angle θ . According to (4.84c), the fitting parameter 3.65 corresponds to the value of $2/3 \times I(\text{O 1s}) / I(\text{Al 2p})$ for $W(\beta_{\text{eff}}, \theta)_{\text{O1s}} / W(\beta_{\text{eff}}, \theta)_{\text{Al2p}} = 1$, i.e., $\psi = 54.7^\circ$ (equal to $\theta = 38.0^\circ$ after (4.85)), and is identical to the matrix relative sensitivity factor $S_{\text{O1s,Al2p,m}} = 3.65 \pm 0.01$ (rms deviation) for matrix Al_2O_3 .

A comparison with theoretical values can be done either with the basic equations (4.41) and (4.50a) when the spectrometer efficiency $G(E_i)$ is known. According to the manufacturer, for the respective kinetic energies (945 eV for O 1s and 1,416 eV for Al 2p) and 100 eV pass energy, the ratio is $G(E_{\text{O1s}}) / G(E_{\text{Al2p}}) = 1.016$ which gives $S_{\text{O1s,Al2p}}^m(\text{theor.}) = 3.99$, a deviation of +9% from the experimental value.

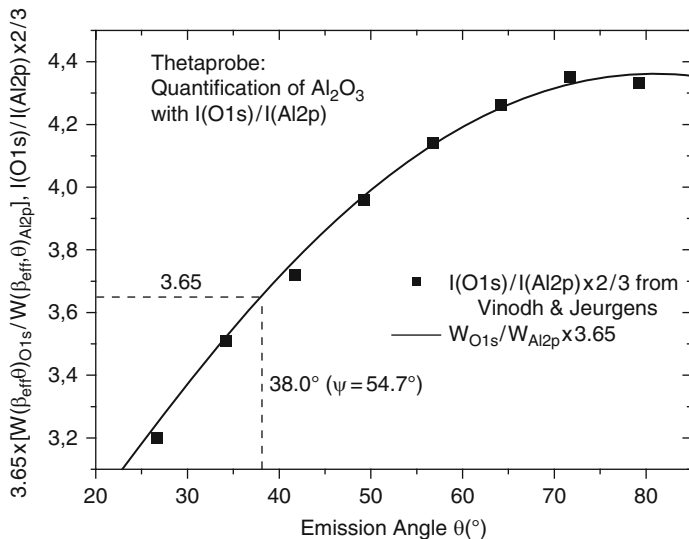


Fig. 4.22 Ratio of the asymmetry factors of O 1s and Al 2p, $W(\beta_{\text{eff}}, \theta)_{\text{O}1s}/W(\beta_{\text{eff}}, \theta)_{\text{Al}2p}$, as a function of the emission angle θ , after the JP approximation [4.33] (solid line in Fig. 4.21), fitted to the experimental intensity data of Vinodh and Jeurgens [4.69] in one point (intensity ratio = 3.65) for $\psi = 54.7^\circ$, corresponding to $\theta = 38.0^\circ$ and the asymmetry factor (ratio) = 1

Ignoring the spectrometer function, the semiempirical elemental relative sensitivity factors after Wagner et al. [4.74] may be used, which give $S_{\text{O,Al}} = 0.66/0.185 = 3.57$, leaving $F^m_{\text{O,Al}} = S_{\text{O,Al}}/S^m_{\text{O,Al}} = 0.98$ for the relative matrix correction factor. This result can be compared to the theoretical value of the latter, for example, by the improved composition-independent relative matrix correction factor given by (4.51). With the relative density values and the attenuation length and energy values from Table 4.4, $F^m_{\text{O,Al}} = 0.998$ is obtained, in good agreement with the experimental matrix correction factor which is fortuitously close to 1. Recently, a fit similar to Fig. 4.22 was shown by Tasneem et al. [4.95] as an application example of the SESSA software [4.94].

If the angular dependence of the asymmetry term, (4.35), is ignored, it is seen from the data in Fig. 4.22 that the empirical matrix relative sensitivity factor varies from 3.2 to 4.35 between $\theta = 27^\circ$ and 79° , that is from -12% to $+19\%$ of the correct value, with a respective deviation from the correct concentration ratio value.

Using the Thetaprobe instrument, measurements performed around emission angle $\theta = 38^\circ$ (e.g., $38^\circ \pm 10^\circ$ and taking the mean value) can be quantified irrespective of the asymmetry term. Angle-resolved measurements, for example, AR-XPS for layer thickness determination (see Sect. 4.3.3), can only be quantified if the asymmetry factor for each peak and matrix is determined and the intensity values are corrected for. At higher emission angles, the surface excitation parameter (SEP) should be additionally taken into account [4.31, 4.45] (see above). Fortunately, the overall effect is diminished if the peak ratio is used. Only when the parameter

β_{eff} for the peaks to be compared is practically the same, the angular dependence will cancel in the determination of matrix relative sensitivity factor correction.

4.3.3 Quantitative XPS Analysis of Thin Surface Layers

4.3.3.1 Generalized Layer-by-Layer Quantification

In general, the solution of (4.39) requires knowledge of the in-depth distribution of composition within the information depth (i.e., about 3 to 4 times the electron escape depth ($\lambda \cos \theta$) (see Sect. 4.2.2.6 and fig. 4.17)), which can principally be obtained by depth profiling (Chap. 7). For the special case of thin surface layers, it is useful to transform the integral in (4.39) into a sum of thin layers (≥ 1 atomic monolayer). Simplifying (4.39) by assuming $\psi = 54.7^\circ$ ($W_A = 1$) and normalizing to $I_{A,m}^0 = (\Delta\Omega/4\pi)I_{\text{hv}}(\alpha)\sigma N_m^0\lambda_{A,E(A),m}\cos\theta$, the intensity contribution of a thin layer in matrix m with constant mole fraction of A, X_A , between depth z_2 and z_1 , $I_{A,m}(z_2 - z_1)$, follows from the solution of the integral in (4.39) as:

$$I_{A,m}(z_2 - z_1) = I_{A,m}^0 X_A (z_2 - z_1) \left\{ \exp\left[-\frac{z_1}{\lambda_{A,E(A),m}\cos\theta}\right] - \exp\left[-\frac{z_2}{\lambda_{A,E(A),m}\cos\theta}\right] \right\}. \quad (4.86)$$

Note that the matrix-related values, $\lambda_{A,E(A),m}$, and $I_{A,m}^0$ have to be used in (4.86), with $I_{A,m}^0 = I_A^0/F_{A,m}$ (4.53). For simplicity, we ignore the matrix correction factor $F_{A,m}$ in the following.

Any in-depth distribution can be considered as a stack of several layers. The totally measured intensity, I_A , normalized to the pure (bulk) intensity of A, I_A^0 , is the sum of the intensity contributions of n layers. With the optimum resolution of one monolayer with thickness $d_{\text{ML}} = z_2 - z_1 = 1 \text{ ML}$ (monolayer) and n of the order of 10–20 ML (the information depth defined by 5λ), we obtain

$$\frac{I_A}{I_A^0} = \sum_{j=1}^n X_{A,j} \left\{ \exp\left[-\frac{(j-1)d_{\text{ML}}}{\lambda_{A,E(A)}\cos\theta}\right] - \exp\left[-\frac{j d_{\text{ML}}}{\lambda_{A,E(A)}\cos\theta}\right] \right\} \quad (4.87)$$

with j being the number of layers from the surface. (Note that I_A^0 and therefore I_A are only valid for a fixed angle θ , see also Chap. 7.) The most simple case is a homogeneous surface layer with constant composition X_A , as for $z_1 = 0$ and $z_2 = \text{total layer thickness } d$ in (4.86). The solution of (4.87) for a stack of n monolayers with $X_A = 1$ results in

$$\frac{I_A}{I_A^0} = 1 - \exp\left[-\frac{n d_{\text{ML}}}{\lambda_{A,E(A)}\cos\theta}\right] = 1 - (\alpha_A^A)^n \quad (4.87a)$$

with

$$\alpha_A^A = \exp \left[-\frac{d_{ML}}{\lambda_{A,E(A)} \cos \theta} \right]. \quad (4.87b)$$

Equation 4.87a was first derived by Gallon [4.96] with the transmission coefficient α_A^A for one monolayer of component A, as expressed by (4.87b) in present notation.

Let us consider the most common cases of thin surface layers: single-element layers, multielement surface layers, segregation layers, evaporation layers (layer growth), and the influence of a contamination layer. The general case for a binary system is schematically shown in Fig. 4.23. Here, we only consider atomically flat surfaces. The influence of roughness is discussed in Chap. 5.

4.3.3.2 Single Component Surface Layer (Layer on Substrate with Full Coverage): Oxide Layer

The strong dependence of the XPS or AES intensity on the depth distribution of the detected species on an atomic scale can be used for the determination of the thickness of a thin overlayer (<5 nm) of one element on another or, in general, of two different components. Typical examples are an evaporated layer of element A on a substrate B, or an oxide layer on a metal substrate. Because the electron binding energy depends on the valence of the respective atom [4.97], the same element in general shows two separate peaks at slightly different energies, one for the metallic and one (or more) for the oxide state (see, e.g., Fig. 3.8), and both states can be treated like different elements. Let us first consider XPS (equivalent to AES with similar backscattering factors of A and B) on a smooth, closed thin layer of element A with thickness d on bulk element substrate B as schematically depicted in Fig. 4.23. Then the solution of the integral over depth z from 0 to d in (4.32), which is equivalent to setting $X_A = X_A^s = 1$, $z_1 = 0$, and $z_2 = d$ in (4.86), gives for the intensity of A, I_A :

$$I_A = I_A^0 \left\{ 1 - \exp \left[-\frac{d}{\lambda_{A,E(A)} \cos \theta} \right] \right\}, \quad (4.88a)$$

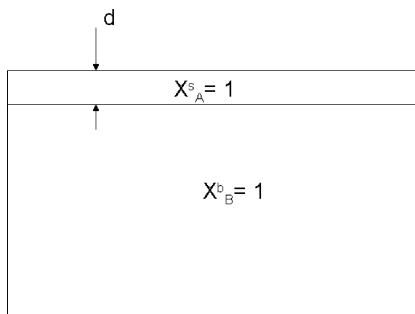


Fig. 4.23 Schematic view of the most simple case of a closed surface layer of component A with layer thickness d on a substrate of component B

where I_A^0 is the intensity of the bulk elemental standard and $\lambda_{A,E(A)}$ is the attenuation length of the signal of A (at kinetic energy E_A) in matrix A. Note that I_A^0 is only valid for a fixed angle θ (usually for $\theta = 0^\circ$, but the θ dependence of I_B^0 (below) is similar). The signal strength I_B of the signal of B (with $X_B = X_B^b = 1$) is attenuated by the overlayer of A with thickness d , and the solution of (4.86) for this case is

$$I_B = I_B^0 \left\{ \exp \left[-\frac{d}{\lambda_{A,E(B)} \cos \theta} \right] \right\}, \quad (4.88b)$$

where I_B^0 is the intensity of the bulk elemental standard and $\lambda_{A,E(A)}$ is the attenuation length of the signal of B at kinetic energy $E(B)$ in matrix A. (Note that measurement of I_B before and I_B^0 after sputter removal of a contamination or oxide layer immediately gives a good estimation of the thickness of that layer in terms of $d/(\lambda_{B,A} \cos \theta)$ after (4.88b).)

Knowledge of the (absolute) standard intensities I_A^0 or I_B^0 for a fixed angle θ enables determination of the relative layer thickness $d/\lambda_{A,E(A)}$ or $d/\lambda_{A,E(B)}$ from (4.88a) or (4.88b). For example, evaporation of an element A on a clean surface of B (where I_B^0 is measured) and knowing the thickness d , for example, from accompanying quartz microbalance measurements, is a means to determine $\lambda_{A,E(B)}$ [4.98, 4.99].

Taking the ratio of both (4.88a) and (4.88b) has the advantage that instrumental parameters such as the angular dependence of the bulk intensity (see (4.41)) cancel, and the ratio of the two intensities, I_A/I_B , normalized by the relative elemental sensitivity factor defined above ($S_A/S_B = I_A^0/I_B^0$) is given by

$$\frac{I_A I_B^0}{I_B I_A^0} = \frac{1 - \exp \left[-\frac{d}{\lambda_{A,E(A)} \cos \theta} \right]}{\exp \left[-\frac{d}{\lambda_{A,E(B)} \cos \theta} \right]}. \quad (4.89)$$

Equation 4.89 allows the determination of the layer thickness d by knowledge of $\lambda_{A,E(A)}$, $\lambda_{A,E(B)}$ (see Sect. 4.2.2) and the measured and normalized intensities of layer A and substrate B for any given emission angle θ .

It is important to keep in mind that for a nonelemental surface layer, for example, an oxide layer, the attenuation lengths, $\lambda_{A,E(A)}$ and $\lambda_{A,E(B)}$, for element A have to be replaced by $\lambda_{s,E(A)}$ and $\lambda_{s,E(B)}$, valid for the surface matrix composition s . While $I_B^0 = S_B$, the elemental RSF of A, $I_A^0 = S_A$, has to be replaced by the matrix RSF, $S_{A,s} = I_{A,s}^0$.

For the special case of a compound layer (e.g., oxide, nitride, carbide) of A on pure substrate of the same metal, both respective photo- and Auger electrons are separated by a small chemical shift as compared to the kinetic energy, i.e., $E(A) \approx E(B)$, $\lambda_{A,E(B)} = \lambda_{A,E(A)}$, and element A is replaced by A_s in matrix s , B is replaced by A_{met} . Then, (4.89) gives

$$\frac{I_{A,s} I_{A,\text{met}}^0}{I_{A,\text{met}} I_{A,s}^0} = \exp \left[\frac{d}{\lambda_{s,E(A)} \cos \theta} \right] - 1, \quad (4.90a)$$

and the explicit result for the relative oxide layer thickness ($s \rightarrow \text{ox}$), $d_{\text{ox}}/\lambda_{\text{ox},E(A)}$ is [4.1, 4.2]

$$\frac{d_{\text{ox}}}{\lambda_{\text{ox},E(A)}} = \cos \theta \ln \left[\frac{I_{A,\text{ox}} I_{A,\text{met}}^0}{I_{A,\text{met}} I_{A,\text{ox}}^0} + 1 \right]. \quad (4.90b)$$

The case of (4.90b) applies, for example, if an oxide layer thickness of element A on metallic A is determined by measurement of the intensity $I_{A,\text{met}}$ of the metallic A, and that of the slightly shifted peak of A in the oxide bond (equivalent to $I_{A,\text{ox}}$ in (4.90b)), as for Ta₂O₅ on Ta [4.100], Al₂O₃ on Al [4.68], or SiO₂ on Si [4.101]. Whereas determination of the relative surface layer thickness, $d_{\text{ox}}/\lambda_{\text{ox},E(A)}$, is straightforward, an appropriate value of $\lambda_{\text{ox},E(A)}$ for the oxide layer has to be known (e.g., from databases [4.37]) to obtain the true oxide layer thickness d_{ox} . Equation 4.90b is valid for an experimentally determined standard intensity for a stoichiometric oxide. If a theoretical oxide sensitivity factor, $(I_{A,\text{ox}}^0)_{\text{theor}}$, is taken for the total atom concentration N_{ox}^0 in the oxide, the latter has to be multiplied by the mole fraction of the metal in the oxide, $X_{\text{met,ox}}$, and $I_{A,\text{ox}}^0 = X_{\text{met,ox}} (I_{A,\text{ox}}^0)_{\text{theor}}$.

An equation similar to (4.90b) can be used to describe oxygen depletion of metal oxides under argon ion bombardment and to obtain the altered layer thickness [4.102] (see (4.106), (7.67b) and Fig. 7.30). Alternatively, if the oxygen and the unresolved bulk and layer peak of the metal are used for layer characterization, the equivalent case of a segregation layer applies here, as shown below.

Because (4.90a) and (4.90b) contain the emission angle θ , variation of this angle, for example, by tilting the sample, offers a means to increase the precision of determination of the relative thickness, $d/\lambda_{A,E(A)}$. Angle-resolved XPS (AR-XPS) provides information about the in-depth distribution of composition and is generally used to check the validity of an assumed layer structure (see Sect. 7.2.1).

4.3.3.3 A Special Case: Al₂O₃ on Al and Determination of the Intrinsic Plasmon Contribution

For constant emission angle, the increase of the oxide layer thickness increases the oxide peak intensity after (4.88a) in the same way as it decreases the bulk metal peak intensity after (4.88b), because $\lambda_{A,E(B)} = \lambda_{A,E(A)}$. Eliminating the exponential expression from both equations shows that these intensities are linearly related by

$$\frac{I_A}{I_A^0} = 1 - \frac{I_B}{I_B^0}. \quad (4.91)$$

Equation 4.91 is represented by the solid line in Fig. 4.24 and is correct for measured standard intensities, for example, for a clean metal surface (I_B^0) and a thick

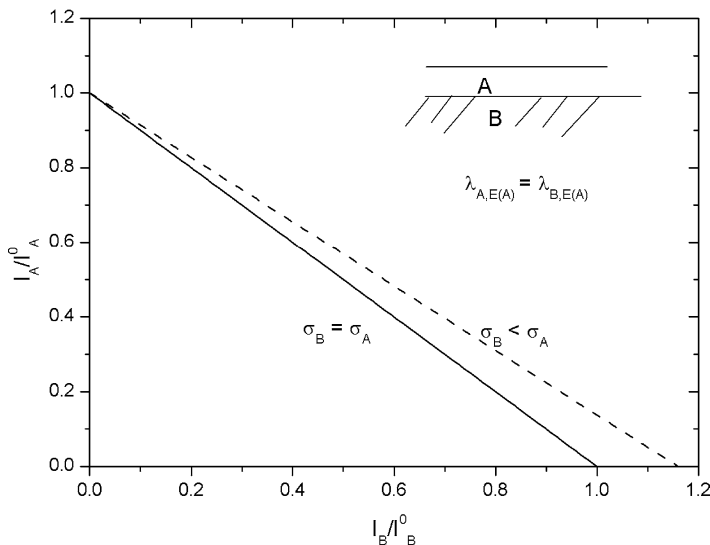


Fig. 4.24 Relation between normalized signal intensity of overlayer (A) and substrate (B) (I_A/I_A^0 , I_B/I_B^0), for $\lambda_{A,E(B)} = \lambda_{A,E(A)}$ and constant emission angle according to (4.91), (4.92), and (4.93). All points on the line are for a thickness of A (e.g., oxide layer thickness) between infinity ($I_A/I_A^0 = 1$) and zero ($I_B/I_B^0 = 1$). If intrinsic plasmon losses are negligible, the photoionization cross sections are equal ($\sigma_B = \sigma_A$, *solid line*), and (4.91) applies. If substrate B shows intrinsic plasmon losses whereas layer A does not ($\sigma_B < \sigma_A$, see (4.96a)), I_B^0 is diminished (4.91), and the *dashed line* is obtained which indicates an apparently higher overlayer thickness

oxide layer ($d > 5\lambda_{A,E(A)} \cos \theta$), (I_A^0). If, however, theoretical standard intensities are used, for example, taken from (4.44), different photoionization cross sections (σ_A, σ_B) of the same element in metal (B) and oxide (A) can be disclosed with (4.91) when measuring I_A and I_B for different oxide layer thickness. According to (4.44), the ratio I_A^0/I_B^0 is given by

$$\frac{I_A^0}{I_B^0} = \frac{\sigma_A N_A^0 \lambda_{A,E(A)}}{\sigma_B N_B^0 \lambda_{B,E(B)}}. \quad (4.92)$$

Because of the generally unknown instrumental parameters, absolute theoretical values for I_A^0 and I_B^0 are difficult to obtain, but for the ratio in (4.92), which is equivalent to the matrix relative sensitivity factor (see (4.57)), the instrumental parameters cancel. This ratio can be introduced by multiplying (4.92) with I_B^0/I_B which gives

$$\frac{I_B^0}{I_B} = 1 + \frac{I_A I_B^0}{I_B I_A^0} = 1 + \frac{I_A \sigma_B N_B^0 \lambda_{B,E(B)}}{I_B \sigma_A N_A^0 \lambda_{A,E(A)}}. \quad (4.93)$$

Equation 4.93 is plotted as a solid line in Fig. 4.25 for $I_B^0 = I_A^0$. According to Wagner [4.74], in general, the (Scofield) photoionization cross sections for an

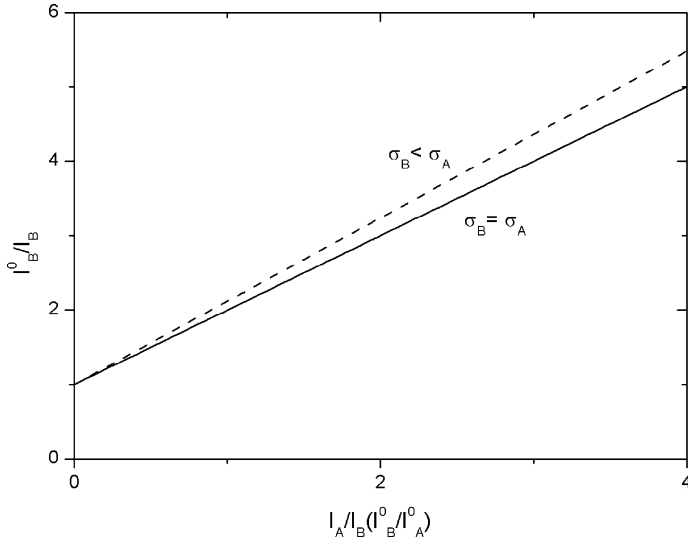


Fig. 4.25 Plot of (4.93) for $\sigma_B = \sigma_A$ (solid line) and for $\sigma_B < \sigma_A$ (dashed line)

atomic core level are the same for an element in a compound, i.e., $\sigma_A = \sigma_B$, and therefore, σ cancels in (4.92) and (4.93). However, this does not apply if there are nonnegligible intrinsic plasmon losses (see Sect. 3.2.6). In this case, the measured intensity I_B is diminished, and $\sigma_B < \sigma_A$ is obtained (dashed line in Fig. 4.25). In particular, metallic Al and Mg show pronounced intrinsic plasmon losses. In contrast to the metal, the valence band electrons are strongly localized in the chemical bond to oxygen in metal oxides, resulting in a strong decrease of the probability of intrinsic (and extrinsic) bulk plasmons and of surface plasmons at the metal/oxide interface [4.103, 4.104]. This difference can be used to extract the contribution of both bulk and surface plasmons from the quantitative evaluation of Al oxide layers on pure Al by exact determination of intensity of the metal and oxide Al 2p peak, as demonstrated by Jeurgens et al. [4.105] (see Fig. 3.8). Because the intrinsic bulk and surface plasmon excitations subtract from the total primary-excitation peak intensity of the metal (represented by the Scofield photoionization cross section), I_{met}^0 measured for the pure metal has to be increased by the factor $(1 + \alpha_p + \beta_p)$, where α_p and β_p denote the intrinsic bulk and surface plasmon contributions, respectively. For the metal peak with oxide overlayer ($I_{\text{met}} < I_{\text{met}}^0$), the surface plasmon vanishes ($\beta_p = 0$), and for the measured oxide peak, there is no plasmon contribution at all. Assuming $\sigma_A = \sigma_B$, replacing overlayer A by oxide (ox) and substrate B by metal (met), and correcting the measured intensities by the appropriate plasmon correction factor, (4.93) is expressed by

$$\frac{I_{\text{met}}^0(1 + \alpha_p + \beta_p)}{I_{\text{met}}(1 + \alpha_p)} = 1 + \frac{I_{\text{ox}}N_{\text{met}}^0\lambda_{\text{met},E(\text{met})}}{I_{\text{met}}(1 + \alpha_p)N_{\text{ox}}^0\lambda_{\text{ox},E(\text{ox})}}, \quad (4.94)$$

which, after some rearrangement, clearly shows a linear relation between the measured peak intensity ratios $I_{\text{met}}/I_{\text{met}}^0$ and $I_{\text{ox}}/I_{\text{met}}$:

$$\frac{I_{\text{met}}^0}{I_{\text{met}}} = \frac{1}{1 + \alpha_P + \beta_P} \left[(1 + \alpha_P) + \frac{I_{\text{ox}} N_{\text{met}}^0 \lambda_{\text{met},E(\text{met})}}{I_{\text{met}} N_{\text{ox}}^0 \lambda_{\text{ox},E(\text{ox})}} \right] \quad (4.95)$$

with slope $((N_{\text{met}}^0 \lambda_{\text{met},E(\text{met})}) / (N_{\text{ox}}^0 \lambda_{\text{ox},E(\text{ox})})) / (1 + \alpha_P + \beta_P)$ and intercept with the ordinate $(1 + \alpha_P) / (1 + \alpha_P + \beta_P)$, as indicated in Fig. 4.25 by the dashed line. With measured data of oxide layers with different thickness lying on this line, the bulk plasmon contribution $\alpha_P = 0.14$ and the surface plasmon contribution $\beta_P = 0.02$ were determined by Jeurgens et al. [4.105] with (4.95) for the Al 2p peak with MgK $_{\alpha}$ excitation at 45° emission angle.

In (4.95), the Scofield cross sections ($= \sigma_{\text{Sc}}$) for metal and oxide were set equal and therefore they cancel. As seen by comparison of (4.94) with (4.95), setting

$$\sigma_{\text{met}} = \frac{\sigma_{\text{Sc}}}{1 + \alpha_P + \beta_P} \quad (4.96a)$$

and

$$\sigma_{\text{ox}} = \sigma_{\text{Sc}}, \quad (4.96b)$$

we obtain

$$\frac{I_{\text{met}}^0}{I_{\text{met}}} = \frac{1 + \alpha_P}{1 + \alpha_P + \beta_P} + \frac{I_{\text{ox}} \sigma_{\text{met}} N_{\text{met}}^0 \lambda_{\text{met},E(\text{met})}}{I_{\text{met}} \sigma_{\text{ox}} N_{\text{ox}}^0 \lambda_{\text{ox},E(\text{ox})}}, \quad (4.97)$$

which is identical to (4.93) if β_P is neglected and the ratio $(1 + \alpha_P) / (1 + \alpha_P + \beta_P)$ is taken as unity, a reasonable approximation in view of total experimental error, since $\beta_P = 0.02$ in the above example. Equation 4.97 means that the usual quantitative equations for thin aluminum oxide layers can be used if the correction is taken into account for the Scofield cross section (4.96a) and therefore for the matrix relative sensitivity factor (4.92), if (4.92) is not determined by reference standard samples. Without the latter and no intrinsic plasmon correction, the error in the thickness determination of aluminum oxide films on aluminum can be as high as +20% [4.106]. Schematically, the effect of a 16% lower photoionization cross section of the metal substrate cross section is indicated by the dashed line in Figs. 4.24 and 4.25.

Note Concerning the Error. Values for the theoretical parameters in (4.95) were given by Jeurgens et al. [4.105] as $N_{\text{met}}^0 = 100.14 \text{ mol/dm}^3$ for Al in Al, $N_{\text{ox}}^0 = 71.85 \text{ mol/dm}^3$ for Al in $\gamma\text{-Al}_2\text{O}_3$ (from Ref. [4.84]), and $\lambda_{\text{Al},E(\text{Al})} = 2.23 \text{ nm}$ and $\lambda_{\text{ox},E(\text{ox})} = \lambda_{\text{ox},E(\text{Al})} = 2.40 \text{ nm}$ were taken as IMFP values calculated by the TPP-2M algorithm [4.13]. It is clear that any error in these values affects the results for α_P and β_P . For example, replacing the IMFP values by the more appropriate average effective attenuation length (EAL) values after the NIST EAL database [4.37] for Al, i.e., $\lambda_{\text{Al},E(\text{Al}2p)} = 2.07 \text{ nm}$, and of Al_2O_3 , $\lambda_{\text{ox},E(\text{Al}2p)} = 2.32 \text{ nm}$ [4.37, 4.107–4.109], the experimental curve in [4.105] yields $(1 + \alpha_P + \beta_P) = 1.125$. Then, the values of α_P and β_P would be obtained as 0.10 and 0.024, respectively, which appear to be closer to theoretical predictions [4.110].

4.3.3.4 Different Kinetic Energies of Bulk and Surface Layer Signals

In general, the binding energies of photoelectron peaks from elements in the bulk and in the surface layer are substantially different, for example, when measuring the metal peak in the bulk and the oxygen peak in the oxide layer. In that case, $\lambda_{A,E(A)} \neq \lambda_{A,E(B)}$, and (4.89) only gives an implicit solution with $d/(\lambda_{A,E(A)} \cos \theta)$, namely,

$$\frac{I_A I_B^0}{I_B I_A^0} = \exp \left[-\frac{d}{\lambda_{A,E(A)} \cos \theta} \frac{\lambda_{A,E(A)}}{\lambda_{A,E(B)}} \right] - \exp \left[-\frac{d}{\lambda_{A,E(A)} \cos \theta} \left(1 - \frac{\lambda_{A,E(A)}}{\lambda_{A,E(B)}} \right) \right]. \quad (4.98)$$

In (4.98), the ratio $\lambda_{A,E(A)}/\lambda_{A,E(B)}$ can be replaced by the ratio of the energy dependence of the attenuation length, because both values refer to the same material A. Adapting the generally valid relation given by $\lambda \propto E^{0.75}$ [4.33] (see (4.19)), with E the kinetic energy of the detected electrons, and replacing the (measured) elemental standard intensities by the elemental RSFs, S_A and S_B , (4.98) can be written as

$$\begin{aligned} \frac{I_A S_B}{I_B S_A} = \exp \left[-\frac{d}{\lambda_{A,E(A)} \cos \theta} \left(\frac{E_A}{E_B} \right)^{0.75} \right] \\ - \exp \left[-\frac{d}{\lambda_{A,E(A)} \cos \theta} \left(1 - \left(\frac{E_A}{E_B} \right)^{0.75} \right) \right]. \end{aligned} \quad (4.99)$$

Of course, the elemental relative sensitivity factors (E-RSFs), S_A and S_B , have to be replaced by the matrix relative sensitivity factors (M-RSFs), $S_{A,m}$ and $S_{B,m}$, if A and B are alloys or compounds. An illustration of (4.98) is shown in Fig. 4.26, where the measured and normalized intensity ratio is plotted as a function of the relative thickness, $d/(\lambda_{A,E(A)} \cos \theta)$, for different values of the kinetic energy ratio of the photoelectrons of surface layer A to substrate B, E_A/E_B . The simple exponential line for $E_B = E_A$ represents (4.90a,b).

A practical example is given for the case of a carbon layer on Fe, where for the Fe2p and the C 1s, the kinetic energies $E_{Fe} = 780$ eV, $E_C = 1202$ eV apply, respectively (for Al K α source), hence $E_A/E_B = E_C/E_{Fe} = 1.54$. Assuming an intensity ratio, I_C/I_{Fe} of 0.5, with the relative elemental sensitivity factors $S_C = 0.25$, $S_{Fe} = 2$ (see Table 4.2), we get $(I_C/S_C)/(I_{Fe}/S_{Fe}) = 4$. In case of application of the simple equation (4.90a), we would obtain the wrong value of 1.61 for the relative thickness $d/(\lambda_{A,E(A)} \cos \theta)$ (dashed line in Fig. 4.26). However, using the correct expression (4.99) with $E_A/E_B = 1.54$, we get $d/(\lambda_{A,E(A)} \cos \theta) = 1.24$ (solid line connection). According to the CS2 relation, for a pure carbon layer, $\lambda_{A,E(A)} = 2.47$ nm. For normal emission ($\theta = 0$), we obtain a carbon layer thickness of $d = 3.06$ nm. (Note that the above relations are not recommended for emission angles $\theta \geq 70^\circ$ because then elastic scattering may considerably increase the effective attenuation length [4.33].)

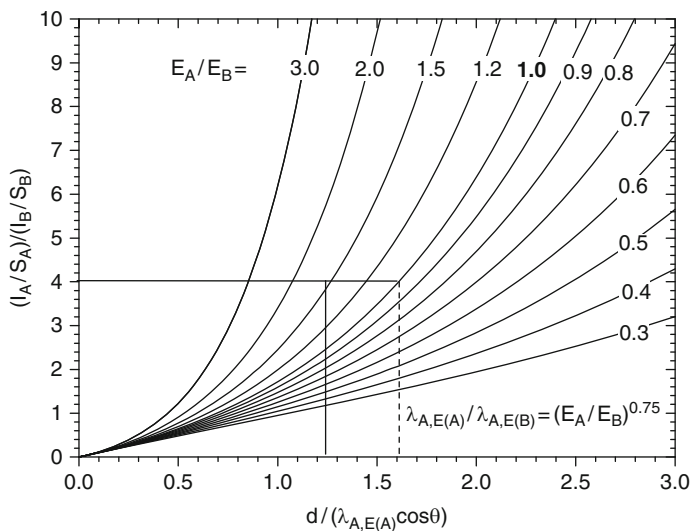


Fig. 4.26 Plot of (4.99) showing the ratio of the normalized intensity of an overlayer, I_A/S_A (with S_A the elemental relative sensitivity factor, E-RSF) with the normalized intensity of the substrate, I_B/S_B , as a function of the relative thickness $d/(\lambda_{A,E(A)} \cos \theta)$. Parameter is the ratio of the kinetic energies of the XPS peak of the overlayer (A) and the substrate (B), E_A/E_B . Note that only for $E_A/E_B = 1$, expression (4.90a) applies. See text for the example shown

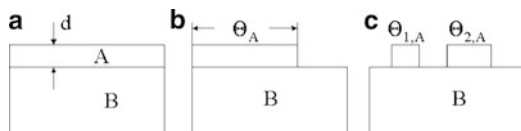


Fig. 4.27 Schematic view of substrate B with (a) full coverage ($\Theta_A = 1$) of A with layer thickness d , (b) fractional coverage ($\Theta_A < 1$), and (c) island formation ($\Theta_{j,A} \ll 1$)

An alternative graphical solution of (4.99) and/or Fig. 4.26 for the determination of the relative layer thickness in the form of a nomogram (named “Thickogram”) was published by Cumpson [4.111].

A typical case for application of (4.97)–(4.99) is (monolayer) surface segregation layer of element A on bulk element B. In this case, the segregation layer is constant, and the amount of enrichment is given by the surface coverage of A. This and more complicated cases are briefly considered in the following paragraphs.

4.3.3.5 Fractional Surface Coverage: Segregation and Evaporation Layers

In evaporation as well as in surface segregation experiments, the substrate B may be covered by only a fraction, Θ_A , of element A, as schematically depicted in Fig. 4.27. In this case, (4.88a) and (4.88b) have to be modified, and the signal intensity from the surface layer is

$$I_A = I_A^0 \Theta_A \left\{ 1 - \exp \left[-\frac{d}{\lambda_{A,E(A)} \cos \theta} \right] \right\} \quad (4.100a)$$

and for the substrate,

$$I_B = I_B^0 \left\{ (1 - \Theta_A) + \Theta_A \exp \left[-\frac{d}{\lambda_{A,E(B)} \cos \theta} \right] \right\}, \quad (4.100b)$$

which gives the ratio

$$\frac{I_A I_B^0}{I_B I_A^0} = \frac{\Theta_A \{1 - \exp[-d/(\lambda_{A,E(A)} \cos \theta)]\}}{1 + \Theta_A \{\exp[-d/(\lambda_{A,E(B)} \cos \theta) - 1]\}}. \quad (4.101)$$

With $\lambda \propto E^{0.75}$ as above,

$$\frac{I_A S_B}{I_B S_A} = \frac{\Theta_A \{1 - \exp[-d/(\lambda_{A,E(A)} \cos \theta)]\}}{1 + \Theta_A \{\exp[-d/(\lambda_{A,E(B)} \cos \theta)[E(A)/E(B)]^{0.75} - 1]\}}. \quad (4.102)$$

Figure 4.28 shows the intensity ratio as a function of the relative layer thickness after (4.102), for $E(A)/E(B) = 1.54$ as in the Fe–C example above, and with the coverage Θ as parameter. It is interesting to note that (a) for very thick layers, the intensity ratio approaches a maximum, limiting value given by the coverage, and (b) for a limited range, each measured intensity ratio for a certain coverage corresponds to a value for full coverage ($\Theta = 1$) but with lower thickness. If the latter yields less than a monolayer, the only physically reasonable explanation is a coverage of a monolayer thickness and $\Theta < 1$. A clear distinction between different coverages is only possible by measurements with different emission angles (see Sect. 7.2) or otherwise known layer thickness. Equations 4.100, 4.101, and 4.102 can be used to distinguish between layer-by-layer and island growth (Fig. 4.27c) using in situ observation of the growth of evaporation layers (see below).

4.3.3.6 Surface Enrichment and Surface Depletion

In the following, we replace the fractional coverage Θ_A (Fig. 4.27b) by the more general mole fraction X_A in a layer of A and B with thickness d (see Fig. 4.29b), keeping in mind that the mole fraction of A is its concentration in atoms per volume, N_A , divided by the sum of the concentrations of all other elements, N_i :

$$X_A = \frac{N_A}{\sum_i N_i}. \quad (4.103)$$

Even in thermodynamic equilibrium, the case of a homogeneous alloy composition from bulk to surface is highly unlikely. In general, the composition of the very first

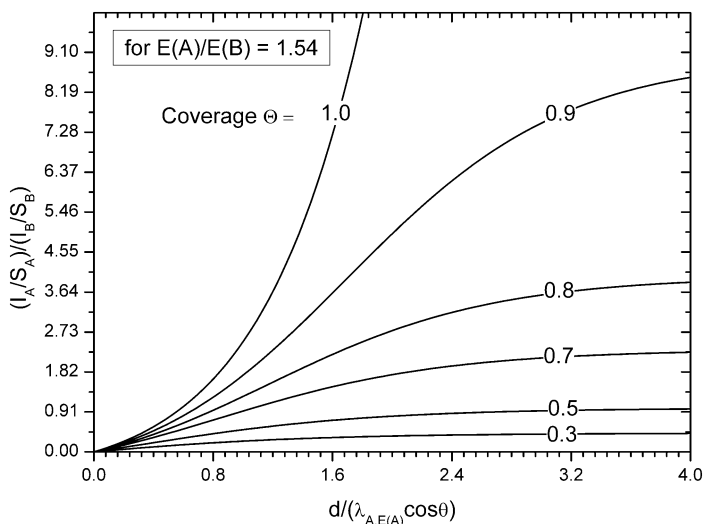


Fig. 4.28 Ratio of the normalized intensity of an overlayer, I_A/S_A (with S_A the relative elemental sensitivity factor, RSF), with the normalized intensity of the substrate, I_B/S_B , as a function of the relative layer thickness $d/(\lambda_{A,E(A)} \cos \theta)$ after (4.101), for $E(A)/E(B) = 1.54$ (as for the example Fe–C in Fig. 4.26). Parameter is the degree of coverage Θ_A of the surface layer A on substrate B. Note the intensity ratio is the same for complete layer coverage and for a given range of fractional coverage with different relative layer thickness

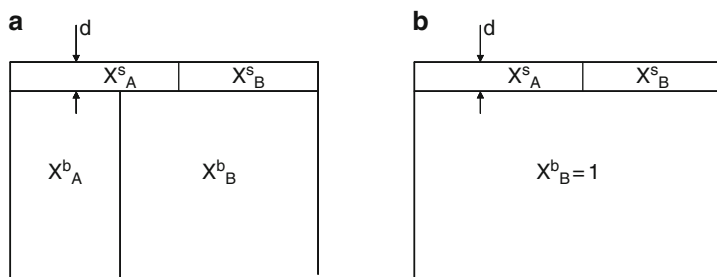


Fig. 4.29 Schematic view of a surface layer of a binary system with components A and B, and layer thickness d . (a) Mole fractions in surface layer X_A^s , X_B^s showing different composition from the bulk with mole fractions X_A^b , X_B^b . (b) Special case for bulk component mole fraction $X_A^b = 0$ ($X_B^b = 1$)

surface layers is different from the bulk composition. This fact is called surface segregation (or interfacial segregation in the case of internal surfaces like grain boundaries) and is usually described by some form of the Langmuir–McLean equation [4.112, 4.113]. AES and XPS are most frequently used to determine the amount of surface enrichment of a component. Let us first consider a binary system A–B with surface layer with thickness d and composition X_A^s , X_B^s and bulk composition X_A^b , X_B^b , as schematically depicted in Fig. 4.29.

In the general case of a binary alloy in the surface layer as well as in the bulk, for quantification, the measured signal intensity of A has to be normalized to the matrix relative sensitivity factor $I_A/I_{A,m}^0 = I_A/S_{A,m}$ (see Sect. 4.3.2). The total intensity consists of two contributions, one from the segregation layer and the other from the bulk, giving

$$\frac{I_A}{I_{A,s}^0} = X_A^s \left\{ 1 - \exp \left[-\frac{d}{\lambda_{s,E(A)} \cos \theta} \right] \right\} + X_A^b \exp \left[-\frac{d}{\lambda_{s,E(A)} \cos \theta} \right] \quad (4.104)$$

when neglecting instrumental parameters. According to Fig. 4.29a, the attenuation length in pure A, $\lambda_{A,E(A)}$, is replaced by $\lambda_{s,E(A)}$ to indicate by subscript *s* the influence of the surface layer composition. If the bulk concentration X_A^b and the intensity of A in a thick surface layer ($d > 5 \lambda_{s,E(A)} \cos \theta$) of matrix composition *s*, $I_{A,s}^0$, are known, X_A^s can be determined. It is important that the bulk standard value is known for the same instrumental conditions as applied in the actual measurement. Frequently, calibration can be performed by an “internal standard,” for example, by removing the segregation layer by fracture of the sample (e.g., transgranular fracture as in grain boundary segregation [4.114, 4.115]). Assuming that the relative sensitivity factors are similarly depending on instrumental parameters, the ratio technique as applied already above proves useful for cancellation of the latter, with the possibility of using elemental relative sensitivity factors from handbooks [4.21, 4.22] combined with relative matrix correction factors (see Sect. 4.3.2).

Writing (4.104) similarly for I_B , X_B , for the binary system shown in Fig. 4.29a, we obtain for the measured intensity ratio I_A/I_B , divided by the respective matrix relative elemental sensitivity factors $I_{A,s}^0/I_{B,s}^0$, the sum of the intensities from the bulk, attenuated by the surface layer, and the contribution of that layer:

$$\frac{I_A I_{B,s}^0}{I_B I_{A,s}^0} = \frac{X_A^s \left\{ 1 - \exp \left[-\frac{d}{\lambda_{s,E(A)} \cos \theta} \right] \right\} + X_A^b \exp \left[-\frac{d}{\lambda_{s,E(A)} \cos \theta} \right]}{X_B^s \left\{ 1 - \exp \left[-\frac{d}{\lambda_{s,E(B)} \cos \theta} \right] \right\} + X_B^b \exp \left[-\frac{d}{\lambda_{s,E(B)} \cos \theta} \right]}. \quad (4.105)$$

The attenuation lengths for the bulk signal of both A and B have are for the surface layer composition of both elements ($\lambda_{s,E(A)}$, $\lambda_{s,E(B)}$). The general expression (4.105) enables quantification of enrichment as well as depletion of a component. For example, depletion of one component is encountered in formation of an altered layer by preferential sputtering (see Chap. 7). In case of ion bombardment of transition metal oxides (e.g., Ta₂O₅, Nb₂O₅) [4.102], depletion of oxygen occurs as schematically visualized by Fig. 4.29. If B is considered as metal in full bonding state (pentoxide), present only in the bulk ($X_B^b = 1$, $X_B^s = 0$), and A as metal in suboxide bonding states with slightly higher binding energy, present only in the surface layer ($X_A^s \neq 0$, $X_A^b = 0$), Fig. 4.29b applies. Therefore, (4.105) can be simplified to

$$\frac{I_A}{I_B} = \frac{X_A^s \left\{ 1 - \exp \left[-\frac{d}{\lambda_{s,E(A)} \cos \theta} \right] \right\}}{X_B^b \exp \left[-\frac{d}{\lambda_{s,E(B)} \cos \theta} \right]} = \frac{X_A^s}{X_B^b} \left\{ \exp \left[\frac{d}{\lambda_{s,E(A)} \cos \theta} \right] - 1 \right\}, \quad (4.106)$$

because $I_{A,s}^0 = I_{B,s}^0$ and $E(B) \cong E(A)$. Since the relative intensities of pentoxide and suboxides determine the stoichiometry of bulk and layer, X_B^b and X_A^s are known, and with the measured XPS intensity ratio, the relative thickness of the altered layer, $d/(\lambda_{A,E(A)} \cos \theta)$, is determined [4.102] (see (9.1) in Sect. 9.2.3).

Equation 4.105 gives the intensity ratio as a function of two variables, X_A^s and d , if bulk composition X_A^b , X_B^b , matrix relative sensitivity factors and matrix-corrected attenuation lengths are known. Replacing X_B^b by $1 - X_A^b$ and X_B^s by $1 - X_A^s$, we may write

$$\frac{I_A}{I_B} S_{B,A,s} = \frac{X_A^s + (X_A^b - X_A^s) \exp \left[-\frac{d}{\lambda_{s,E(A)} \cos \theta} \right]}{1 - X_A^s + (X_A^s - X_A^b) \exp \left[-\frac{d}{\lambda_{s,E(B)} \cos \theta} \right]}. \quad (4.107)$$

Equation 4.107 is a generalized description of a surface layer of a binary system with different compositions from the bulk (Fig. 4.29a). It is especially useful to quantify interfacial segregation in binary alloy systems, for example, NiAl [4.115] or Fe₃Al [4.109].

Equation 4.107 can be considerably simplified for dilute systems, if the bulk concentration of the segregant is below 1 at% and can therefore be ignored (e.g., O in Nb [4.116], Sn in Cu [4.117], S in Cu [4.118], and P, C, and Si in Fe) [4.108], as schematically shown in Fig. 4.29b. Thus, we can simplify (4.107) by setting $X_A^b = 0$, $X_B^b = 1$. In principle, A and B in the surface may form a new two-dimensional structure which will determine $\lambda_{s,E(A)}$ and $\lambda_{s,E(B)}$. However, it appears reasonable to assume that the surface layer, according to Fig. 4.29b, consists of a fractional layer of A on B. Then, the attenuation lengths $\lambda_{s,E(A)}$ and $\lambda_{s,E(B)}$ are represented by $\lambda_{A,E(A)}$ and $\lambda_{A,E(B)}$, and we obtain

$$\frac{I_A I_B^0}{I_A^0 I_B} = \frac{I_A}{I_B} S_{B,A} = \frac{X_A^s \left\{ 1 - \exp \left[-\frac{d}{\lambda_{A,E(A)} \cos \theta} \right] \right\}}{1 - X_A^s \left\{ 1 - \exp \left[-\frac{d}{\lambda_{A,E(B)} \cos \theta} \right] \right\}}, \quad (4.108)$$

where the matrix relative sensitivity factor $S_{B,A,m}$ is now replaced by the elemental relative sensitivity factor $S_{B,A}$. Note that (4.108) is identical to the usual Langmuir-McLean equation for surface segregation [4.1, 4.2, 4.108, 4.112], given by (4.101), with X_A^s being replaced by the coverage of A, Θ_A , in fractions of a monolayer.

Referring to the ratio of mole fraction in the surface layer, X_A^s/X_B^s , with $X_A^s + X_B^s = 1$, we may rewrite (4.108) and get

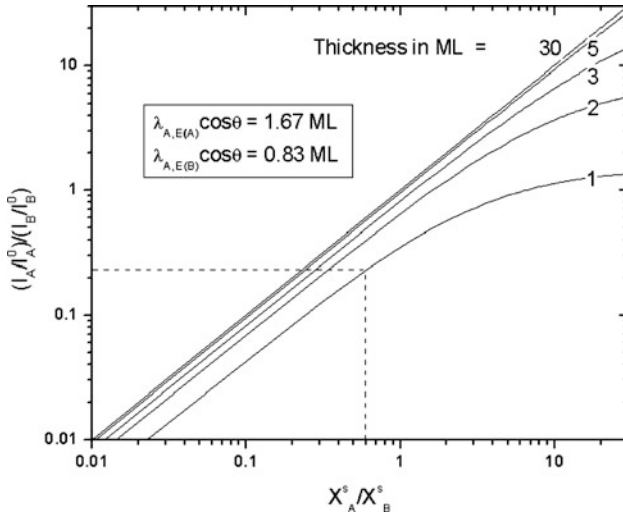


Fig. 4.30 Example of the intensity ratio $(I_A/I_A^0)/(I_B/I_B^0)$ is as a function of the surface layer composition X_A^s/X_B^s after (4.109), with the assumption that $\lambda_{A,E(A)} \cos \theta = 1.67$ ML and $\lambda_{A,E(B)} \cos \theta = 0.83$ ML are known and given in monolayer (ML) thickness [4.119]. For higher thicknesses (here > 5 ML), the bulk solution is obtained. For monolayer segregation (Langmuir–McLean), a linear relation is obtained for $X_A^s/X_B^s \leq 0.6$ (indicated by dashed lines) (see Fig. 4.35)

$$\frac{I_A I_B^0}{I_A^0 I_B} = \frac{\frac{X_A^s}{X_B^s} \left\{ 1 - \exp \left[-\frac{d}{\lambda_{A,E(A)} \cos \theta} \right] \right\}}{\frac{X_A^s}{X_B^s} \exp \left[-\frac{d}{\lambda_{A,E(B)} \cos \theta} \right] + 1}. \quad (4.109)$$

In the past, (4.109) was used to estimate the relative layer thickness and amount of oxygen coverage during surface segregation of oxygen on niobium [4.119]. A diagram of (4.109) is shown in Fig. 4.30. In case of monolayer segregation, d is given by the monolayer thickness, and knowing the attenuation lengths of A and B and the elemental relative sensitivity factor ratio, I_A^0/I_B^0 (or standard intensities), we obtain directly X_A/X_B from the intensity ratio I_A/I_B in (4.109). If the segregation layer thickness is not known (e.g., for multilayer segregation), we can at least find a maximum layer thickness for a maximum intensity ratio at full layer coverage of A, i.e., for $X_A^s/X_B^s \rightarrow \infty$. Thus, $(I_A/I_B)/(I_A^0/I_B^0)_{\max} = 1.5$ for 1 ML full coverage in the example of Fig. 4.30 [4.119].

Using the relation $\lambda_{A,E(B)} = (E_B/E_A)^{0.75} \lambda_{A,E(A)}$ defined above (see (4.19)), the normalized intensity ratio as a function of two variables, the amount of segregation and the relative segregation layer thickness, $d/(\lambda_{A,E(A)} \cos \theta)$, is given by

$$\frac{I_A I_B^0}{I_A^0 I_B} = \frac{\frac{X_A^s}{X_B^s} \left\{ 1 - \exp \left[-\frac{d}{\lambda_{A,E(A)} \cos \theta} \right] \right\}}{\frac{X_A^s}{X_B^s} \exp \left[-\frac{d}{\lambda_{A,E(A)} (E_B/E_A)^{0.75} \cos \theta} \right] + 1}. \quad (4.110)$$

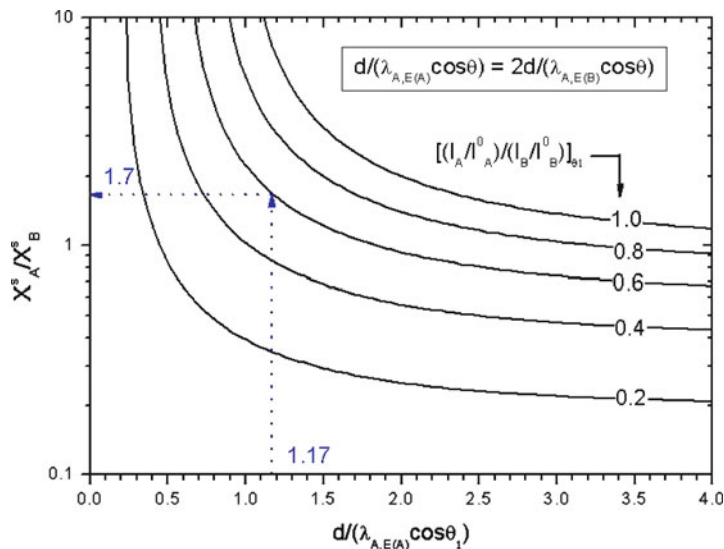


Fig. 4.31 Example of the relation between the mole fraction ratio X_A^s/X_B^s of the components A, B of a surface segregation layer and the relative layer thickness $d/(\lambda_{A,E(A)} \cos \theta_1)$ with $\theta_1 = 0^\circ$, for the case of $\lambda_{A,E(B)} = 2\lambda_{A,E(A)}$, i.e., $(E_A/E_B)^{0.75} = 2$, after (4.111). Parameter is the normalized relative intensity $(I_A/I_A^0)/(I_B/I_B^0)_{\theta_1}$. If the latter value is 0.6 and $d/(\lambda_{A,E(A)} \cos \theta_1) = 1.17$, $X_A^s/X_B^s = 1.7$ is obtained (see blue arrows)

If $d/\lambda_{A,E(A)} \cos \theta$ is known, X_A^s/X_B^s is determined. Figure 4.31 shows a plot of (4.110) for an assumed value of $(E_B/E_A)^{0.75} = 2.0$ ($\lambda_{A,E(B)} \cos \theta = 2\lambda_{A,E(A)} \cos \theta$) for different amounts of segregation, given by X_A^s/X_B^s . The mole fraction ratio X_A^s/X_B^s corresponds to $X_A^s/(1 - X_A^s)$, the logarithm of which is proportional to $-\Delta H/(RT)$ where ΔH is the segregation enthalpy for ideal Langmuir–McLean behavior [4.108]. Rewriting (4.110), we obtain

$$\begin{aligned} \frac{X_A^s}{X_B^s} &= \frac{X_A^s}{1 - X_A^s} \\ &= \frac{1}{\frac{1}{\left(\frac{I_A/I_A^0}{I_B/I_B^0}\right)} \left[1 - \exp\left(-\frac{d}{\lambda_{A,E(A)} \cos \theta}\right) \right] - \exp\left[-\frac{d}{\lambda_{A,E(A)} (E_B/E_A)^{0.75} \cos \theta}\right]}. \end{aligned} \quad (4.111)$$

If standard measurements are not available, the ratio I_A^0/I_B^0 may be replaced by the elemental relative sensitivity factor S_A/S_B defined in Sect. 4.3.2. Most important is the relative layer thickness, i.e., the ratio of thickness and mean escape depth, $d_A/(\lambda_{A,E(A)} \cos \theta)$, as obvious from Fig. 4.30. In the limiting case of a very thick layer of A, $d \gg \lambda_{A,E(A)}$, the exponential terms in (4.107)–(4.111) approach zero, and we get a linear relation equivalent to a homogeneous bulk condition, $(I_A/I_A^0)/(I_B/I_B^0) = X_A^s/X_B^s$.

Equations 4.105, 4.106, 4.107, 4.108, 4.109, 4.110, and 4.111 can be used to determine the layer thickness, if the mole fraction of X_A^s is known (e.g., from stoichiometric compounds in the example above). In general, X_A^s is unknown and has to be determined. This requires the relative layer thickness, $d/(\lambda_{A,E(A)})$, to be known, as in monolayer segregation. As obvious from Fig. 4.30, if segregation (or evaporation) builds up a second layer after saturation of the first layer ($X_A^s/X_B^s \gg 10$), the normalized intensity ratio indicates this fact (e.g., $(I_A/I_A^0)/(I_B/I_B^0) > 1.5$ in Fig. 4.30) and thus enables calculation of the second layer coverage analogous to (4.102).

A second equation is necessary to determine layer composition and layer thickness independently, for example, by two measurements with different electron escape depths. This can be achieved either by two measurements at different emission angles θ , or by using two peaks of the same element with different binding energies (see, e.g., (4.12) in Ref. [7.2]).

The effect of measurements at two different emission angles θ is obvious from Fig. 4.31 (see also AR-XPS and AR-AES, Sect. 7.2.1). Eliminating (X_A^s/X_B^s) from (4.111) by taking the ratio for $\theta = \theta_1$ and $\theta = \theta_2$, we get the following relation between the intensities measured for both angles and the relative layer thickness:

$$\left(\frac{I_A I_B^0}{I_A^0 I_B} \right)_{\theta_2} = \left(\frac{I_A I_B^0}{I_A^0 I_B} \right)_{\theta_1} \left[1 - \exp \left(-\frac{d}{\lambda_{A,E(A)} \cos \theta_2} \right) \right] / \left\{ \left(\frac{I_A I_B^0}{I_A^0 I_B} \right)_{\theta_1} \left[\exp \left(-\frac{d}{\lambda_{A,E(A)} (E_B/E_A)^{0.75} \cos \theta_2} \right) - \exp \left(-\frac{d}{\lambda_{A,E(A)} (E_B/E_A)^{0.75} \cos \theta_1} \right) \right] + 1 - \exp \left(-\frac{d}{\lambda_{A,E(A)} \cos \theta_1} \right) \right\}. \quad (4.112a)$$

This implicit equation can be solved for $d/(\lambda_{AE(A)})$. As an example, let us assume the conditions given in Fig. 4.31 and two measured and normalized intensities, $(I_A/I_A^0)/(I_B/I_B^0)_{\theta_1} = 0.6$ for $\theta_1 = 0^\circ$ ($\cos \theta_1 = 1$) and $(I_A/I_A^0)/(I_B/I_B^0)_{\theta_2} = 1.0$ for $\theta_2 = 60^\circ$ ($\cos \theta_2 = 0.5$). From these data, we can find the appropriate value of $d/\lambda_{A,E(A)} \cos \theta_1 = 1.17$ from (4.112a) and $X_A^s/X_B^s = 1.7$ from (4.111).

The solution of the implicit equation (4.12a) can be found graphically as indicated in Fig. 4.32. The two normalized intensity ratios connected by the blue line determine the relative layer thickness, $d/\lambda_{A,E(A)} \cos \theta_1 = 1.17$ (dashed blue arrow). With that value, we use Fig. 4.31 to find $X_A^s/X_B^s = 1.7$ for $(I_A/I_A^0)/(I_B/I_B^0)_{\theta_1} = 0.6$.

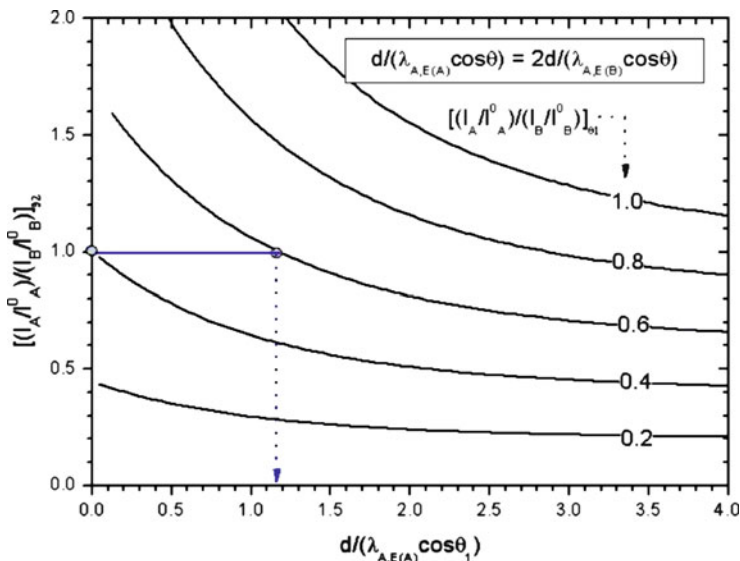


Fig. 4.32 Plot of expression (4.112a) for the graphical determination of the relative layer thickness by intensity measurements at two different emission angles from the two normalized intensity ratios $(I_A/I_A^0)/(I_B/I_B^0)_{\theta_1}$ and $(I_A/I_A^0)/(I_B/I_B^0)_{\theta_2}$. With the resulting $d/(\lambda_{A,E(A)} \cos \theta_1)$ transferred to Fig. 4.31, the layer composition X_A^s/X_B^s is found. An example is shown by blue lines and arrows. For details, see text

An elegant method, where only one measurement (e.g., at θ_1) is necessary, is the use of two different peaks of the same element at very different energies, which is possible for a number of elements (e.g., in XPS: Fe 2p_{3/2}: $E_b = 707$ eV, $E_k(\text{AlK}\alpha) = E_{B1} = 780$ eV; Fe3p : $E_b = 53$ eV, $E_k = E_{B2} = 1434$ eV; in AES, the energy difference is often larger, see, e.g., Fig. 7.2). With two energies of the substrate, E_{B1} , E_{B2} and constant θ_1 , (4.112a) is given by

$$\left(\frac{I_A I_{B2}^0}{I_A^0 I_{B2}} \right)_{E(B2), \theta_1} = \left(\frac{I_A I_{B1}^0}{I_A^0 I_{B1}} \right)_{E(B1), \theta_1} \left[1 - \exp \left(- \frac{d}{\lambda_{A,E(A)} \cos \theta_1} \right) \right] / \left\{ \left(\frac{I_A I_{B1}^0}{I_A^0 I_{B1}} \right)_{E(B1), \theta_1} \left[\frac{\exp \left(- \frac{d}{\lambda_{A,E(A)} (E_{B2}/E_A)^{0.75} \cos \theta_1} \right)}{- \exp \left(- \frac{d}{\lambda_{A,E(A)} (E_{B1}/E_A)^{0.75} \cos \theta_1} \right)} \right] + 1 - \exp \left(- \frac{d}{\lambda_{A,E(A)} \cos \theta_1} \right) \right\}. \quad (4.112b)$$

Of course, in addition to I_{B1}^0 , a second standard intensity I_{B2}^0 or equivalent elemental relative sensitivity factor is necessary. Equation 4.112b is an implicit relation between the two measured intensities of the high- and low-energy peak

and the relative layer thickness $d/\lambda_{A,E(A)} \cos \theta_1$ at constant angle θ_1 which is plotted in Fig. 4.33 for the above values of XPS measurements at an Al layer on Fe, with $E_A(\text{Al } 2p) = 1416 \text{ eV}$. It is obvious that the sensitivity of the layer thickness determination is low for thick layers (vanishing I_{B1} , I_{B2}) and for very thin layers (vanishing I_A). The optimum is found when both signal-to-noise ratios (see Chap. 6) are similar, i.e., $(I_A/I_A^0)^{0.5} = (I_{B1}/I_{B1}^0)^{0.5}$. After (4.110) and assuming $X_A = X_B$, $I_A^0 = I_{B1}^0$, this condition is met at about $d/\lambda_{A,E(A)} \cos \theta_1 = 0.5$. The procedure to determine the relative layer thickness from Fig. 4.33 is analogous to that in Fig. 4.32. With $(I_A/I_A^0)/(I_{B1}/I_{B1}^0)_{E(B1)} = 0.6$, $(I_A/I_A^0)/(I_{B2}/I_{B2}^0)_{E(B2)} = 0.53$ (blue line), we get $d/\lambda_{A,E(A)} \cos \theta_1 = 1.17$ as before, and $X_A/X_B = 1.7$ is obtained from Fig. 4.31.

Although for a single-component segregation layer we should not expect any matrix correction terms, the *atomic density in the segregation layer* has to be considered. While a major contribution is contained in the matrix relative sensitivity factor, it is seen from (4.105) that the matrix-corrected attenuation lengths do not cancel. This is, for example, obvious for low segregation levels and/or specific segregation structures on single-crystal surfaces with only partial coverage. As an approximation, we may define the coverage level in terms of the atomic density of the substrate surface structure. If that areal density is larger than that of the

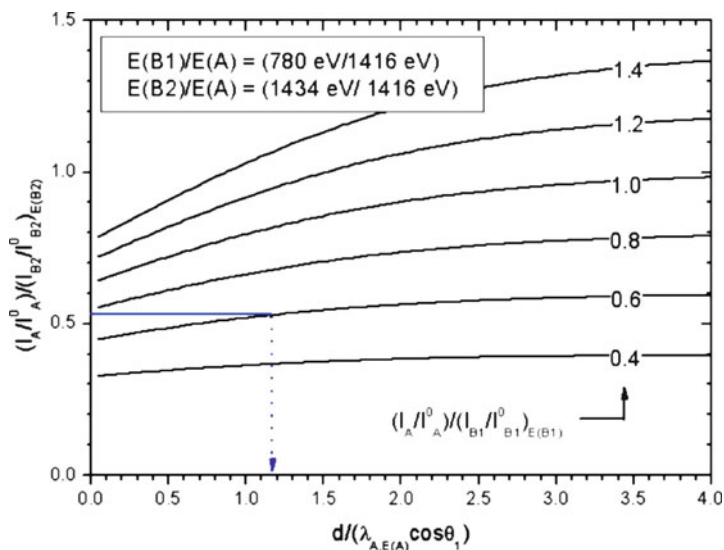


Fig. 4.33 Example of (4.112b) for the determination of the relative layer thickness $d/(\lambda_{A,E(A)} \cos \theta_1)$ from the measured values of $(I_A/I_A^0)/(I_{B1}/I_{B1}^0)_{E(B1)}$ (curves parameter) and $(I_A/I_A^0)/(I_{B2}/I_{B2}^0)_{E(B2)}$ (ordinate). The values indicated by the blue line are selected to give $d/(\lambda_{A,E(A)} \cos \theta_1) = 1.17$ (dashed blue arrow). This value is used in Fig. 4.31 to yield the surface layer composition $X_A^s/X_B^s = 1.7$

bulk structure of the segregant, the latter will not cover all of the areas, but if the attenuation length is for the bulk structure, the apparent coverage has to be corrected [4.120].

It is seen from (4.111) and in Fig. 4.30 that for the usual case of monolayer segregation, a linear relation is obtained only for $X_A^s/X_B^s < 0.6$, i.e., $X_A^s < 0.4$. Here and in the following it is generally assumed that segregation takes place in the first monolayer. Owing to the discrete contribution of each layer according to (4.87a, b), a distinction is possible between segregation in the first, second, or third monolayer [4.113, 4.121] (see Fig. 4.30).

A consequence of (4.111) is the fact that a linear relation between X_A^s/X_B^s and the intensity ratio I_A/I_B is only obtained for very small values of both $(I_A/I_A^0)/(I_B/I_B^0)$ and $d/(\lambda_{A,E(A)} \cos \theta)$ [4.1, 4.2] (see Fig. 4.30). If these conditions are not valid, as, for example, in the case of segregation of A at higher coverage, (4.87) has to be applied [4.113, 4.121]. To clarify this point, (4.111) is rewritten to directly show the amount of segregation in terms of the segregant mole fraction (or monolayer fraction), X_A^s , in the segregation layer:

$$X_A^s = \frac{\frac{I_A I_B^0}{I_B I_A^0}}{1 - \exp \left[-\frac{d}{\lambda_{A,E(A)} \cos \theta} \right] + \frac{I_A I_B^0}{I_B I_A^0} \left\{ 1 - \exp \left[-\frac{d}{\lambda_{A,E(B)} \cos \theta} \right] \right\}}. \quad (4.113)$$

Frequently, a linear relation between the measured intensity and the amount of segregant enrichment is recommended [4.1, 4.2]. As pointed out by Seah [4.122], if we neglect the attenuation of the bulk signal by the segregated solute layer ($1 - \exp[-d/(\lambda_{A,E(B)} \cos \theta)] \approx 1$) and approximate the exponential function (for $d/(\lambda_{A,E(A)} \cos \theta) \ll 1$) by $(1 - d/(\lambda_{A,E(A)} \cos \theta))$, (4.113) simplifies to

$$X_A^s = \frac{I_A I_B^0}{I_B I_A^0} \frac{\lambda_{A,E(A)} \cos \theta}{d}. \quad (4.114)$$

The deviation between (4.113) and (4.114) depends mainly on the value of the relative attenuation length, as seen in a comparison of both equations in Fig. 4.34. An example for segregation of C on Fe ($A = C$, $B = Fe$) with the parameters for XPS given in Table 4.2 and emission angle $\theta = 0^\circ$ is shown in Fig. 4.35. In this case, it is clearly seen that above a segregation level of about 0.5 ML an increasing deviation from a linear relation between X_A^s and the normalized intensity ratio is evident. For increasing values of θ , the deviation increases (see Fig. 4.30). Therefore, the use of (4.114) instead of (4.113) is not recommended for exact quantification [4.113].

As evident from Figs. 4.23 and 4.29, the above equations describing segregation can be used equally well to quantify evaporated layers of elements and alloys, if smooth, layer-by-layer deposition prevails. Additional modifications are necessary to describe general mechanisms of thin-film deposition.

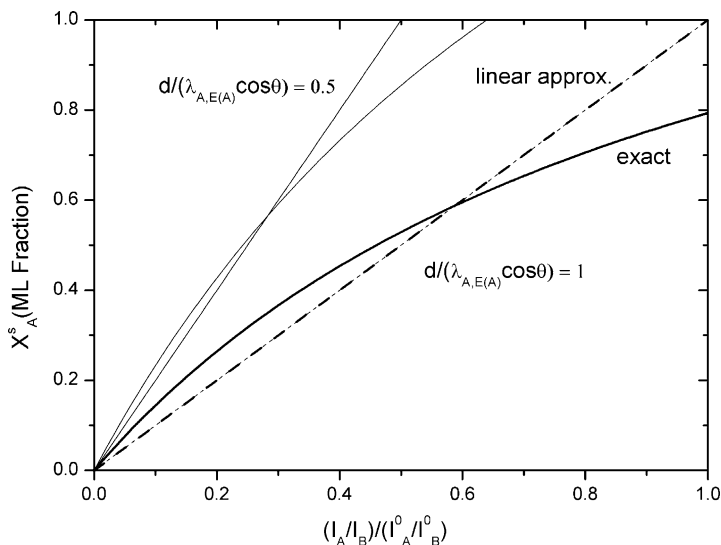


Fig. 4.34 Visualization of the exact quantification of monolayer segregation after (4.113) (solid lines) and linear approximation (dashed lines) after (4.114), for assumed relative layer thickness $d/(\lambda_{A,E(A)} \cos \theta) = 1$ (thick lines) and 0.5 (thin lines)

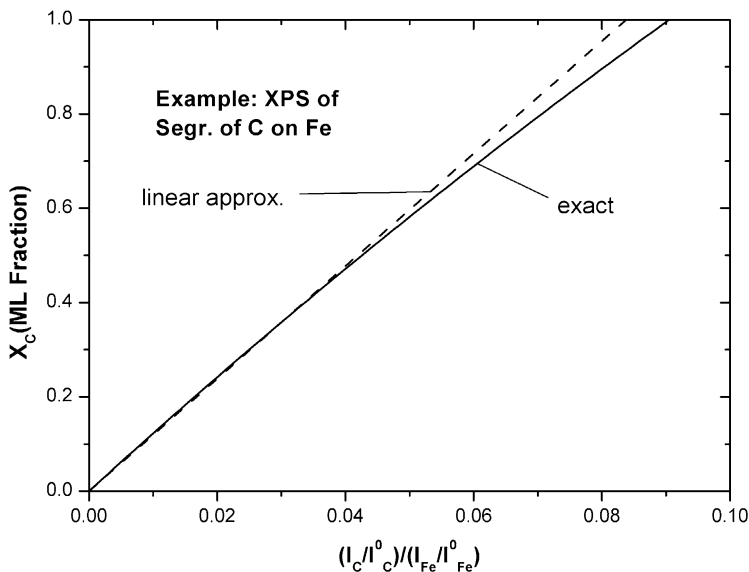


Fig. 4.35 Relation between segregant coverage (in monolayer fractions) and normalized intensity ratio, calculated with (4.113) (full line) for segregation of C on Fe with the data from Table 4.3 (carbon layer thickness $d = 0.207$ nm and the attenuation $\lambda_{A,E(A)} = \lambda_{C,E(C)} = 2.47$ nm, $\lambda_{B,A} = \lambda_{Fe,C} = 1.75$ nm), $\theta = 0$. The linear approximation after (4.114) is shown by the dashed line

4.3.3.7 Thin-Film Deposition and Growth

Quantitative analysis of thin surface layers can be applied to thin-film deposition and growth. For example, the surface component A can be present as a pure element or representing a component in an alloy or a compound, for example, a metal peak in an oxide bonding state. Measurement of adsorbate and bulk intensities can be used to quantify thin layer growth via (4.88)–(4.114) (see Fig. 4.27). Layer growth may occur in different modes: (a) in a layer-by-layer growth (Franck–van der Merwe (FM) mode), island growth (Volmer–Weber (VW) – mode), layer plus island growth (Stranski–Krastanov (SK) mode), and simultaneous multilayer (SM) growth mode [4.123]. For example, layer-by-layer growth (FM) is described by the well-known Gallon equations [4.96, 4.98] which are obtained by expressing the exponential functions in (4.88a) and (4.88b) as in (4.87a) and (4.87b) by adsorbate (α_A^A) and substrate (α_B^A) transmission coefficients per atomic monolayer (ML), (4.87a) and (4.87b), and ($d = 1$ ML and λ in ML), $\alpha_A^A = \exp[-1/(\lambda_{A,E(A)} \cos \theta)]$ and $\alpha_B^A = \exp[-1/(\lambda_{A,E(B)} \cos \theta)]$. After (4.87a), for a coverage of n complete monolayers, we get, for the normalized signal intensity of the adsorbate,

$$\frac{I_A(n)}{I_A^0} = 1 - (\alpha_A^A)^n, \quad (4.115a)$$

and for the normalized signal intensity of the substrate,

$$\frac{I_B(n)}{I_B^0} = (\alpha_B^A)^n. \quad (4.115b)$$

Validity of (4.115a) and (4.115b) requires negligible bulk diffusion and full surface diffusion of the adsorbate. For constant flux of adsorbate atoms, J , the change of the intensities with time t is linear until completion of each layer. The slope of $I_A(t)$ is given by (4.115a) and decreases with higher n , as shown in Fig. 4.36 (full line). Such FM growth was observed, for example, for Sn on Cu, Cu on W, and Te on Fe [4.123].

Without surface diffusion, the growth rate (coverage change per time, $d\Theta/dt$) for the n th layer is proportional to the flux J of sticking adatoms and to the difference of coverage $\Theta_{n-1} - \Theta_n$ between the neighboring layers [4.123, 4.124]:

$$\frac{d\Theta_n}{dt} = J(\Theta_{n-1} - \Theta_n). \quad (4.116)$$

Since the intensity is proportional to the fractional coverage of each layer, it is easy to show that the intensity–thickness relations are now exponential functions with total equivalent layer thickness Jt [4.98, 4.123, 4.124]:

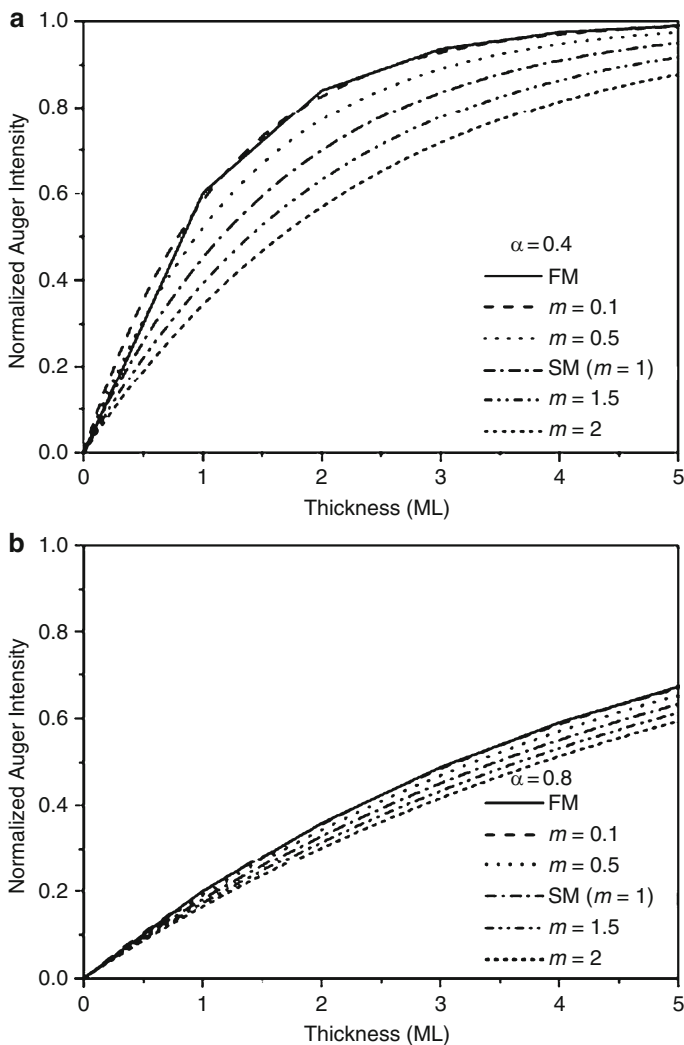


Fig. 4.36 Increase of normalized adsorbate signal intensity (AES or XPS) after (4.121a) (DCSM, model I) for different values of m , and two different transmission coefficients, (a) $\alpha_A^A = 0.4$ ($\lambda_{A,E(A)} \cos \theta = 1.1$ ML), (b) $\alpha_A^A = 0.8$ ($\lambda_{A,E(A)} \cos \theta = 4.5$ ML) (Reproduced from Q. Fu and T. Wagner [4.127]), with permission of Elsevier B.V.)

$$\frac{I_A(Jt)}{I_A^0} = 1 - \exp[-(1 - \alpha_A^A) Jt], \quad (4.117a)$$

$$\frac{I_B(Jt)}{I_B^0} = \exp[-(1 - \alpha_B^A) Jt]. \quad (4.117b)$$

If the total amount of adsorbate, Jt (in monolayers), is known (e.g., by measurement of quartz crystal frequency shift), the transmission coefficients α_A^A , α_B^A and therefore the attenuation lengths $\lambda_{A,E(A)}$, $\lambda_{A,E(B)}$ can be determined. Indeed, one of the first experimental determinations of attenuation length for Be, Ag, and C was reported by Seah [4.98] using (4.117a) and (4.117b). Many AES (and XPS) results of exponential signal variation during growth were interpreted as simultaneous multilayer (SM) growth [4.98, 4.123, and references therein]. It is obvious that both extreme cases of surface diffusion being fast (FM growth mode) or practically zero (SM growth mode) are rarely fulfilled. To describe appropriately intermediate cases, a so-called diffusion-corrected simultaneous multilayer (DCSM) model was introduced by Fu and Wagner [4.125]. This model takes into account dynamic change of layer coverage by vertical diffusion including up-step and down-step movement of adatoms which modifies SM growth. A diffusion-correction coefficient, f , was introduced, resulting in a modified growth rate according to

$$\frac{d\Theta_1}{dt} = J(1 - \Theta_1) + fJ(\Theta_1 - \Theta_1^2), \quad (4.118)$$

$$\frac{d\Theta_n}{dt} = J(\Theta_{n-1} - \Theta_n) + fJ(\Theta_{n-1}^2 - \Theta_{n-1} - \Theta_n^2 - \Theta_n) \quad \text{for } n > 1. \quad (4.119)$$

Down-step diffusion is obtained for $0 < f \leq 1$, with $f = 0$ (no diffusion) corresponding to the SM growth mode, and with $f = 1$ approaching the FM growth mode. Up-step diffusion results in island growth behavior (VM) and is characterized by $f < 0$ with a typical lower adsorbate intensity increase as compared to FM and SM [4.123]. Equations 4.118 and 4.119 can be used to calculate the coverage Θ_n for each individual layer as a function of the total number of adsorbate layers (or thickness) and given values of f . Then, the coverage-dependent XPS or AES intensities are given by

$$\frac{I_A(Jt)}{I_A^0} = (1 - \alpha_A^A) \left[\Theta_1 + \alpha_A^A \Theta_2 + (\alpha_A^A)^2 \Theta_2 + \cdots (\alpha_A^A)^n \Theta_{n+1} + \cdots \right] \quad (4.120a)$$

and

$$\frac{I_B(Jt)}{I_B^0} = 1 - (1 - \alpha_B^A) \left[\Theta_1 + \alpha_B^A \Theta_2 + (\alpha_B^A)^2 \Theta_2 + \cdots (\alpha_B^A)^n \Theta_{n+1} + \cdots \right]. \quad (4.120b)$$

Experimental data can be fitted to the above equations to determine the parameters α_A^A , α_B^A , and f . The advantage of the DCSM model is that the growth mode can be directly derived from these data. However, simulation of experimental data can only be done numerically. Therefore, Fu and Wagner developed a semiempirical analytical relation for the description of growth mode by introducing a new parameter called m [4.124]. Using the SM mode as a basis, their modification of (4.117a) and (4.117b) is given by

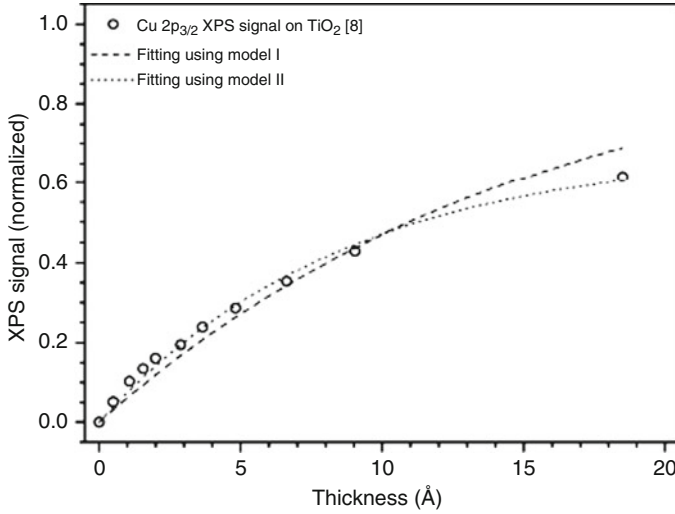


Fig. 4.37 Increase of the normalized $\text{Cu}2p_{3/2}$ XPS signal intensity for room temperature deposition of Cu on TiO_2 (110) surface. Open points are experimental results from Diebold et al. [4.126], the *dashed line* is a fit with (4.121a) (model I, Fig. 4.36), and the *dotted line* is an improved semiempirical analytical model (model II) (Reproduced from Q. Fu and T. Wagner [4.124], with permission of Elsevier B.V.)

$$\frac{I_A}{I_A^0} = 1 - \exp \left\{ - \left[1 - (\alpha_A^A)^m \right] \frac{Jt}{m} \right\} \quad (4.121a)$$

and

$$\frac{I_B}{I_B^0} = \exp \left\{ - \left[1 - (\alpha_B^A)^m \right] \frac{Jt}{m} \right\}. \quad (4.121b)$$

For $m > 1$, up-step diffusion leads to island growth mode (VW). Simultaneous multilayer growth mode (SM) is characterized by $m = 1$, and for $0 < m < 1$, down-step diffusion leads gradually to layer-by-layer growth mode (FM). These cases are shown in Fig. 4.36. The upper picture (A) is for low-energy photo- or Auger electrons ($\alpha_A^A = 0.4$ corresponds to $\lambda_{A,E(A)} = 1.1$ ML for $\theta = 0^\circ$), and the lower picture (B) is for high-energy electrons ($\alpha_A^A = 0.4$ gives $\lambda_{A,E(A)} = 4.5$ ML). Obviously, low-energy electrons (frequently used in AES) are more sensitive to thickness change and therefore to mechanism detection than high-energy electrons. A test of island growth (VW mode) can already be made by (4.100a) and (4.100b). For example, for a total amount of deposit corresponding to 2 ML in Fig. 4.36(A), full-layer coverage after (4.100a) gives $I_A/I_A^0 = 0.84$ (line FM or $m = 0.1$). For $m = 2$, $I_A/I_A^0 = 0.57$ is obtained after (4.121a). Since the amount $Jt = \Theta d = \text{const.} = 2$, (4.100a) gives an implicit equation for which yields $\Theta = 0.6$, corresponding to islands of average thickness $d = 3.3$ ML.

Using XPS, Diebold et al. [4.126] observed island growth (VW mode) when Cu is deposited on a clean TiO_2 substrate. A comparison of their main result with the models of Fu and Wagner is given in Ref. [4.124] and reproduced in Fig. 4.37.

The dashed line (fitting with model I) shows the fit with (4.121a) which yields $\alpha^{Cu}_{Cu(2p)} = 0.77$ and $m = 6$, in accordance with an electron escape depth of 3.8 ML (0.8 nm) and pronounced island growth. A slightly better fit is obtained with an improved analytical approximation (dotted line, called model II in Ref. [4.124]) of the more correct descriptions via (4.118) and (4.119), and (4.120a).

4.3.3.8 Grain Boundary Segregation: Fracture Surfaces

A prerequisite for studies of interfacial segregation is a well-defined surface with negligible contamination. Therefore, a sufficiently good ultrahigh vacuum (UHV) $< 10^{-7}$ Pa (see Sect. 2.1) is required, and all sample processing should be done in the UHV chamber, including intergranular, brittle fracture to “open” the grain boundary to surface analysis. Even then, however, slow contamination of the measured surface occurs, and therefore, a correction of the measured data is often necessary [4.127]. Usually, boundary cohesion is reduced by the segregants [4.112]. In some cases, a reduction of the fracture temperature (by liquid nitrogen) or a saturation of the sample by hydrogen facilitates brittle fracture. Although only one side of the sample is usually analyzed, a special sample holder can be used that gives access to both fracture surfaces [4.128] (see Fig. 8.2). Frequently, calibration can be performed by an “internal standard,” for example, by analyzing a part of the fracture layer generated by transgranular fracture which shows the bulk composition of the sample [4.114, 4.115].

After intergranular brittle fracture, the composition of the two resulting fracture surfaces can be analyzed by AES or XPS. Comparison with surface segregation is visualized in Fig. 4.38. The fracture path is schematically depicted in Fig. 4.38b by the bold line. The surface regions of fracture surface 1, FS1, and of surface 2, FS2, are partially covered with the amount Θ_1 and $\Theta_2 = (1 - \Theta_1)$ of the total interfacial segregation layer. The remaining surface parts without segregation layer possess the bulk composition. For component A, we get two equations, one for free surface 1, FS1,

$$\begin{aligned} \left(\frac{I_A}{I_A^0} \right)_{FS1} &= \Theta_1 X_A^s \left\{ 1 - \exp \left[-\frac{d}{\lambda_{s,E(A)} \cos \theta} \right] \right\} \\ &+ \Theta_1 X_A^b \exp \left[-\frac{d}{\lambda_{s,E(A)} \cos \theta} \right] + (1 - \Theta_1) X_A^b \end{aligned} \quad (4.122a)$$

and a corresponding equation for free surface 2, FS2,

$$\begin{aligned} \left(\frac{I_A}{I_A^0} \right)_{FS2} &= (1 - \Theta_1) X_A^s \left\{ 1 - \exp \left[-\frac{d}{\lambda_{s,E(A)} \cos \theta} \right] \right\} \\ &+ (1 - \Theta_1) X_A^b \exp \left[-\frac{d}{\lambda_{s,E(A)} \cos \theta} \right] + \Theta_1 X_A^b \end{aligned} \quad (4.122b)$$

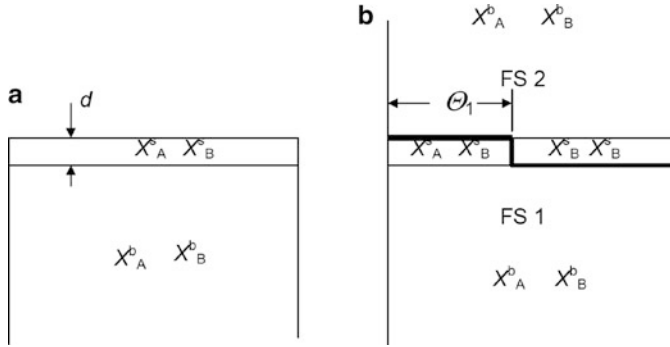


Fig. 4.38 Schematic representation of the studied surfaces in (a) surface segregation and (b) grain boundary segregation, showing interfacial brittle fracture for a binary system with surface and bulk compositions X_A^s , X_B^s and X_A^b , X_B^b , respectively, and segregation layer thickness d . FS1 and FS2 denote the free surfaces after fracture, Θ_1 the coverage of FS1, and the **bold line** indicates the fracture path. It is evident that in case of FS2, the surface coverage is $1-\Theta_1$

For the sum of (4.122a) and (4.122b), the expressions with coverage Θ_1 cancel, and we obtain

$$\left(\frac{I_A}{I_A^0}\right)_{\text{FS1}} + \left(\frac{I_A}{I_A^0}\right)_{\text{FS2}} = X_A^s \left[1 - \exp\left(-\frac{d}{\lambda_{s,E(A)} \cos \theta}\right) \right] + X_A^b \left[1 + \exp\left(-\frac{d}{\lambda_{s,E(A)} \cos \theta}\right) \right], \quad (4.122c)$$

and instead of (4.104), X_A^s is given by

$$X_A^s = \frac{\left(\frac{I_A}{I_A^0}\right)_{\text{FS1}} + \left(\frac{I_A}{I_A^0}\right)_{\text{FS2}} - X_A^b \left\{ 1 + \exp\left[-\frac{d}{\lambda_{s,E(A)} \cos \theta}\right] \right\}}{1 - \exp\left[-\frac{d}{\lambda_{s,E(A)} \cos \theta}\right]}. \quad (4.123)$$

At symmetrical boundaries, the distribution of the segregants between two FSs is homogeneous, $(I_A)_{\text{FS1}} = (I_A)_{\text{FS2}}$, and we may simply double the measured signal of one FS to obtain the amount of X_A^s in the grain boundary [4.128]. For asymmetrical grain boundaries, in general, $(I_A)_{\text{FS1}} \neq (I_A)_{\text{FS2}}$ and both FSs have to be studied. An example is shown in Fig. 4.39, for the two free surfaces obtained after intergranular fracture (performed in an AES instrument) through a (001)/(011) asymmetrical tilt boundary of an annealed Fe(Si,P,C) bicrystal [4.128]. The relative Auger intensities measured at both fracture surfaces are shown for phosphorus and silicon as a function of the annealing temperature. As seen from Fig. 4.39, a systematic difference exists between the chemical composition of the two FSs: the FS along the grain boundary plane (011) with the more dense structure exhibits less “segregation effects” than the FS along the plane (001) [4.128].

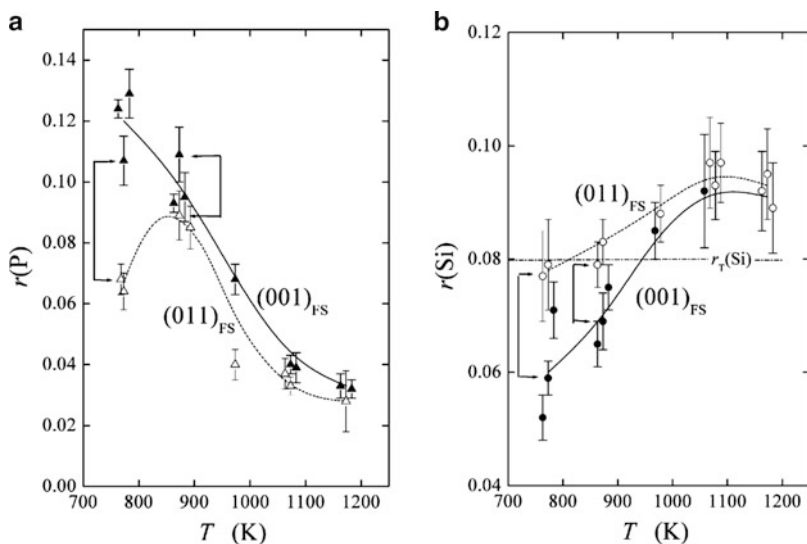


Fig. 4.39 Measured relative Auger intensities at both matching fracture surfaces (free surfaces, FS) of the (001)/(011) asymmetrical tilt grain boundary in Fe, for (a) phosphorus and (b) silicon [4.128]. The measured intensity ratios are $r(P) = I_P/I_{Fe}$ and $r(Si) = I_{Si}/I_{Fe}$ for the (001)_{FS} (solid symbols, full line) and (011)_{FS} (empty symbols, dotted line). The arrows connecting two points designate the one-to-one analysis at the same points of the matching fracture surfaces. $r_T(Si)$ designates the value of $r(Si)$ corresponding to the bulk (transgranular) state (From P. Lejček and S. Hofmann [4.128])

4.3.3.9 Influence of a Contamination Layer

In general, any sample is covered with a thin contamination layer that is difficult to remove without changing the underlying sample surface. The most frequently used method is sputter cleaning which is likely to change an alloy or oxide composition because of different element-specific sputtering rates of the components (preferential sputtering, see Sect. 7.1). Therefore, quantification of a sample below a surface contamination layer (the thickness and composition of which is unknown) is frequently required. Let us consider the following two cases: (1) a homogeneous alloy below a contamination layer, and (2) a thin film with a contamination layer (double layer structure).

(1) Contamination Layer on a Homogeneous Substrate

The most common case is that of a thin contamination layer on a homogeneous binary system as depicted in Fig. 4.40a. For the case where the electron energies of the components are similar, their attenuation by the overlayer is the same, and the exponential term cancels in the intensity ratio. However, this is rarely the case. For an alloy (or an oxide with unknown stoichiometry), peaks with different electron energies have to be considered. The contamination layer most frequently consists of

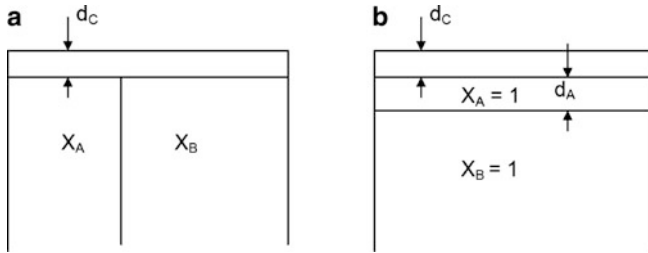


Fig. 4.40 Schematic view of a contamination layer of thickness d_C on a sample with (a) a homogeneous binary bulk composition with mole fractions X_A , X_B , and (b) a layer of thickness d_A of pure A on pure B with a second layer on top

a hydrocarbon layer for which the attenuation length is difficult to obtain. However, as, for example, shown by Thomas and Hofmann [4.129], an indirect method can be applied which uses the intensity of the measured carbon peak to characterize the influence of the contamination layer, as pointed out in the following.

Because the elemental signal strength of both components A, B is attenuated by $\exp[-d_C/(\lambda_{C,E(A)} \cos \theta)]$, the expected normalized intensity ratio is given by

$$\begin{aligned} \frac{I_A I_{B,m}^0}{I_{A,m}^0 I_B} &= \frac{X_A}{X_B} \frac{\exp\left[-\frac{d_C}{\lambda_{C,E(A)} \cos \theta}\right]}{\exp\left[-\frac{d_C}{\lambda_{C,E(B)} \cos \theta}\right]} = \frac{X_A}{X_B} \exp\left[-\frac{d_C}{\lambda_{C,E(A)} \cos \theta} \left(1 - \frac{\lambda_{C,E(A)}}{\lambda_{C,E(B)}}\right)\right] \\ &= \frac{X_A}{X_B} \exp\left[-\frac{d_C}{\lambda_{C,E(C)} \cos \theta} \left(\frac{E_C}{E_A}\right)^{0.75} \left(1 - \left(\frac{E_A}{E_B}\right)^{0.75}\right)\right], \end{aligned} \quad (4.124a)$$

where X_A , X_B are the mole fractions of A and B, d_C is the thickness of the contamination layer, and $\lambda_{C,E(A)}$, $\lambda_{C,E(B)}$, and $\lambda_{C,E(C)}$ are the attenuation lengths of the respective signals of A, B, and C in the carbonaceous contamination layer. Using again the relation $\lambda_{C,E(i)}/\lambda_{C,E(C)} = (E_i/E_C)^{0.75}$ with E_i , E_C the kinetic energies of the emitted Auger- or photoelectrons of element i ($=A$ or B) and carbon (C), we obtain the normalized intensity ratio $(I_A/I_{A,m}^0)/(I_B/I_{B,m}^0)$ for a given composition X_A/X_B as a function of the contamination layer thickness $d_C/(\lambda_{C,E(C)} \cos \theta)$ from (4.124a). It is important to keep in mind that the standard elemental intensities I_A^0 , I_B^0 have to be replaced by the matrix-corrected standard intensities $I_{A,m}^0$ and $I_{B,m}^0$ (or in the ratio by the matrix relative sensitivity factors $S_{A,m}/S_{B,m} = S_{A,B,m}$ (see Sect. 4.3.2)). Equation 4.124a is plotted for $I_A/I_B = I_O/I_{Si}$ in Fig. 4.41 for a typical example of a carbonaceous contamination layer on SiO_2 ($X_A/X_B = X_O/X_{Si} = 2$) and with the respective parameters for an AlK_α source, $E_O(1s) = 954 \text{ eV}$, $E_{Si}(2p) = 1387 \text{ eV}$, and $E_C(1s) = 1202 \text{ eV}$, assuming carbon C 1s as representative for a carbonaceous contamination layer, and I_A^0/I_B^0 is replaced by $S_{O,m}/S_{Si,m} = 3.11$ [4.2] (see Sect. 4.3.2).

For another relation, that of the ratio of the contamination signal intensity (usually that of carbon, I_C , in a CH_xO_y matrix) to that of one of the elements,

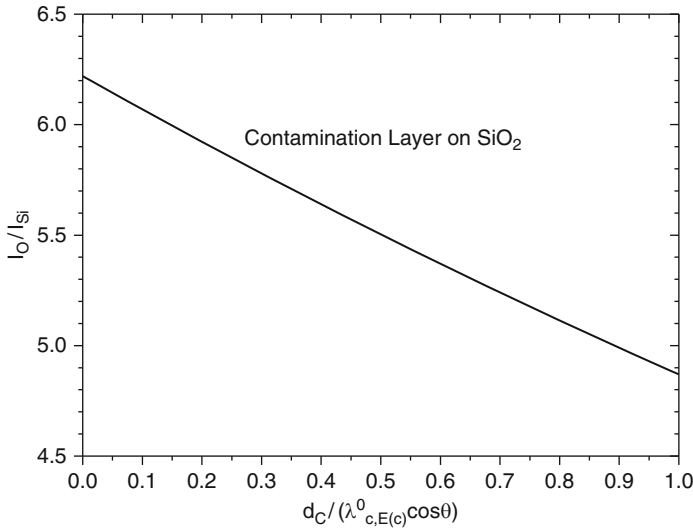


Fig. 4.41 Measured intensity ratio I_O/I_{Si} as a function of relative contamination layer thickness, $d_C/(\lambda_{C,E(C)} \cos \theta)$ for stoichiometric SiO_2 , $X_O/X_{Si} = 2.0$, after (4.124a), with $I_A^0/I_B^0 = S_{O,m}/S_{Si,m} = 3.11$ [4.2] (see Sect. 4.3.2)

for example, B, we obtain, in analogy to (4.98), the ratio of the normalized layer element intensity to the intensity of one element in the bulk, for example, B, $(I_C/I_{C,m}^0)/(I_B/I_{B,m}^0)$, with mole fraction $X_B = 1/(1 + X_A/X_B)$ in the bulk

$$\frac{I_C I_{B,m}^0}{I_{C,m}^0 I_B} = X_B \left\{ \exp \left[-\frac{d_C}{\lambda_{C,E(B)} \cos \theta} \right] - \exp \left[-\frac{d_C}{\lambda_{C,E(C)} \cos \theta} \left(1 - \frac{\lambda_{C,E(C)}}{\lambda_{C,E(B)}} \right) \right] \right\} \quad (4.124b)$$

and with the kinetic-energy approximation for the attenuation lengths as above:

$$\frac{I_C I_{B,m}^0}{I_{C,m}^0 I_B} = \left(\frac{1}{1 + \frac{X_A}{X_B}} \right) \left\{ \exp \left[-\frac{d_C}{\lambda_{C,E(C)} \cos \theta} \left(\frac{E_C}{E_B} \right)^{0.75} \right] - \exp \left[-\frac{d_C}{\lambda_{C,E(C)} \cos \theta} \left(1 - \left[\frac{E_C}{E_B} \right]^{0.75} \right) \right] \right\}. \quad (4.124c)$$

Because the exact composition of the contamination layer is unknown, we assume for simplicity a pure C layer with respect to attenuation length and sensitivity factors ($I_{C,m}^0 = I_C^0$). This simplification is only of importance if the thickness and composition of the contamination layer is required. The dependence of the normalized intensity ratio $(I_C/I_C^0)/(I_B/I_B^0)$ (for $B = Si$) on the relative contamination layer thickness, $d_C/(\lambda_{C,E(C)} \cos \theta)$, after (4.124b) and (4.124c) is shown in Fig. 4.42 using the same parameters as for Fig. 4.41.

By combination of (4.124a) and (4.124c), we can eliminate $d_C/(\lambda_{C,E(C)} \cos \theta)$ and obtain the ratio X_A/X_B as an implicit function of the measured and normalized intensity ratios $(I_C/I_B)/(I_C^0/I_B^0)$ and $(I_A/I_B)/(I_A^0/I_B^0)$:

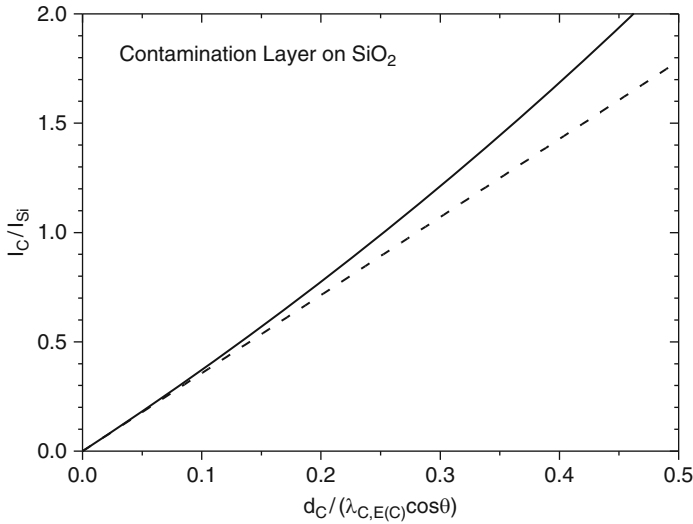


Fig. 4.42 Measured intensity ratio I_C/I_{Si} of stoichiometric SiO_2 as a function of the relative contamination layer thickness, $d_C/(\lambda_{C,E(C)} \cos \theta)$ (solid line) after (4.124c), and linear approximation after (4.125). Note that the contamination layer influence is only a correction

$$\frac{I_C I_B^0}{I_C^0 I_B} = \left(\frac{1}{1 + \frac{X_A}{X_B}} \right) \left\{ \begin{array}{l} \exp \left[-\frac{1}{\left(\frac{E_C}{E_B} \right)^{0.75} - 1} \ln \left(\frac{I_A I_{B,m}^0 X_B}{I_B I_{A,m}^0 X_A} \right) \right] \\ - \exp \left[-\frac{\left(\frac{E_B}{E_C} \right)^{0.75} - 1}{\left(\frac{E_B}{E_A} \right)^{0.75} - 1} \ln \left(\frac{I_A I_{B,m}^0 X_B}{I_B I_{A,m}^0 X_A} \right) \right] \end{array} \right\}. \quad (4.124d)$$

Equation 4.124d couples the measured intensity ratios I_C/I_B and I_A/I_B with the correct bulk composition of the sample below the surface layer, X_A/X_B , without the necessity of explicit determination of the thickness of the contamination layer [4.99]. If the stoichiometry of a standard sample with a contamination layer on top is known, the layer thickness is known from (4.124d) and (4.124c), and the ratio of the matrix-corrected relative sensitivity factors can be obtained from (4.124a).

For low levels of contamination, (4.124d) can be simplified. If $d_C/(\lambda_{C,E(C)} \cos \theta) \ll 1$, the exponential functions in (4.124c) can be developed which gives the linear relation (indicated in Fig. 4.42)

$$\frac{I_C}{I_B} = \frac{I_C^0}{I_B^0} \left(\frac{1}{1 + \frac{X_A}{X_B}} \right) \frac{d_C}{\lambda_{C,E(C)} \cos \theta}. \quad (4.125)$$

Equation 4.125 can be introduced in (4.124a) by elimination of $d_C/(\lambda_{C,E(C)} \cos \theta)$, giving

$$\frac{I_A}{I_B} = \frac{I_{A,m}^0}{I_{B,m}^0} \frac{X_A}{X_B} \left\{ \exp \left[- \left(\frac{I_C I_B^0}{I_B I_C^0} \right) \right] \left(\frac{1}{1 + \frac{X_A}{X_B}} \right) \left(\frac{E_C}{E_A} \right)^{0.75} \left(1 - \left(\frac{E_A}{E_B} \right)^{0.75} \right) \right\}. \quad (4.126)$$

A graphical solution of (4.126) is shown in Fig. 4.43 for a carbonaceous contamination layer on silicon dioxide, with A = O(1s), and B = Si(2p), assuming carbon C 1s as representative of the contamination layer, and the matrix relative sensitivity factors and kinetic energies as pointed out in Sect. 4.3.2 [4.2]. A similar diagram with the respective values for MgK_α radiation was reported by Thomas and Hofmann [4.129] to disclose the stoichiometry of SiO_2 in the presence of contamination layers of various thicknesses. A comparison with the exact (4.124d) shows that even for a high ratio $I_C/I_{Si} = 1$, the error is only about 1%.

Of course, the above equations apply also to general overlayer structures. In the following, we will consider the next more complicated case of a contamination overlayer on a thin film, or a bilayer on a homogeneous bulk.

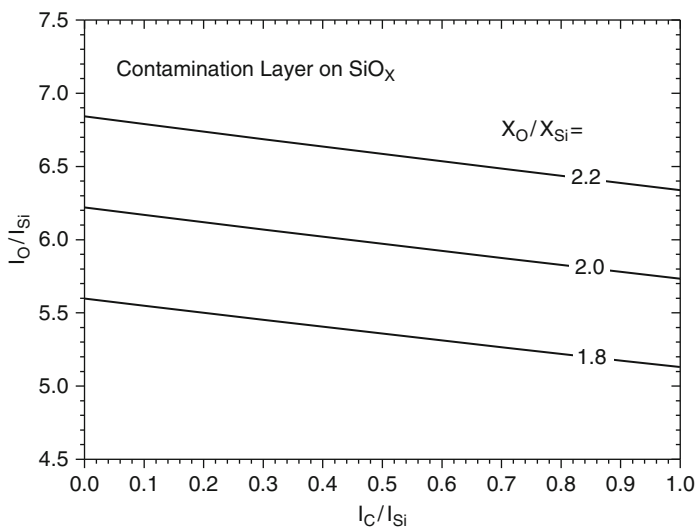


Fig. 4.43 Effect of a carbonaceous contamination layer, represented by the intensity ratio of carbon (1s) to silicon (2p), I_C/I_{Si} , on the measured ratio of intensities of O 1s to Si 2p, I_O/I_{Si} , for silicon oxide with different oxygen/silicon mole fraction ratios X_O/X_{Si} , after (4.126), with sensitivity factors as in Figs. 4.41 and 4.42. The measured intensity ratio values determine a point in the diagram that lies on a line given by the mole fraction X_O/X_{Si}

(2) Contamination Layer on a Thin Film: Double-Layer Structure

A more complicated situation arises when the contamination layer is not on a homogeneous binary alloy as described above (see Fig. 4.40a) but on a layered structure as depicted in Fig. 4.40b. A typical case is evaporation of a layer of A on B or segregation of A if the bulk concentration of A in B is negligible [4.127,4.128] (see Fig. 4.29b), both covered with a contamination layer. Of course, Fig. 4.40b applies to any two layers of C and A on substrate B (double-layer structure), for example, for interfacial layers (A) beneath a surface layer (C) (see Sect. 4.3.3.10). Let us consider the layer structure depicted in Fig. 4.40b and in the inset of Fig. 4.4. The normalized intensity I_A/I_A^0 of layer A with thickness d_A is given by (4.88a) multiplied with the weakening factor of layer C with thickness d_C given by (4.88b). With the electron attenuation lengths $\lambda_{C,E(A)}$ and $\lambda_{A,E(A)}$ for $E(A)$ in layer C and in layer A, respectively, we get

$$\frac{I_A}{I_A^0} = \exp \left[-\frac{d_C}{\lambda_{C,E(A)} \cos \theta} \right] \left\{ 1 - \exp \left[-\frac{d_A}{\lambda_{A,E(A)} \cos \theta} \right] \right\}. \quad (4.127a)$$

The intensity of element B is attenuated by two layers, A and C,

$$\frac{I_B}{I_B^0} = \exp \left[-\frac{d_A}{\lambda_{A,E(B)} \cos \theta} \right] \exp \left[-\frac{d_C}{\lambda_{C,E(B)} \cos \theta} \right], \quad (4.127b)$$

and the intensity of the contamination layer peak is

$$\frac{I_C}{I_C^0} = 1 - \exp \left[-\frac{d_C}{\lambda_{C,E(C)} \cos \theta} \right]. \quad (4.127c)$$

Combining (4.127a) and (4.127b), and introducing the kinetic-energy relation for different attenuation lengths in the same matrix as above, we get for the normalized intensity ratio

$$\frac{I_A I_B^0}{I_B I_A^0} = \left\{ \exp \left[-\left(\frac{d_C}{\lambda_{C,E(C)} \cos \theta} \right) \left[\left(\frac{E_C}{E_A} \right)^{0.75} - \left(\frac{E_C}{E_B} \right)^{0.75} \right] \right] \right. \\ \left. \times \left[\exp \left[\left(\frac{d_A}{\lambda_{A,E(A)} \cos \theta} \right) \left(\frac{E_A}{E_B} \right)^{0.75} \right] - \exp \left[-\left(\frac{d_A}{\lambda_{A,E(A)} \cos \theta} \right) \right] \left(1 - \left(\frac{E_A}{E_B} \right)^{0.75} \right) \right] \right\}. \quad (4.127d)$$

Equation 4.127d gives the measured intensity ratio I_A/I_B as a function of both the relative layer thickness of A and of the contamination layer C. It is clear that for the same kinetic energy of A and B, $E_A = E_B$, the first exponential function in (4.127c) is unity, and (4.127d) is equal to (4.90a). For example, using the zero valence peak and the oxide peak of Si for determination of the thickness of an SiO_2 layer on Si,

the latter is immediately obtained from the ratio of both Si peaks, and independent of the contamination layer thickness and composition.

If $E_A \neq E_B$, the intensity ratio of layer A to substrate B depends on both the thickness of layer A and that of the contamination layer. For a given intensity ratio, there is an infinite number of combinations of d_A and d_C , mainly depending on the peak energies. However, with the measured and normalized intensities in (4.127a, b, c), a solution for the thickness of the two layers can be given. Replacing the term with d_C in (4.127b) by that in (4.127c) and correcting for the different energies gives

$$\frac{I_B}{I_B^0} = \exp \left[\frac{d_A}{\lambda_{A,E(A)} \cos \theta} \left(\frac{E_A}{E_B} \right)^{0.75} \right] \left(1 - \frac{I_C}{I_C^0} \right)^q \quad (4.127e)$$

and

$$\frac{d_A}{\lambda_{A,E(A)} \cos \theta} = \left(\frac{E_B}{E_A} \right)^{0.75} \ln \left[\frac{\left(1 - \frac{I_C}{I_C^0} \right)^q}{\left(\frac{I_B}{I_B^0} \right)} \right], \quad (4.127f)$$

with the exponent $q = (E_B/E_C)^{0.75}$. Inserting (4.128b) in (4.127a) gives for the outer (contamination) layer thickness:

$$\frac{d_C}{\lambda_{C,E(C)} \cos \theta} = \left(\frac{E_A}{E_B} \right)^{0.75} \ln \left[\frac{1 - \exp \left(-\frac{d_A}{\lambda_{A,E(A)} \cos \theta} \right)}{\left(\frac{I_A}{I_A^0} \right)} \right]. \quad (4.127g)$$

An illustration of (4.128a–c) with a graphical solution is given in Figs. 4.44 and 4.45. As an example, let us assume a layer of Al (= A) on bulk Fe (= B) with a carbon contamination layer (= C) on top. With the respective kinetic energies of C 1s ($E_C = 1202$ eV), Al 2p ($E_A = 1416$ eV), and Fe 2p_{3/2} ($E_B = 780$ eV) [4.23], the relative layer thickness of Al, $d_A/(\lambda_{A,E(A)} \cos \theta)$, is determined by the measured and normalized intensities, I_C/I_C^0 and I_B/I_B^0 , after (4.128a, b), as shown by the blue dashed lines in Fig. 4.44 for $I_C/I_C^0 = 0.4$, and $I_B/I_B^0 = 0.3$. With the value for $d_A/(\lambda_{A,E(A)} \cos \theta) = 1.31$ thus obtained, we get from (4.128c) the relative top (contamination) layer thickness using the measured and normalized intensity $I_B/I_B^0 = 0.5$, as demonstrated in Fig. 4.45 (blue dashed arrows).

A disadvantage of the above method is the necessity of standard intensity values. For example, using as an approximation the elemental relative sensitivity factors (E-RSFs) after Wagner [4.74] for I_i^0 , we get for the relative intensity of the measured values (in arbitrary units) in the above example $I_C = 0.4/I_C^0 = 1.6$, $I_{Al} = 0.5/I_{Al}^0 = 2.7$, and $I_{Fe} = 0.3/I_{Fe}^0 = 0.15$. Angle-resolved measurements can be used to overcome the problem of using standard intensities, as shown below.

An alternative method to solve the contamination layer-on-layer problem was proposed by Cumpson [4.111], namely, to tilt the sample until the intensity of the substrate (B) vanishes and the contamination layer can be treated as a single film

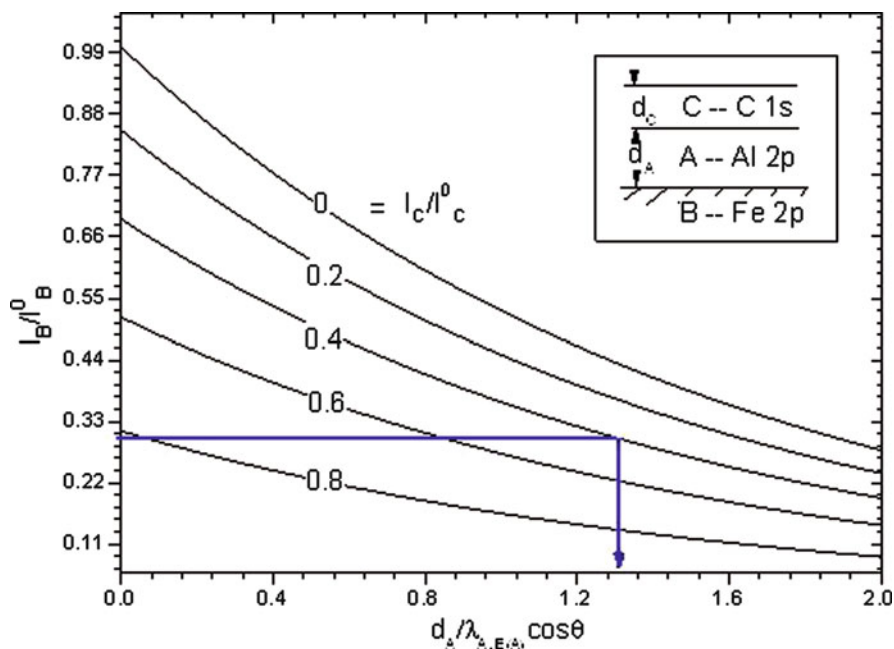


Fig. 4.44 Dependence of the normalized intensity of substrate element B, I_B/I_B^0 , on the relative layer thickness of A, $d_A/(\lambda_{A,E(A)} \cos \theta)$, for different normalized intensities I_C/I_C^0 of the (contamination) layer of C, for the layer structure shown in the *inset*, after (4.127e, f). The respective kinetic energies are for C = carbon layer, $E_C = E(\text{C } 1s) = 1202 \text{ eV}$, A = Al layer, $E_A = E(\text{Al } 2p) = 1416 \text{ eV}$, and B = Fe = bulk, $E_B = E(\text{Fe } 2p_{3/2}) = 780 \text{ eV}$ [4.23]. Blue lines show determination of $d_A/(\lambda_{A,E(A)} \cos \theta)$ using $I_B/I_B^0 = 0.3$, $I_C/I_C^0 = 0.4$. For details, see text

of C on (quasibulk) substrate A as above with (4.99) to determine the contamination layer thickness first. Then, (4.127d) can be solved. However, this method requires careful sample tilt and is restricted to rather thick overlayers because the useful tilt angle should be below $60\text{--}70^\circ$ to avoid the influence of elastic scattering. In contrast, the direct method explained above works for constant emission angle, i.e., without sample tilt. However, the advantage of using two different angles enables standardless determination of the two layer thicknesses.

4.3.3.10 A Special Case: Interface Layer Between Metal and Full Oxide Layer

It is obvious that the contamination layer can be replaced by any other layer of a component. Therefore, the above equations can be used to quantify any double-layer system, as frequently encountered in alloy oxidation [4.131, 4.132, 4.133, 4.134, 4.135] and transition metal oxidation [4.134, 4.135, 4.136]. (Such layer structures are advantageously studied with emission angle-resolved XPS or AES (see Sect. 7.2).)

A simple case is observation of the growth of an oxide layer on an initially generated suboxide layer in low-temperature oxidation of transition metals, for

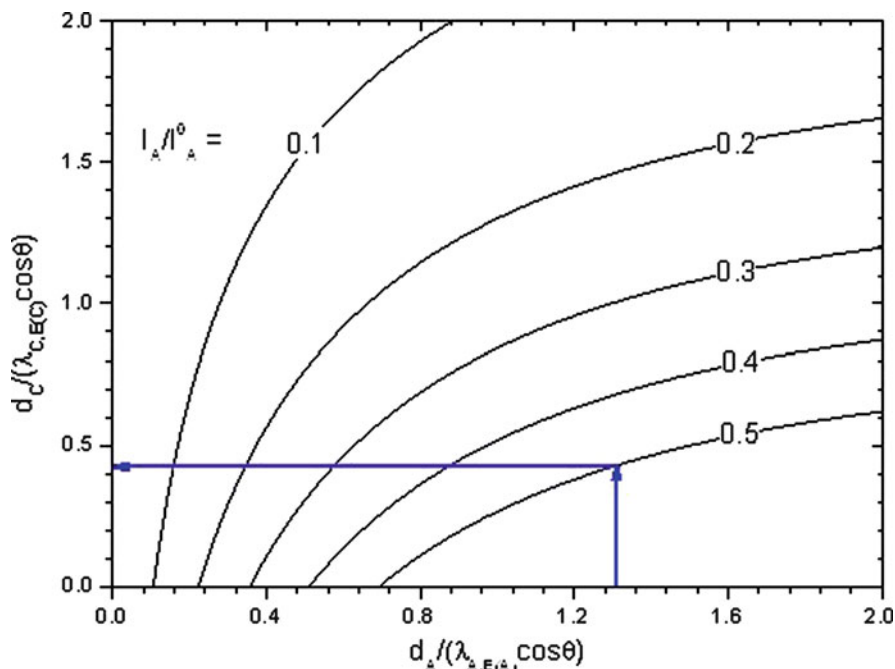


Fig. 4.45 Relation between the relative contamination layer thickness, $d_C/(\lambda_{C,E(C)} \cos \theta)$, and the relative thickness of layer A, $d_A/(\lambda_{A,E(A)} \cos \theta)$, for different values of the normalized intensity of A, I_A/I_A^0 , after (4.127g). Elements and kinetic energy values as in Fig. 4.44 (A = Al, B = Fe). Blue arrows refer to the example of Fig. 4.44 described in the text

example, Ta and Nb [4.136]. The bulk intensity is given by the metallic element peak, the suboxide layer by the same peak shifted about 1 eV to higher binding energy, and the pentoxide by the Me^{5+} peak shifted a few eV further. Therefore, all attenuation length values are the same in (4.127a)–(4.127d). For A denoting the suboxide (so) interlayer of constant thickness, $I_A/I_A^0 = I_{\text{so}}/I_{\text{so}}^0$ (4.127a), C the growing oxide $I_C/I_C^0 = I_{\text{ox}}/I_{\text{ox}}^0$, (4.127c), and B the metal substrate $I_B/I_B^0 = I_{\text{met}}/I_{\text{met}}^0$, (4.127b), the dependencies of the intensities on the oxide layer thickness are directly obtained, as shown in the inset of Fig. 4.46. Here, simultaneous multilayer (SM) growth is assumed (see (4.121a) and (4.121b), $m = 1$, and Fig. 4.36). An example for oxidation of Ta is given in Fig. 9.15.

With $I_A/I_A^0 = I_{\text{so}}/I_{\text{so}}^0$, the simplified conditions $E_A = E_C = E_{\text{ox}} = E_{\text{so}}$, and $\lambda_{\text{ox}} = \lambda_{\text{so}} = \lambda$, we get from (4.127d), for the relative suboxide layer thickness, d_{so}/λ :

$$\frac{d_{\text{so}}}{\lambda} = \cos \theta \ln \left[1 + \frac{I_{\text{so}} I_{\text{met}}^0}{I_{\text{so}}^0 I_{\text{met}}} \right]. \quad (4.128a)$$

Introducing the oxide intensity (corresponding to d_C in (4.127c)) in (4.127b) with $I_B/I_B^0 = I_{\text{met}}/I_{\text{met}}^0$ yields another expression for the thickness of the suboxide interlayer:

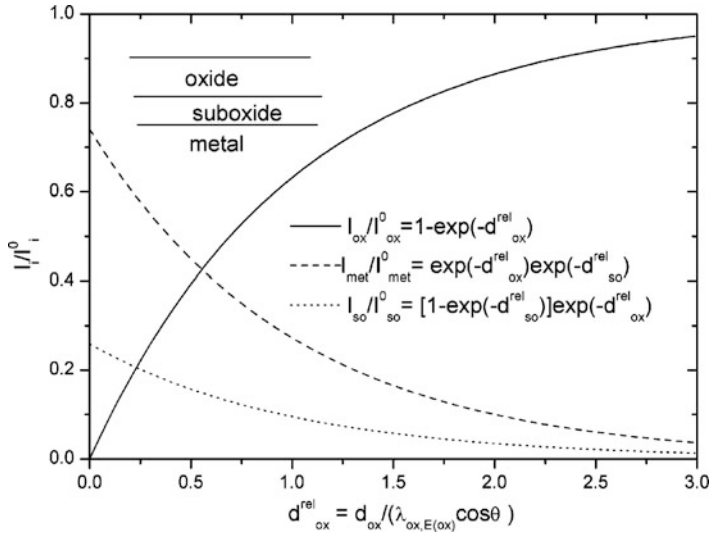


Fig. 4.46 Intensities of a system of 2 layers on a substrate, according to (4.127a)–(4.127c) for all λ values equal, $\cos \theta = 1$, as a function of the relative layer thickness d_{ox}/λ of the first layer (e.g., oxide layer, I_{ox}) after formation of a given constant relative interlayer thickness, $d_{so}/\lambda = 0.3$ (e.g., suboxide, I_{so}) on a metal substrate, I_{met}

$$\frac{d_{so}}{\lambda} = \cos \theta \ln \left[\frac{I_{met}^0}{I_{met}} \left(1 - \frac{I_{ox}}{I_{ox}^0} \right) \right]. \quad (4.128b)$$

Expressions (4.128a) can be used to test the interrelations between the three measured intensities and thus for determination of the standard intensity I_{so}^0 which is difficult to obtain. However, the interface layer thickness for a given oxide thickness can be obtained without the need of any standard intensity by two measurements at two different emission angles θ_1 , θ_2 in (4.127a) and (4.127b) which gives

$$\frac{I_{so}(\theta_1)/I_{so}^0(\theta_1)}{I_{so}(\theta_2)/I_{so}^0(\theta_2)} = \frac{\left\{ 1 - \exp \left[-\frac{d_{so}}{\lambda \cos \theta_1} \right] \right\} \exp \left[-\frac{d_{ox}}{\lambda \cos \theta_1} \right]}{\left\{ 1 - \exp \left[-\frac{d_{so}}{\lambda \cos \theta_2} \right] \right\} \exp \left[-\frac{d_{ox}}{\lambda \cos \theta_2} \right]}, \quad (4.128c)$$

where all the quantities independent of θ cancel and $I_{so}^0(\theta_2)/I_{so}^0(\theta_1) = \cos \theta_2 / \cos \theta_1$ (see (4.41)). With (4.128c), the explicit solution for the relative oxide layer thickness above the suboxide layer is given by

$$d_{ox}/\lambda = \frac{\cos \theta_1 \cos \theta_2}{(\cos \theta_1 - \cos \theta_2)} \ln \left(\frac{\left\{ 1 - \exp \left[-\frac{d_{so}}{\lambda \cos \theta_2} \right] \right\} \cos \theta_2 I_{so}(\theta_1)}{\left\{ 1 - \exp \left[-\frac{d_{so}}{\lambda \cos \theta_1} \right] \right\} \cos \theta_1 I_{so}(\theta_2)} \right). \quad (4.128d)$$

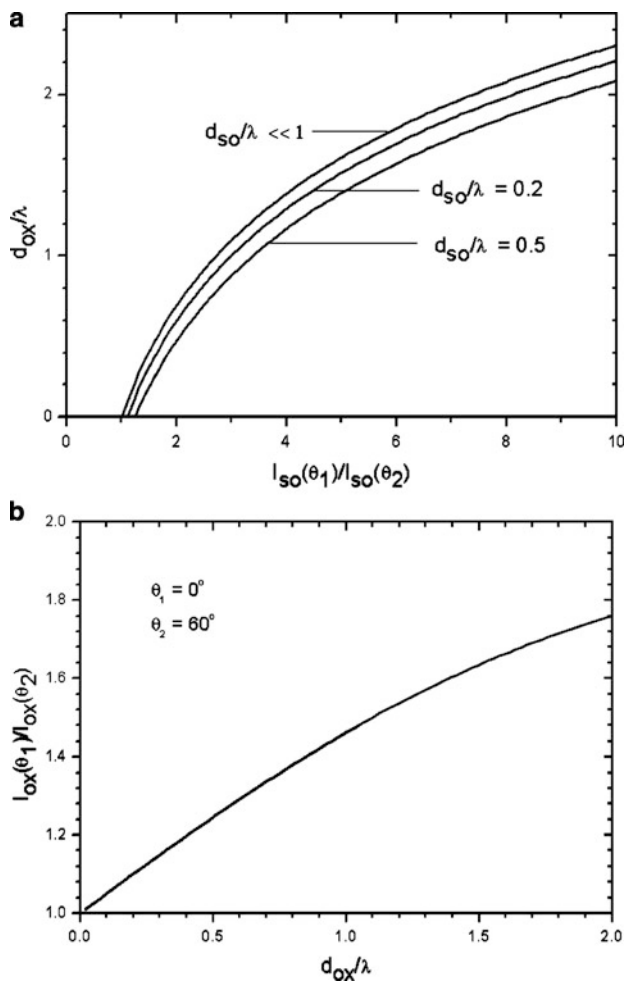


Fig. 4.47 (a) Relative oxide layer thickness d_{ox}/λ as a function of the ratio of interfacial suboxide layer intensity, $I_{so}(\theta_1)/I_{so}(\theta_2)$, for $\theta_1 = 0^\circ$, $\theta_2 = 60^\circ$ and for three different values of $d_{so}/\lambda = 0.2, 0.5$, and $d_{so}/\lambda \ll 1$, after (4.128d). Note the shift to lower values d_{ox}/λ with increasing d_{so}/λ . (b) Relation between the intensity ratio of the oxide peak $I_{ox}(\theta_1)/I_{ox}(\theta_2)$ at $\theta_1 = 0^\circ$ and $\theta_2 = 60^\circ$ after (4.128f). With d_{ox}/λ obtained here, d_{so}/λ can be determined in (a).

For a very thin interfacial suboxide layer, $d_{so}/\lambda \ll 1$ and the respective exponential functions in (4.128d) can be developed resulting in

$$d_{ox}/\lambda = \frac{\cos \theta_1 \cos \theta_2}{(\cos \theta_1 - \cos \theta_2)} \ln \left(\frac{I_{so}(\theta_1)}{I_{so}(\theta_2)} \right). \quad (4.128e)$$

For $\theta_1 = 0$ and $\theta_2 = 60^\circ$, (4.128d) and (4.128e) are depicted in Fig. 4.47a for different values of d_{so}/λ . For any finite thickness of the interfacial suboxide layer, the exact equation (4.128d) has to be used, as shown in Fig. 4.47. Thus, expression (4.128e) does not represent the “effective depth” ($< z >$) of the suboxide layer as

assumed in [4.132, 4.133]. For the layer structure considered here, the latter is given by $\langle z \rangle \approx d_{\text{ox}} + d_{\text{so}}/2$, i.e., the depth of the center of the suboxide layer. This demonstrates that the “effective depth” depends on the actual in-depth distribution of composition (layer structure, see (4.87)).

Equation 4.127c provides an implicit expression for the relative oxide layer thickness as a function of the ratio of oxide intensities at the two emission angles θ_1 and θ_2 , given by

$$\frac{I_{\text{ox}}(\theta_1)}{I_{\text{ox}}(\theta_2)} = \frac{\cos \theta_1}{\cos \theta_2} \frac{\left\{ 1 - \exp \left[-\frac{d_{\text{ox}}}{\lambda \cos \theta_1} \right] \right\}}{\left\{ 1 - \exp \left[-\frac{d_{\text{ox}}}{\lambda \cos \theta_2} \right] \right\}}. \quad (4.128f)$$

Expression (4.128f) is shown in Fig. 4.47b for $\theta_1 = 0^\circ$ and $\theta_2 = 60^\circ$. The oxide intensity ratio determines d_{ox}/λ which in turn is used to determine d_{so}/λ with the measured ratio $I_{\text{so}}(\theta_1)/I(\theta_2)$ in Fig. 4.47a.

Note that expressions (4.128a)–(4.128f) are valid for the asymmetry factor $W(\psi) = W(54.7^\circ) = 1$. For measurements with changing $\psi(\theta)$, the measured intensities $I_{\text{so}}(\theta_1)$ and $I_{\text{so}}(\theta_2)$ have to be multiplied with $W(\psi(\theta_1))$ and $W(\psi(\theta_2))$, respectively [4.132, 4.133] (see Sect. 4.3.2, Thetaprobe).

4.4 Quantitative AES

4.4.1 Fundamental Quantities for AES

Most of the basic relations for AES are formally similar to those for XPS. The fundamental equation for AES intensities is similar to (4.32) and (4.39), except that the photoelectron intensity, photoionization cross section, and angular asymmetry term are replaced by the following new parameters: electron-induced ionization cross section, probability of Auger transition after ionization, and backscattering factor. Because the Auger-electron emission is isotropic, the asymmetry term vanishes, and the AES intensity, $I_{\text{A},\text{XYZ}}$, of a pure element A with transition XYZ is given by [4.1]

$$I_{\text{A},\text{XYZ}} = n_{\text{A},\text{X}} \sigma_{\text{A},\text{X}}(E_{\text{p}}) \gamma_{\text{A},\text{XYZ}} \times \int_0^\infty I_{\text{p}}(\alpha, z) [(1 + r_{m,U(\text{A})}(E_{\text{A},\text{X}}, E_{\text{p}}, \alpha, \theta, z))] N_{\text{A}}(z) \exp \left[-\frac{z}{\lambda_{m,E(\text{A})} \cos \theta} \right] dz \quad (4.129)$$

where $n_{\text{A},\text{X}}$ is the population of level X, $\sigma_{\text{A},\text{X}}(E_{\text{p}})$ is the ionization cross section of level X for primary electrons with energy E_{p} , γ_{XYZ} is the XYZ transition probability, and $I_{\text{p}}(\alpha, z)$ is the primary current excitation depending on incidence angle α and depth z . The typical parameter in AES is the backscattering factor $1 + r_{m,U(\text{A})}(E_{\text{A},\text{X}}, E_{\text{p}}, \alpha, \theta, z)$, with the backscattering term $r_{m,U(\text{A})}$, given by the ratio between the Auger-electron intensity generated by the backscattered electrons to

that generated by the primary electrons [4.140] (see below in this section). The term $r_{m,U(A)}$ depends on the ionization energy of core level X , $E_{A,X}$, the primary energy E_p , the electron incidence angle α , the emission angle θ , and depth z . The subscripts m and $U(A)$ in $r_{m,U(A)}$ denote the preponderant influence of matrix m and “overvoltage” $U(A) = U = E_p/E_{A,X}$, respectively, on the value of $r_{m,U(A)}$. The atomic density of A atoms is given by $N_A(z)$, and $\lambda_{m,E(A)} = f(m, E_{A,XYZ})$ is the attenuation length of Auger electrons with kinetic energy $E_{A,XYZ}$ in matrix m and emission angle θ measured from the surface normal. It is important to note that $\lambda_m(E_{A,XYZ}, \theta)$ depends on the matrix composition. Only if the sample mainly consists of element A, m can be replaced by A and $\lambda_{m,E(A)}$ becomes the usually written $\lambda_{A,E(A)}$ [4.1, 4.2].⁸ If the matrix composition changes with depth, the attenuation length will be depth dependent too (see (4.9)). The ionization cross section depends on the overvoltage $U = E_p/E_{A,XYZ}$ (with $U \geq 1$), and starts at zero for $U = 1$, increases with U through a broad maximum around $U = 2$ and moderately decreases for higher U values [4.1, 4.2]. Equation 4.129 includes excitations other than by primary excitation, namely, Auger and Coster–Kronig transitions (inner-shell rearrangement) and ionization of core levels by X-rays generated to increase extent at higher primary energies ($E_p > 10$ keV) (see, e.g., [4.1] for details).

The basic differences between AES (4.129) and XPS (4.32) are, besides the asymmetry factor, the primary electron energy-dependent cross section for electron-excited ionization of level X of element A, $\sigma_{A,X}(E_p)$, the probability of an XYZ Auger transition, $\gamma_{A,XYZ}$, and the backscattering factor $R_{m,U(A)} = 1 + r_{m,U(A)}(E_{A,X}, E_p, \alpha, \theta)$, which are briefly considered in the following.

4.4.1.1 Electron-Induced Ionization Cross Section

The most popular predictive formulae for the electron-induced inner-shell ionization cross section, $\sigma_{A,X}(E_p)$, are those of Drawin [4.138], Gryzinski [4.139], and Casnati et al. [4.137]. All three give a fairly good description of the shape and magnitude of the cross section as a function of primary energy. The formula of Casnati et al. was developed from fits to measured K-shell cross sections and has been found satisfactory for describing cross sections for L- and M-shell ionization [4.40]. Figure 4.48 shows the experimental results of Takeuchi and Goto [4.80] for the intensity of the $\text{AgM}_{5}\text{N}_{4.5}\text{N}_{4.5}$ transition as a function of the overpotential $U = E_p/E_i$, with E_p the primary electron and $E_i = E_{A,X}$ the ionization energy of A, respectively. It is clear that the ionization cross section starts to increase from zero for $E_p/E_i \leq 1$ and decreases after a theoretical maximum between E_p/E_i of about 2 to 4. This is the reason why the primary electron gun for AES is usually working with energies at or above 3 keV to cover the AES energy region up to 2400 eV.

⁸Note that the inelastic mean free path is exactly the same for Auger- and photoelectrons of the same kinetic energy. However, attenuation lengths between AES and XPS may differ slightly because of the different effects of elastic scattering for symmetric and asymmetric emission (see Sects. 4.2.2 and 4.3.1).

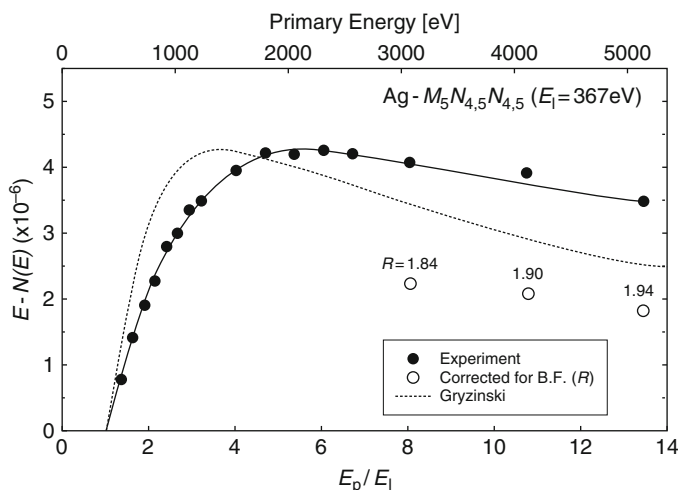


Fig. 4.48 Intensity of the Ag $M_5N_{4.5}N_{4.5}$ Auger line measured as a function of $U = E_p/E_i$ with E_p the primary electron energy and E_i the ionization energy of Ag M_5 , compared to the theoretical Gryzinski function and to some values corrected for the backscattering contribution (Reproduced from Y. Takeuchi and K. Goto [4.81], with permission of J. Wiley & Sons Ltd.)

Measurements show that the maximum intensity extends to higher overpotentials because of the backscattering effect (see below), a correction of which is also indicated in Fig. 4.48. This is one of the reasons why today's Auger spectrometers frequently work at 10 keV primary electron energy. Even higher primary energies are useful if better lateral resolution is required (see Fig. 2.9).

4.4.1.2 Auger Transition Probability

The probability of an XYZ Auger transition, γ_{XYZ} ("Auger yield"), which competes with the X-ray emission probability ("fluorescence yield") is unity for light elements and decreases with increasing transition energy. Therefore, the Auger transition probability decreases with increasing atomic number at first for the K- and then for the L-shell ionization and so on [4.89]. This is the main reason why the more intense Auger transitions that are analytically useful are below 2.5 keV. Thus, KLL transitions are most sensitive for elements $Z = 3-14$, LMM transitions for elements $Z = 12-40$, and MNN transitions for the heavier elements. This fact is reflected in the elemental sensitivity factors for AES [4.25] (see Fig. 4.49).

4.4.1.3 Backscattering Factor (BF) and Backscattering Correction Factor (BCF)

Consideration of electron backscattering by primary is essential in quantitative AES (see (4.129)) and characterized by the backscattering factor (BF) [4.140, 4.141,

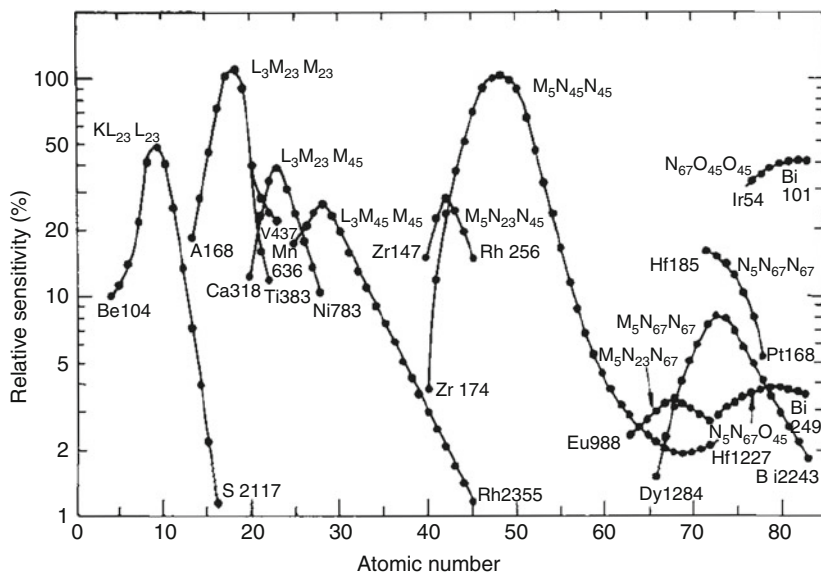


Fig. 4.49 AES relative elemental sensitivity factors $I_i^0/I_{Ag}^0 = S_{i,Ag}$ in % of I_{Ag}^0 (set to 100), for Auger peak-to-peak height (APPH), derived experimentally with primary energy $E_p = 5$ keV and zero incidence angle after Davis et al. [4.21], with annotations by Seah [4.25] (Reproduced with permission of J. Wiley & Sons Ltd., from M. P. Seah [4.2]. Crown Copyright 1990)

4.142], $R_{m,U(A)} = 1 + r_{m,U(A)}$ defined above, with $r_{m,U(A)}$ the backscattering term for element A in matrix m . This term additionally depends on the incidence angle, on the emission angle, and on depth z (if there are concentration gradients or layer structures).

Unfortunately, different usages of the backscattering factor exist. The original definition of the backscattering factor ($R = 1 + r$) adopted here is not encouraged by the ISO vocabulary [4.155] that recommends use of r as a “factor defining the fractional increase in the Auger electron current due to additional ionizations in the sample caused by backscattered electrons above that arising directly from the primary electrons.” This definition has been shown to be unsatisfactory by Jablonski [4.144] since the “fractional increase” can be negative at low energies near the ionization threshold, $E_{A,X}$, and for very high incidence angles. Therefore, a new name and definition is being considered by the ISO Technical committee 201 on Surface Chemical Analysis. The new backscattering correction factor (BCF) is defined as a “factor equal to the ratio of the Auger-electron current arising from ionizations in the sample caused by both the primary electrons and the backscattered electrons to the Auger-electron current arising directly from the primary electrons.” Monte Carlo simulations according to the new model are shown below (see Figs. 4.52 and 4.53).

Ichimura–Shimizu Equations: Traditionally, the backscattering factor is based on the extensive work of Ichimura and Shimizu [4.140]. They performed Monte Carlo simulations of electron transport in solids and approximated these results by easy to

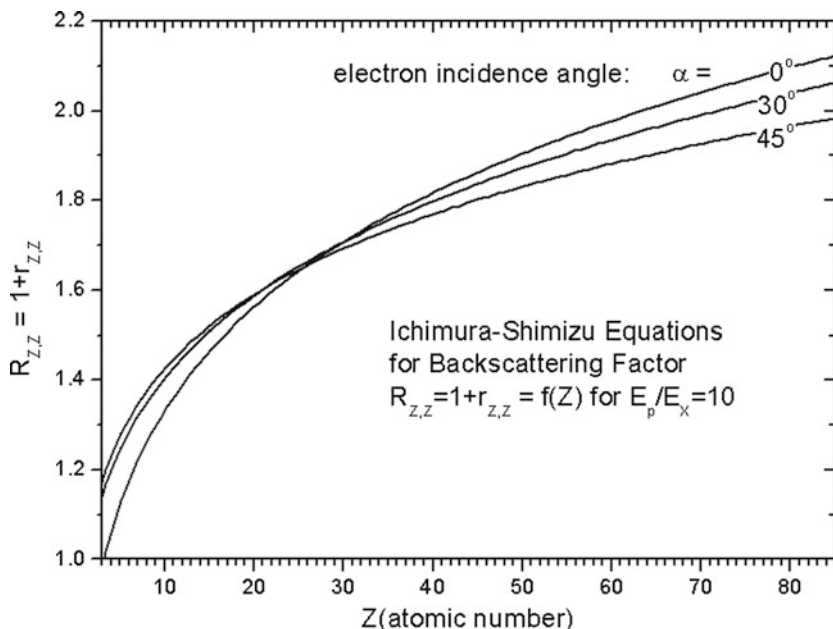


Fig. 4.50 Plot of Ichimura–Shimizu equations (4.130) for the backscattering factor $R_{Z,Z} = 1 + r_{Z,Z}$ as a function of the atomic number Z for $U = E_p/E_X = \text{const.} = 10$, with E_p = primary electron energy and E_X = ionization energy, for electron incidence angles $\alpha = 0^\circ, 30^\circ$, and 45°

use analytical expressions, the so-called Ichimura–Shimizu equations. The accuracy of these equations was further improved by Shimizu [4.141] and Shimizu et al. [4.142] who proposed the following expressions for the three electron incidence angles $\alpha = 0^\circ, 30^\circ$, and 45° :

$$\begin{aligned} r &= (2.34 - 2.10Z^{0.14})U^{-0.35} + (2.58Z^{0.14} - 2.98) \quad \text{for } \alpha = 0^\circ, \\ r &= (0.462 - 0.777Z^{0.20})U^{-0.35} + (1.15Z^{0.20} - 1.05) \quad \text{for } \alpha = 30^\circ, \\ r &= (1.21 - 1.39Z^{0.13})U^{-0.33} + (1.94Z^{0.13} - 1.88) \quad \text{for } \alpha = 45^\circ, \end{aligned} \quad (4.130)$$

where Z is the average atomic number of the respective sample material, and $U = E_p/E_X$, the ratio of the primary electron energy and the binding energy (= ionization energy) of the considered Auger transition XYZ . In practice, the expressions (4.130) are extremely useful for the practical analyst because they enable a quick determination of the backscattering factor for typical experimental situations when the sample composition is known. Incidence angles between 0° and 30° or 30° and 45° can be taken into account by linear interpolation. After having first determined the sample composition without consideration of the backscattering factor, the latter can then be calculated with (4.130) and introduced in the respective quantitative expression (see, e.g., (4.129)) to obtain improved results. Figure 4.50 shows the dependence of the backscattering factor on the atomic number Z after (4.130) for the incidence angles $0^\circ, 30^\circ$, and 45° and an overpotential of $U = 10$ (e.g., 10 keV primary voltage and 1000 eV ionization energy). (The notation $r = r_{Z,U(Z)}$)

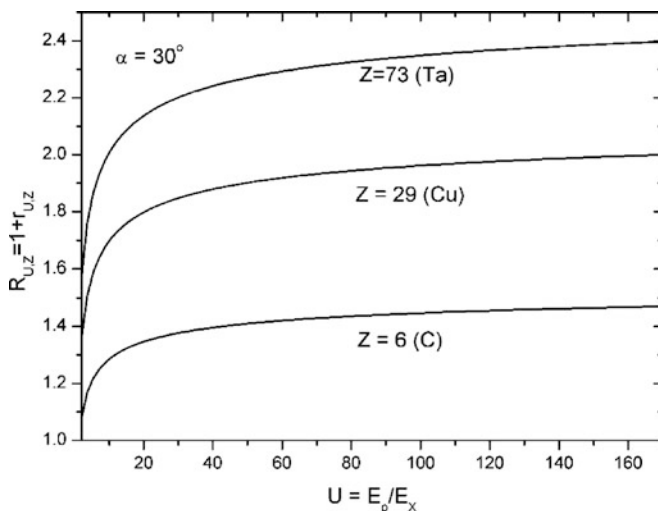


Fig. 4.51 Plot of Ichimura–Shimizu equations (4.130) for the backscattering factor $R_{U,Z} = 1 + r_{U,Z}$ as a function of the overvoltage $U = E_p/E_X$ with primary electron energy, E_p , and ionization energy, E_X , for $\alpha = 30^\circ$ electron incidence angle and three typical matrices with $Z = 6$ (C), 29 (Cu), and 73 (Ta)

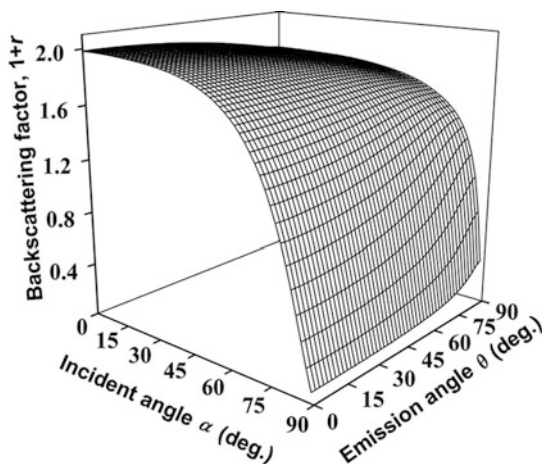


Fig. 4.52 Calculated backscattering factor for Ta $M_5N_{6,7}$ Auger electrons (179 eV) in pure Ta for $E_p = 5$ keV as a function of incidence angle and emission angle (Reprinted with permission from R. G. Zeng et al. [4.146]. Copyright 2008, American Institute of Physics)

is abridged to $r_{Z,Z}$.) For alloys, the average atomic number can be used. Figure 4.51 depicts the dependence on U for three representative atomic numbers and an incidence angle of 30° .

A reformulation and extension of the Ichimura–Shimizu equations to 30 keV primary energy and to 60° incidence angle has been given by Tanuma [4.143].

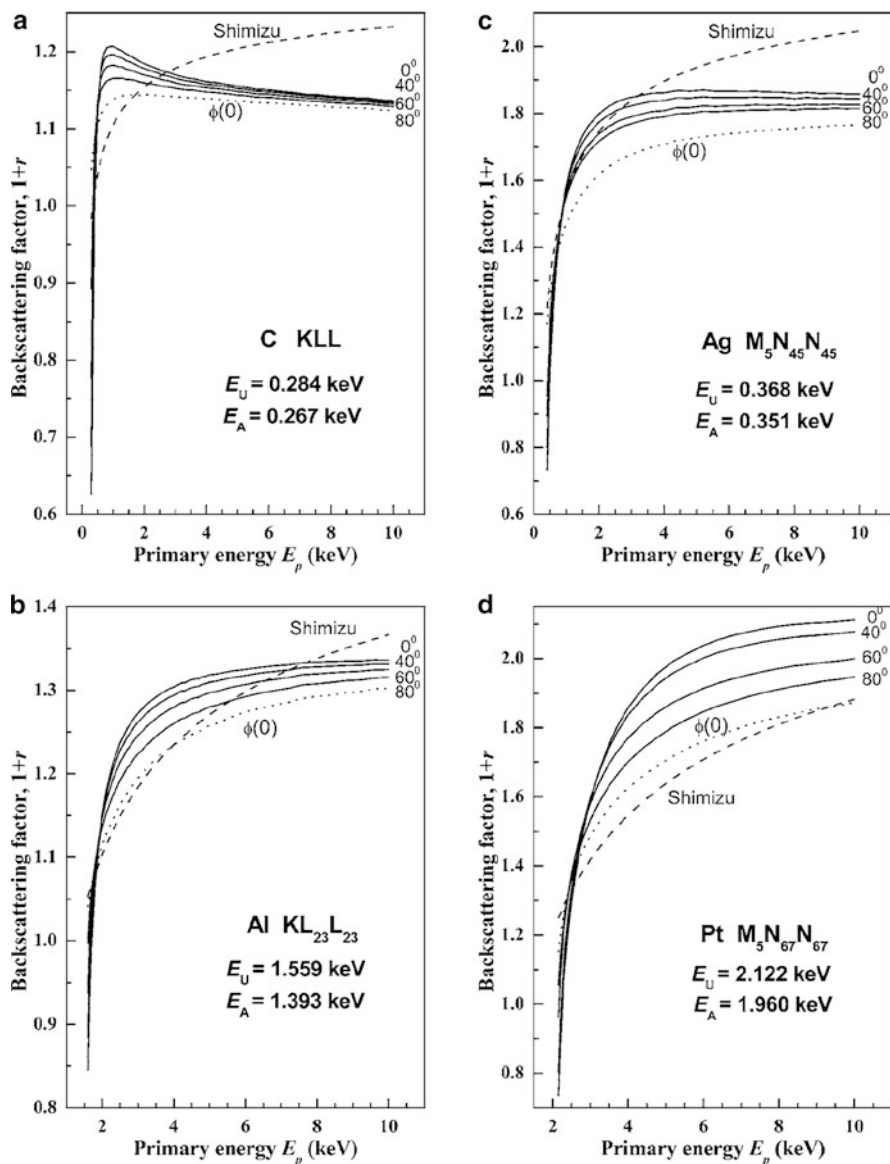


Fig. 4.53 Calculated backscattering factor $R = 1 + r$ for 4 selected elements as a function of the primary energy and 4 different emission angles and for normal incidence angle, for (a) C(KLL), (b) Al($KL_{2,3}L_{2,3}$), (c) Ag($M_5N_{4,5}N_{4,5}$), and (d) Pt($MN_{6,7}N_{6,7}$). Dashed lines show the corresponding result of the Ichimura-Shimizu expression (4.130) for $\alpha = 0$ (Reprinted with permission from Z. J. Ding et al. [4.30]. Copyright 2006, American Institute of Physics)

Backscattering Correction Factor (BCF) after Jablonski: A refined theoretical approach to backscattering was introduced by Jablonski [4.144] by considering the angular, energy, and element dependencies of the excitation depth distribution function (EXDDF) and the emission depth distribution function (EMDDF) outlined in expression (4.7). Based on this work, Jablonski et al. [4.29, 4.145] and Ding et al. [4.30] were able to show that the backscattering factor for pure elements can deviate up to 20% from the Ichimura–Shimizu values that – in addition to the incidence angle (α) – there is a dependence on the emission angle (θ) of up to 10%. Both dependencies are shown for Ta (179 eV) in Fig. 4.52 [4.146]. In contrast to former theories, the backscattering coefficient, r , may even become negative for low primary energies ($U < 2$) (Fig. 4.53) and for very high incidence angles ($\alpha > 80^\circ$) (Fig. 4.52). An example of the work of Ding et al. [4.30] is shown in Fig. 4.53 (= Fig. 3b in [4.30]). The backscattering factor of pure C(KLL), Al(KL_{2,3}L_{2,3}), Ag(M₅N_{4,5}N_{4,5}) and Pt(MN_{6,7}N_{6,7}) is plotted as a function of the primary electron energy E_p . The deviation of the new calculations from the Ichimura–Shimizu results is clearly recognized, as well as a slight emission angle (θ) dependence not considered by Ichimura and Shimizu. A new database for backscattering factors $r_{A,U(A)}$ has been published by Ding and coworkers in 2008 [4.146]. Recent calculations by Jablonski and Powell [4.53, 4.147] show an additional dependence of the backscattering factor on the analyzer acceptance angle. In spring 2011, these authors launched a NIST database for the backscattering correction factor (BCF) [4.149]. This database (SRD 154) provides BCF values from Monte Carlo simulations for two models (BF and BCF). BCFs can be determined for a user-specified solid of arbitrary composition. In future works, this database will replace the Ichimura–Shimizu equations. It is recommended to replace the term $(1 + r_{m,U(A)})$ in these equations below by the BCF from [4.149]. However, the practically important backscattering influence of a nonconstant in-depth distribution of composition has yet to be explored in detail. A first step in that direction was the quantitative description of a layer thickness-dependent backscattering contribution introduced already in 1979 [4.151]. Later, this approach was extended by Hofmann et al. [4.130] in sputter depth profiling of multilayer structures. Recently, these results were basically confirmed by Monte Carlo calculations for samples with compositions varying with depth [4.156] (see below, Sect. 4.4.3) and for similar multilayers [4.157, 4.158] (see Sect. 7.1.8).

4.4.2 Quantitative AES Analysis of Homogeneous Material

Assuming I_p to be constant over the escape depth of the Auger electrons, for an amorphous solid and for homogeneous composition with depth, i.e., constant $N_A(z) = N_A$, the integral in (4.129) can be solved. With the geometry depicted in Figs. 4.13 and 5.1a, the total, emitted Auger-electron intensity $I_{A,XYZ,em}$ can be written – in analogy to (4.40) – as

$$I_{A,XYZ,em} = n_{A,X} \sigma_{A,X}(E_p) \gamma_{A,XYZ}(E_p) \frac{I_p}{\cos \alpha} [1 + r_{m,U(A)}(E_{A,X}, E_p, \alpha, \theta, m)] \times N_A \lambda_{m,E(A)} \cos \theta. \quad (4.131)$$

Introducing the analyzer characteristic function, $G(E_{A,XYZ})$ (total analyzer efficiency given by the Intensity/Energy Response Function (IERF), see Sect. 4.3.2.1), we obtain the detected Auger-electron intensity:

$$I_{A,XYZ} = n_{A,X} \sigma_{A,X}(E_p) \gamma_{A,XYZ}(E_p) G(E_{A,XYZ}) \times \frac{I_p}{\cos \alpha} [1 + r_{m,U(A)}(E_{A,X}, E_p, \alpha, \theta, m)] N_A \lambda_{m,E(A)} \cos \theta. \quad (4.132)$$

With the analyzer acceptance angle $\Delta\Omega$ and the detector (channel plate) efficiency $D(E)$, the number of Auger electrons detected in the energy window ΔE is proportional to the analyzer efficiency:

$$G(E_{A,XYZ}) = \frac{\Delta\Omega}{4\pi} \Delta E D(E) = \frac{\Delta\Omega}{4\pi} \left(\frac{\Delta E}{E} \right) E D(E). \quad (4.133)$$

For a CMA and CHA with constant retard ratio, $\Delta E/E = \text{const.}$ (and $D(E) = \text{const.}$), the measured intensity (obtained in count rate $N(\text{s}^{-1})$) is proportional to $N(E)E$. This has to be taken into account if absolute intensities after the basic equations are considered. For relative intensities, this small systematic error is unimportant.

Although in principle elemental sensitivity factors can be estimated after the basic equations [4.25], in general, elemental sensitivity factors are empirically determined for a specific instrument, frequently for 0.5% or 0.6% energy resolution and for differential spectra [4.21] (see Fig. 4.49).

4.4.2.1 Quantification Using Elemental Relative Sensitivity Factors (E-RSFs)

The general equation for XPS relative sensitivity factors (4.44) has to be modified for AES. In close analogy to XPS, a reference element transition, usually the Ag ($M_{5.5}N_{4.5}M_{4.5}$) transition at 350 eV is chosen, and the elemental relative sensitivity factors (E-RSFs) for AES are given for the Auger peak-to-peak height (APPH) of a certain (KLL, LMM, or MNN) transition of element A to that of the above Ag transition in the differentiated spectrum. It is essential to keep in mind that these data as compiled in a popular handbook [4.21] are only valid for a CMA with the same resolution (0.6%) and with identical incidence and emission angles. The basic equation for the relative sensitivity factor of element A, S_A , is formally similar to that for XPS (4.44), but the latter has to be modified by the appropriate variables and above all by the backscattering factor $(1 + r_{A,A})$ for element A in A and $(1 +$

$r_{\text{Ag,Ag}}$) for the usual silver standard (see Sect. 4.4.1). For brevity, the population $n_{\text{A},X}$ is included in σ_{AX} for a given subshell X of A. With the parameters defined in (4.129)–(4.133), we get in analogy to (4.45)

$$\frac{I_{\text{A}}^0}{I_{\text{Ag}}^0} = \frac{\sigma_{\text{A},X}(E_{\text{p}})\gamma_{\text{A},XYZ}(E_{\text{p}})[1 + r_{\text{A},U(\text{A})}(E_{\text{A},X}, E_{\text{p}}, \alpha, \theta)]G(E_{\text{A}})\lambda_{\text{A},E(\text{A})}N_{\text{A}}^0}{\sigma_{\text{Ag},X}(E_{\text{p}})\gamma_{\text{Ag},XYZ}(E_{\text{p}})[1 + r_{\text{Ag},U(\text{Ag})}(E_{\text{Ag},X}, E_{\text{p}}, \alpha, \theta)]G(E_{\text{Ag}})\lambda_{\text{Ag},E(\text{Ag})}N_{\text{Ag}}^0} = S_{\text{A}}. \quad (4.134)$$

Usually, AES is performed with constant retarding ratio of the spectrometer, where, as for a CMA, the electron optical transmission is proportional to the kinetic energy. Because of the more complicated dependence of the quantities in (4.132) on many not exactly understood parameters and instrumental characteristics, theoretical evaluations of the relative elemental sensitivity factors have been not very convincing in the past [4.25, 4.150]. Although newer data, particularly for the attenuation length, give a somewhat better agreement with experimental data, the latter are still to be preferred (see Fig. 4.49). Elemental intensities measured by well-defined parameters with the particular instrument used are expected to be most reliable in any quantification procedure. Using the elemental relative sensitivity factors $S_{i,\text{Ag}} = S_i$, either determined with elemental standards or, as a second choice, taken from instrument suppliers manuals or from a handbook [4.21], (4.134) can be used, for example, for quantification of a multielement system. As discussed in the case of XPS (see Sect. 4.3.2.2 and (4.48)), the use of E-RSFs neglects matrix effects which will be considered in the following.

4.4.2.2 Quantification Including Matrix Effects (AES)

Let us consider a binary system of elements A and B. From (4.84), in analogy to (4.51), according to (4.132) and (4.134), the ratio of the intensity of A in matrix m , I_{A} , to the standard intensity for the pure element, I_{A}^0 , can be expressed as

$$\frac{I_{\text{A}}}{I_{\text{A}}^0} = \frac{[1 + r_{m,U(\text{A})}(E_{\text{A},X}, E_{\text{p}}, \alpha, \theta)]\lambda_{\text{A},E(\text{A}),m}N_{\text{A}}}{[1 + r_{\text{A},U(\text{A})}(E_{\text{A},X}, E_{\text{p}}, \alpha, \theta)]\lambda_{\text{A},E(\text{A})}N_{\text{A}}^0}, \quad (4.135)$$

where the subscript m denotes matrix-related terms. Other terms except the backscattering term are like in (4.51) for XPS [4.1]. Of course, for constant α and θ , the terms in (4.132) related to atomic or instrumental properties like $\sigma_{\text{A},X}(E_{\text{p}})\gamma_{\text{XYZ}}(E_{\text{p}})G(E_{\text{A}})I_{\text{p}} \cos \theta / \cos \alpha$ cancel in (4.135).

Rearranging (4.132), keeping in mind the complicated dependencies of the backscattering factor, and replacing the atomic densities by mole fractions via $N_{\text{A}} = X_{\text{A}}N_m^0$, we obtain, for the mole fraction X_{A} of A in matrix m ,

$$X_{\text{A}} = \frac{I_{\text{A},m}}{I_{\text{A}}^0} \frac{[1 + r_{\text{A},U(\text{A})}]\lambda_{\text{A},E(\text{A})}N_{\text{A}}^0}{[1 + r_{m,U(\text{A})}]\lambda_{m,E(\text{A})}N_m^0} = \frac{I_{\text{A},m}}{I_{\text{A}}^0} \frac{S_{\text{A}}}{S_{\text{A},m}} = \frac{I_{\text{A},m}}{I_{\text{A}}^0} F_{\text{A},m}. \quad (4.136)$$

The simple Palmberg relation (4.5) can be used when replacing the E-RSF, S_A , by the matrix relative sensitivity factor (M-RSF) $S_{A,m} = S_A/F_{A,m}$. According to (4.136), the matrix relative correction factor $F_{A,m}$ for element A in matrix m is given by

$$F_{A,m} = \frac{[1 + r_{A,U(A)}]\lambda_{A,E(A)}N_A^0}{[1 + r_{m,U(A)}]\lambda_{m,E(A)}N_m^0}, \quad (4.137a)$$

and for B in matrix m ,

$$F_{B,m} = \frac{[1 + r_{B,U(B)}]\lambda_{B,E(B)}N_B^0}{[1 + r_{m,U(B)}]\lambda_{m,E(B)}N_m^0}. \quad (4.137b)$$

In contrast to XPS, in addition to the attenuation length and the atomic densities, we have to consider the backscattering factor (at present to be taken from the Ichimura–Shimizu equations (4.130), see Sect. 4.4.1).

As for XPS, a convenient key parameter in quantification is the (binary) relative matrix correction factor $F_{A,B}^m$, given by the ratio of the above expressions (4.137a) and (4.137b):

$$F_{A,B}^m = \frac{\lambda_{A,E(A)}N_A^0\lambda_{m,E(B)}(1 + r_{A,U(A)})(1 + r_{m,U(B)})}{\lambda_{B,E(B)}N_B^0\lambda_{m,E(A)}(1 + r_{B,U(B)})(1 + r_{m,U(A)})} = \frac{1}{F_{B,A}^m} \quad (4.138a)$$

with $(1 + r_{A,U(A)})$, $(1 + r_{B,U(B)})$ denoting the backscattering factor for overvoltage $U_A = E_p/E_{A,X}$, $U_B = E_p/E_{B,X}$, for primary energy E_p and ionization energy $E_{A,X}$, $E_{B,X}$ in pure A and B, respectively, and $(1 + r_{m,U(A)})$, $(1 + r_{m,U(B)})$ that for A and B in matrix m .

Similar to Sect. 4.3.2, a matrix composition-dependent correction term for the backscattering factors $(1 + r_{m,U(A)})$, $(1 + r_{m,U(B)})$ was introduced by Holloway [4.86]. To get an idea of the role of the backscattering factor ratio in a changing matrix composition, let us have a look on the dependence shown in Fig. 4.54 as an example. The backscattering factors for 30° incidence angle after (4.130) are shown for the C KLL and the Fe LVV peaks with 285 and 707 eV ionization energy as a function of the composition, given by the (average) atomic number. The matrix-dependent backscattering ratio in (4.138a), $(1 + r_{m,U(B)})/(1 + r_{m,U(A)})$, with A = Carbon, B = Fe clearly shows a remarkable constancy with less than 2% variation over the whole range considered, from atomic number $Z = 6$ (0.94) to $Z = 60$ (0.93). This means we can choose practically any value for m and get the same ratio of $(1 + r_{m,U(B)})/(1 + r_{m,U(A)})$. Replacing $\lambda_{m,E(B)}/\lambda_{m,E(A)}$ by $(E(B)/E(A))^{0.75}$ (with $E(B)$ and $E(A)$ the respective Auger-electron energies, see Sect. 4.2.2) and taking again the traditional silver standard, $m = \text{Ag}$ for the backscattering term, we get

$$F_{A,B}^m = \frac{\lambda_{A,E(A)}N_A^0(1 + r_{A,U(A)})(1 + r_{\text{Ag},U(B)})}{\lambda_{B,E(B)}N_B^0(1 + r_{B,U(B)})(1 + r_{\text{Ag},U(A)})} \left(\frac{E(B)}{E(A)} \right)^{0.75} = \frac{1}{F_{B,A}^m}. \quad (4.138b)$$

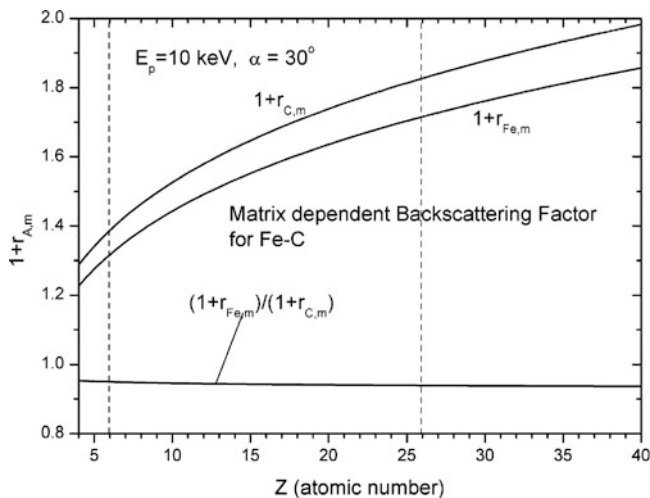


Fig. 4.54 Backscattering factors ($\alpha = 30^\circ$) for Fe ($E(\text{Fe}) = 703 \text{ eV}$, $E_{X,\text{Fe}} = 707 \text{ eV}$) and C ($E(\text{C}) = 272 \text{ eV}$, $E_{X,\text{C}} = 285 \text{ eV}$) and their ratio as a function of the matrix composition characterized by the average matrix atomic number Z , after Ichimura–Shimizu (4.130). For the Fe–C example, the relevant region between pure C and pure Fe is indicated by *dashed lines*

In Sect. 4.3.2, the matrix composition-independent attenuation length correction was pointed out. Equations 4.138a and 4.138b, based on Fig. 4.54, establish the matrix composition-independent (relative binary) backscattering factor correction recommended below.

4.4.2.3 Comparison of Different Approaches to Matrix Correction Factors

In the following, we briefly reiterate the main approaches for matrix correction factors for XPS (Sect. 4.3.2.3) but now with the backscattering extension.

1. Matrix Correction Factor for Dilute Alloys After Hall and Morabito (AES)

In the binary dilute alloy case, the matrix can be taken approximately as the second element, and (4.137a) and (4.137b) can be rewritten for A in matrix B

$$F_{A,B}(\text{HM}) = \frac{(1 + r_{A,U(A)})\lambda_{A,E(A)}N_A^0}{(1 + r_{B,U(A)})\lambda_{B,E(A)}N_B^0}, \quad (4.139a)$$

and for B in matrix A

$$F_{B,A}(\text{HM}) = \frac{[1 + r_{B,U(B)}]\lambda_{B,E(B)}N_B^0}{[1 + r_{A,U(B)}]\lambda_{A,E(B)}N_A^0}. \quad (4.139b)$$

Equations 4.139a and 4.139b are similar to (4.60a) and (4.60b) except the additional backscattering terms. The matrix dependence of the backscattering factor ratio considered by Holloway [4.86] is negligible (see Fig. 4.54). Thus, (4.37a) and (4.34b) can be used for nondilute systems too, as shown below.

2. Simplified Matrix Correction Factor After Payling (AES)

Although Payling [4.87] considers quantitative AES, he ignores backscattering and reduces the matrix correction factor to a relative density factor given already in (4.66). As seen in the comparison in Table 4.6, this results in a correction that is too weak, as discussed in Sect. 4.3.2.

3. Average Matrix Approach (Seah–Gilmore) (AES)

The approach after Seah and Gilmore is related to that of Payling, with a hypothetical average matrix chosen to give less variation in the matrix correction factors for a large number of elements [4.64]. Replacing the reference element Ag in (4.138a) by the average matrix (subscript av) and writing $\lambda = \lambda_{in}Q$, these authors give the following expression for an average matrix relative sensitivity factor (AM-RSF) [4.27, 4.89]:

$$S_{A,m} = \frac{S_A}{F_{A,m}} = \frac{N_{av}^0 Q_{av,E(A)} \lambda_{in,av,E(A)} (1 + r_{av,U(A)})}{N_A^0 Q_{A,E(A)} \lambda_{in,A,E(A)} (1 + r_{A,U(A)})} S_A \quad (4.140)$$

with N_{av}^0 , Q_{av} , $\lambda_{in,av}$ given by (4.73a)–(4.73c) and the hypothetical backscattering matrix by atomic number $Z = 40.5$ to be used in the Ichimura–Shimizu relations (4.130) to generate $(1 + r_{av,U(A)})$. In analogy to (4.138a), the relative (binary) matrix correction factor for the average matrix based on (4.140) is obtained as

$$\frac{F_{B,av}}{F_{A,av}} = F_{A,B}^{av} = \frac{N_A^0 \lambda_{A,E(A)} \lambda_{av,E(B)} (1 + r_{A,U(A)}) (1 + r_{av,U(B)})}{N_B^0 \lambda_{B,E(B)} \lambda_{av,E(A)} (1 + r_{B,U(B)}) (1 + r_{av,U(A)})}. \quad (4.141)$$

Expression (4.141) is identical to (4.138a) if the actual matrix (m) is replaced by the average matrix (av). Because of the recommended usage of binary (matrix-less) correction factors introduced below, the choice of reference matrix appears to be unimportant. For an extended discussion, see Sect. 4.3.2.

4. Binary Relative Matrix Correction Factors Without Standard Matrix

In analogy to Sect. 4.3.2.3 item (4), an improved composition-independent Payling–Hall–Morabito approach can be formulated. The basic expression (4.138a) for the relative matrix correction factor $F_{A,B}^m$ takes into account the matrix dependence of the attenuation length and the backscattering factor. While the former can

be replaced by a simple relative energy dependence (see (4.138b)), this dependence is much more complicated for the backscattering term. In contrast to XPS, the reference matrix, $m = \text{Ag}$ or av , is still contained in the backscattering factor ratio of $F_{A,B}^m$ (see (4.138b)). However, as seen in Fig. 4.54, the ratio $(1 + r_{m,U(A)})/(1 + r_{m,U(B)})$ is practically independent of the choice of the reference matrix. Therefore, we may take B as matrix m . Setting $(1 + r_{m,U(A)})/(1 + r_{m,U(B)}) = (1 + r_{B,U(A)})/(1 + r_{B,U(B)})$ in (4.138a), the standardless binary relative matrix correction factor $F_{A,B}^{\text{rel}}$ follows as

$$F_{A,B}^{\text{rel}} = \frac{\lambda_{A,E(A)} N_A^0 (1 + r_{A,U(A)})}{\lambda_{B,E(A)} N_B^0 (1 + r_{B,U(A)})} = \frac{\lambda_{A,E(A)} (\rho_A/M_A) (1 + r_{A,U(A)})}{\lambda_{B,E(B)} (\rho_B/M_B) (1 + r_{B,U(A)})} \left(\frac{E(B)}{E(A)} \right)^{0.75}, \quad (4.142a)$$

and for element B, we get

$$F_{B,A}^{\text{rel}} = \frac{\lambda_{B,E(B)} N_B^0 (1 + r_{B,U(B)})}{\lambda_{A,E(B)} N_A^0 (1 + r_{A,U(B)})} = \frac{\lambda_{B,E(B)} (\rho_B/M_B) (1 + r_{B,U(B)})}{\lambda_{A,E(A)} (\rho_A/M_A) (1 + r_{A,U(B)})} \left(\frac{E(A)}{E(B)} \right)^{0.75}, \quad (4.142b)$$

and combining (4.14a) and (4.14b) yields

$$F_{B,A}^{\text{rel}} = \frac{(1 + r_{A,U(A)})(1 + r_{B,U(B)})}{(1 + r_{B,U(A)})(1 + r_{A,U(B)})} \frac{1}{F_{A,B}^{\text{rel}}} \cong \frac{1}{F_{A,B}^{\text{rel}}}. \quad (4.143)$$

Thus, the binary matrix relative sensitivity factor to be used in (4.5) is expressed by

$$S_{A,B}^{\text{rel}} = \frac{S_{A,B}}{F_{A,B}^{\text{rel}}} = \frac{\lambda_{B,E(A)} (\rho_B/M_B) (1 + r_{B,U(A)})}{\lambda_{A,E(A)} (\rho_A/M_A) (1 + r_{A,U(A)})} S_{A,B} \quad (4.144)$$

Expressions (4.142a), (4.142b), and (4.144) establish universal, matrix composition-independent, binary matrix relative correction factors and binary matrix relative sensitivity factors, respectively. These factors correspond to the Hall–Morabito equations (4.142a) and (4.142b) and can be used for a multielement system. They are expected to be most accurate if the major constituent is chosen as reference element (see also (4.5), (4.6a)–(4.6c)).

Choosing an arbitrary reference element, for example, the traditional element Ag for AES, we may set for matrix m in (4.137a) the element Ag and obtain

$$F_{A,\text{Ag}} = \frac{(1 + r_{A,U(A)}) \lambda_{A,E(A)} N_A^0}{(1 + r_{\text{Ag},U(A)}) \lambda_{\text{Ag},E(A)} N_{\text{Ag}}^0} = \frac{(1 + r_{A,U(A)}) \lambda_{A,E(A)} (\rho_A/M_A)}{(1 + r_{\text{Ag},U(A)}) \lambda_{\text{Ag},E(A)} (\rho_{\text{Ag}}/M_{\text{Ag}})}. \quad (4.145)$$

Thus, for any element A, a relative matrix correction factor can be precalculated (see Table 4.5). The relative binary matrix correction factors are obtained by the ratio $F_{A,B}^{\text{rel}} = F_{A,\text{Ag}}/F_{B,\text{Ag}}$ and correspond to (4.142a) because the reference matrix (Ag) related parameters cancel, as seen from (4.142c).

Table 4.5 Quantification data for AES analysis of Fe–Cr and Fe–C systems

Element (<i>i</i>)	Fe	Cr	C	Ag	Average matrix
(ρ/M) (mol/cm ³)	0.1411	0.1383	0.1883	0.0973	0.086
<i>a</i> (nm)	0.228	0.229	0.207	0.258	0.268
<i>Z</i>	26	24	6	47	40.57 for (4.130)
<i>E</i> (eV)	703	529	272	351	
<i>E</i> _{<i>i,x</i>} (eV)	707	574	285	368	
$\lambda_{i,E(\text{Fe})}$ (nm) (CS2)	1.03	1.07	1.61	0.988	
$\lambda_{i,E(\text{Cr})}$ (nm) (CS2)	0.841	0.872	1.47	0.814	
$\lambda_{i,E(\text{C})}$ (nm) (CS2)	0.544	0.563	0.800	0.541	
$\lambda_{i,E(\text{Ag})}$ (nm) (CS2)	0.638	0.661	0.957	0.628	
($\lambda_{\text{in}}Q$) _{<i>i,E(Fe)</i>} (nm)	1.18	1.20	2.02	1.04	1.69
($\lambda_{\text{in}}Q$) _{<i>i,E(Cr)</i>} (nm)	0.953	0.972	1.63	0.851	1.37
($\lambda_{\text{in}}Q$) _{<i>i,E(C)</i>} (nm)	0.611	0.616	1.01	0.576	0.869
($\lambda_{\text{in}}Q$) _{<i>i,E(Ag)</i>} (nm)	0.718	0.782	1.21	0.660	1.03
$1 + r_{i,U(\text{Fe})}$	1.72 1.75*) 1.63**)	1.69 1.64**)	1.32 1.31**)	1.91 1.77**)	
$1 + r_{i,U(\text{Cr})}$	1.74 1.64**)	1.72 1.67*) 1.67**)	1.34 1.28**)	1.95 1.79**)	
$1 + r_{i,U(\text{C})}$	1.79 1.65**)	1.80 1.61**)	1.39 1.30*) 1.19**)	2.04 1.77**)	
$1 + r_{i,U(\text{Ag})}$	1.79 1.68**)	1.77 1.67**)	1.37 1.30**)	2.00 1.85*) 1.77**)	1.95
$1 + r_{\text{Ag},U(i)}$	1.91 1.77**)	1.95 1.79**)	2.04 1.77**)	2.00 1.85*) 1.77**)	
$1 + r_{\text{av},U(i)}$	1.86	1.89	2.00	1.95	
E-RSF (PHI, 5 keV) <i>S_i</i> (Ag)	0.21	0.31	0.14	1.00	
E-RSF (JEOL, 10 keV) <i>S_i</i> (Ag)	0.355	0.468	0.128	1.00	
$F^m_{i,\text{av}} (\lambda_{\text{in}}Q)$	1.06	1.04	1.77	0.744	1.00
$F^m_{i,\text{Ag}} (\text{CS2})$	1.36	1.34	1.95	1.00	
$F^m_{i,\text{Ag}} (\lambda_{\text{in}}Q)$	1.48	1.43	2.31	1.00	
$F^{\text{rel}}_{i,\text{Fe}} (\lambda_{\text{in}}Q)_{\text{av}}$	1.00	0.981	1.67	0.702	

(continued)

Table 4.5 (continued)

Element (<i>i</i>)	Fe	Cr	C	Ag	Average matrix
$F_{i,Fe}^{rel} (CS2)_{Ag}$	1.00	0.985	1.43	0.735	
$F_{i,Fe}^{rel} (\lambda_{in} Q)_{Ag}$	1.00	0.966	1.56	0.676	
$S_{i,Ag}^m (JEOL)(=$	0.26	0.35	0.066	1.0	
$S_{i,Ag} / F_{i,Ag}^m (CS2))$					
$S_{i,Ag}^m (JEOL)(=$	0.24	0.33	0.055	1.0	
$S_{i,Ag} / F_{i,Ag}^m (\lambda_{in} Q))$					

With (ρ/M) = molar density [4.84]; a = atomic distance (4.18); Z = atomic number; E = Auger-electron energy; $E_{i,X}$ = ionization energy of element i ; λ = attenuation length, either from CS2 (4.17) or as $\lambda_{in} Q$ [4.37]; $1 + r_{i,U(j)}$ = backscattering factor of matrix i on Auger intensity of element j ; for $E_p = 10$ keV, $\alpha = 30^\circ$ (4.130), E-RSF data, APPH-based, from PHI Handbook [4.23] and from JEOL 7830F instrument manual ($S_{i,C}(RSF)$ data for values for AlK α excitation are from Wagner et al. [4.74])

Abbreviations in parentheses: (CS2): expression (4.17), (Payling): (4.69), (4.70); ($H-M$): (4.60a, b); ($S-G$): (4.73a–c), (4.77), (4.78); (Syn): (4.80), (4.81)

Average matrix data after Refs. [4.10, 4.93]: (ρ/M) (mol/cm³) = 0.0864, $a = 0.268$ nm

*) Values in italics: with one star *): From backscattering factor database by Zeng et al. Ref. [4.146]; with two stars **): From BCF database by Jablonski and Powell [4.149]

For AES, where many elements have strong lines below 500 eV, it is recommended to use the exact expression for the attenuation length given by $\lambda_{A,E(B)} = Q_{A,E(B)} \lambda_{in,A,E(B)}$ (4.20) and not the replacement by $\lambda_{A,E(B)} = \lambda_{A,E(A)} \times (E(B)/E(A))^{0.75}$ which may lead to errors of up to 10% (see Table 4.5).

4.4.2.4 Numerical Example of Quantitative AES: Fe–Cr and Fe–C

As an example of the application of different approaches to matrix effect corrections, we consider two systems in the following, Fe–Cr with similar atomic number and density values, and Fe–C with rather different ones. As for XPS in Sect. 4.3.2, results are given for the following approaches described above:

- Elemental relative sensitivity factors (E-RSFs)
- Payling simplified approximation M-RSF [4.87]
- Dilute alloy approximation (Hall-Morabito M-RSF) [4.85]
- Average matrix approach (Seah and Gilmore) (AM-RSF) [4.10]
- “Matrix-less” binary matrix relative sensitivity factors (BM-RSF)

Table 4.5 gives the necessary numerical data for the calculations for primary energy 10 keV, 30° incidence angle. Attenuation length values are either calculated from CS2 (4.17) or from $\lambda_{in} Q$ data after Ref. [4.37]. Ichimura–Shimizu equations ((4.130) for 10 keV, 30°) are used for backscattering factors. For comparison, data from new databases [4.146, 4.149] are also given the deviation from the former values is generally less than –6%, with exception of the elemental matrix values for C and Ag (–14%). Two different sets of relative elemental sensitivity factors

Table 4.6 Comparison of the expected AES results for Fe–Cr and Fe–C from (4.83) (for normalized elemental intensities $I_A/S_A = X_A$ with S_A the E-RSF value [4.74], giving mole fractions of X_{Cr} or $X_C = 0.1$ and 0.5 without matrix correction), calculated using different matrix correction factors (see text) with corresponding values from Table 4.5 (with AL either from CS2 (4.17) or from $\lambda_{in}Q$ [4.37])

System	Fe–ca 10 at% Cr	Fe–ca 50 at% Cr	Fe–ca 10 at% C	Fe–ca 50 at% C
	X_{Cr}	X_{Cr}	X_C	X_C
El Sens. (E-RSF)	0.100	0.500	0.100	0.500
Payling corr. M-RSF) ($\lambda_{in}Q$)	0.099	0.498	0.114	0.537
Dilute approx. (Hall – Morabito M-RSF) ($\lambda_{in}Q$)	0.099	0.497	0.160	0.631
Average matrix corr. (S-G, AM-RSF) ($\lambda_{in}Q$)	0.098	0.495	0.157	0.626
Improved corr. (BM-RSF) (Syn) (CS2)	0.099	0.496	0.137	0.589
Improved corr. (BM-RSF) (Syn) ($\lambda_{in}Q$)	0.099	0.497	0.160	0.631

(RSFs), both based on APPHs with reference to the Ag(350eV) peak, are given, one for a CMA system with 0.6% resolution and 5 keV primary energy (PHI), and the other for a CHA system with 0.5% resolution and 10 keV primary energy (JEOL) (from respective handbooks or manufacturer data [4.21, 4.24]). In the following, we refer to the JEOL set of data.

A comparison of results for Fe–Cr and Fe–C of the five different approaches to quantification outlined above using the respective matrix relative correction factors $F^m_{i,j}$ after (4.83) is summarized in Table 4.6. As expected, when compared to E-RSF, almost no change is found for Cr in Fe because of similar atomic data. In contrast, for C in Fe, the correct, matrix-corrected values deviate by about 30% (Fe–16at%C) and by about 20% (Fe–61at%C) from the uncorrected E-RSF values (10 and 50at%, respectively). All approaches deviate in the same direction. While the Payling approach is too weak because of only density and no backscattering correction, the other approaches give values that are within 2 at% scatter (15at%C) and 4at%C (61at%C). Supposing (SG) and (Syn) $\lambda_{in}Q$ values to be most reliable, the latter are less than 1 at% (15at%C) or 2 at% (61 at%) apart. At present, the proposed matrix-less binary matrix correction factors based on appropriate $\lambda_{in}Q$ values from the NIST EAL database [4.37] seem to yield the most accurate quantitative values. In the future, the convenient but less accurate Ichimura–Shimizu equations (4.130) will be replaced by new, improved databases [4.149].

The above quantification schemes are only valid for homogeneous composition from the very first surface layer to at least a depth given by the information depth of the measured photo- or Auger electrons (about 5 times the attenuation

length). In most practical cases, a sample is covered by a thin surface layer with different compositions from the bulk, which will change the relative intensities of the sample constituents and give an incorrect sample composition. Only if the layer composition and thickness is known (e.g., by angle-resolved studies with AR-XPS or AR-AES) (see Sect. 7.2.1), a contamination layer correction can be made. Because sputter cleaning of a multicomponent sample generally changes the surface composition (see, e.g., preferential sputtering in Sect. 7.1.4), this method cannot be recommended for correct determination of a homogeneous bulk composition. However, angle-resolved spectrometry in combination with sputter depth profiling can be used to determine composition and thickness of the altered layer (i.e., the atomic mixing length; see Sect. 7.1.8). Usually, only intragranular fracture surfaces of a homogenized alloy give a sufficiently well-defined, constant in-depth distribution.

According to (4.129), determination $N_A(z)$ by measurement of I_A alone is generally ambiguous. Figure 4.13 shows schematically how the same XPS or Auger-electron intensity can be obtained for quite different distributions of layer compositions near the surface. An unambiguous relation between N_A and I_A is only possible for two simple cases: a constant concentration with depth, as shown above in this section, and a (constant) concentration confined to a thin surface layer of constant thickness, as shown in the next section. In general, determination of $N_A(z)$ is only possible by depth profiling, as presented in Chap. 7.

4.4.3 Quantitative AES Analysis of Thin Surface Layers

4.4.3.1 Generalized Layer-by-Layer Quantification

In close analogy to XPS, the intensity contribution of a thin layer of A with constant mole fraction X_A between depth z_2 and z_1 , $I_A(z_2 - z_1)$, given by (4.85), has to be extended by the AES backscattering factor $(1 + r_{m,A})$ (see Sect. 4.4.1), resulting in

$$I_A(z_2 - z_1) = \frac{I_A^0 X_A (z_2 - z_1)}{1 + r_{A,U(A)}} \left\{ \left[1 + r_{m,U(A)}(z_1) \right] \exp \left[-z_1 / (\lambda_{m,E(A)} \cos \theta) \right] - \left[1 + r_{m,U(A)}(z_2) \right] \exp \left[-z_2 / (\lambda_{m,E(A)} \cos \theta) \right] \right\} \quad (4.146)$$

with $1 + r_{A,U(A)}$ the backscattering factor of pure elemental matrix A for element A (according to the ionization energy of the respective electron level X of A), and $1 + r_{m,U(A)}$ that of matrix m for element A. The division with $1 + r_{A,U(A)}$ is necessary because the standard elemental bulk intensity I_A^0 already contains the intrinsic pure elemental backscattering factor.

If the backscattering factor for the analyzed element is different from that of the matrix, the change in local concentration is accompanied by a change of the local backscattering factor, which can only be approximately calculated by iterative approaches to in-depth composition. A proposal for multilayers [4.130] can be transferred to special layer structures, as shown below.

4.4.3.2 Full Coverage: Single Component Layer of A on Substrate B

Monolayer Approximation: As already shown in Sect. 4.4.1, the fundamental difference between the sensitivity factor for XPS and AES is the dependence of the latter on the backscattering factor that has to be taken into account for matrix correction factors in bulk systems. For a thin overlayer on a bulk substrate, the intensity of the overlayer is additionally increased by backscattering from both within the layer and from the substrate. Considering a freestanding layer, it is clear that for a thick layer, we have practically bulk conditions, whereas for a very thin layer of the order of a monolayer, the intrinsic backscattering effect will approach zero. For such a thin overlayer of element (or homogeneous component) A on substrate B, the overlayer intensity I_A is increased by the respective backscattering factor for the substrate material B with respect to the ionization energy of the overlayer material A, i.e., $1 + r_{B,U(A)}$. Therefore, (4.146) with $z_1 = 0$ and $z_2 = d$, with d being the overlayer thickness, yields

$$I_A = I_A^0 \frac{1 + r_{B,U(A)}}{1 + r_{A,U(A)}} \{1 - \exp[-d/(\lambda_{A,E(A)} \cos \theta)]\}, \quad (4.147a)$$

where I_A^0 is the intensity of the 100% bulk elemental standard and $\lambda_{A,E(A)}$ is the attenuation length of the signal of A (at kinetic energy E_A) in matrix A. The intensity I_B of the signal of B is attenuated by the overlayer and is given by

$$I_B = I_B^0 \exp[-d/(\lambda_{A,E(B)} \cos \theta)] \quad (4.147b)$$

where I_B^0 is the AES intensity of the bulk elemental standard and $\lambda_{B,A}$ is the attenuation length of the signal of B (at kinetic energy E_B) in matrix A. From the ratio of both expressions, (4.147a) and (4.147b), the relative overlayer thickness $d/(\lambda_{A,E(A)})$ can be found if the ratio of the two standard intensities I_A^0/I_B^0 (i.e., the elemental relative sensitivity factor $S_{A,B}$) and the backscattering factor ratio are known:

$$\frac{I_A I_B^0}{I_B I_A^0} = \frac{(1 + r_{B,U(A)})}{(1 + r_{A,U(A)})} \frac{\{1 - \exp[-d/\lambda_{A,E(A)} \cos \theta]\}}{\exp[-d/\lambda_{A,E(B)} \cos \theta]}. \quad (4.148)$$

For $\lambda_{A,E(A)} = \lambda_{A,E(B)}$, i.e., when the energies of the emitted photo- or Auger electrons of A and B are close to each other (note the material A is the same), (4.148) gives an explicit result for $d/\lambda_{A,E(A)}$:

$$\frac{d}{\lambda_{A,E(A)}} = \cos \theta \ln \left[\frac{(1 + r_{A,U(A)}) I_A I_B^0}{(1 + r_{B,U(A)}) I_B I_A^0} + 1 \right]. \quad (4.149)$$

The case of (4.149) applies, for example, if an oxide layer thickness of element B is determined on B by measurement of the intensity of the pure metallic and the slightly shifted peak of B in an oxide bond.

In general, $\lambda_{A,E(A)} \neq \lambda_{A,E(B)}$ (4.148) – as in (4.98) for XPS; the attenuation length, $\lambda_{A,E(B)}$, can be replaced by $\lambda_{A,E(A)}\lambda_{A,E(B)}/\lambda_{A,E(A)}$, and we obtain the following implicit solution for $d/(\lambda_{A,E(A)} \cos \theta)$:

$$\begin{aligned} \frac{(1 + r_{A,U(A)})}{(1 + r_{B,U(A)})} \frac{I_A I_B^0}{I_B I_A^0} &= \exp \left[\frac{d}{\lambda_{A,E(A)} \cos \theta} \frac{\lambda_{A,E(A)}}{\lambda_{A,E(B)}} \right] \\ &- \exp \left[-\frac{d}{\lambda_{A,E(A)} \cos \theta} \left(1 - \frac{\lambda_{A,E(A)}}{\lambda_{A,E(B)}} \right) \right], \end{aligned} \quad (4.150)$$

which is similar to (4.98) but with the additional backscattering factor ratio on the left side. As in (4.99), the ratio $\lambda_{A,E(A)}/\lambda_{A,E(B)}$ can be replaced by the ratio of the kinetic energy dependence of the attenuation length, $(E_B/E_A)^{0.75}$ after (4.19), and in analogy to (4.99), we get

$$\begin{aligned} \frac{(1 + r_{A,U(A)})}{(1 + r_{B,U(A)})} \frac{I_A/S_A}{I_B/S_B} &= \exp \left[\frac{d}{\lambda_{A,E(A)} \cos \theta} \left(\frac{E_A}{E_B} \right)^{0.75} \right] \\ &- \exp \left[-\frac{d}{\lambda_{A,E(A)} \cos \theta} \left(1 - \left(\frac{E_A}{E_B} \right)^{0.75} \right) \right], \end{aligned} \quad (4.151)$$

with S_A and S_B being the elemental relative sensitivity factors.

Equation 4.151 results in dependences similar to those in Fig. 4.27, if the intensity ratio is modified by the backscattering factor ratio. Note that (4.145)–(4.151) are only valid for very thin layers of the order of $d = 1\text{ML}$. For a layer thickness of two or more monolayers (ML), a thickness-dependent backscattering factor has to be used to give correct results.

Thickness Dependence: Nanolayers: The approximations given in (4.145)–(4.151) are only valid, when the backscattered electrons from substrate B with high enough energy are not yet substantially attenuated by the overlayer, i.e., for a very thin layer of A. For a very thick overlayer, the bulk backscattering factor of A applies. Within this range, typical for nanolayers of thickness $d = 0.5\text{--}50\text{ nm}$, the backscattering effect of substrate B gradually vanishes with thickness d . Hofmann et al. [4.130, 4.151, 4.152] proposed a simple model for the dependence of the backscattering effect on layer thickness, which is represented by an exponential decay function of the backscattering factor with depth. Compared to recently published more elaborate approaches [4.156, 4.157, 4.158], this simple model has the advantage of straightforward application for the practical analyst and appears to be basically in accordance with those approaches. With decreasing layer thickness, the mean backscattering effect of A in layer A decreases, and at the same time that of substrate B on layer A increases. If both effects are assumed to follow an exponential decay function, (4.147a) can be extended by replacing d by the variable layer thickness $z_0 - z$, where z_0 denotes the A/B interface [4.151, 4.152]:

$$\begin{aligned}
\frac{I_A(1 + r_{A,U(A)})}{I_A^0} &= \left\{ 1 - \exp \left[\frac{z_0 - z}{\lambda_{A,E(A)} \cos \theta} \right] \right\} \\
&\times \left\{ 1 + r_{A,U(A)} \left(1 - \exp \left[\frac{z_0 - z}{L_{A,A,A}} \right] \right) \right. \\
&\left. + r_{B,U(A)} \exp \left[\frac{z_0 - z}{L_{B,A,A} \cos \theta} \right] \right\}. \quad (4.152)
\end{aligned}$$

In (4.152), a new parameter, L , is introduced, the so-called mean effective backscattering decay length (MEBDL) [4.130,4.152]. It is based on the heuristic assumption that the backscattered electrons lose energy approximately in an exponential fashion with distance in backward direction. The notation $L_{A,A,A}$ gives the MEBDL for the backscattering factor of element A on the ionization level of A in material A. Likewise, $L_{B,A,A}$ means the MEBDL of substrate B on the ionization level of A in material A. At present, the value of the MEBDL cannot be predicted, but it is obvious that it has to be larger than the IMFP for the primary electron energy but smaller than half their projected range [4.130]. Comparison with experimental depth profiling results [4.130,4.152] shows that we may approximately set $L_{A,A,A} = L_{B,A,A}$ which simplifies (4.152) to

$$\frac{I_A}{I_A^0} = \left\{ 1 - \exp \left[\frac{z_0 - z}{\lambda_{A,E(A)} \cos \theta} \right] \right\} \left\{ 1 + \left(\frac{1 + r_{B,U(A)}}{1 + r_{A,U(A)}} - 1 \right) \exp \left[\frac{z_0 - z}{L_{B,A,A} \cos \theta} \right] \right\}. \quad (4.153)$$

Equation 4.153 was originally derived for applications to depth profiling, therefore for increasing z , the layer gets thinner. For the limit of a very small layer thickness $z_0 - z \ll L_{B,A,A}$, (4.147a) results, and for similar backscattering factors (or backscattering terms) of layer and of substrate on A, $r_{A,U(A)} = r_{B,U(A)}$, the general equation (4.88a) with $d = -(z_0 - z)$ is obtained.

Figure 4.55 shows a plot of (4.153) with typical values of $\lambda_{A,E(A)} \cos \theta = 1$ nm, $L_{B,A,A} = 10$ nm for 5 different ratios of the bulk backscattering factors $((1 + r_{B,U(A)})/(1 + r_{A,U(A)}))$ is equal to $(1 + r_{BA})/(1 + r_{AA})$ in short form writing). For a value of this ratio > 1 , the backscattering effect of the substrate increases the measured intensity in the vicinity of the substrate, with a broad maximum for layers of typically several nanometers thickness, whereas for the values of the ratio < 1 , the intensity falls off more steeply than without backscattering influence, i.e., a ratio of unity. (For more details, see Chap. 7 on backscattering influence on depth profiling.)

As an example, Fig. 4.56 (from [4.151]) shows an application of (4.153) to the results of Tarnag and Wehner [4.153], where the Auger peak-to-peak height of Mo (120 eV) is measured during evaporation of Mo on W. The full drawn line corresponds to (4.153) with $(1 + r_{B,U(A)})/(1 + r_{A,U(A)}) = 1.35$, $L_{W,Mo,Mo} = 20$ ML (1 ML = 0.25 nm). The numerical deviation from the value calculated with the Ichimura–Shimizu equations for the backscattering ratio ($= 1.20$ after (4.130), $\alpha = 30^\circ$) is not unexpected (see, e.g., Fig. 4.53).

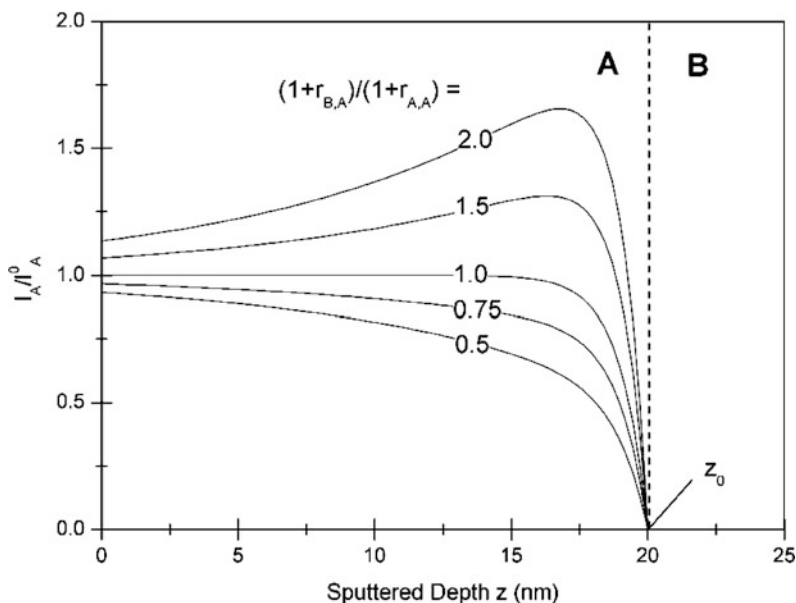


Fig. 4.55 Dependence of the measured AES intensity of A in a layer of A on substrate B on the thickness of the layer, for different backscattering factor ratios $(1 + r_{B,A})/(1 + r_{A,A}) = (1 + r_{B,U(A)})/(1 + r_{A,U(A)})$, normalized to $(1 + r_{A,U(A)}) = 1$, according to (4.153) with $\lambda_{A,E(A)} \cos \theta = 1$ nm, $L_{B,A,A} = 10$ nm. Note that (4.153) and Fig. 4.55 were originally developed for sputter depth profiling. For evaporation of A, the start is at $z_0 = 0$ ($z = 20$ nm) and the end at $z = 0$ corresponds to 20 nm thickness (Reproduced from S. Hofmann, J.Y. Wang [4.152]. Copyright J. Wiley & Sons Ltd. 2007)

It is interesting to calculate the error when neglecting the depth dependence of the ratio of the layer/substrate backscattering factors as a function of layer thickness. By comparing (4.153) with (4.147a), we get for the intensity error $\Delta(I_A/I_A^0)$,

$$\Delta \left(\frac{I_A}{I_A^0} \right) (\%) = \left\{ \frac{\left(\frac{1 + r_{B,A}}{1 + r_{A,A}} \right)}{\left[1 + \left(\frac{1 + r_{B,A}}{1 + r_{A,A}} - 1 \right) \exp \left(-\frac{d}{L_{B,A,A}} \right) \right]} - 1 \right\} \times 100. \quad (4.154a)$$

Equation 4.154a is depicted in Fig. 4.57 for a typical value of $L_{B,A,A} = 10$ nm as a function of backscattering factor ratios between extreme but possible values of 0.5 and 2.0 (see, e.g., (4.130)) and different layer thicknesses (1–2–3–10–30 monolayers, 1ML = 0.3 nm). The error increases strongly with backscattering ratio and with layer thickness, but even for 1ML, the error can be a few percent.

If backscattering is not at all taken into account, the error increases considerably:

$$\Delta \left(\frac{I_A}{I_A^0} \right) (\%) = \left\{ 1 / \left[1 + \left(\frac{1 + r_{B,A}}{1 + r_{A,A}} - 1 \right) \exp \left(-\frac{d}{L_{B,A,A}} \right) \right] - 1 \right\} \times 100. \quad (4.154b)$$

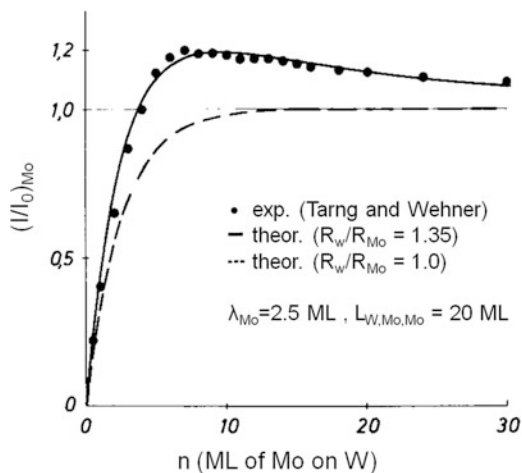


Fig. 4.56 Application of (4.153) to the results of Tarng and Wehner [4.153], showing the measured, normalized Auger peak-to-peak height of Mo (120 eV) as a function of the number of monolayers of Mo evaporated on W. The *full drawn line* corresponds to (4.153) with $(1 + r_{B,A})/(1 + r_{A,A}) = R_W/R_{Mo} = 1.35$, $L_{W,Mo,Mo} = 20\text{ML}$ (1ML = 0.25 nm). The *dashed line* is the “true profile” corrected for the backscattering influence. *Solid and dashed lines* were calculated according to the assumptions shown in the figure (Reproduced from S. Hofmann [4.151])

Compared to Fig. 4.57, the dependence on layer thickness is completely different in Fig. 4.58. Here, the error is largest for a monolayer and decreases for thicker layers. For very thick layers, there is no error because backscattering from the substrate vanishes.

In order to avoid an error larger than 10%, as a consequence of Fig. 4.58, it is necessary to apply (4.147a) in the monolayer regime with a fixed backscattering factor ratio, if the latter exceeds 1.0 ± 0.1 . In contrast, Fig. 4.51 shows that in case of a monolayer of A, even extreme values of the backscattering factor ratio, the error does not exceed 3%. Only for thicker layers $>3\text{ML}$, an error above 10% is expected and has to be avoided by thickness-dependent backscattering factor correction after (4.153).

The composition and depth dependence of the backscattering factor complicates quantitative AES considerably as compared to quantitative XPS. This is particularly obvious for partial coverage and for island formation in thin layer deposition (e.g., (4.100)–(4.102)). For example, by replacing a smooth layer by islands with increased thickness and less coverage (see, e.g., Fig. 4.23 and (4.120a)), the average layer thickness is increased and, according to (4.153), the average backscattering correction factor decreases. Thus, surface roughness is expected to decrease the backscattering correction (see also MRI model extension in Chap. 7).

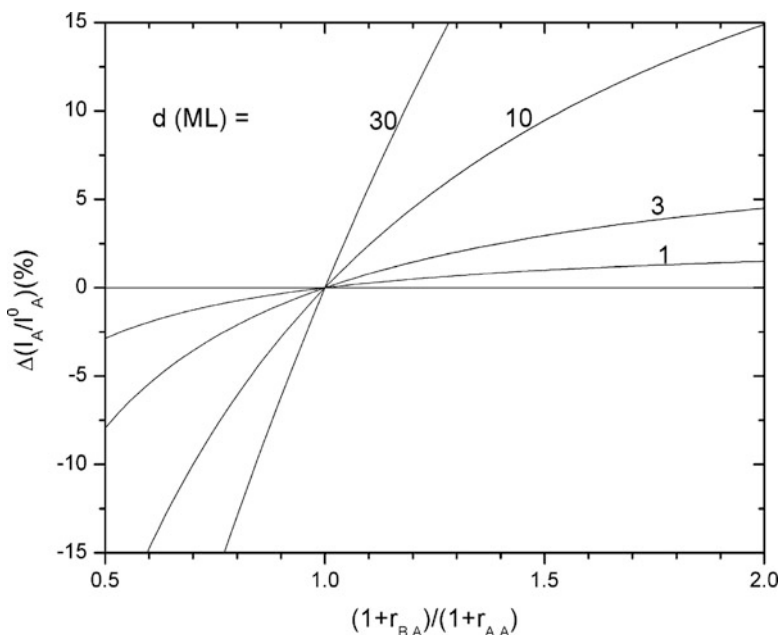


Fig. 4.57 Relative intensity error $\Delta(I_A/I_A^0)$ (%) between constant (for $d \rightarrow 0$) and depth-dependent backscattering correction for different layer thickness of A on B in monolayers (1ML = 0.3 nm), after (4.154a), assuming a typical value of $L_{B,A,A} = 10$ nm (33 ML) as a function of backscattering factor ratios between substrate B and layer A

4.4.3.3 Fractional Coverage: Surface Segregation Layer

For the most frequently studied case of monolayer surface segregation of a dilute solute A in matrix B, Fig. 4.29 and (4.148) apply. For the more general case depicted in Fig. 4.29, for monolayer segregation, the relative sensitivity factors (already matrix-corrected by attenuation length and density effects as in XPS, see Sect. 4.3.2) have to be multiplied by the backscattering factor ratio terms for A and B, and (4.106) for AES is given by

$$\frac{I_A I_{B,m}^0 (1 + r_{A,U(A)})(1 + r_{m,U(B)})}{I_B I_{A,m}^0 (1 + r_{B,U(B)})(1 + r_{m,U(A)})} = \frac{X_A^s + (X_A^b - X_A^s) \exp \left[-\frac{d}{\lambda_{E(A),s} \cos \theta} \right]}{1 - X_A^s + (X_A^s - X_A^b) \exp \left[-\frac{d}{\lambda_{E(B),s} \cos \theta} \right]}, \quad (4.155)$$

where the ratio $(1 + r_{m,B})/(1 + r_{m,A})$ takes into account the effect of (bulk) matrix m , composed of A and B, on the backscattering factor for A and B in the bulk and its effect on the intensity of the first monolayer. As in (4.106), the subscript s for the attenuation lengths refers to the composition s of the surface layer.

For thicker layers, the correction gets more complicated because the thickness dependence of the backscattering effect has to be taken into account, as described by (4.153).

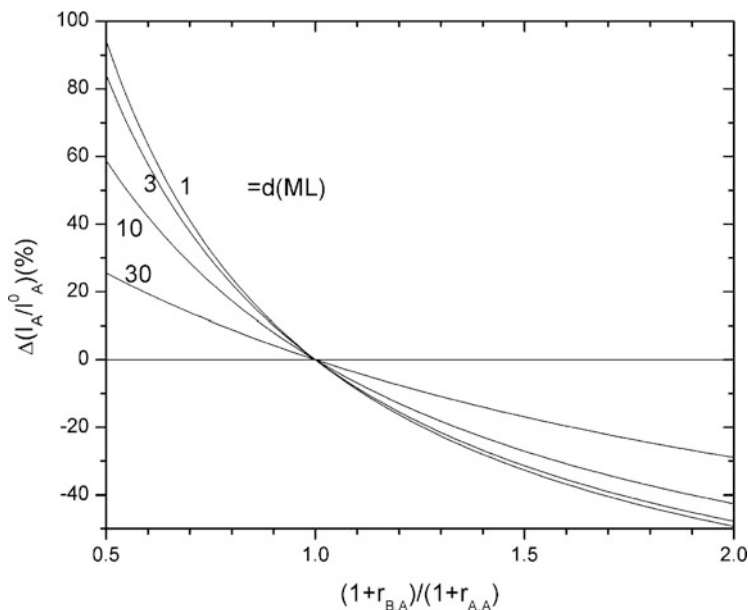


Fig. 4.58 Relative error $\Delta(I_A/I_A^0)$ (%) if backscattering correction is ignored as compared to full, depth-dependent backscattering correction, for different layer thickness of A on B in monolayers (1ML = 0.3 nm), after (4.149b), assuming a typical value of $L_{B,A,A} = 10$ nm, as a function of backscattering factor ratios between substrate B and layer A

For the simpler case of a dilute solute A in a matrix of almost pure B (Fig. 4.30), $X_A^b = 0$ and $(1 + r_{m,U(B)}) = (1 + r_{B,U(B)})$, $(1 + r_{m,U(A)}) = (1 + r_{B,U(A)})$, (4.155) gives, in analogy to (4.110),

$$\frac{I_A I_B^0 (1 + r_{A,U(A)})}{I_B I_A^0 (1 + r_{B,U(A)})} = \frac{X_A^s / X_B^s \{1 - \exp[-d/\lambda_{A,A} \cos \theta]\}}{X_A^s / X_B^s \exp[-d/\lambda_{A,A} (E_B/E_A)^{0.75} \cos \theta] + 1}. \quad (4.156)$$

For Auger analysis of surface segregation of O (= A) on Nb (= B) [4.119], the backscattering factor ratio after (4.130) is $(1 + r_{A,U(A)})/(1 + r_{B,U(A)}) = 1.42/1.80 = 0.79$. According to (4.156), this means that the measured, normalized intensity ratio of O to Nb has to be lowered by the factor 0.79 to give the correct X_A/X_B . Figure 4.59 shows a plot according to (4.156), in analogy to Fig. 4.30, with (full drawn line) and without (dashed lines) backscattering correction for monolayer segregation and $(1 + r_{A,U(A)})/(1 + r_{B,U(A)}) = 0.79$. A result for Nb–O similar to this figure was reported earlier [4.119, 4.154], but without taking the backscattering factor into account. As obvious from Fig. 4.58, the effect of backscattering strongly decreases with increasing layer thickness.

In analogy to (4.113), the amount of surface concentration X_A^s including the backscattering extension for AES is given by

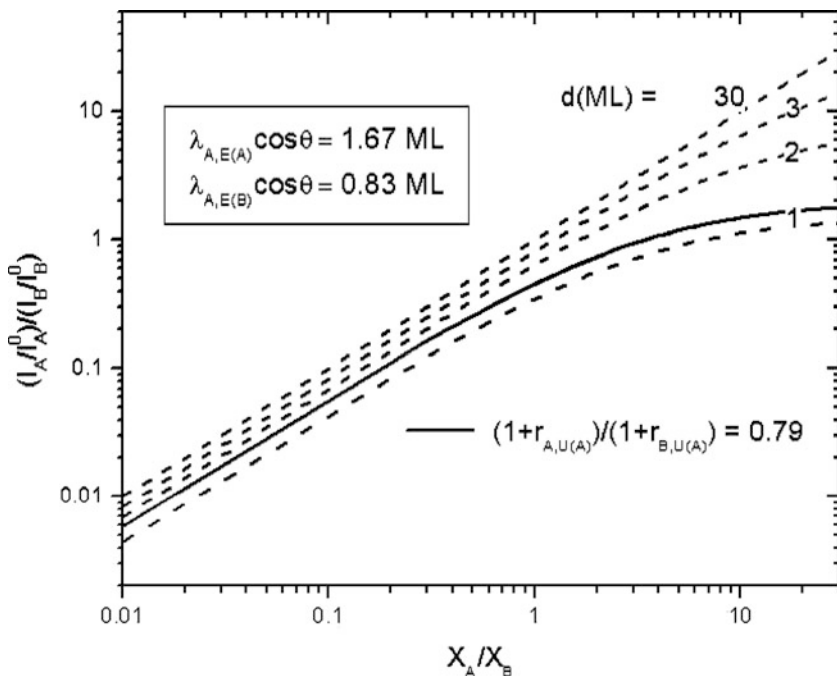


Fig. 4.59 Normalized intensity ratio $(I_A/I_A^0)/(I_B/I_B^0)$ of a segregation or evaporation layer with composition given by X_A/X_B on substrate B according to (4.156), with respective $\lambda \cos \theta$ values given in the *inset* and thickness between 1 and 30 monolayers (ML). Dashed lines are without backscattering correction as in Fig. 4.30, but the first monolayer is additionally shown with backscattering factor ratio correction (*full drawn line*)

$$X_A^s = \frac{\frac{I_A I_B^0 (1+r_{A,U(A)})}{I_B I_A^0 (1+r_{B,U(A)})}}{1 - \exp[-d/\lambda_{A,E(A)} \cos \theta] + \frac{I_A I_B^0 (1+r_{A,U(A)})}{I_B I_A^0 (1+r_{B,U(A)})} \{1 - \exp[-d/\lambda_{A,E(B)} \cos \theta]\}}. \quad (4.157)$$

The linear approximation for $\exp(-d/(\lambda_{A,E(A)} \cos \theta)) \ll 1$ follows from (4.157) as [4.1]

$$X_A^s = \frac{I_A I_B^0 (1+r_{A,U(A)})}{I_B I_A^0 (1+r_{B,U(A)})} \frac{\lambda_{A,E(A)} \cos \theta}{d}. \quad (4.158)$$

As an example, let us assume surface segregation of carbon (=A) on iron (=B). With (4.130), we get $(1.39/1.85) = 0.76$ for the backscattering correction factor $(1+r_{A,U(A)})/(1+r_{B,U(A)})$ in (4.157). Figure 4.60 depicts the exact relation (4.156) (black solid line) together with several common approximations. The linear approximation (4.156) (black dashed line) shows an error of about 10% at $(I_C/I_C^0)/(I_{Fe}/I_{Fe}^0) = 0.1$ for both cases with and without backscattering correction (blue solid and dashed lines, respectively). Here, ignoring the backscattering correction gives the high error of about 28% for the whole range of X_C . Of course,

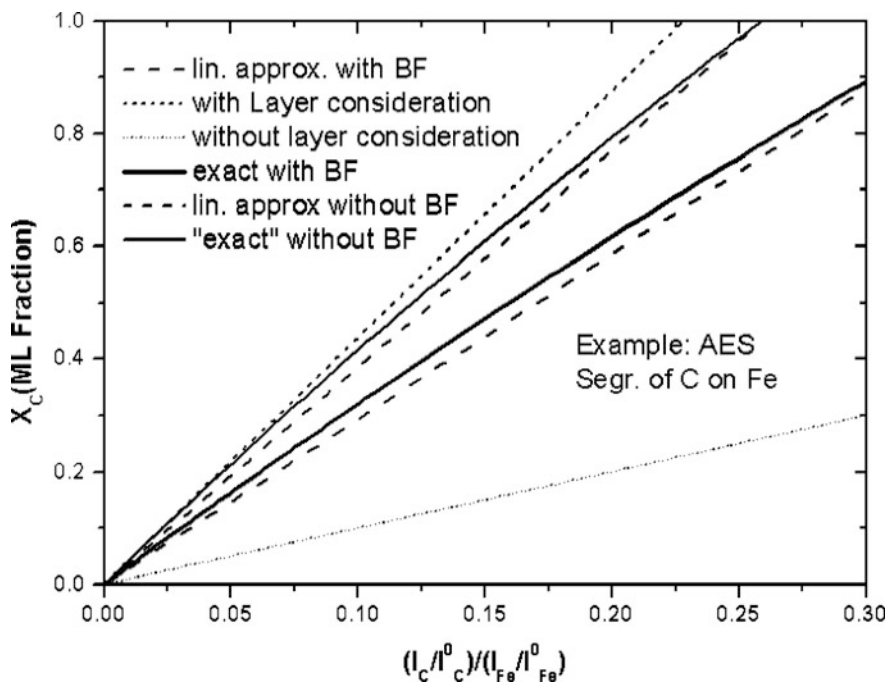


Fig. 4.60 Surface segregation layer of carbon on iron in the monolayer regime, showing the monolayer fraction of C, X_C , as a function of the measured signal strength ratio, I_C/I_{Fe} , normalized by the elemental relative sensitivity factor (or element standard intensity ratio) I_{Fe}^0/I_C^0 taking into account the backscattering factor (BF) correction (*black solid line*) after (4.157) with respective parameter values from Table 4.5. The linear approximation after (4.158) is shown as *black dashed line*. In addition, both lines without BF correction are shown (*solid and dashed lines*, respectively). Furthermore, the *straight lines* for taking into account only the layer structure but ignoring bulk signal attenuation (*short dashed line*) and the “naïve” evaluation completely neglecting the layer structure (*dotted line*)

the “naïve” quantification, by treating the segregation layer signal like a bulk signal, gives a completely wrong result with an apparent monolayer fraction of a factor of 2.9 too low (*dotted magenta line*). Taking into account the confinement in a thin layer but not the attenuation of the bulk Fe signal intensity shows about 10% error at $(I_C/I_C^0)/(I_{Fe}/I_{Fe}^0) = 0.2$ which increases with coverage (*short dashed blue line*).

Further examples of quantitative analysis of surface and grain boundary segregation are given in Sects. 9.1.4 and 9.2.5.

Fractional surface coverage in the monolayer regime is represented by expressions (4.50)–(4.52) if X_A^s is replaced by Θ_A , as obvious by comparing Figs. 4.23b and 4.25b. For higher layer thickness (0.5–5 nm, see above), (4.147)–(4.149) apply for fraction Θ_A , while fraction $(1 - \Theta_A)$ is unaffected by the overlayer.

4.4.3.4 Influence of a Contamination Layer

Basically, the same formalism as with XPS applies here, the main difference being the backscattering factor. As seen in the section on segregation above, for a thin film, the backscattering factor can be looked upon as a change in the relative sensitivity factor.

Contamination Layer on a Homogeneous Binary System

The most common case is that of a thin contamination layer on a homogeneous binary system, as depicted in Fig. 4.40. For the case of a carbonaceous contamination layer (C) on an oxide or alloy (A,B), the normalized intensity ratio is described as in (4.124a):

$$\frac{I_A I_{B,m}^0}{I_{A,m}^0 I_B} = \frac{X_A}{X_B} \exp \left[-\frac{d_C}{\lambda_{C,E(C)}^0 \cos \theta} \left(\frac{E_C}{E_A} \right)^{0.75} \left(1 - \left(\frac{E_A}{E_B} \right)^{0.75} \right) \right]. \quad (4.159a)$$

However, the standard matrix elemental intensity ratio contains the backscattering correction factor which is included in the AES matrix correction factor (see, e.g., (4.139)). In contrast, the second equation necessary to get the contamination layer thickness in (4.159a) has to take into account the backscattering factor ($1 + r_{m,C}$) of matrix m (A,B) on the carbon signal and writes instead of (4.124c)

$$\frac{I_C I_{B,m}^0 (1 + r_{C,U(C)})}{I_{C,m}^0 I_B (1 + r_{m,U(C)})} = \left(\frac{1}{1 + \frac{X_A}{X_B}} \right) \left\{ \frac{\exp \left[-\frac{d_C}{\lambda_{C,E(C)} \cos \theta} \left(\frac{E_C}{E_B} \right)^{0.75} \right]}{-\exp \left[-\frac{d_C}{\lambda_{C,E(C)} \cos \theta} \left(1 - \left[\frac{E_C}{E_B} \right]^{0.75} \right) \right]} \right\}. \quad (4.159b)$$

The backscattering factor of the unknown matrix can be estimated by assuming an average atomic number (e.g., from quantification without backscattering) to be inserted in the Ichimura–Shimizu equations (4.130) and repeating the quantification. Quantitative evaluation proceeds as shown above for XPS in Sect. 4.3.3.

Contamination Layer on a Thin Film (Double-Layer Structure)

In case of a layered structure as depicted in Fig. 4.40, (4.127a)–(4.127c) apply with the backscattering correction factor for the intensities. Thus, I_A^0 is replaced by $I_A / I_A^0 (1 + r_{A,U(A)}) / (1 + r_{B,U(A)})$. However, this factor is modified by the dependence of the effect of B on the layer thickness of A, d_A , $(1 + r_{B,U(A)}) = f(d_A)$, as described by (4.153) and visualized in Fig. 4.55. Two different depth-dependent backscattering factors apply for the contamination layer, $(1 + r_{B,U(C)}) = f(d_A)$,

multiplied by $(1 + r_{A,U(C)}) = f(d_A)$. While the first factor decreases with d_A , the second factor increases with d_A . This fact is explained in detail in Sect. 7.1.8.

Note that all calculations can first be done without taking into account the backscattering factor correction. With the “uncorrected” layer structure obtained in such a way, the layer thickness dependence (4.153) can be used to obtain the backscattering factors that give the correct signal strength for the thin film at the interface thin film/contamination layer and for correction of the contamination layer intensity. With these corrected intensities, the whole calculation can easily be repeated to get the correct layer structure values.

4.5 Summary and Conclusion

Quantification of experimental data is the key to understanding materials properties and behavior. Today, a fairly reliable framework of quantification procedures is available, owing to contributions of many researchers, but above all to the outstanding work of Seah and Powell. The starting quantity of all quantification approaches is the measured intensity of a specific elemental peak in XPS or AES spectra, which is proportional to the peak area obtained by appropriate background subtraction. Depending on the purpose and accuracy required, simple linear subtraction or more sophisticated methods may be used in XPS, whereas in AES, frequently, differentiation prevails. To avoid exact knowledge of instrumental and materials parameters, the peak ratio method is generally applied to get elemental mole fraction ratios, based on elemental relative sensitivity factors (E-RSFs). Correction of matrix effects requires exact knowledge of the electron attenuation length of the Auger- and photoelectrons, a key parameter in any quantification for which now fairly reliable databases are available. Matrix correction factors are used to establish a database of matrix relative sensitivity factors (M-RSFs) for improved quantification. In special cases, asymmetry of photoelectron emission, intrinsic plasmon, and surface excitation effects in XPS have to be considered. In addition, the higher background intensity in AES as compared to XPS and the electron backscattering effect in AES require somewhat different routes for quantification. Therefore, quantitative XPS and AES are treated separately. Results of new theoretical advances in electron backscattering are now gradually replacing older databases. In any case, knowledge of the in-depth distribution of composition is indispensable for correct quantification, at least within the information depth of about 5 times the electron escape depth (and beyond for AES when variations in backscattering factor are important). The in-depth distribution is revealed by compositional depth profiling methods summarized in Chap. 7.

There are two limiting cases where the convolution integral of the intensity can be easily resolved: homogeneous distribution of the composition and thin surface layers. Partial layer and multilayer coverage considerations disclose connections of quantitative surface analysis with nanostructure. Recent results on thickness-dependent backscattering effects on layer analysis with AES show new ways

for correct quantification. For many applications, it is necessary to correct for carbonaceous contamination layers that are frequently met even in UHV systems. These corrections can be performed with reasonable accuracy. The developed formalism can be directly applied to double-layer structures as well as fractional layers encountered in different growth mechanisms of adsorbate evaporation.

It should be kept in mind that the accuracy of any quantification is limited by assumptions and simplifications that are inevitably involved. Therefore, it is important to get an idea of probable errors when using particular approaches, as outlined in several paragraphs.

References

- 4.1. M.P. Seah, Quantification in AES and XPS, in *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, Chap. 13, ed. by D. Briggs, J.T. Grant (IM Publication, Chichester, 2003), pp. 345–375
- 4.2. M.P. Seah, Quantification of AES and XPS, in *Practical Surface Analysis*, Chap. 5, 2nd edn., ed. by D. Briggs, M.P. Seah, vol. 1: *AES and XPS* (Wiley, Chichester, 1990), pp. 206–251
- 4.3. M.V. Zakhvatova, F.Z. Gil'mutdinov, D.V. Surnin, *Phys. Met. Metallogr.* **104**, 157 (2007)
- 4.4. D.A. Shirley, *Phys. Rev. B* **5**, 4707 (1972)
- 4.5. J. Vegh, *J. Electron Spectrosc. Relat. Phenom.* **151**, 93 (2001)
- 4.6. H.E. Bishop, *Surf. Interface Anal.* **3**, 272 (1981)
- 4.7. S. Tougaard, *Surf. Sci.* **216**, 343 (1981)
- 4.8. S. Tougaard, *J. Vac. Sci. Technol. A* **14**, 1415 (1996)
- 4.9. M.P. Seah, *Surf. Sci.* **420**, 285 (1999)
- 4.10. M.P. Seah, I.S. Gilmore, S.J. Spencer, *J. Electron Spectrosc. Relat. Phenom.* **120**, 93 (2001)
- 4.11. C.J. Powell, J.M. Conny, *Surf. Interface Anal.* **41**, 804 (2009)
- 4.12. M.P. Seah, I.S. Gilmore, H.E. Bishop, G. Lorang, *Surf. Interface Anal.* **26**, 701 (1998)
- 4.13. S. Hofmann, *J. Vac. Sci. Technol. A* **4**, 2789 (1986)
- 4.14. R. Kosiba, J. Liday, G. Ecke, O. Ambacher, J. Breza, P. Vogrincic, *Vacuum* **80**, 990 (2006)
- 4.15. M.P. Seah, M.T. Anthony, *J. Electron Spectrosc. Relat. Phenom.* **32**, 73 (1983)
- 4.16. I.S. Gilmore, M.P. Seah, *Appl. Surf. Sci.* **93**, 273 (1996)
- 4.17. W. Pamler, *Surf. Interface Anal.* **13**, 55 (1988)
- 4.18. W.F. Stickle, The Use of Chemometrics in AES and XPS Data Treatment, in *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, Chap. 14, ed. by D. Briggs, J.T. Grant (IM Publications, Chichester, 2003), pp. 377–396
- 4.19. J.D. Cox, *Pure Appl. Chem.* **54**, 1239 (1982)
- 4.20. W. Palmberg, *Anal. Chem.* **45**, 549A (1973)
- 4.21. L.E. Davis, N.C. MacDonald, P.W. Palmberg, G.E. Riach, R.E. Weber, *Handbook of Auger Electron Spectroscopy*, 2nd edn. (Perkin-Elmer Corp., Eden Prairie, 1978); K.D. Childs, B.A. Carlson, L.a. LaVanier, J.F. Moulder, D.F. Paul, W.F. Stickle, D.G. Watson, *Handbook of Auger Electron Spectroscopy*, 3rd edn. (Physical Electronics Inc., Eden Prairie, 1995)
- 4.22. C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, G.E. Muilenberg, *Handbook of X-Ray Photoelectron Spectroscopy* (Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie, 1979)
- 4.23. J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy* (Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie, 1992)

- 4.24. N. Ikeo, Y. Iijima, N. Niimura, M. Sigematsu, T. Tazawa, S. Matsumoto, K. Kojima, Y. Nagasawa, *Handbook of X-Ray Photoelectron Spectroscopy* (JEOL, Tokyo 1991)
- 4.25. M.P. Seah, Surf. Interface Anal. **9**, 85 (1986)
- 4.26. Geller Microanalytical Laboratory, Topsfield. www.gellermicro.com
- 4.27. M.P. Seah, I.S. Gilmore, Phys. Rev. B **73**, 174113 (2006)
- 4.28. C.S. Fadley, J. Electron Spectrosc. Relat. Phenom. **5**, 725 (1974)
- 4.29. A. Jablonski, C.J. Powell, Surf. Sci. **574**, 219 (2005)
- 4.30. Z.J. Ding, W.S. Tan, Y.G. Li, J. Appl. Phys. **99**, 084903 (2006)
- 4.31. Y.F. Chen, Surf. Sci. **435**, 213 (1996)
- 4.32. C.J. Powell, Surf. Sci. **299/300**, 34 (1994)
- 4.33. A. Jablonski, C.J. Powell, Surf. Sci. Rep. **47**, 33 (2002)
- 4.34. A. Jablonski, C.J. Powell, J. Vac. Sci. Technol. **A 27**, 253 (2009)
- 4.35. C.J. Powell, A. Jablonski, J. Electron Spectrosc. Relat. Phenom. **178–179**, 331 (2010)
- 4.36. M.P. Seah, W.A. Dench, Surf. Interface Anal. **1**, 2 (1979)
- 4.37. C.J. Powell, A. Jablonski, *NIST Electron Effective-Absorption-Length Database, ver. 1.2*, SRD 82 (National Institute of Standards and Technology, Gaithersburg, 2009). <http://www.nist.gov/srd/nist82.cfm>
- 4.38. S. Tanuma, C.J. Powell, D.R. Penn, Surf. Interface Anal. **21**, 165 (1994)
- 4.39. A. Jablonski, Surf. Sci. **188**, 164 (1987)
- 4.40. M.P. Seah, I.S. Gilmore, Surf. Interface Anal. **26**, 815 (1998)
- 4.41. S. Tanuma, C.J. Powell, D.R. Penn, Surf. Interface Anal. **17**, 911 (1991)
- 4.42. S. Tanuma, C.J. Powell, D.R. Penn: Surf. Interface Anal. **17**, 927 (1991)
- 4.43. P.J. Cumpson, M.P. Seah, Surf. Interface Anal. **25**, 430 (1997)
- 4.44. S. Tanuma, C.J. Powell, D.R. Penn, Surf. Interface Anal. **43**, 689 (2011)
- 4.45. Y.F. Chen, Surf. Sci. **519**, 115 (2002)
- 4.46. Y.F. Chen, C.M. Kwei, Surf. Sci. **364**, 131 (1996)
- 4.47. S. Tanuma, S. Ichimura, K. Goto, Surf. Interface Anal. **30**, 212 (2000)
- 4.48. F. Yubero, S. Tougaard, Surf. Interface Anal. **19**, 269 (1992)
- 4.49. W.S.M. Werner, C. Eisenmenger-Sittner, J. Zemek, P. Jiricek, Phys. Rev. B **67**, 155412 (2003)
- 4.50. K. Salma, Z.J. Ding, H.M. Li, Z.M. Zhang, Surf. Sci. **600**, 1526 (2006)
- 4.51. N. Pauly, S. Tougaard, Surf. Sci. **603**, 2158 (2009)
- 4.52. W.S.M. Werner, W. Smekal, C. Tomasik, H. Stoeri, Surf. Sci. **486**, L461 (2001)
- 4.53. A. Jablonski, J. Zemek, Surf. Sci. **601**, 3409 (2007)
- 4.54. S. Tanuma, T. Shiratori, T. Kimura, K. Goto, S. Ichimura, C.J. Powell, Surf. Interface Anal. **37** 833 (2005)
- 4.55. G. Gergely, S. Gurban, M. Menyhard, A. Jablonski, L. Zommer, K. Goto, Vacuum **84**, 134 (2010)
- 4.56. W.S.M. Werner, L. Köver, S. Egri, J. Toth, D. Varga, Surf. Sci. **585**, 85 (2005)
- 4.57. T. Nagatomi, K. Goto, Appl. Surf. Sci. **256**, 1200 (2009)
- 4.58. T. Nagatomi, S. Tanuma, Anal. Sci. **26**, 165 (2010)
- 4.59. A. Jablonski, Surf. Sci. **364**, 380 (1987)
- 4.60. ISO 18115, *Surface Chemical Analysis Vocabulary* (ISO, Geneva, 2001)
- 4.61. [4.34] A. Jablonski, C.J. Powell, J. Vac. Sci. Technol. **A 27**, 253 (2009).
- 4.62. A. Jablonski, C.J. Powell, J. Electron Spectrosc. Relat. Phenom. **100**, 137 (1999)
- 4.63. A. Jablonski, C.J. Powell, Phys. Rev. B **50**, 4739 (1994)
- 4.64. M.P. Seah, I.S. Gilmore, Surf. Interface Anal. **31**, 835 (2001)
- 4.65. M.P. Seah, Surf. Interface Anal. **20**, 243 (1993)
- 4.66. R.F. Reilmann, A. Msezane, S.T. Manson, J. Electron Spectrosc. **8**, 389 (1976)
- 4.67. S. Hofmann, J.M. Sanz, Surf. Interface Anal. **6**, 75 (1984)
- 4.68. P. Marcus, C. Hinnen, I. Olefjord, Surf. Interface Anal. **20**, 923 (1993)
- 4.69. M.S. Vinodh, L.P.H. Jeurgens, Surf. Interface Anal. **36**, 1629 (2004).
- 4.70. M.P. Seah, Surf. Interface Anal. **33**, 640 (2002)
- 4.71. C.J. Powell, A. Jablonski, Surf. Interface Anal. **33**, 211 (2002)
- 4.72. C.S. Fadley, J. Electron Spectrosc. Relat. Phenom. **178–179**, 2 (2010)

- 4.73. J.H. Scofield, J. Electron Spectrosc. Relat. Phenom. **8**, 129 (1976)
- 4.74. C.D. Wagner, L.E. Davis, M.V. Zeller, J.A. Taylor, R.H. Raymond, L.H. Gale, Surf. Interface Anal. **3**, 211 (1981)
- 4.75. J. Yeh, I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985)
- 4.76. F. Nevedov, J. Electron Spectrosc. Relat. Phenom. **100**, 1 (1999)
- 4.77. A. Jablonski, Surf. Interface Anal. **23**, 29 (1995)
- 4.78. M.P. Seah, S.J. Spencer, F. Boderio, J.J. Pireaux, J. Electron Spectrosc. Relat. Phenom. **87**, 159 (1997)
- 4.79. D.W.O. Heddle, J. Phys. E Sci. Instrum. **4**, 589 (1971)
- 4.80. Y. Takeichi, K. Goto, Surf. Interface Anal. **25**, 17 (1997)
- 4.81. M.P. Seah, C.G. Smith, Surf. Interface Anal. **17**, 855 (1991)
- 4.82. *NPL Systems for the Intensity Calibration of Auger- and Photoelectron Spectrometers, A1 and X1* (NPL, Teddington). <http://www.npl.co.uk/npl/cmmnt/index.html>
- 4.83. ISO 1818:2004, *Surface Chemical Analysis – Auger Spectroscopy and X-Ray Photoelectron Spectroscopy – Guide to the Use of Experimentally Determined Relative Sensitivity Factors for the Quantitative Analysis of Homogeneous Materials* (Int. Org. for Standardization, Geneva, 2004)
- 4.84. D.R. Lide (ed.), *Handbook of Chemistry and Physics*, 85th edn. (2004)
- 4.85. P.M. Hall, J.M. Morabito, Surf. Sci. **83**, 391 (1979)
- 4.86. P.H. Holloway, Surf. Sci. **66**, 479 (1977)
- 4.87. R. Payling, J. Electron Spectrosc. Relat. Phenom. **36**, 99 (1985)
- 4.88. M.P. Seah, I.S. Gilmore, Surf. Interface Anal. **26**, 723 (1998)
- 4.89. M.P. Seah, I.S. Gilmore, Surf. Interface Anal. **26**, 908 (1998)
- 4.90. D.R. Penn, J. Electron Spectrosc. Relat. Phenom. **9**, 29 (1976)
- 4.91. A.I. Zagorenko, V.I. Zaporozhenko, Surf. Interface Anal. **14**, 438 (1989)
- 4.92. M.P. Seah, I.S. Gilmore, J. Spencer, Surf. Interface Anal. **31**, 778 (2001)
- 4.93. C.J. Powell, A. Jablonski, Nucl. Instrum. Methods Phys. Res. A **601**, 54 (2009)
- 4.94. W.S.M. Werner, W. Smekal, C.J. Powell, *NIST Database for the Simulation of Electron Spectra for Surface Analysis (SESSA), SRD 100, Ver. 1.3* (National Institute of Standards and Technology, Gaithersburg, 2011). <http://www.nist.gov/srd/nist100.cfm>
- 4.95. G. Tasneem, W.S.M. Werner, W. Smekal, C.J. Powell, Surf. Interface Anal. **42**, 1072 (2010)
- 4.96. T.E. Gallon, Surf. Sci. **17**, 486 (1969)
- 4.97. R. Holm, S. Storp, Fres. Z. Anal. Chem. **290**, 273 (1978)
- 4.98. M.P. Seah, Surf. Sci. **32**, 703 (1972)
- 4.99. J. Zemek, P. Jifíček, J. Houdková, K. Olejnik, A. Jablonski, Surf. Interface Anal. **39**, 916 (2007)
- 4.100. S. Hofmann, J.M. Sanz, Microchim. Acta Suppl. **10**, 135 (1983)
- 4.101. M.P. Seah, J. Vac. Sci. Technol. A **22**, 1564 (2004)
- 4.102. S. Hofmann, J.M. Sanz, J. Trace Anal. Microprobe Technol. **1**, 213 (1982–1983)
- 4.103. A.M. Bradshaw, W. Wyrobisch, J. Electron Spectrosc. Relat. Phenom. **7**, 45 (1975)
- 4.104. A.M. Bradshaw, W. Domcke, L.S. Cederbaum, Phys. Rev. B **16**, 1480 (1977)
- 4.105. L.P.H. Jeurgens, W.G. Sloof, C.G. Borsboom, F.D. Tichelaar, E.J. Mittemeijer, Appl. Surf. Sci. **161**, 139 (2000)
- 4.106. L.P.H. Jeurgens, W.G. Sloof, C.G. Borsboom, F.D. Tichelaar, E.J. Mittemeijer, Appl. Surf. Sci. **144–145**, 11 (1999)
- 4.107. A. Akkerman, T. Boutboul, A. Breskin, R. Chechik, A. Gibrekhterman, Y. Lifshitz, Phys. Stat. Sol. B **198**, 769 (1996)
- 4.108. P. Lejček, S. Hofmann, Crit. Rev. Solid State Mater. Sci. **20**, 1 (1995)
- 4.109. P. Lejček, S. Hofmann, Surf. Interface Anal. **36**, 938 (2004)
- 4.110. P. Steiner, H. Hoehst, S. Hüfner, Z. Phys. B **30**, 129 (1978)
- 4.111. P.J. Cumpson, Surf. Interface Anal. **29**, 403 (2000)
- 4.112. E.D. Hondros, M.P. Seah, S. Hofmann, P. Lejček, Interfacial and Surface Microchemistry, in *Physical Metallurgy*, 4th edn., ed. by R.W. Cahn, P. Haasen (North-Holland, Amsterdam, 1996), pp. 1201–1289

- 4.113. P. Lejček, S. Hofmann, Crit. Rev. Solid State Mater. Sci. **33**, 133 (2008)
- 4.114. J. Janovec, P. Lejček, J. Pokluda, M. Jenko, Kovové Mater. **44**, 81 (2006)
- 4.115. P. Lejček, S. Hofmann, V. Paidar, Scr. Mater. **38**, 137 (1998)
- 4.116. S. Hofmann, G. Blank, H. Schultz, Z. Metall. **67**, 189 (1976)
- 4.117. J. Erlewein, S. Hofmann, Surf. Sci. **68**, 71 (1977)
- 4.118. S. Hofmann, R. Frech, Anal. Chem. **57**, 716 (1985)
- 4.119. S. Hofmann, Microchim. Acta Suppl. **7**, 109 (1977)
- 4.120. S. Hofmann, J. Erlewein, Microchim. Acta **I**, 65 (1979)
- 4.121. S. Hofmann, P. Lejček, Int. J. Mater. Res. **100**, 1167 (2009)
- 4.122. M.P. Seah, p. 368 in Ref. [4.2].
- 4.123. C. Argile, C.E. Rhead, Surf. Sci. Rep. **10**, 277 (1989)
- 4.124. Q. Fu, T. Wagner, Appl. Surf. Sci. **240**, 189 (2005)
- 4.125. Q. Fu, T. Wagner, Phys. Rev. Lett. **90**, 106105 (2003)
- 4.126. U. Diebold, J.-M. Pan, T.E. Madey, Phys. Rev. B **47**, 3868 (1993)
- 4.127. U. Otterbein, S. Hofmann, Surf. Interface Anal. **24**, 263 (1996)
- 4.128. P. Lejček, S. Hofmann, Surf. Sci. **307–309**, 798 (1994)
- 4.129. J.H. Thomas III, S. Hofmann, J. Vac. Sci. Technol. A **3**, 1921 (1985)
- 4.130. S. Hofmann, J.Y. Wang, A. Zalar, Surf. Interface Anal. **39**, 787 (2007)
- 4.131. J. Steffen, S. Hofmann, Surf. Interface Anal. **11**, 617 (1988)
- 4.132. L.P.H. Jeurgens, M.S. Vinodh, E.J. Mittemeijer, Appl. Surf. Sci. **253**, 627 (2006)
- 4.133. E. Panda, L.P.H. Jeurgens, E. Mittemeijer, J. Appl. Phys. **106**, 114913 (2009)
- 4.134. S. Nemsak, T. Skala, M. Yoshitake, N. Tsud, K.C. Prince, V. Matolin, Surf. Sci. **604**, 2073 (2010)
- 4.135. L.P.H. Jeurgens, A. Lyapin, E.J. Mittemeijer, Surf. Interface Anal. **38**, 727 (2006)
- 4.136. J.M. Sanz, S. Hofmann, J. Less Common Met. **92**, 317 (1983)
- 4.137. E. Casnati, A. Tartari, C. Baraldi, J. Phys. B **15**, 155 (1982)
- 4.138. H.-W. Drawin, Z. Phys. **164**, 513 (1961)
- 4.139. M. Gryzinski, Phys. Rev. A **138**, 336 (1965)
- 4.140. S. Ichimura, R. Shimizu, Surf. Sci. **112**, 386 (1981)
- 4.141. R. Shimizu, Jpn. J. Appl. Phys. **22**, 1631 (1983)
- 4.142. S. Ichimura, D.-Z. Jun, R. Shimizu, Surf. Interface Anal. **13**, 149 (1988)
- 4.143. S. Tanuma, J. Surf. Anal. **15**, 312 (2009)
- 4.144. A. Jablonski, Surf. Sci. **499**, 219 (2002)
- 4.145. A. Jablonski, C.J. Powell, S. Tanuma, Surf. Interface Anal. **37**, 861 (2005)
- 4.146. R.G. Zeng, Z.J. Ding, Y.G. Li, S.F. Mao, J. Appl. Phys. **104**, 114909 (2008)
- 4.147. A. Jablonski, C.J. Powell, Surf. Sci. **604**, 1928 (2010)
- 4.148. A. Jablonski, C.J. Powell, J. Surf. Anal. **17**, 213 (2011)
- 4.149. A. Jablonski, C.J. Powell, *NIST Backscattering-Correction-Factor Database for Auger Electron Spectroscopy, SRD 154, Version 1.0* (National Institute of Standards and Technology, Gaithersburg, 2011). <http://www.nist.gov/srd/nist154.cfm>
- 4.150. S. Mroczkowski, J. Vac. Sci. Technol. A **7**, 1529 (1989)
- 4.151. S. Hofmann, Mikrochim. Acta Suppl. **8**, 71 (1979)
- 4.152. S. Hofmann, J.Y. Wang, Surf. Interface Anal. **39**, 324 (2007)
- 4.153. M.L. Tarnag, G.K. Wehner, J. Appl. Phys. **44**, 1534 (1973)
- 4.154. S. Hofmann, Auger Electron Spectroscopy, in *Wilson and Wilson's Comprehensive Analytical Chemistry*, vol. IX, ed. by G. Svehla (Elsevier, Amsterdam, 1979), pp. 89–172
- 4.155. ISO 18115:2001 – *Surface Chemical Analysis – Vocabulary* (ISO, Geneva, 2001)
- 4.156. L. Zommer, A. Jablonski, J. Phys. D Appl. Phys. **41**, 055501 (2008)
- 4.157. L. Zommer, A. Jablonski, L. Kotis, M. Menyhard, J. Phys. D Appl. Phys. **41**, 155312 (2008)
- 4.158. L. Zommer, A. Jablonski, L. Kotis, G. Safran, M. Menyhard, Surf. Sci. **604**, 633 (2010)
- 4.159. A. Jablonski, Computer Physics Comm. **183**, 1773 (2012)
- 4.160. A. Jablonski, C.J. Powell, Surf. Sci. **606**, 644 (2012)
- 4.161. M.P. Seah, S.J. Spencer, Surf. Interface Anal. **43**, 744 (2012)
- 4.162. N. Pauly, M. Novák, A. Dubus, S. Tougaard, Surf. Interface Anal. **44**, 1147 (2012)

Chapter 5

Optimizing Measured Signal Intensity: Emission Angle, Incidence Angle and Surface Roughness

The primary aim of any analysis is a high signal intensity (count rate) that ensures a high signal to noise ratio and therefore a high sensitivity. While the ultimate limit is given by the properties of the respective instrument, its optimum settings can be chosen by the analyst within those limits. Besides primary excitation energy and power (current), the most important other parameters which can be varied and optimized by the analyst are set by the geometry between excitation source, sample, and analyzer. In any modern instrument, the sample can be tilted with respect to the analyzer axis. In this way, the angle of incidence of the primary photons or electrons and the angle of emission of Auger- or photoelectrons can be varied (Sects. 5.1 and 5.2). This variation cannot only be used to find optimum signal intensity but also to provide nondestructive depth profiles by angle-resolved XPS (AR-XPS) and AES (AR-AES) (see Sect. 7.2.1).

Assuming a rough surface to consist of a statistical distribution of differently inclined microplanes, the angular dependencies of XPS and AES can be used to describe at least approximately the effect of surface roughness on the signal intensity [5.45] including different sample tilt angles (Sects. 5.1.3 and 5.2.3).

5.1 XPS: Intensity Dependence on Emission and Incidence Angles

The principal dependence of the Auger- or photoelectron signal intensity on both the incidence angle (α) and the emission angle (θ) is given by the fundamental equations for quantification of homogeneous material [4.1, 4.2, 5.1, 5.2] (see (4.37) (XPS), (4.126) (AES) in Chap. 4). For XPS instruments operating with the “magic angle” of $\psi = 54.7^\circ$, we can neglect the dependence of β_{eff} on the emission angle. In AES, backscattering depends slightly on the emission angle through the parameter Q but can be ignored when emission angles above 80° are excluded.

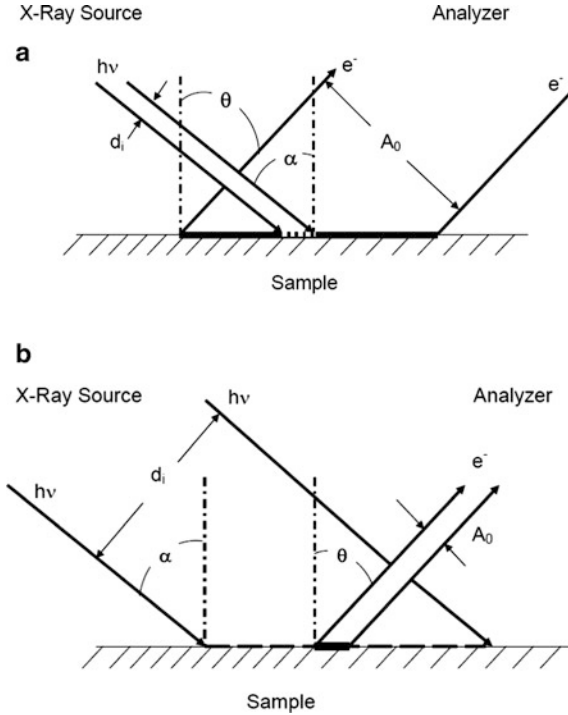


Fig. 5.1 Schematic view of geometry between the focused, (a) monochromatic X-ray beam ($h\nu$) with diameter d_i and analyzer with analyzed area A_0 , for the case $d_i^2\pi/4 \ll A_0$, and (b) wide nonmonochromatic X-ray beam and analyzer with a small analyzed area, $d_i^2\pi/4 \gg A_0$. The beam incidence angle is denoted by α and the emission angle to the analyzer by θ . The irradiated area is indicated by the bright points on the sample surface, and the acceptance area of the analyzer by the *thicker solid line*. Note that in reality, the angles α and θ are mean angles with a slight divergence. In contrast to (a), the analyzed area in (b) is $A_0/\cos\theta$

Because under the conditions above, all other parameters are practically angle independent; (4.41) and (4.132) can be written as

$$I(\alpha, \theta) = K_1 \frac{\cos\theta}{\cos\alpha}, \quad (5.1)$$

where K_1 is constant for given instrument parameters considered in Sect. 4.1 (4.38) with $K_1 = \text{const.}$ (5.1) describes the case of Fig. 5.1a, showing a fine focused X-ray beam within a wide analyzed area. Note that the term $\cos\theta$ in the nominator of (4.37) and of (5.1) stems from the integration of (4.36). Although the analyzed area increases with θ by $A_0/\cos\theta$, this is irrelevant for the measured intensity provided the excited area stays within the analyzed area. For this condition, the excitation intensity is independent of α . Therefore, $K_1 = \text{const.}$ in (5.1). This case is usually met in small spot XPS and in AES (see also Fig. 4.14 and Sect. 5.2.1).

However, for conventional XPS instruments with a nonmonochromatic wide beam X-ray source and a comparably small analyzer aperture, the angular dependences in (5.1) cancel as already shown by Fadley et al. [5.1]. This can be understood when comparing Fig. 5.1b with Fig. 5.1a. In Fig. 5.1b, the analyzed area covers only a small part of the wide X-ray beam, even when θ increases. This means the projection of A_0 on the surface (= the analyzed area) and therefore the measured intensity increases with θ by $A_0/\cos\theta$. However, the photon flux in the analyzed area decreases with the incidence angle α by $d_i \cos\alpha$, therefore $K_1 = \text{const.} \times \cos\alpha/\cos\theta$ in (5.1). Therefore, the angular terms cancel and the measured intensity is independent of incidence and emission angles [5.1, 5.2] (with the exception of extremely high angles α and θ , see Sects. 5.1.4 and 5.2.1). A similar case is usually met by imaging XPS (see Sect. 2.5.4).

Of course, complications arise as soon as one spot falls outside the other. Then we will get a somewhat mixed situation between both extreme cases depicted in Fig. 5.1a, b. Indeed, some instruments increase efficiency by raising the input lens magnification to match the X-ray illumination more closely and then a shift from the case of Fig. 5.1b to Fig. 5.1a either within one angular tilt experiment or during an energy scan.

In general, the angle between excitation source and analyzer direction is fixed, and therefore, the incidence angle changes together with the emission angle during sample tilt.

In special cases, the incidence angle can be kept constant, and only the emission angle is changed, for example, if there is a movable analyzer [5.2] or an analyzer aperture with variable angular acceptance. Experimentally, this possibility is realized in the double-pass CMA with drum device and with the Thetaprobe instrument (see Sects. 2.5 and 5.1.2).

According to (5.1), for a concentric hemispherical analyzer (CHA), the intensity dependence on the emission angle in case of a fixed incidence angle is basically described by a cosine law that is exactly valid if we only consider inelastic scattering and neglect elastic scattering of the photo- or Auger electrons (see Sect. 4.2.2). For a given depth below the surface, the electron traveling length gets larger with the emission angle θ (measured to the normal to the sample surface). Therefore, the signal detected without energy loss stems from a surface region that decreases with $\cos\theta$. Assuming the focused beam condition in Fig. 5.1a, the intensity, I , detected by a CHA analyzer is

$$I(\theta) = K_2 \cos\theta, \quad (5.2)$$

where K_2 is a constant depending on the excitation parameters, sample (peak), and on analyzer and detector characteristics. When the backscattering term in AES and the asymmetry term in XPS emission (see Sect. 4.3.1) are ignored, (5.2) holds for XPS as well as for AES [4.1, 4.2]. This means that (5.2) is strictly valid only for isotropic emission (i.e., for background emission (see Fig. 5.3) or if the angle between X-ray and analyzer direction is constant and $\psi = 54.7^\circ$).

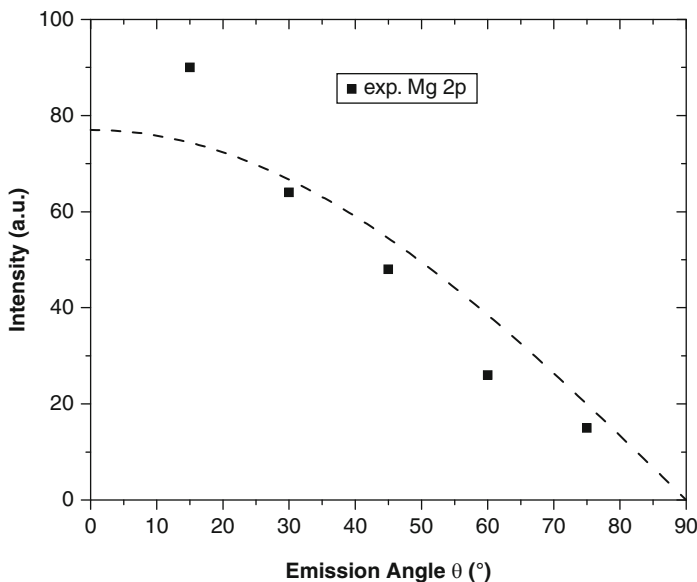


Fig. 5.2 Dependence of the intensity of the Mg 2p peak on the emission angle measured with a Quantum 2000 instrument (quick test measurement). Note that the tilt angle was changed by tilting the sample in front of the CHA analyzer and the angle between the monochromatic X-ray source and the analyzer was kept constant at 54.7° . For deviations from the cosine law (*dashed line*), see text

5.1.1 Sample Tilt Using CHA

For most instruments with concentric hemispherical analyzer (CHA) and fixed X-ray source and analyzer positions, the intensity change after (5.2) can only be measured by tilting the sample that means by changing at the same time the incidence and emission angles. Figure 5.2 shows the result of a measurement on a sputter-cleaned Mg surface, with the intensity of the Mg 2p peak shown for different emission angles. Comparison with the cosine law shows similar monotonic intensity dependence but marked differences. One of the reasons for the deviation is due to the fact that the analyzer acceptance area gets increasingly elliptic when θ increases. The large axis of this ellipse varies with $1/\cos\theta$, and regions at the rim of the excitation spot (with generally decreased X-ray intensity) are inevitably contributing to the signal intensity. Therefore, the measured signal in general decreases stronger than the cosine dependence predicts. Obviously, the matching between analyzed area and X-ray excitation is optimum for $\theta = 15^\circ$ but drops sharply for higher θ values, presumably caused by noncentric sample tilt. To compensate for this effect, intensity ratio measurements are necessary (e.g., for layer thickness determination, see Sect. 7.2.1). Note that the angle between X-ray excitation and analyzer axis is fixed and usually at 57.4° , where the asymmetry term for the 2p peak vanishes (see Sect. 4.3.1). In any case, Fig. 5.2 clearly shows that the optimum intensity is

obtained when the emission angle is in the vicinity of 0° , i.e., when the analyzer axis is close to the normal to the sample surface.

5.1.2 Double-Pass Cylindrical Mirror Analyzer (DP-CMA) and Thetaprobe (CHA)

Instead of tilting the sample, a fixed sample position is advantageous because of constant excitation conditions. Generally, the intensity change after (5.2) for fixed sample position can be done in two ways: (a) variation of the analyzer position and (b) variation of the analyzer aperture position with fixed sample. Method (a) is straightforward but complicated in practice, whereas for method (b), two analyzers have become popular: the double-pass CMA (DP-CMA) developed by Palmberg [5.3] at the company PHI in 1977 and the more recently developed Thetaprobe instrument of Thermo Scientific company. The cosine law of (5.2) is well represented for the Thetaprobe measurement in Fig. 5.3. Note that only the background shows approximately isotropic emission, whereas the $\text{Ag}5d_{3/2}$ peak intensity is modified by the asymmetry factor (see Sect. 4.3.1.2).

For the DP-CMA (see Sect. 2.5.1, Fig. 2.15), the drum device in the second CMA is important [5.4]. This is a movable slit around the emission cone of the CMA. Depending on the fixed tilt angle of the sample, each azimuth angle of the slit is correlated with a specific emission angle [5.4–5.6]. Figure 5.4 shows the

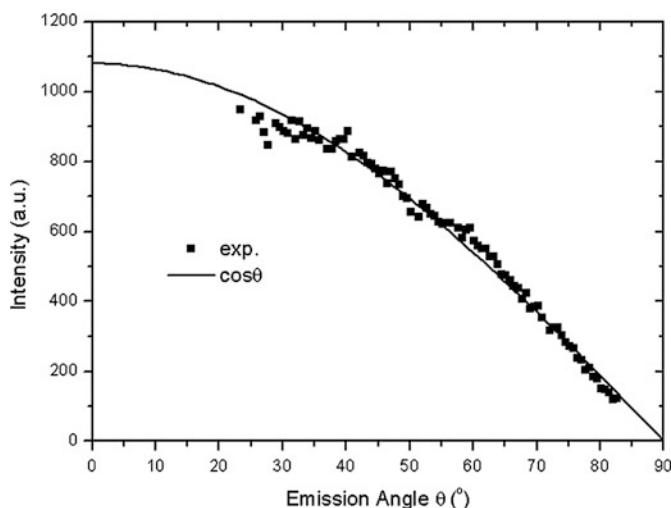


Fig. 5.3 “Signature” of a Thetaprobe instrument, showing the intensity of the background on the lower kinetic energy side of the $\text{Ag } 5d_{3/2}$ XPS peak as a function of the emission angle between 23° and 82° , measured on a polycrystalline sample with small grain size. Solid line shows the cosine law after (5.2) (Courtesy of L.P.H. Jeurgens, Max-Planck-Institute for Metals Research)

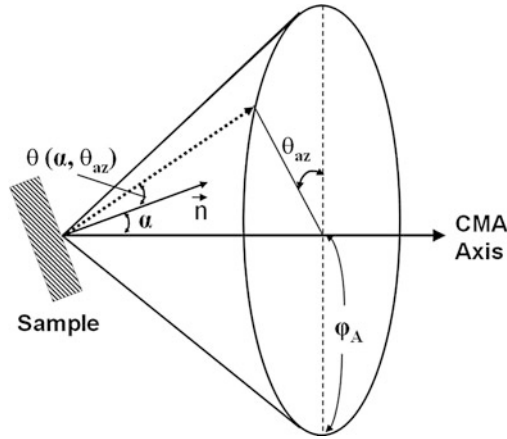


Fig. 5.4 Schematic view of the cone of the emitted electrons which are detected in a CMA with angle $\varphi_A = 42.3^\circ$ cone angle. The emission angle to the sample surface normal $\mathbf{n}$ is $\theta(\alpha, \theta_{az})$. For a concentric electron gun, the sample tilt angle α is equal to the electron incidence angle. Changing the azimuth angle θ_{az} in a double pass CMA with a movable drum with a slit (6° opening angle) cuts out an emission angle θ given by (5.3). (Adapted from S. Hofmann and J.Y. Wang [5.11])

geometrical relations for a CMA with the usual opening angle of the acceptance cone of $\varphi_A = 42.3^\circ$ [5.4]. The angle θ is the electron emission angle, angle α is the incidence angle (i.e., angle between the normal to the sample surface and the CMA axis with concentric gun), and the angle θ_{az} is the azimuth angle along the circumference of the acceptance cone. These angles are connected by the basic geometry relation [5.4–5.12]

$$\begin{aligned} \cos \theta(\alpha, \theta_{az}) &= \sin \alpha \sin \varphi_A \cos \theta_{az} + \cos \alpha \cos \varphi_A \\ &= 0.673 \sin \alpha \cos \theta_{az} + 0.74 \cos \alpha \end{aligned} \quad (5.3)$$

Equation 5.3 shows how the emission angle, θ , depends on both the tilt angle α and the azimuth angle θ_{az} . For $\alpha = 0$, $\cos \varphi = \cos \varphi_A = 0.74$. Note that for a CMA, the maximum electron escape depth, $\lambda_{\max} = \lambda \cos \varphi_A = 0.74\lambda$, when λ is the practical effective attenuation length (EAL) (whereas for the CHA and $\alpha = 0$, $\lambda_{\max} = \lambda$). For a given tilt angle α , $\cos \theta$ and $\cos \theta_{az}$ are linearly related [5.5]. The maximum variation is obtained for $\alpha = 42.3^\circ$, when $(\cos \theta)_{\max} = 1$ and the corresponding $\cos \theta_{\min} = \cos(84.6^\circ)$, therefore

$$\cos \theta(42.3^\circ, \theta_{az}) = 0.453 \cos \theta_{az} + 0.547 \quad (5.4)$$

The azimuth angle, θ_{az} , can be experimentally changed by a drum device (with a slit with 12° or 6° opening angle) that can be rotated from outside by 360° .

Validity of (5.3) and (5.4) was demonstrated by Frech [5.8] in Fig. 5.5, which shows the Auger signal intensity for the Au MVV transition for a full circle variation of the azimuth angle θ_{az} and a tilt angle of $\alpha = 30^\circ$. The theoretically expected $\cos \theta$ relation is excellently fulfilled when a slight correction is introduced, a straggling of

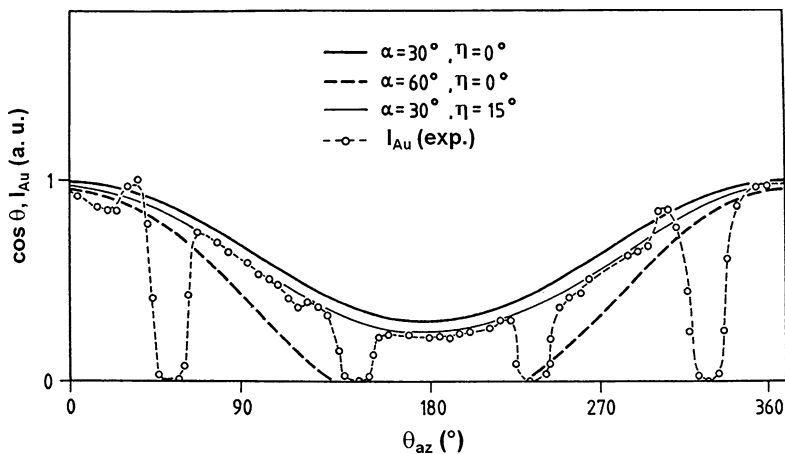


Fig. 5.5 Dependence of the Auger intensity (proportional to $\cos \theta$) on the azimuth angle, θ_{az} , for a double pass CMA (DP-CMA). Measured values are for the Au (MVV) transition and for a sample tilt angle of $\alpha = 30^\circ$ (= electron incidence angle). Calculations are for $\alpha = 30$ and 60° , with angle η denoting a slight deviation or straggling, for example, by sample mount and/or bending (see text). The four equidistant minima of the measurement (*open circles*) indicate the four solid bridges holding the meshes of the inner cylinder. (Adapted from R. Frech [5.8])

$\pm 15^\circ$ (for details see [5.5]). With today's knowledge, that effect may be probably attributed to elastic scattering (maximum deviation from ideal cosine function at the maximum emission angle at x -axis value = 180° (see Sect. 4.2.2)). The four metal bridges that hold the grids of the inner cylinders are indicated by zero intensity, as are distortions of the electric field and/or electron scattering near the edges. In contrast to sample tilt measurements, the excitation spot is fixed, and therefore, the errors introduced by sample movement vanish.

Using the double-pass CMA with XPS, the change of the angle ψ between excitation and emission has to be taken into account. This method became popular for angle-dependent studies in the 1970s and 1980s, when the company PHI offered a double-pass (DP)CMA for XPS studies [5.3]. Together with a so-called drum device with a small and a large slit (equal to 6° or 12° opening angle) the DP-CMA enables angle-resolved XPS (AR-XPS) with constant tilt angle of the sample [5.4]. In the CMA, this is possible because of the change of the emission angle θ with the angle θ_{az} according to (5.3) and (5.4). For example, for $\alpha = \text{const.} = 45^\circ$ (slightly below the critical angle $\alpha_c = 47.7^\circ$), (5.3) gives $\cos \theta = 0.523 + 0.476 \cos \theta_{az}$. However, the angle ψ and therefore the asymmetry factor $W(\psi)$ changes according to (4.35) in Sect. 4.3.1.2. For the case of Cu $2p_{3/2}$, the asymmetry parameter from [4.53], $\beta = 1.4 \approx \beta_{\text{eff}}$ applies. With an angle between the CMA axis and the X-ray source of 90° , $\psi = \arccos(\cos \psi^0 \times \cos \theta_{az})$ where $\psi^0(\theta_{az} = 0) = 90^\circ - \varphi_A = 47.7^\circ$ (see Figs. 4.10 and 5.4). Then, (4.35) is given by

$$W(\text{Cu}2p) = 1 + 0.7 \left\{ 1.5 \sin^2 \left[\arccos(\cos \psi^0 \cos \theta_{az}) \right] - 1 \right\} \quad (5.5)$$

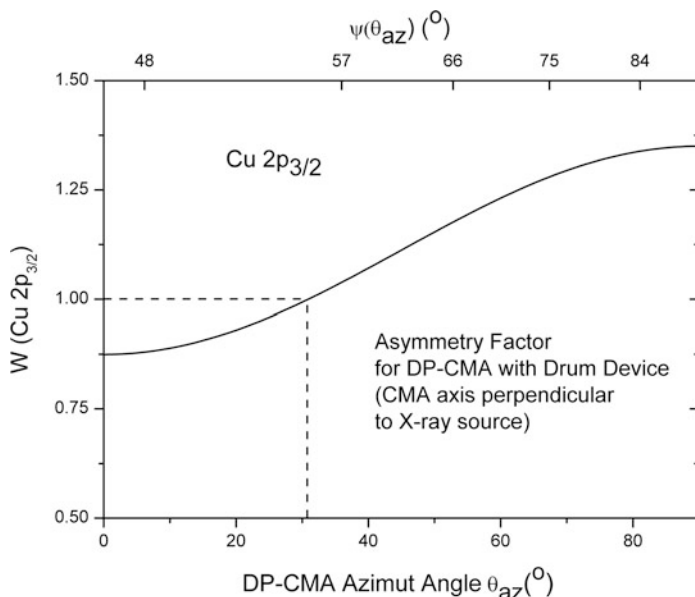


Fig. 5.6 AR-XPS with a double-pass CMA, for Cu $2p_{3/2}$, MgK α radiation, and photon beam direction perpendicular to CMA axis: the intensity is proportional to the Reilman asymmetry factor $W(\text{Cu}2p_{3/2})$, shown as a function of the CMA azimuth angle θ_{az} according to (5.5). Note that $W = 1$ for $\theta_{az} = 30.8^{\circ}$, because then $\psi = 54.7^{\circ}$ (see text)

Equation 5.5 is plotted in Fig. 5.6. It is seen that there is a continuous increase of the intensity toward higher θ , i.e., glancing angle emission. The value $W = 1$ is obtained at $\theta_{az} = 30.8^{\circ}$ where $\psi = \arccos(\cos \psi^0 \times \cos \theta_{az}) = 54.7^{\circ}$ corresponds to the “magic angle” (see Sect. 4.3.1.2).

The DP-CMA was frequently used in the past to determine nondestructively the composition and thickness of thin layers, for example, contamination layers [5.6, 5.7], oxide layers in alloys [5.9], or altered layers in sputter depth profiling [5.10] (see, e.g., Fig. 9.15). Nowadays, the DP-CMA is used for very special applications such as gas phase photoemission studies [5.13] or Auger-photoelectron coincidence spectroscopy (APECS) [5.14].

In contrast to the DP-CMA, where emission under different angles is measured sequentially, the modern “Thetaprobe” XPS instrument introduced in 1999 by Thermo Scientific Company provides parallel detection of the emitted photoelectrons within an emission angle range between 23° and 82° . Consequently, a similar change of the asymmetry factor with the emission angle occurs with this method as for the DP-CMA.

An example of Thetaprobe application (quantitative analysis of Al_2O_3) is presented in Sect. 4.3.2.6 (see Figs. 4.21, 4.22).

5.1.3 Total Reflection XPS (TR-XPS)

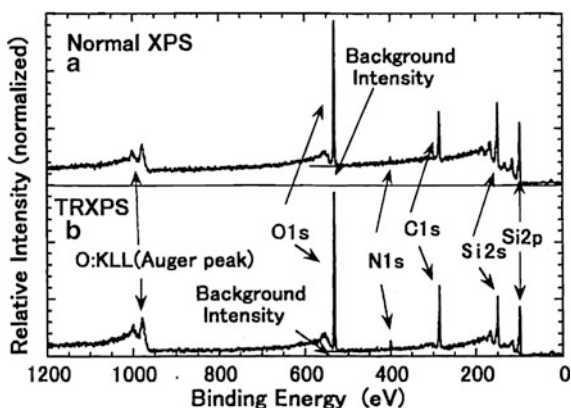
Because the excitation range of the X-rays is orders of magnitude larger than the attenuation length of the photoelectrons, the angle of incidence of the former is unimportant and (5.2) is applicable. This picture changes completely when the X-ray incidence angle is close to the critical angle of total reflection, as employed in total reflection XPS (TR-XPS) [5.15] or grazing incidence XPS (GI-XPS) [5.16]. In that case, the characteristic length for the excitation becomes comparable to the photoelectron attenuation length, and the effective analyzed depth, d_{eff} , is given by [5.17]

$$d_{\text{eff}} = \frac{1}{\frac{\cos \theta}{\lambda} + \frac{1}{L_{\text{exc}}(\alpha)}}, \quad (5.6)$$

where λ is the attenuation length, θ is the emission angle, and $L_{\text{exc}}(\alpha)$ is the X-ray penetration length depending on the incidence angle α . Theoretical calculations [5.15, 5.16] show that the intensity at the critical angle for total reflection angle (depending on the material, usually in the vicinity of $1\text{--}2^\circ$ to the surface ($\alpha_{\text{crit}} = 88\text{--}89^\circ$)) is increased by a factor of up to 4. For $\text{AlK}\alpha$ radiation and Cu, $L_{\text{exc}}(\alpha_{\text{crit}} = 2.17^\circ) = 4.0\text{ nm}$. The confinement of the excitation to a shallow surface has several typical advantages:

- The background is considerably reduced, as obvious from Fig. 5.7 leading to an increased signal to noise figure (see Chap. 6).
- The detection limit is improved to about 10–100 times as compared to conventional XPS. The detection limit for Fe and Cu was found to be 1×10^{11} and $9 \times 10^{10}\text{ at/cm}^2$, respectively [5.18].
- Variation of L_{exc} with the incidence angle results in a change of the sampling depth and enables nondestructive depth profiling within limits given by the minimum attainable sampling depth relative to the attenuation length which can be increased using high energy X-rays [5.19].

Fig. 5.7 Comparison of survey-scan spectra acquired (a) with normal XPS ($\alpha = 10^\circ$) and (b) TR-XPS ($\alpha = 1.1^\circ$) of a silicon wafer surface stored in air after HF treatment. The signals of O and C from the contamination layer are increased in (b), while the background is considerably reduced. (Reproduced from Y. Iijima et al. [5.18], with permission of J. Wiley & Sons Ltd.)



A disadvantage of TR-XPS is the necessity of a flat, smooth, and relatively large surface. Furthermore, a collimated X-ray beam should be used as is available from synchrotron radiation (see Sect. 2.2.4).

5.1.4 XPS Intensity Dependence on Surface Roughness

5.1.4.1 Simplified Model of Surface Roughness

Although theoretical work on quantitative AES and XPS generally assumes atomically flat surfaces (of amorphous samples), most of the surfaces in practice (e.g., in corrosion, oxidation studies, or after fracture or sputter depth profiling) are rough and corrugated. The influence of surface roughness on the intensity of XPS and AES signals, particularly with respect to angular geometries, was early recognized [5.1, 5.20, 5.21]. Despite the numerous works done since then, up to now, no generally applicable, quantitative model seems to exist. This fact reflects the complicated nature of practical surface morphology. While in early work roughness was characterized by a single parameter, for example, the mean (linear) departure of a surface profile from a straight line, R_a , or the root-mean-square (rms) roughness [5.22–5.24], the importance of areal distribution of microplanes with specific inclination angles was recognized in later work [5.25–5.30]. More recently, the use of an AFM enables knowledge of surface topography in microscopic detail [5.23, 5.31, 5.32].

Generally, roughness affects both the excitation distribution function and the emission distribution function [5.1, 5.2]. However, the excitation function in XPS is little influenced by roughness because the X-ray range is more than a factor of 10 larger than the photoelectron attenuation length and the angular variation of the exciting beam of photons can be practically ignored (except for extremely glancing incidence, see Sect. 5.1.3) [5.25, 5.26, 5.29, 5.30]. The situation is different in AES, where the focused electron beam causes a strong change of the excitation depth distribution with the incidence angle α (approximately with $1/\cos\alpha$, see Sect. 5.2).

Therefore, the easier case of XPS is considered first, neglecting elastic scattering, although it will have a measureable effect at higher emission angles (see, e.g., [5.27, 5.31]).

The emission angle dependence of the bulk XPS signal of a prism-like surface corresponds to that of a flat surface [5.1, 5.29] below a critical angle. However, for increasing emission angle, shadowing caused by surface protrusions has to be taken into account. For that case, the discrepancy between various authors is reflected in different roughness definitions and different models for the influence of roughness.

Frequently, roughness effect calculations are based on simplified assumptions about surface morphology, such as triangular, sinusoidal, pyramidal, etc., shapes, and these surfaces are often assumed only as two-dimensional and with one characteristic parameter. For example, such a parameter is the relative total surface area as compared to the projected surface area of a flat sample [5.25–5.27]. It is

obvious that in practice, the roughness structure is much more complicated. Based on AFM measurements [5.28, 5.31], a given surface roughness can be rather well described (see example below). For the influence of roughness on XPS (and AES), the areal distribution of microplanes with characteristic inclination angles to the “average,” macroscopic surface is most important. Therefore, it is customary to describe roughness in terms of such inclination angles [5.28]. In reality, there will be a distribution of various inclination angles. However, for simplicity and to demonstrate the basic effect of roughness, a simple prismatic surface roughness is adopted here with the two-dimensional cross section being an isosceles triangle depicted in in Fig. 5.8 [5.27, 5.29]. Such a simplified model of the surface structure enables description by only one parameter, the base angle φ_r of the slope of the different area parts right and left of the top edge, a_r and a_l , with their normals $\vec{n}_l$ and $\vec{n}_r$ at the roughness angle $+\varphi_r$ and $-\varphi_r$ to the normal, $\vec{n}$, of the average, macroscopic surface. The electron emission angle between the local surface normal and the direction to the analyzer (e^-) is different for the two surfaces; it is $\theta + \varphi_r$ for the plane left of the prism peak (a_l) and $\theta - \varphi_r$ for the right plane (a_r). It is seen in Fig. 5.8 that a critical angle is $\theta = 90 - \varphi_r$, where shadowing arises (that some authors [5.26, 5.29] do not take into account). Below that angle, both parts of the surface contribute with $1/2$ of the total area to the signal. Above $\theta = 90 - \varphi_r$, the left plane is completely in the shadow and does not contribute to electron emission. Furthermore, the right plane is increasingly shadowed with increasing θ (as indicated by the dashed electron emission at θ in Fig. 5.8). Let us first consider a homogeneous bulk material sample without an overlayer.

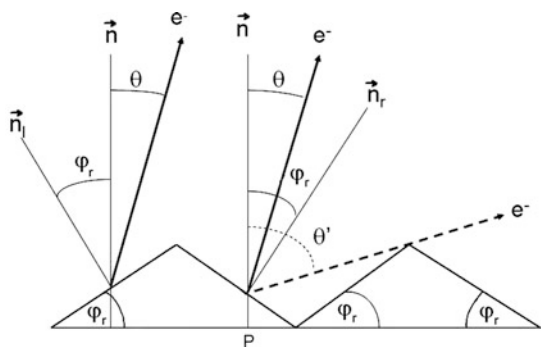


Fig. 5.8 Schematic view on the cross section of a prismatic roughness with symmetric roughness angle φ_r to the average, macroscopic surface (=horizontal line). The electron emission angle θ is denoted by e^- , $\vec{n}$ is the normal to the average surface plane, and $\vec{n}_l$ and $\vec{n}_r$ are the normals to the partial planes with areas a_l , a_r located *left* and *right* from the *top* of the triangular structure, respectively. The *dashed line* (for $\theta = \theta'$) denotes the situation when neighbor shadowing is important. The part to the right from point P, a_r^s , is shadowed by the right prism and therefore gives no detectable signal

5.1.4.2 Homogeneous Sample Without Overlayer

According to Fig. 5.8, we have to consider the two sides of the prism separately, each of which contributes to half of the total intensity. From (5.2), it follows for the normalized intensity, $I(\theta)/I(0)$ of a rough surface,

$$\frac{I(\theta)}{I(0)} = 0.5 \cos(\theta + \varphi_r) + 0.5 \cos(\theta - \varphi_r) = \cos \theta \cos \varphi_r \quad (5.7a)$$

for $0 < \theta < 90 - \varphi_r$.

Here, $I(0)$ is the intensity for a flat surface ($\varphi_r = 0$) and emission angle $\theta = 0$. For $\theta > 90 - \varphi_r$, we have only to take into account the right part because the left part is completely shadowed and therefore does not contribute any more to the signal intensity. The right part is shadowed completely as seen in Fig. 5.8. Applying basic trigonometry, we see that the ratio of the shadowed part (right of point P in Fig. 5.8) to the total area, a_r^s/a_r , is for $\theta > 90 - \varphi_r$ given by

$$\frac{a_r^s}{a_r} = \frac{\cos(\theta + \varphi_r)}{\cos(\theta - \varphi_r)}. \quad (5.7b)$$

The part contributing to emission is $(1 - a_r^s/a_r)$. Figure 5.9 shows this fraction of the nonshadowed area as a function of the emission angle for different roughness values characterized by $\varphi_r = 0^\circ, 30^\circ, 45^\circ, 60^\circ$, and 75° . The part of a_r in (5.7a) and (5.7b) combines for the range $90 - \varphi_r < \theta < 90$ to give

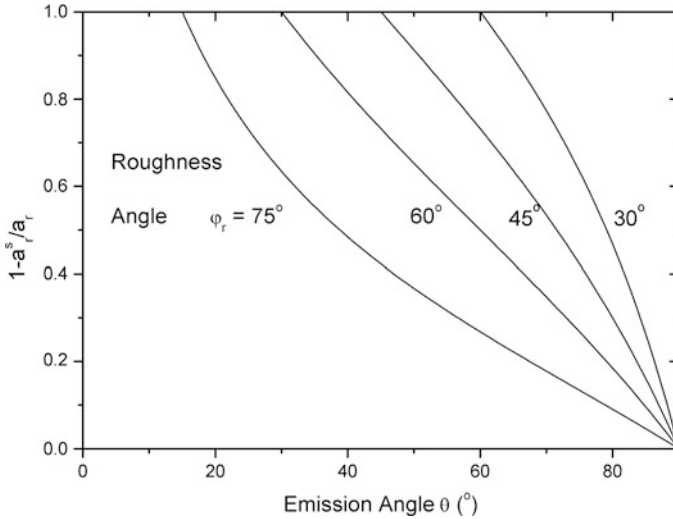


Fig. 5.9 Fraction of the nonshadowed area of the *right* side of the roughness pyramid in Fig. 5.8, $1 - a_r^s/a_r$, as a function of the emission angle, θ , after (5.7b), for different roughness values characterized by $\varphi_r = 0^\circ, 30^\circ, 45^\circ, 60^\circ$, and 75°

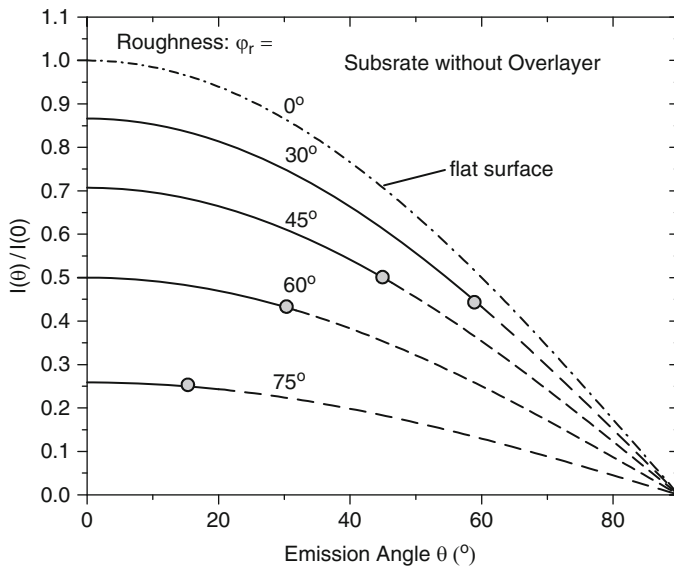


Fig. 5.10 Emission angle θ dependence of the normalized intensity for homogeneous bulk after (5.7a) and (5.8) for different roughness parameters ϕ_r . The open points mark the onset of shadowing at $\theta = (90 - \phi_r)$

$$\frac{I(\theta)}{I(0)} = \frac{1}{2} \left(1 - \frac{a_r^s}{a_r} \right) \cos(\theta - \phi_r) = \cos \theta \cos \phi_r. \quad (5.8)$$

In this case, the same result is obtained for both regions. Compared with the angular dependence of a flat surface (5.1), it is obvious that its shape is a $\cos \theta$ dependence for the rough surfaces too, as already pointed out by Fadley [5.1], with $\cos \phi_r$ as a parameter for the intensity. As shown in Fig. 5.10, the photoelectron emission intensity of a rough surface is lower than that of a flat surface, as already demonstrated by Dawson et al. [5.24] and confirmed by others [5.21, 5.28]. Only a roughness factor has to be considered in quantification [4.2], but standard and unknown specimen measurements have to be performed with the same roughness to ensure correct quantification. This is not always the case when sputter cleaning is involved (see Chap. 7).

The simple emission angle dependence becomes more complicated for special surface morphologies [5.32] or when a substrate is covered with a thin overlayer (see below) and in angle dependent studies of layer structures (see also Sect. 7.2.1).

5.1.4.3 Homogeneous Sample with Overlayer

(1) Substrate Intensity

For the case of an overlayer with thickness d , we obtain with (5.2, 5.7a) for the normalized substrate intensity $I_{\text{sub}}(\theta)/I_{\text{sub}}^0(0)$,

for $0 < \theta < 90 - \varphi_r$

$$\frac{I_{\text{sub}}(\theta)}{I_{\text{sub}}^0(0)} = \frac{1}{2} \cos(\theta + \varphi_r) \exp\left[-\frac{d}{\lambda_{\text{sub}} \cos(\theta + \varphi_r)}\right] + \frac{1}{2} \cos(\theta - \varphi_r) \exp\left[-\frac{d}{\lambda_{\text{sub}} \cos(\theta - \varphi_r)}\right], \quad (5.9a)$$

and for $90 - \varphi_r < \theta < 90$

$$\frac{I_{\text{sub}}(\theta)}{I_{\text{sub}}^0(0)} = \frac{1}{2} \frac{a'_r}{a_r} \cos(\theta - \varphi_r) \exp\left[-\frac{d}{\lambda_{\text{sub}} \cos(\theta - \varphi_r)}\right] = \cos \theta \cos \varphi_r \exp\left[-\frac{d}{\lambda_{\text{sub}} \cos(\theta - \varphi_r)}\right]. \quad (5.9b)$$

Here, I_{sub}^0 is the “standard” intensity for a substrate without overlayer, i.e., for $\theta = 0$, $\varphi_r = 0$, $d = 0$, and λ_{sub} denotes the attenuation length for the substrate photoelectrons in the overlayer material. Figure 5.11 shows the result for a roughness angle of $\varphi_r = 30^\circ$, and for three values of $d/\lambda = 0.01, 0.3$ and 1.0 ($\lambda = \lambda_{\text{sub}}$). With the first value of an almost vanishing overlayer, the emission angle dependence of the normalized intensity is seen to be identical with that of the substrate without an overlayer (see Fig. 5.10). Let us consider now the emission angle dependence of the overlayer signal.

(2) Overlayer Intensity

Introducing the overlayer intensity in (5.7a), we get

for $0 < \theta < 90 - \varphi_r$

$$\frac{I_{\text{ov}}(\theta)}{I_{\text{ov}}^0(0)} = \frac{1}{2} \cos(\theta + \varphi_r) \left\{ 1 - \exp\left[-\frac{d}{\lambda_{\text{ov}} \cos(\theta + \varphi_r)}\right] \right\} + \frac{1}{2} \cos(\theta - \varphi_r) \left\{ 1 - \exp\left[-\frac{d}{\lambda_{\text{ov}} \cos(\theta - \varphi_r)}\right] \right\} \quad (5.10a)$$

and for $90 - \varphi_r < \theta < 90$

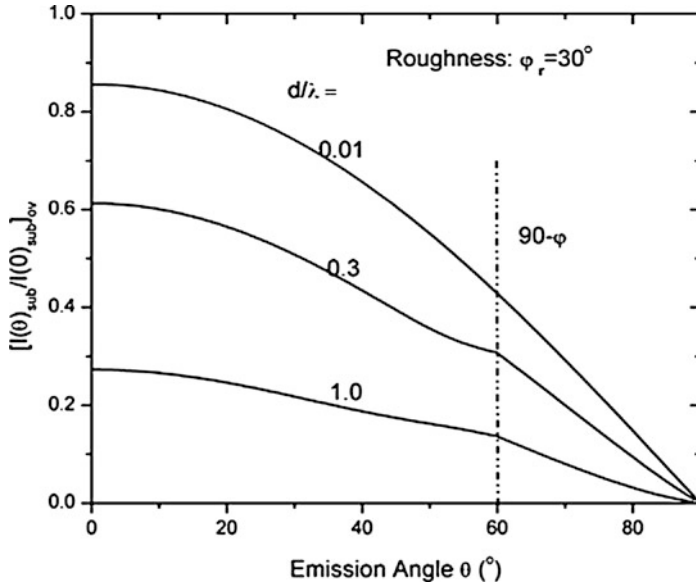


Fig. 5.11 Normalized substrate intensity $[I_{\text{sub}}(\theta)/I_{\text{sub}}^0(0)]_{\text{ov}}$ after (5.9a,b) (with $\lambda = \lambda_{\text{sub}}$), for a substrate with an overlayer of thickness d , as a function of the emission angle θ , for a roughness angle of $\varphi_r = 30^\circ$, and three values of $d/\lambda = 0.01, 0.3$, and 1.0 .

$$\begin{aligned} \frac{I_{\text{ov}}(\theta)}{I_{\text{ov}}^0(0)} &= \frac{1}{2} \frac{a'_r}{a_r} \cos(\theta - \varphi_r) \left\{ 1 - \exp \left[-\frac{d}{\lambda_{\text{ov}} \cos(\theta - \varphi_r)} \right] \right\} \\ &= \cos \theta \cos \varphi_r \left\{ 1 - \exp \left[-\frac{d}{\lambda_{\text{ov}} \cos(\theta - \varphi_r)} \right] \right\}. \end{aligned} \quad (5.10b)$$

In (5.10a) and (5.10b), $I_{\text{ov}}^0(0)$ is the standard overlayer intensity for $\theta = 0$, $\varphi_r = 0$, $d > 5\lambda$, and with λ_{ov} denoting the overlayer electron attenuation length in that layer. In Fig. 5.12, the overlayer intensity is shown for three different relative overlayer thickness values. With the above relations, the overlayer thickness can be determined for rough layers. However, with respect to additional experimental errors, for example, when tilting the sample, it is better to use the ratio approach.

(3) Ratio of Overlayer and Substrate Intensities:

Layer Thickness and Apparent Layer Thickness

Using the ratio method to determine an overlayer thickness from the ratio of (5.9a) and (5.9b) and (5.10a) and (5.10b) requires the generally different values λ_{sub} and λ_{ov} . In the following, we will simplify the equations by setting $\lambda_{\text{sub}} = \lambda_{\text{ov}} = \lambda$. Then, the respective ratios are

$$\text{for } 0 < \theta < 90 - \varphi_r$$

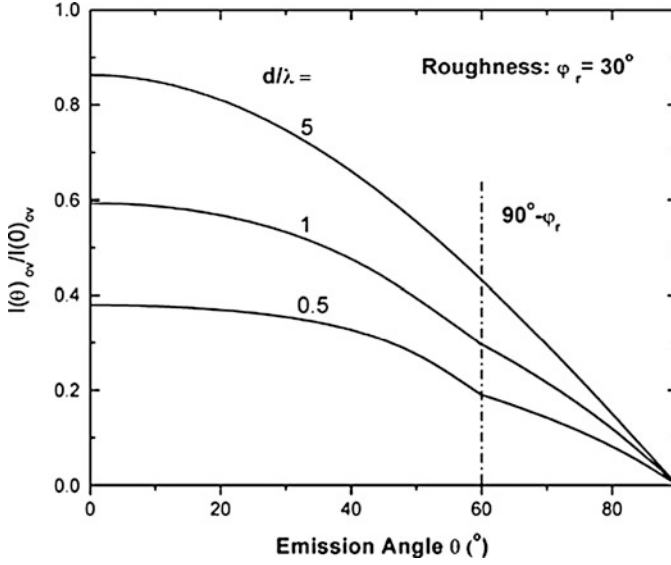


Fig. 5.12 Emission angle dependence of the normalized overlayer intensity for the roughness parameter $\varphi_r = 30^\circ$ and three different relative overlayer thickness values $d/\lambda = 0.5, 1$, and 5 , after (5.10a) and (5.10b) with $\lambda = \lambda_{ov}$

$$\frac{I_{ov}(\theta)I_{sub}^0(0)}{I_{ov}^0(0)I_{sub}(\theta)} = \frac{\cos(\theta + \varphi_r) \left\{ 1 - \exp \left[-\frac{d}{\lambda \cos(\theta + \varphi_r)} \right] \right\} + \cos(\theta - \varphi_r) \left\{ 1 - \exp \left[-\frac{d}{\lambda \cos(\theta - \varphi_r)} \right] \right\}}{\cos(\theta + \varphi_r) \exp \left[-\frac{d}{\lambda \cos(\theta + \varphi_r)} \right] + \cos(\theta - \varphi_r) \exp \left[-\frac{d}{\lambda \cos(\theta - \varphi_r)} \right]} \quad (5.11a)$$

and for $90 - \varphi_r < \theta < 90$, with (5.9b), (5.10b), and $\lambda_{ov} = \lambda_{sub} = \lambda$:

$$\frac{I_{ov}(\theta)I_{sub}^0(0)}{I_{ov}^0(0)I_{sub}(\theta)} = \exp \left[\frac{d}{\lambda \cos(\theta - \varphi_r)} \right] - 1. \quad (5.11b)$$

The intensity ratio after (5.11a) and (5.11b) is depicted in Fig. 5.13 for a roughness angle of $\varphi_r = 30^\circ$ and $d/\lambda_0 = 0.5$ and 1 . These curves are obviously different from the corresponding ones for flat surfaces shown as dashed lines in Fig. 5.13. Besides the discontinuous change at the critical angle $(90 - \varphi_r)$, it is seen that the overall change of the ratio is smaller for rough surfaces and decreases with increasing roughness, as demonstrated in Fig 5.14 for $\varphi_r = 0, 30$ and 45° . Comparison of measured intensity ratios for different emission angles with dependencies like those depicted in Figs. 5.13 and 5.14 yields the relative (and constant!) overlayer thickness in case of rough surfaces.

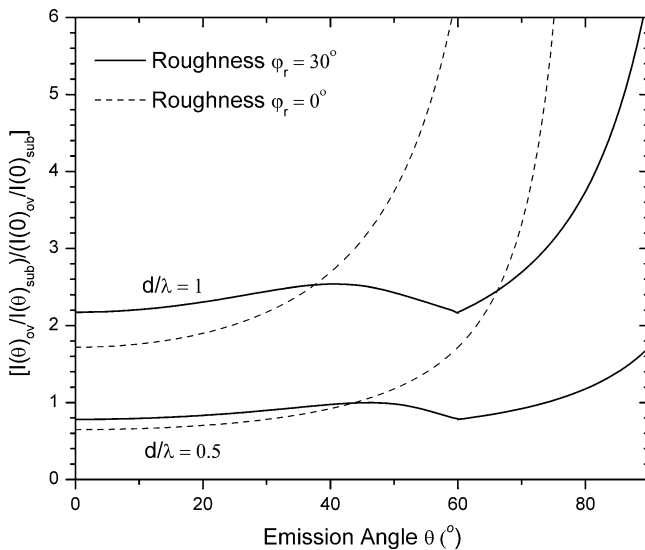


Fig. 5.13 The overlayer/substrate intensity ratio after (5.11a) and (5.11b) for a roughness angle of $\varphi_r = 30^\circ$ and relative overlayer thickness $d/\lambda = 0.5$ and 1 , compared to a flat surface with $\varphi_r = 0^\circ$

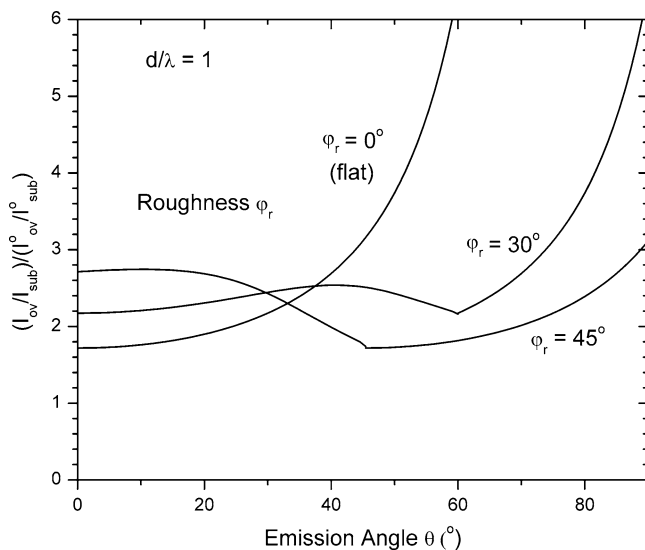


Fig. 5.14 Overlayer/substrate intensity ratio after (5.11a) and (5.11b) as a function of the emission angle θ for relative overlayer thickness $d/\lambda = 1$ and three roughness parameter values $\varphi_r = 0, 30$ and 45°

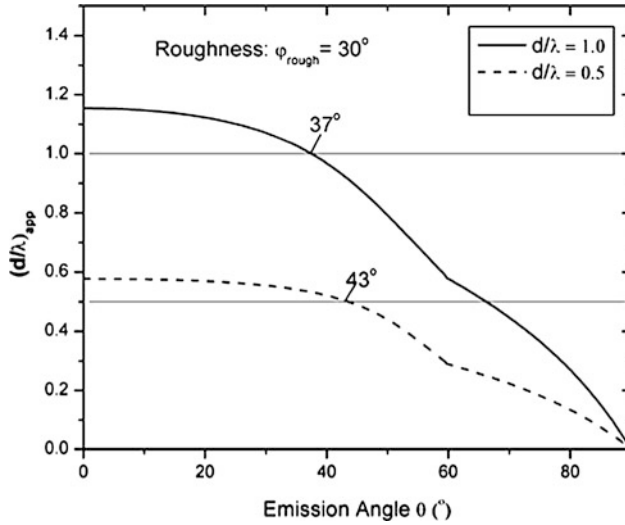


Fig. 5.15 Deviation involved when the thickness of an overlayer on a rough surface is determined using the flat surface expressions (e.g., (4.89), giving $(d/\lambda)_{app}$ instead of the roughness corrected value d/λ after (5.11a) and (5.11b), shown for a roughness angle of $\varphi_r = 30^\circ$ and for $d/\lambda = 0.5$ and 1. Note that $(d/\lambda)_{app} = d/\lambda$ for $\theta_{co} = 43^\circ$ and 37° , respectively

When the roughness effect is ignored and the layer thickness on rough samples is determined with expressions for flat surfaces such as (4.90a) or (4.90b) (with $\varphi_r = 0$), a considerable deviation from the correct values after (5.11a) and (5.11b) for $\varphi_r \neq 0$ is expected. The latter values correspond to the measured overlayer/substrate intensity ratio. When these data are evaluated with (5.11a) and (5.11b) for $\varphi_r = 0$, an apparent but generally incorrect relative layer thickness, $(d/\lambda)_{app}$, is obtained. The dependence of the latter on the emission angle is shown in Fig. 5.15 for a roughness angle of $\varphi_r = 30^\circ$ and $d/\lambda = 0.5$ and 1. As qualitatively obvious, the apparent layer thickness $(d/\lambda)_{app}$ is higher than the true layer thickness d/λ in the vicinity of $\theta = 0$ but lower than that for larger emission angles (e.g., $\theta > 50^\circ$). Therefore, at some angle between very low and very high emission angles, $(d/\lambda)_{app} = d/\lambda$, i.e., at $\theta = 37^\circ$ and 43° for $d/\lambda = 1$ and 0.5 , respectively. The relative deviation at $\theta = 0^\circ$ is +18%, and at $\theta = 70^\circ$, it is -55%, almost independent of d/λ .

Roughness Dependence of the Apparent Layer Thickness

Figure 5.16 shows a comparison of the deviation of $(d/\lambda)_{app}$ from the correct value d/λ , for $d/\lambda = 1$ and for different roughness values ($\varphi_r = 15^\circ$, 30° , and 45°). As expected, the deviation increases with the degree of roughness. In Figs. 5.14 and 5.15, the marked cusp in the curves denotes the critical angle for shadowing, $90^\circ - \varphi_r$. For a more moderate roughness ($= 15^\circ$), the error at $\theta = 0$ is only +4%, but at $\theta = 70^\circ$, it is about -35%. Despite different roughness models and

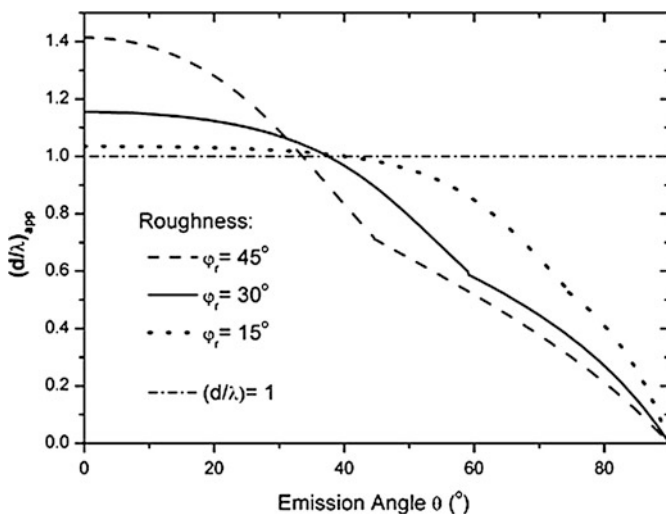


Fig. 5.16 Influence of different roughness values ($\varphi_r = 15^\circ$, 30° , and 45°) on the apparent layer thickness $(d/\lambda)_{app}$ determined using flat surface assumption (4.89) instead of the correct expressions (5.11a) and (5.11b) resulting in $d/\lambda = 1$

calculation methods, most of the results of various authors [5.1, 5.7, 5.8, 5.12, 5.14] agree with those of Figs. 5.14 and 5.15 at least semiquantitatively.

“Magic” Angle

Despite the fact that there is no magic in science, some authors like to denote a special, distinguished value of a parameter “magic.” It is recognized that the angle for which $(d/\lambda)_{app} = d/\lambda$ depends on the value of d/λ and on the roughness. For the conditions in Fig. 5.15, this angle, θ_{co} , has a value of 37° and 43° for $d/\lambda = 1$ and 0.5, respectively. As shown in Fig. 5.16 for $d/\lambda = 1$ and for $\varphi_r = 15^\circ$, 30° and 45° , respectively, θ_{co} varies between 37° and 41° . Several authors call θ_{co} a “magic angle” but report values between 35° [5.8, 5.9] and 55° [5.14], depending on the roughness model and on further assumptions and simplifications used. In view of the simple two-dimensional results given here, and with the rather large spread between different authors, it is obvious that there is no well-defined “magic angle” at all (as, e.g., in contrast to the theoretically well-defined “magic angle” for vanishing asymmetry factor in XPS, see Sect. 4.3.1.2). The “magic” here seems to be caused by the simple fact that θ_{corr} has to be some angle between 0° and 90° but far enough away from these extremes, i.e., somewhere around 45° . Therefore, an important conclusion can be drawn: When angle-resolved measurements are performed on a sample with unknown roughness, the value around $\theta = 35$ to 45° is expected to be close to the true value of d/λ that would have been obtained for a flat surface.

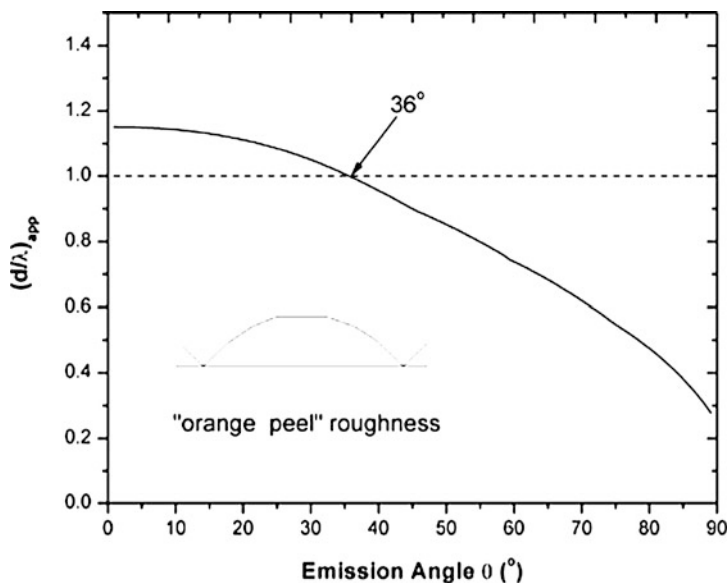


Fig. 5.17 Emission angle dependence of the apparent relative layer thickness $(d/\lambda)_{app}$, for correct relative layer thickness $d/\lambda = 1$, calculated for an equal areal distribution of $\varphi_r = 0^\circ, 15^\circ, 30^\circ$, and 45° resembling an “orange peel” type roughness (see *inset*). Both thickness values are equal for $\theta_{co} = 36^\circ$

Realistic Example

More realistic than the above calculations for one given roughness angle (Figs. 5.15, 5.16) is a mixture of several angles, weighed by their statistical participation, i.e., their areal distribution [5.28]. Assuming schematically a simple case of an equal areal distribution of the three roughness angles shown in Fig. 5.16 (and adding $\varphi_r = 0$ for a flat part of the surface), the apparent layer thickness functions ((5.10a) and (5.10b)) have to be summed up and divided by four, i.e., $(d/\lambda)_{app} = 1/4[(d/\lambda)_{flat} + (d/\lambda)_{15} + (d/\lambda)_{30} + (d/\lambda)_{45}]$. The result is shown in Fig. 5.17. The inset depicts the corresponding surface morphology resembling an “orange peel” type roughness. It is recognized that the deviation between $(d/\lambda)_{app}$ and d/λ is less pronounced than for $\varphi_r \geq 30^\circ$ in Fig. 5.16, with +18% at $\theta = 0^\circ$, and –30% at $\theta = 70^\circ$ (i.e., even lower than that for $\varphi_r = 15^\circ$ in Fig. 5.16). Because the apparent layer thickness an observer (i.e., the analyzer) “sees” is $d_{obs} = d/\cos \theta$, a plot of d_{obs} as a function of $1/\cos \theta$ gives a straight line for a flat sample but deviates for a rough sample. Plotting the data of Fig. 5.17 in that way ($d_{obs}/\lambda = d_{app}/\lambda$) yields the curve shown in Fig. 5.18. The “orange peel” type roughness in Fig. 5.17 is rather similar to an array of ball-shaped segments covered by a thin layer considered by Kappen et al. [5.32] and illustrated in Fig. 5.19. Figure 5.20 shows their results for different roughness. Although the way of roughness influence calculation is different in [5.32], the result for $a/b = 25:50$ in Fig. 5.20 agree fairly well with

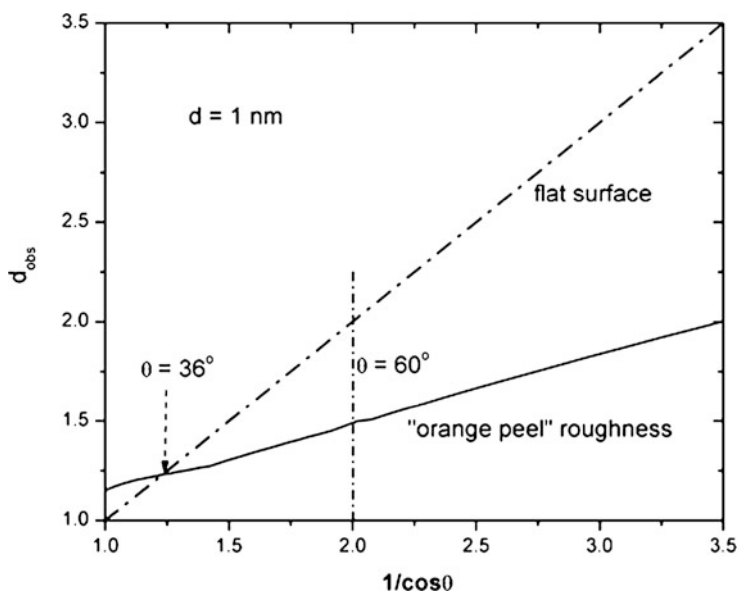


Fig. 5.18 Different plot of Fig. 5.17 for comparison with Fig. 5.20. The observed layer thickness, $d_{\text{obs}} = d_{\text{app}} / \cos \theta$, as a function of $1 / \cos \theta$ gives a straight line for a flat sample surface (*dash-dotted line*). The *solid line* corresponds to the line in Fig. 5.17 for the “orange peel” roughness

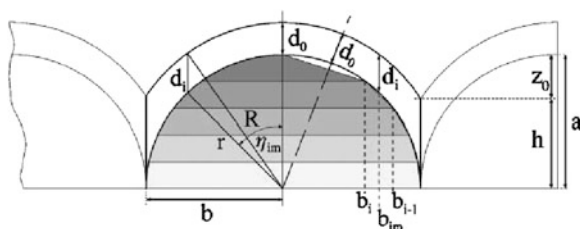


Fig. 5.19 Cross section of hemispheres ($a = b = r$) coated with a thin film of thickness d_0 (Reproduced from P. Kappen et al. [5.32], with permission of Elsevier B.V.)

that of Fig. 5.18. This is obvious too when compared with experimental XPS results for a monolayer of *n*-octanethiol adsorbed on a hexagonal close-packed and gold-coated latex beads (500-nm diameter) on a silicon wafer shown in Fig. 5.21.

The above geometrical models can easily be adapted for any type of angular distributions. Although they are only for one dimension (in the most important tilt angle plane), the main features are fairly well represented. More elaborate models are given, for example, in Ref. [5.31], and Ref. [5.33] gives a review of XPS at corrugated surfaces. The consequences of roughness for the signal-to-noise figure are presented in Chap. 6.

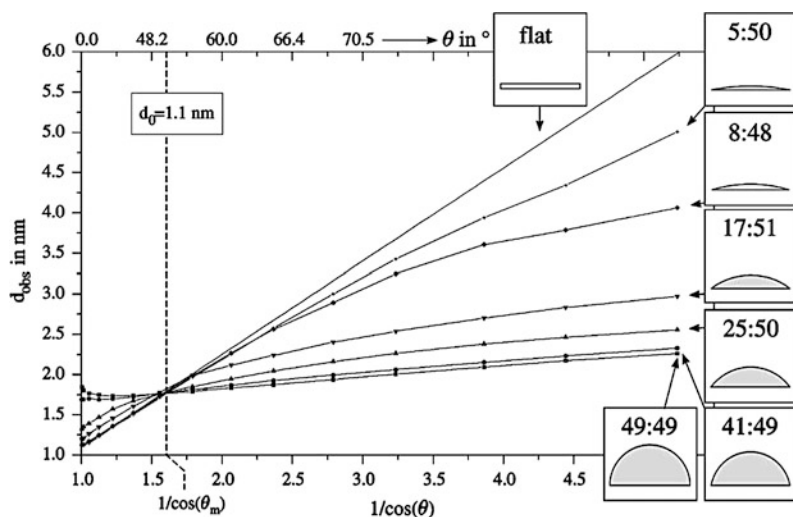


Fig. 5.20 Emission angle resolved results of calculations of d_{obs} for surfaces with different roughness given by different a/b ratios (see *inset*) explained in Fig. 5.19. Note similarity with Fig. 5.18 for $a/b = 25:50$ (Reproduced from P. Kappen et al. [5.32], with permission of Elsevier B.V.)

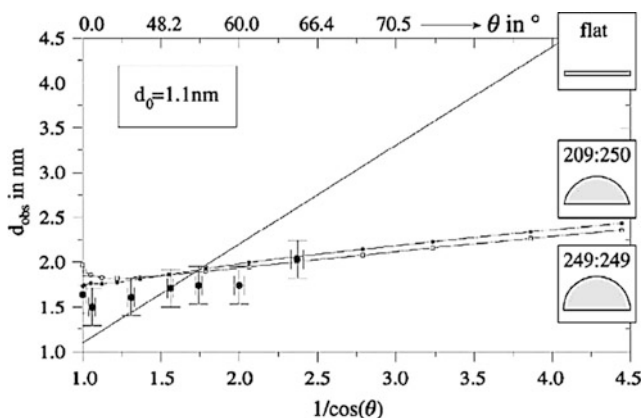


Fig. 5.21 Experimental results (solid circles) of angle resolved XPS applied to a monolayer of n -octanethiol on a hexagonal close-packed layer of 50-nm gold-coated latex beads (500-nm diameter) compared to theoretical results corresponding to the shape shown on the right side (see also similarity with Fig. 5.17 where d_0 corresponds to 1.0 nm) (Reproduced from P. Kappen et al. [5.32], with permission of Elsevier B.V.)

5.2 AES: Intensity Dependence on Emission and Incidence Angles

5.2.1 Sample Tilt Using CHA for AES

Because of the different electron excitation and acceptance angle geometry, the cylindrical mirror analyzer (CMA) and the concentric hemispherical analyzer (CHA) (outlined in Sect. 2.5) have a markedly different dependence of peak intensity and peak-to-background ratio on the electron beam incidence angle. At first, AES using a CHA is considered.

The Auger signal intensity is generated by two contributions: One from the directly incident beam and one from the excitations by the backscattered electrons with energies above the ionization energy of the respective peak. Let us first have a look at the geometrical relations for typical CHA equipment as schematically depicted in Fig. 4.17 [5.34]. Ignoring the backscattering contribution and considering only the primary excitation, we see the following: The primary electron beam with incidence angle α to the normal to the sample surface (dotted line) generates Auger electrons along its way, L , in the sample. Auger electrons that are created within a thickness z from the surface are emitted with an emission angle θ and are detected in the CHA analyzer. In the usual approximation, we assume an exponential law for electron attenuation and write for the total number of Auger electrons, N_{AE} , emitted from the surface, and having survived the inelastic and elastic scattering during their path $z/\cos\theta$ from generation to the surface,

$$N_{\text{AE}} = \int_0^{\infty} n_{\text{AE}} \exp\left(-\frac{k_{\text{A}} z}{\cos\theta}\right) dL = \int_0^{\infty} n_{\text{AE}} \exp\left(-\frac{k_{\text{A}} L \cos\alpha}{\cos\theta}\right) dL = \frac{n_{\text{AE}} \cos\theta}{k_{\text{A}} \cos\alpha}, \quad (5.12)$$

where n_{AE} is the number of Auger electrons generated per unit length, k_{A} is the attenuation coefficient ($=1/\lambda$), and $z = L \times \cos\alpha$ as seen in Fig. 4.17. The detected Auger electron intensity, I , is assumed to be proportional to N_{AE} . Therefore, we may write for the measured intensity I , in accordance with (5.1), as a function of incidence and emission angles,

$$I(\alpha, \theta) = \text{const} \frac{\cos\theta}{\cos\alpha}, \quad (5.13)$$

incidence and emission angles where the constant includes the attenuation length and the totally emitted Auger electrons multiplied by the transmission function of the spectrometer and $I(0) = I(\alpha = 0, \theta = \Phi_1)$ are the reference intensity for $\alpha = 0$ (see Fig. 4.17).

As seen in Fig. 4.13, the incidence and emission angles are connected by the angle between the electron gun and the analyzer axis ϕ_1 , giving $\theta = \phi_1 - \alpha$. Therefore, after (5.13), $I(0) = I(\alpha = 0) = \text{const.} \times \cos\Phi_1$, and the following

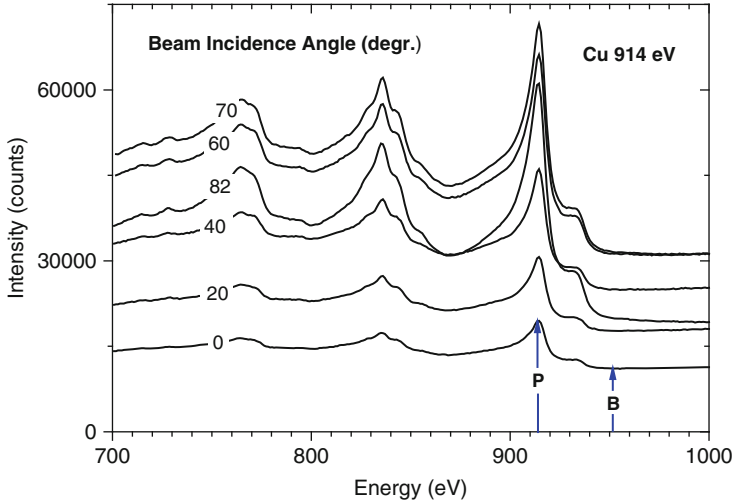


Fig. 5.22 LMM (914 eV) Auger spectra of pure Cu for different electron-beam incidence angles as indicated in the figure, measured with a CHA (Jeol 7830F) at 10 keV primary beam energy, beam current 10 nA, 1 eV/step, 1s/step (10 sweeps of 100 ms each, energy resolution 0.4%). Peak (P) and background (B) determinations for Fig. 5.23 are indicated at 0° incidence angle

expression is obtained for the Auger electron intensity at the analyzer entrance as a function of α :

$$\begin{aligned} \frac{I(\alpha)}{I(0)} &= \frac{1}{\cos \phi_I} \frac{\cos(\phi_I - \alpha)}{\cos \alpha} = \frac{1}{\cos \phi_I} \frac{\cos \phi_I \cos \alpha + \sin \phi_I \sin \alpha}{\cos \alpha} \\ &= (1 + \tan \phi_I \tan \alpha) \end{aligned} \quad (5.14)$$

In general, the angle ϕ_I between the primary electron beam and the analyzer axis is fixed and characterize for a specific instrument. For many instruments, for example, for the Jeol JAMP 7830F instrument, ϕ_I is close to 60°. For this value, $\tan \phi_I = \sqrt{3}$, and (5.14) simplifies to

$$\frac{I(\alpha)}{I(0)} = 1 + \sqrt{3} \tan \alpha. \quad (5.15)$$

Thus, for the Jeol JAMP 7830F (and for any other instrument with $\phi_I \cong 60^\circ$), the measured Auger intensity ratio is expected to be proportional to the ratio $I(\alpha)/I(0)$ as demonstrated by Tsutsumi et al. [5.34]. As an example, Fig. 5.22 shows the intensity of the Cu LMM peak at 914 eV of pure Cu (sputter cleaning with 1 keV Ar ions after sputter deposition on a silicon wafer) measured for different electron-beam incidence angles. Here, the intensity is given as peak height ($P - B$)(θ) with P the peak (in total counts) and B the background at the minimum of counts just above the peak energy, here at 953 eV, both for a set counting time. Taking $(P - B)(\theta)/(P - B)(\theta = 0) = I(\alpha)/I(0)$, Fig. 5.23 shows the result of measurements as in Fig. 5.22 compared to (5.15). Fairly good agreement up to about

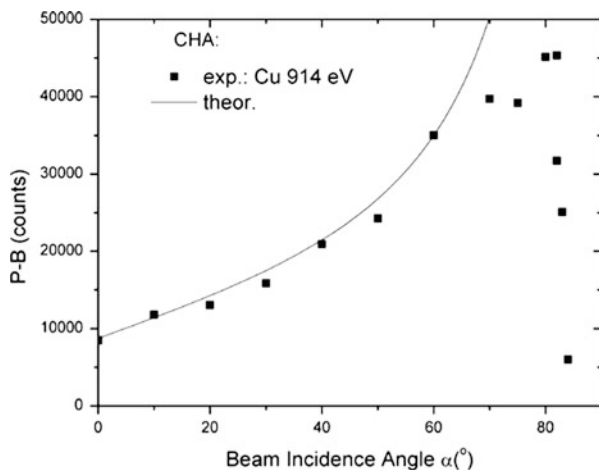


Fig. 5.23 Dependence of the signal intensity of Cu LMM (914 eV), $(P - B) = I$ on the electron-beam incidence angle α (see Fig. 5.22), compared with the theoretical prediction of (5.15)

$\alpha = 60^\circ$ is found. Beyond that value, $P - B$ is lower than predicted by (5.15) because the latter expression ignores both backscattering and roughness effects.

5.2.1.1 Backscattering Contribution

The backscattering contribution to AES signal intensity (see Sect. 4.4.1) is expected to follow a dependence similar to the peak as in (5.12)–(5.15) up to about $\alpha = 45^\circ$, when it becomes weaker since an increasing amount of the lateral straggling part of the primary beam is directly emitted from the surface without creation of Auger electrons. This is recognized by comparison of the Monte Carlo simulations shown in Fig. 5.24a ($\alpha = 0$) with Fig. 5.24b ($\alpha = 80^\circ$) [5.34]. Therefore, the signal intensity $(P - B)$ (see Fig. 5.22) will follow (5.15) until about $\alpha = 45^\circ$, and then start to deviate to generally lower values and, after, a maximum around 70 – 80° , and will eventually decline to a much lower value near 90° incidence angle. Because the main amount of the background is caused by inelastic backscattering, B is closely related to the backscattering intensity. The different behavior of peak and background intensity is seen in Fig. 5.22, with strongly decreasing background for $\alpha > 70^\circ$.

The peak-to-background ratio (P/B), as a function of the incidence angle is shown in Fig. 5.25 and reveals the above-discussed behavior. The nearly constant value up to $\alpha = 45^\circ$ follows from the similar variation of peak and background. The strong increase of P/B between 60° and 80° corresponds to the decreasing backscattering contribution in that range. Above 80° , the decline of P/B corresponds to the decrease in signal intensity and can be explained by the combined effect of decreasing excitation intensity (negative backscattering term $r_{A,U(A)}$ after [5.35–5.37]) and of

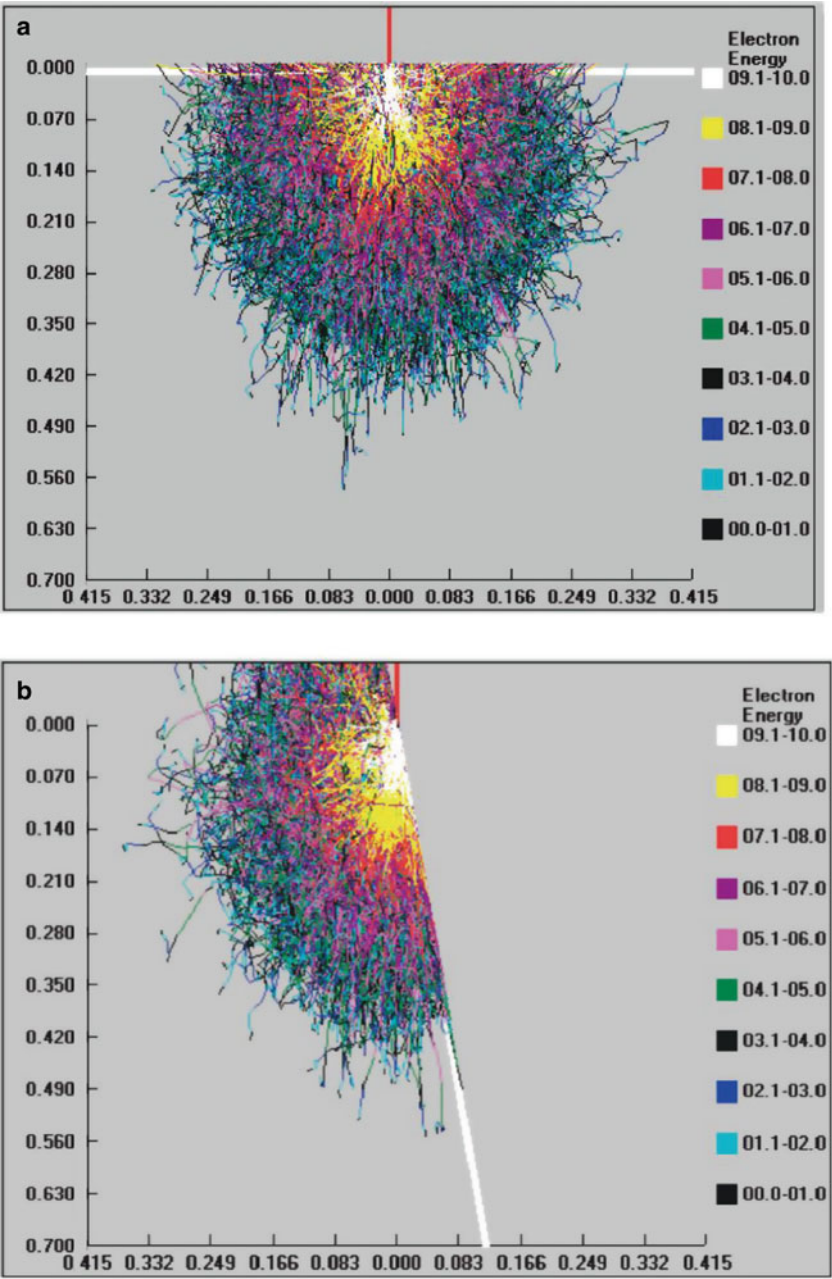


Fig. 5.24 Monte Carlo simulation of the electron scattering for a 10 keV beam impinging on a metallic sample, with incidence angle (a) $\alpha = 0^\circ$ and (b) $\alpha = 80^\circ$. Depth and lateral scale are in μm units; the energy on the color scale on the right side is in keV. The thin white layer on *top* (a few nm thickness) denotes the information depth of AES. The excitation volume center is about 70 nm from the surface (Reproduced from K. Tsutsumi et al. [5.34], with permission of JEOL Ltd.)

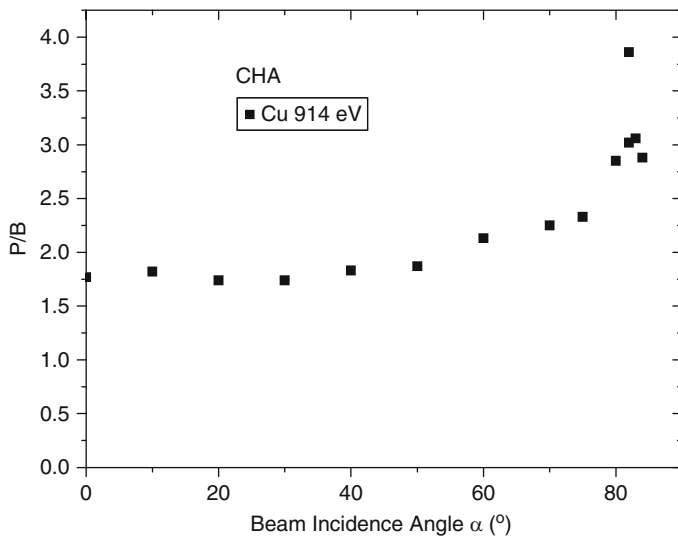


Fig. 5.25 Peak-to-background (P/B) ratio of Cu LMM (914 eV) as a function of the electron-beam incidence angle α from measurements depicted in Fig. 5.22

the influence of residual surface roughness [5.22, 5.23, 5.28] (see Fig. 5.40). The P/B ratio still increases although the Auger signal intensity already decreases at higher incidence angles, as evident by comparison of Fig. 5.25 with Fig. 5.22. Taking into account the backscattering factor dependence of element A on incidence angle α , the experimental result, normalized to $\alpha = 0$, should be better represented by

$$\frac{I_A(\alpha)}{I_A(0)} = \frac{1 + r_{A,U(A)}(\alpha)}{1 + r_{A,U(A)}(0)} (1 + \sqrt{3} \tan \alpha) = \frac{R_{A,U(A)}(\alpha)}{R_{A,U(A)}(0)} (1 + \sqrt{3} \tan \alpha), \quad (5.16)$$

where $R_{A,U(A)} = (1 + r_{A,U(A)})$ is the backscattering factor defined in Sect. 4.4.1, with backscattering term $r_{A,U(A)}$ for species A (here element A) and “overvoltage” $U(A) = E_P/E_{A,X}$, where E_P is the primary electron energy and $E_{A,X}$ the ionization energy of electron level X of element A . The incidence angle dependence of the backscattering factor has been discussed by several authors.

While the classical Ichimura–Shimizu equations only provide backscattering values for $\alpha = 0^\circ$, 30° and 45° (see Sect. 4.4.1.3, (4.130) and Fig. 4.50), there are a number of different approaches to the continuous dependence of $r_{A,U(A)}$ on α [5.35–5.39]. For the Cu LMM (914 eV) peak, the approach by Cazaux [5.39] shows a decrease of $r_{A,U(A)}$ to about 40% near $\alpha = 90^\circ$, whereas Smith and Seah [5.38] assume a decrease to zero, but both authors and Refs. [5.35, 5.36, 5.37] agree that, up to $\alpha = 45^\circ$, there is practically no incidence angle dependence. A new model of Auger electron excitation and emission led to new Monte Carlo (MC) calculations by Jablonski et al. [5.35, 5.36] and by Ding et al. [5.37] (see Sect. 4.4.1). These authors show that $r_{A,U(A)}$ can become negative, i.e., the backscattering factor

$R_{A,U(A)} < 1$ for $\alpha > 80^\circ$. In addition, $r_{A,U(A)}$ slightly depends on the emission angle θ (which is ignored in the following). Taking the values for Cu LMM and for Si KLL at 10 keV primary energy from the database of Zeng et al. [4.151], we get the incidence angle dependencies shown in Fig. 5.26 for the normalized backscattering correction factor $R_{A,U(A)}(\alpha)/R_{A,U(A)}(0) = (1 + r_{A,U(A)}(\alpha))/(1 + r_{A,U(A)}(0))$. The result of multiplication with the theoretical function without backscattering correction after (5.16) and comparison with the latter is shown in Fig. 5.27 for Cu LMM and in Fig. 5.28 for Si KLL.

From a comparison of Fig. 5.27 with Fig. 5.23, it is obvious that the magnitude of the backscattering effect is not sufficient to explain the too low experimental values for $\alpha > 60^\circ$. Most probably, there is an additional roughness influence.

A smooth Si wafer surface will have a much lower roughness as compared to the sputter-deposited copper layer. Therefore, we expect (5.15) to hold for higher incidence angles in case of Si KLL as compared to Cu LMM (Fig. 5.23). Indeed, the measured relation $(P - B) = f(\alpha)$ for Si as shown in Fig. 5.29 shows good agreement with (5.16) up to about $\alpha = 80^\circ$. A plot of the measured P/B ratio as a function of α is shown in Fig. 5.30. The strong increase of the P/B ratio at $\alpha = 80^\circ$ and above yields an even stronger increase of the signal-to-noise (S/N) ratio (see Chap. 6) and therefore of detection sensitivity. This has led to the technique of grazing incidence AES.

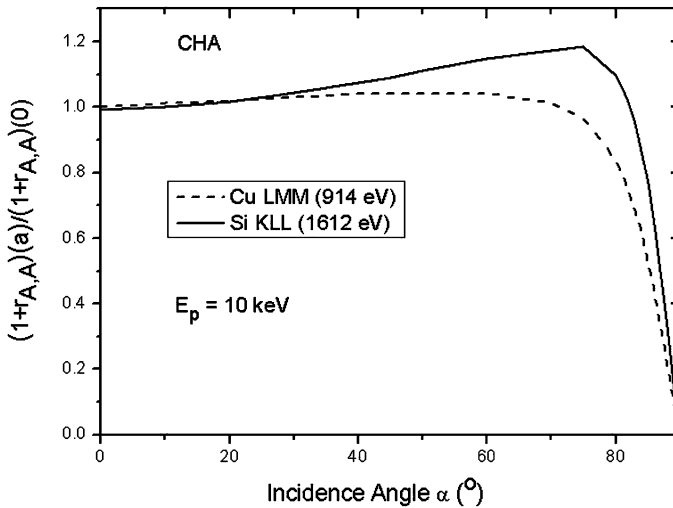


Fig. 5.26 Incidence angle, α , dependence of the backscattering factor normalized to $\alpha = 0$, $(1 + r_{A,A}(\alpha))/(1 + r_{A,A}(0))$ for $A = \text{Cu LMM (914 eV)}$ and for $A = \text{Si KLL (1,612 eV)}$, respectively, at a primary electron energy of 10 keV (Data from the database of Zheng et al. [4.151])

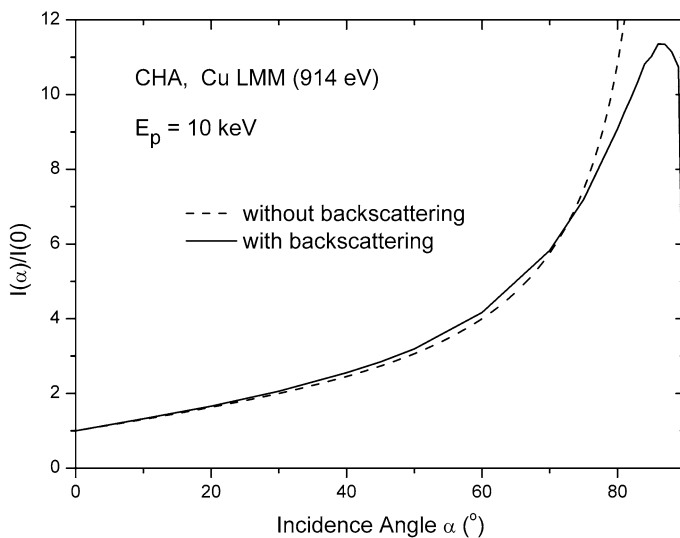


Fig. 5.27 Dependence of the normalized intensity $I(\alpha)/I(0)$ on the incidence angle α without backscattering correction after (5.15) and with backscattering correction after (5.16). Backscattering data are for Cu (LMM) from Fig. 5.26

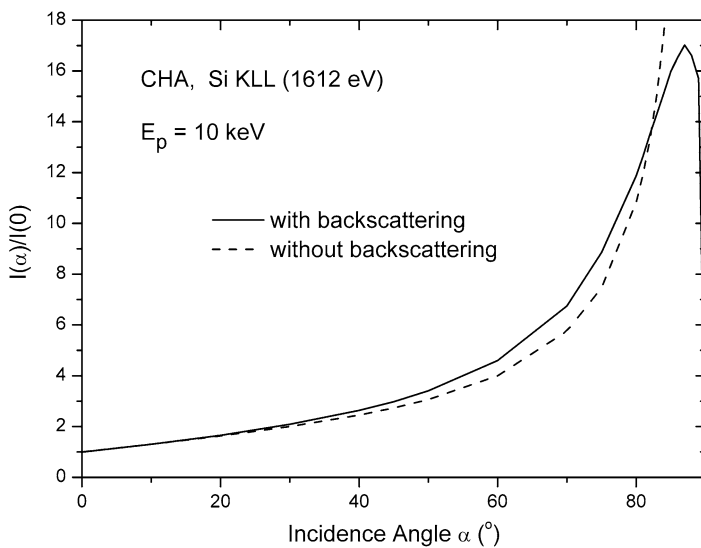


Fig. 5.28 Dependence of the normalized intensity $I(\alpha)/I(0)$ on the incidence angle α without backscattering correction after (5.15) and with backscattering after (5.16). Backscattering for Si KLL are from Fig. 5.26

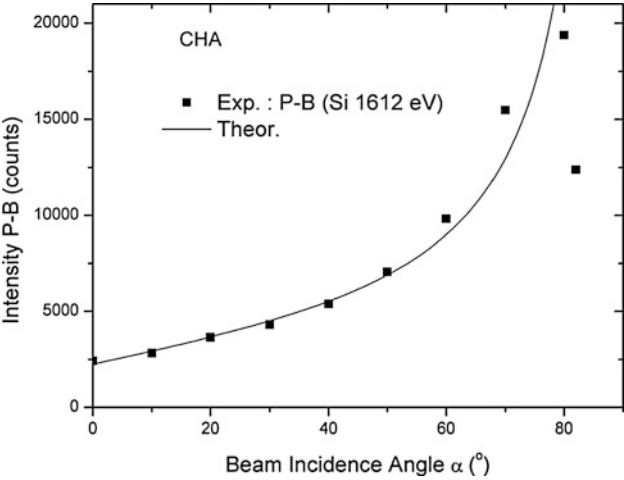


Fig. 5.29 Measured data of the intensity ($P - B$) of the Si KLL (1612 eV) Auger peak as a function of the electron-beam incidence angle α and fit of (5.15) with $I = (P - B)$

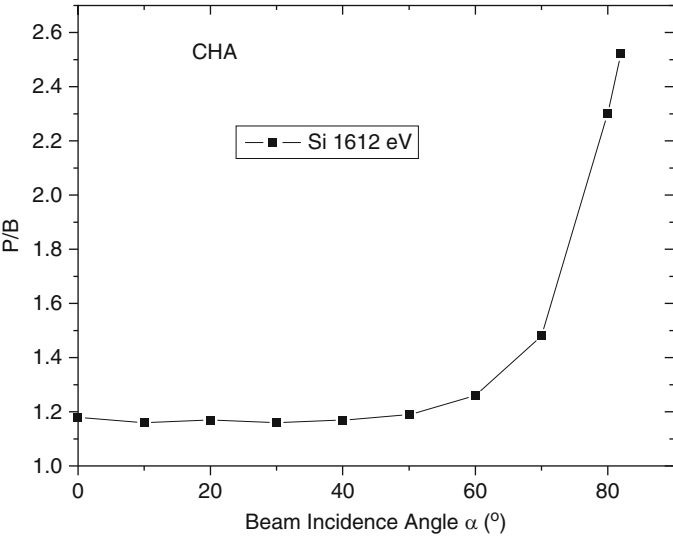


Fig. 5.30 Measured peak-to-background (P/B) ratio as a function of the electron-beam incidence angle α for the Si KLL peak (1612 eV)

5.2.1.2 Grazing Incidence AES (GI-AES)

According to Fig. 5.30, the peak-to-background ratio (P/B) for the Si 1,612 eV Auger signal intensity increases by a factor of more than 2 above 60° and the corresponding signal-to-noise ratio (S/N) by more than a factor of 6 (see Fig. 6.5).

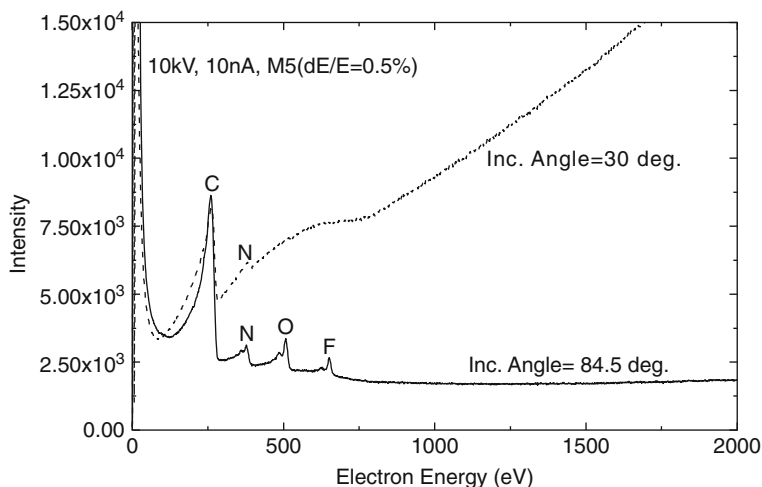


Fig. 5.31 Determination of traces of residual fluorine in the lubrication film on a hard disk by changing the electron-beam incidence angle of the usual 30° to the extreme glancing incidence at 84.5° (grazing incidence AES). Note that in the latter case, the background is extremely low since the matrix is hardly excited, and besides N, the presence of O and F in the outermost layers is clearly disclosed (Reproduced from K. Tsutsumi et al. [5.34], with permission of JEOL Ltd.)

Correspondingly, the relative uncertainty ($N/S = \sigma_R$, see Chap. 6) decreases from 7% to 1.1%. This expected increase in detection sensitivity by grazing incidence AES (GI-AES) has been used by Tsutsumi et al. [5.34] to determine contamination elements in the lubrication film on a hard disk that cannot be seen in the spectrum at an incidence angle of 30° . The example in Fig. 5.31 shows that, at 84.5° incidence angle, the background is extremely low since the matrix is hardly excited, and besides O and N, the presence of fluorine in the surface film is clearly seen. Of course, application of grazing incidence AES is restricted to extremely smooth surfaces. The influence of roughness on AES is discussed in Sect. 5.2.3.

5.2.2 Sample Tilt Using CMA

The schematic cross section of a cylindrical mirror analyzer (CMA) is shown in Fig. 2.12 (Chap. 2). The spatial distribution of the electron path from sample to analyzer follows approximately the shape of an American football. The special, cone-shaped geometry of the electron acceptance visualized in Fig. 5.4 reduces the sensitivity to incidence angle variations. This fact, together with the coaxial electron gun, has often been used as an argument for analyzing ball-shaped objects or rough surfaces in general, as compared to the unidirectional electron acceptance of the CHA. However, exact quantification gets more complicated, and at higher incidence

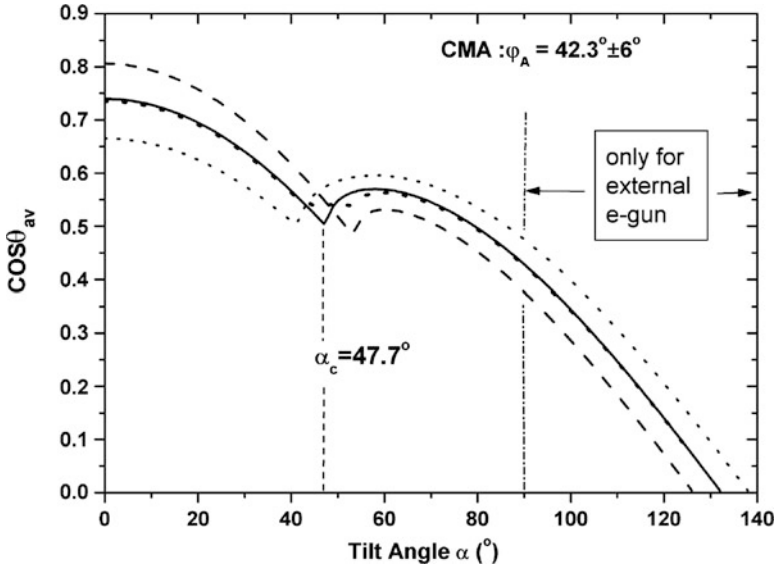


Fig. 5.32 Average of the cosine of the emission angle θ , $\cos \theta_{av}$, as a function of the tilt angle, for the CMA cone angle $\varphi_A = 42.3^\circ$ (cf. Fig. 4.2 of Ref. [5.1]) (full drawn line after (5.17) and (5.18)), including the limiting curves for the acceptance angle $\alpha \pm 6^\circ$ (dotted and dashed line, respectively). Owing to the corresponding range of θ values, the mean curve for $\cos \theta_{av}$ is slightly deviating from the full drawn line in the vicinity of the critical angle $\alpha_c = 47.7^\circ$ (indicated by thick dots). Note that for the usual CMA with a coaxial electron gun, tilt angles above 90° are impossible (From Ref. [5.11])

angles (above 47.7° , see below), there is a gradual loss of transmission because of shadowing of the acceptance cone (cf. Figs. 5.32 and 5.33).

5.2.2.1 Average Cosine of the Emission Angle

According to (5.1), the Auger peak intensity depends directly on the cosine of the emission angle θ . Whereas θ is clearly defined for a concentric hemispherical analyzer (CHA), it covers a range of values in case of a CMA if the normal to the sample surface does not coincide with the analyzer axis. For simplification, however, we can derive an average $\cos \theta_{av}$ that depends on the tilt angle α and serves to replace $\cos \theta$ in (5.1), as shown in the following.

Fig. 5.4 depicts the basic geometrical relations in case of a CMA with the usual opening angle of the acceptance cone of $\varphi_A = 42.3^\circ$, where second-order focusing is obtained [2.5]. The electron emission angle θ depends on both the tilt angle α between the normal to the sample surface and the CMA axis, and on the azimuth angle θ_{az} along the circumference of the acceptance cone.

Equation 5.3 shows how the emission angle, θ , depends on both the tilt angle α and the azimuth angle θ_{az} . Only for $\alpha = 0$, the emission angle is independent of

θ_{az} and $\cos \theta = \cos \varphi_A = \cos 42.3^\circ = 0.74$. As a consequence, for a CMA, the maximum electron escape depth is restricted to $\lambda = \lambda \cos \varphi_A = 0.74\lambda$, where λ is the attenuation length (see Sect. 4.2.2).

As shown by Bungo et al. [5.40], a rigorous treatment for quantification when using a tilted sample in front of the CMA has to take into account the dependence of the Auger electron escape depth on each azimuth angle θ_{az} through $\cos \theta(\theta_{az})$ given by (5.4). Much simpler is an alternative, approximate method to calculate an average $\cos \theta_{av}$ resulting in an average escape depth $\lambda \cos \theta_{av}$. According to Hofmann and Wang [5.11], the deviation from the rigorous treatment is less than 3%.

Assuming a directionally independent emission, the mean value of $\cos \theta_{av}$ when integrating over all azimuth angles θ_{az} is

$$\begin{aligned} \cos \theta_{av} &= \frac{\int_0^{\theta_{\max}} \cos \theta d\theta_{az}}{\int_0^{\theta_{\max}} d\theta_{az}} = \cos \phi_A \cos \alpha \dots (\alpha \leq \alpha_c) \\ &= \cos \phi_A \cos \alpha + \frac{\sin \phi_A \sin \theta_{az,\max} \sin \alpha}{\theta_{az,\max}} \dots (\alpha > \alpha_c) \end{aligned} \quad (5.17)$$

with $\theta_{az,\max}$ in units of π .

The angle $\theta_{az,\max}$ denotes the maximum azimuth angle for which electrons can be detected, and the critical tilt angle is $\alpha_c = 90^\circ - \varphi_A = 47.7^\circ$. For α values below that value, in principle, all emitted electrons around the azimuth are detected, and $\theta_{az,\max} = 2\pi$. In practice, the azimuth regions that are shielded by metal bridges holding the entrance grids of the inner cylinder have to be subtracted, as seen in Fig. 5.5. Above the critical angle, a part of the analyzer's acceptance cone is increasingly "shadowed" by the sample ($\theta_{az,\max} < 2\pi$), and the signal from those angles ($\theta_{az} \geq \theta_{az,\max}$) cannot be detected (see Fig. 5.4). Note that in [5.5, 5.6] there is a slight error for $\theta_{az,\max}$ in the region $\alpha > \alpha_c$ which was corrected in Ref. [5.8]).

The maximum azimuth angle is given by [5.11]

$$\cos \theta_{\max} = -\cot \phi_A \cot \alpha. \quad (5.18)$$

Combining (5.17) and (5.18) results in the average value for a CMA, $\cos \theta_{av}$, as a function of the incidence angle α , plotted in Fig. 5.32. The decisive role of the critical angle, $\alpha_c = 47.7^\circ$, is clearly seen. Because the usual opening angle of the CMA is $\pm 6^\circ$ [2.7], the curves for the limiting angles (48.3° and 36.3°) are also shown in Fig. 5.32, together with the resulting, smoother average curve for the mean value near the critical angle α_c . The surprising increase in $\cos \theta_{av}$ just above α_c is due to the fact that the lowest emission angles are the first ones to be cut away by shadowing. Note that by changing the tilt angle from 0° to 90° (i.e., of the analyzer axis from parallel to perpendicular to the normal to the sample surface), $\cos \theta_{av}$ (and proportionally the electron escape depth) only varies between 0.74 and 0.43. In contrast, for the CHA, $\cos \theta_{av} = \cos \theta$ varies from 1 to 0. However, as pointed

out in Sect. 5.1.2, the so-called double-pass CMA with drum device can be used to obtain angle-resolved AES and XPS data with the advantage of fixed tilt angle of the sample [5.6–5.10]. According to Fig. 5.32, $\cos \theta_{av} \rightarrow 0$ can be principally obtained with a CMA too, if the electron gun is outside the CMA and the sample is tilted to $-\varphi_A$ ($\alpha = 132.3^\circ$).

5.2.2.2 AES Intensity as a Function of the Tilt Angle (CMA)

In contrast to the CHA, the geometrical transmission, given by the total angular aperture T_{ap} , varies with the sample tilt angle above the critical angle $\alpha_c = 47.7^\circ$ because of the increasing shadowing of the acceptance cone. T_{ap} is decreasing from a constant value T_{ap}^0 to $0.5T_{ap}^0$ at $\alpha = 90^\circ$. The aperture angle $\Delta\Omega$ determines T_{ap} . For $\alpha = 0$, $T_{ap}^0 = \Delta\Omega/4\pi$, and for the usual CMA with $\pm 6^\circ$ aperture angle, $\Delta\Omega = 12 \times (\pi/180) \times 2\pi$ and $\Delta\Omega/(4\pi) = 0.105$. This is about 10% for a tilt angle of $0 < \alpha < 47.7^\circ$ (or, more precisely, until $47.7 - 6^\circ = 41.7^\circ$). Above that tilt angle, $T_{ap}/T_{ap}^0 = f(\alpha) = \theta_{max}/180^\circ$, with θ_{max} determined by (5.18). Fig. 5.33 shows T_{ap}/T_{ap}^0 and the AES intensity transmitted through the analyzer, $(T_{ap}/T_{ap}^0) \cos \theta_{av}$, as a function of the incidence angle α . With the latter expression in (5.13), the measured intensity for the CMA, normalized to $I_A(\theta = 0)$, is given by

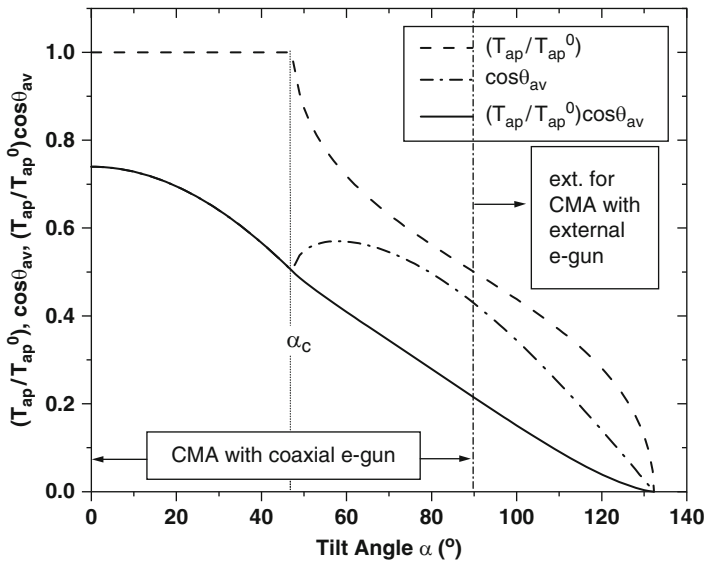


Fig. 5.33 Normalized geometrical analyzer transmission, (T_{ap}/T_{ap}^0) (dashed line), $\cos \theta_{av}$ from Fig. 5.32 (full drawn ($\alpha < \alpha_c$) and dashed-dotted line), and AES electron intensity detected by the analyzer, $[I(\alpha)/I(0)] \cos \varphi_A$, according to (5.19) (full drawn line), as a function of the incidence or sample tilt angle α between the normal to the sample surface and the CMA axis (Adapted from S. Hofmann and J.Y. Wang [5.11])

$$\frac{I(\alpha)}{I(0)} = \frac{T_{\text{ap}} \cos \theta_{\text{av}}}{T_{\text{ap}}^0 \cos \varphi_A} \frac{1}{\cos \alpha} \quad (5.19)$$

In contrast to the CHA, for tilt angles larger than $\alpha_c = 47.7^\circ$, the acceptance angle of the CMA depends on the tilt angle and therefore additionally decreases the measured Auger intensity. In Fig. 5.34, measured values for the Cu LMM (914 eV) Auger peak ($I = P - B$) (normalized to $I(\alpha = 0)$) of a smooth, pure Cu sample, excited with a 10 keV electron beam are shown together with prediction from (5.19) with $\cos \theta_{\text{av}}(\alpha)$ given by (5.17) and (5.18).

As in (5.13), the backscattering effect is ignored in (5.19). Usually, the amount of backscattering is represented by a backscattering factor $R_{A,A} = [1 + r_{A,E(A)}(E_p, \alpha)]$ (see Sect. 4.4.1.3), where the backscattering coefficient $r_{A,E(A)}$ is a function of the material (A), of the ionization energy $E(A)$ for the considered Auger transition, of the primary electron energy, E_p , and of the electron-beam incidence angle, α . Through the normalization ($I(\alpha)/I(0) = 1$ for $\alpha = 0$), the backscattering factor is already considered in the comparison with experimental intensity values for $\alpha = 0$. After adopting (5.16) and Fig. 5.26 and extending (5.19), we get

$$\frac{I_A(\alpha)}{I_A(0)} = \frac{[1 + r_{A,U(A)}(\alpha)]}{[1 + r_{A,U(A)}(0)]} \frac{T_{\text{ap}} \cos \theta_{\text{av}}}{T_{\text{ap}}^0 \cos \varphi_A} \frac{1}{\cos \alpha}, \quad (5.20)$$

where $r_{A,U(A)}$ is the backscattering term for element A and overvoltage $U(A)$ as explained in Sect. 4.4.1.3.

Fig. 5.34 shows a considerably improved agreement between theory and experiment when the simple theory (5.19) is extended by the backscattering factor correction (5.20) with values taken from the database of Zeng et al. [4.151] (see Fig. 5.26). In earlier work [5.11], we adopted the semiquantitative, heuristic relation of Smith and Seah [5.38] which gave less agreement with measured data for Cu LMM.

The P/B values for CMA measurements of the Cu LMM (914 eV) Auger peak are shown in Fig. 5.35. While this figure is not markedly different from Fig. 5.25, the peak intensity dependence on α is weaker for the CMA as compared to the CHA, as obvious when comparing Fig. 5.34 with Fig. 5.23. Hence, incidence angle and therefore sample tilt angle effects are less pronounced for the CMA, which in practice is an advantage when studying rough samples (see Sect. 5.2.3 below).

5.2.3 AES Intensity Dependence on Surface Roughness

5.2.3.1 AES Using CHA

Homogeneous Sample Without Overlayer

The main difference between AES and XPS are the effects of the electron-beam excitation, namely, the dependence of the excitation intensity and of the

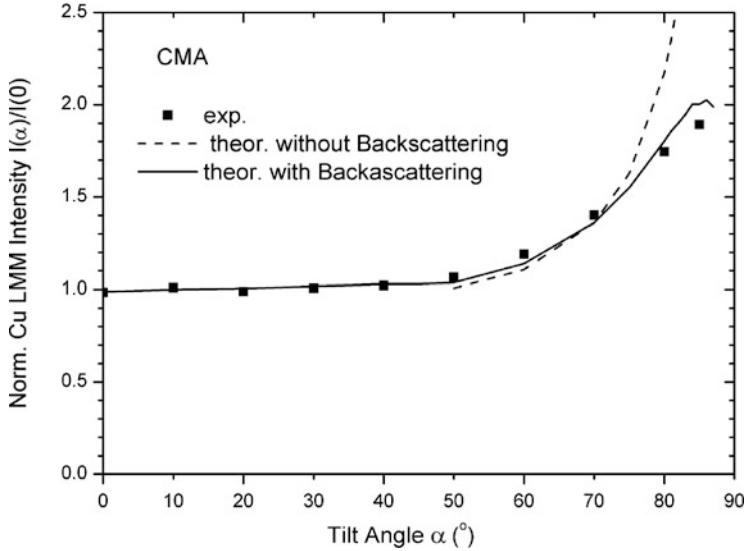


Fig. 5.34 Normalized total Auger intensity $I_{Cu}/I_{Cu}(\alpha = 0)$ as a function of tilt angle α for a CMA with concentric electron gun, compared with measured values for the Cu LMM (914 eV) intensity $(P - B)/(P - B)(0)$. *Dashed line*: without electron backscattering factor $(1 + r_{A,U(A)} = 1)$, after (5.19). *Full drawn line*: with backscattering factor after (5.20). Measured values (10 keV, 10 nA) were provided by E. Nold, Forschungszentrum Karlsruhe

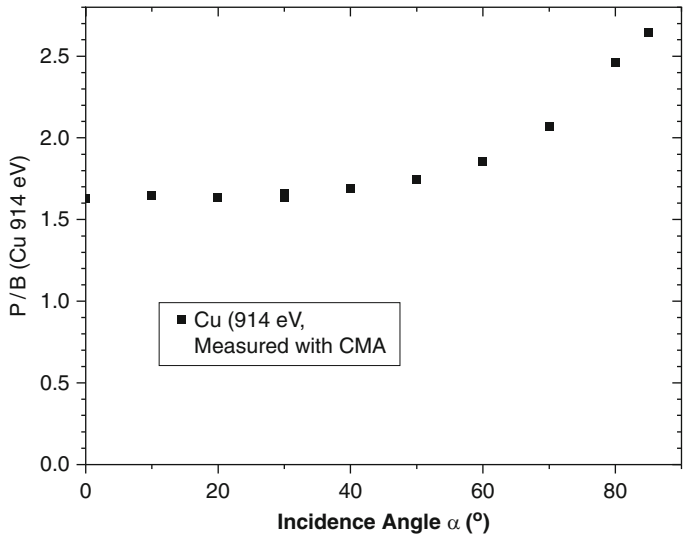


Fig. 5.35 Measured P/B values as a function of the electron-beam incidence angle for CMA measurements of the Cu LMM (914 eV) Auger peak. Measurement conditions as in Fig. 5.34

backscattering factor on the beam incidence angle (see Sect. 5.1.4) [5.24]. As evident from Fig. 4.13, the emission angle θ is given by

$$\theta = \phi_1 - \alpha. \quad (5.21)$$

where ϕ_1 is the angle between the electron beam and the CHA analyzer axis (=retardation lens axis) and α is the electron-beam incidence angle normal to the sample surface. Because ϕ_1 is generally fixed and given for an instrument, the emission angle cannot be changed without changing the electron-beam incidence angle. The detected intensity varies with $\cos \theta$ and the excitation intensity of the electron beam with $1/\cos \alpha$ (5.1). Ignoring the effect of the angle α on the backscattering factor, the normalized intensity $I(\alpha)/I(\alpha = 0)$ for a flat surface is given by (5.14).

The incidence angle α corresponds to the tilt angle of the sample, measured as the angular difference between the vertical electron gun column and the normal to the sample surface.

For the Jeol JAMP 7830F, $\phi_1 = 60^\circ$, and (5.15) is obtained.

As shown in Sect. 5.2.1, (5.15) agrees fairly well to experimental data, with a small deviation caused by the dependence of the backscattering factor on α . Because this deviation becomes measurable only at very high incidence angles (usually for $\alpha > 75^\circ$) (see Fig. 5.34), we will ignore the backscattering effect in the following. Replacing α in (5.15) by $\phi_1 - \theta$ (cf. (5.21)), we get for the emission angle dependence of the intensity

$$\frac{I(\alpha)}{I(0)} = 1 + \sqrt{3} \tan(\phi_1 - \theta) \quad (5.22)$$

Equation 5.22 is shown as the upper curve in Fig. 5.36. For comparison, the respective emission angle dependence of the XPS intensity is additionally shown, both for $\phi_1 = 60^\circ$, i.e., normalized to $\alpha = 0$ or $\theta = 60^\circ$. Whereas above about $\theta = 50^\circ$, AES and XPS intensities show the same angular dependence – they diverge considerably for lower emission angles. When θ approaches -30° ($\alpha \rightarrow 90^\circ$), the intensity gain in AES is very high, although some loss of intensity is expected from the decreasing backscattering factor for angles $\alpha > 75^\circ$ (see Sect. 5.2.1). The signal-to-noise enhancement at glancing incidence angle AES is restricted to a thin surface layer (see Fig. 5.31).

As pointed out in Sect. 5.1.4 (see Fig. 5.8), we describe surface roughness by small pyramids with a characteristic slope angle φ_r . In general, the result will be different from that for XPS (see Sect. 5.1.4), because of the significance of the excitation intensity factor $1/\cos \alpha$ for AES. If the electron-beam incidence angle α varies, three cases may be considered:

- (a) Without shadowing of emission and excitation
- (b) With shadowing of emission only
- (c) With shadowing of excitation and emission

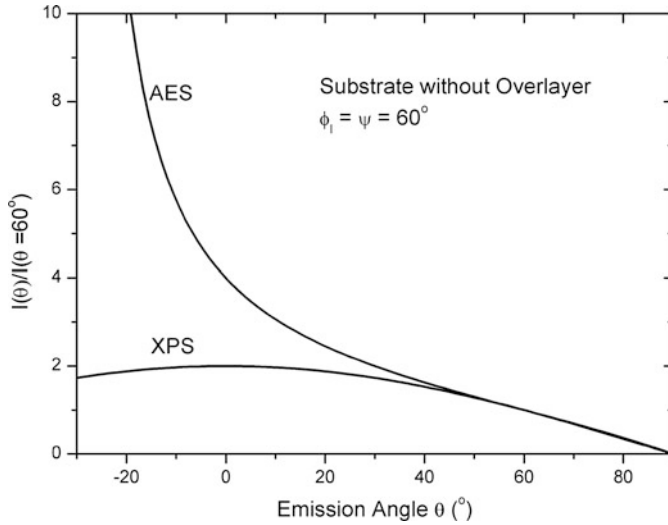


Fig. 5.36 Emission angle dependence of the normalized intensity, $I(\theta)/I(\theta = 60^\circ)$, of AES and XPS for a smooth, flat surface of a homogeneous sample, according to (5.2) (XPS) and (5.22) (AES). Since $\alpha = (\theta - \phi_I) = 0$ for $\theta = 60^\circ$, this figure corresponds to the calculated curves in Figs. 5.2 and 5.23 on a reverse but extended x -axis

Ad (a), without shadowing of emission: According to Fig. 5.8 and $\alpha = 0^\circ$, no shadowing of the electron emission with roughness angle φ_r occurs if the roughness angle fulfills the condition $\varphi_r < 90 - \phi_I$. This corresponds to a critical $\alpha_c = 90 - \phi_I - \varphi_r$ below which there is no shadowing of the emission. The excitation varies with $1/\cos(\alpha - \varphi_r)$ for the right side and with $1/\cos(\alpha + \varphi_r)$ for the left side of the roughness pyramid. Replacing θ by $\phi_I - (\alpha \pm \varphi_r)$ in (5.7a), and multiplying with the AES excitation factor, the following expression is obtained:

$$\frac{I(\alpha)}{I(0)} = \frac{1}{\cos \phi_I} \left[\frac{0.5 \cos(\phi_I - \alpha - \varphi_r)}{\cos(\alpha + \varphi_r)} + \frac{0.5 \cos(\phi_I - \alpha + \varphi_r)}{\cos(\alpha - \varphi_r)} \right]. \quad (5.23)$$

For $\theta = \phi_I - \alpha$ in (5.23), the emission angle dependence is

$$\frac{I(\theta)}{I(\theta = \phi_I)} = \frac{1}{\cos \phi_I} \left[\frac{0.5 \cos(\theta - \varphi_r)}{\cos(\phi_I - \theta + \varphi_r)} + \frac{0.5 \cos(\theta + \varphi_r)}{\cos(\phi_I - \theta - \varphi_r)} \right]. \quad (5.24)$$

With $\phi_I = 60^\circ$, (5.23) is shown in Fig. 5.37a and (5.24) in Fig. 5.37b. Shadowing at $\alpha = 0^\circ$ is only excluded for $\varphi_r \leq 30^\circ$, and a critical tilt angle $\alpha_s = \varphi_r - 30$ exists below which there is emission shadowing (e.g., for $\varphi_r = 45^\circ$ indicated in Fig. 5.37a). The upper limit for nonshadowing is given by the critical angle $\alpha_c = 90 - \varphi_r$, marking the onset of electron-beam incidence shadowing. Corresponding to the critical values of α are those of θ in Fig. 4.31b. The emission angle $\theta = 60^\circ$

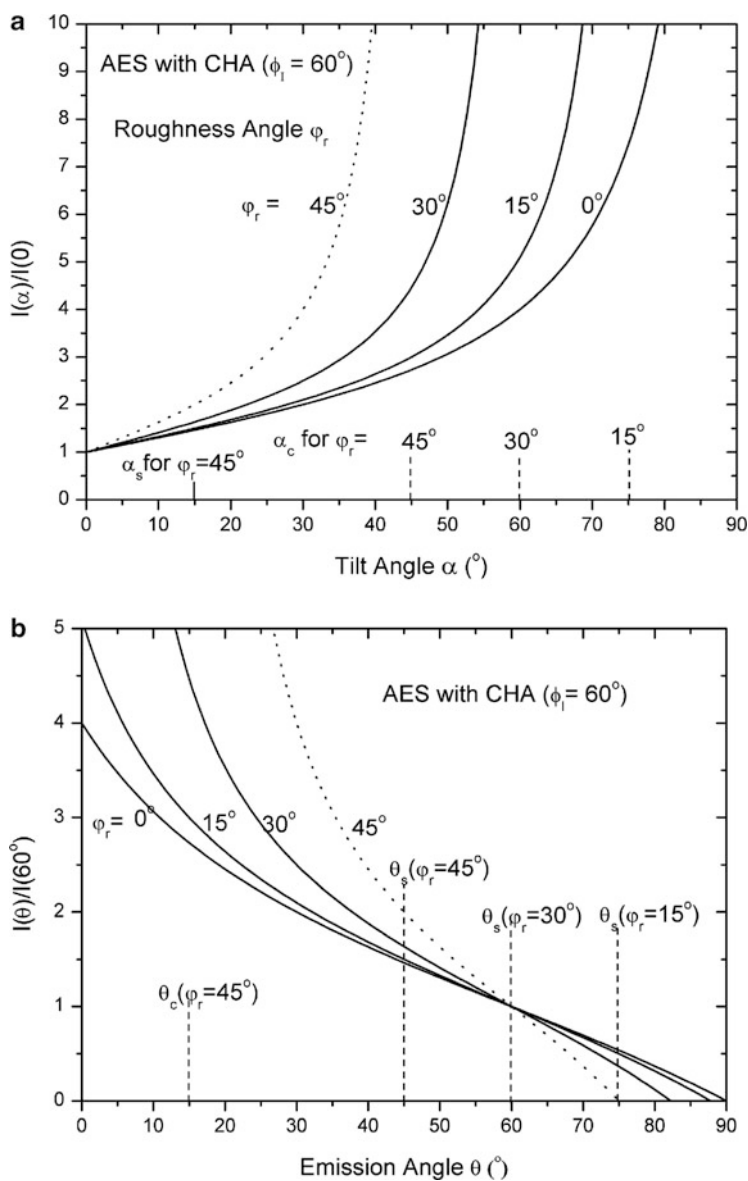


Fig. 5.37 (a) Dependence of the normalized AES signal intensity $I(\alpha)/I(0)$ on the sample tilt angle α (=incidence angle) after (5.23) with $\phi_i = 60^\circ$ for different roughness angles ϕ_r . Critical angles $\alpha_c = 90 - \phi_r$ denote the maximum α before incidence shadowing, and angle $\alpha_s = \phi_r - 30$ for $\phi_r = 45^\circ$ denotes the minimum α below which there is incidence shadowing. (b) Dependence of the normalized AES signal intensity $I(\theta)/I(\theta = 60^\circ)$ on the emission angle $\theta = 60 - \alpha$. The critical angle $\theta_c = 60 - (90 - \phi_r)$ for $\phi_r = 45^\circ$ denotes the minimum below which there is incidence shadowing, and $\theta_s = 60 + (30 - \phi_r)$ marks the maximum θ above which there is emission shadowing

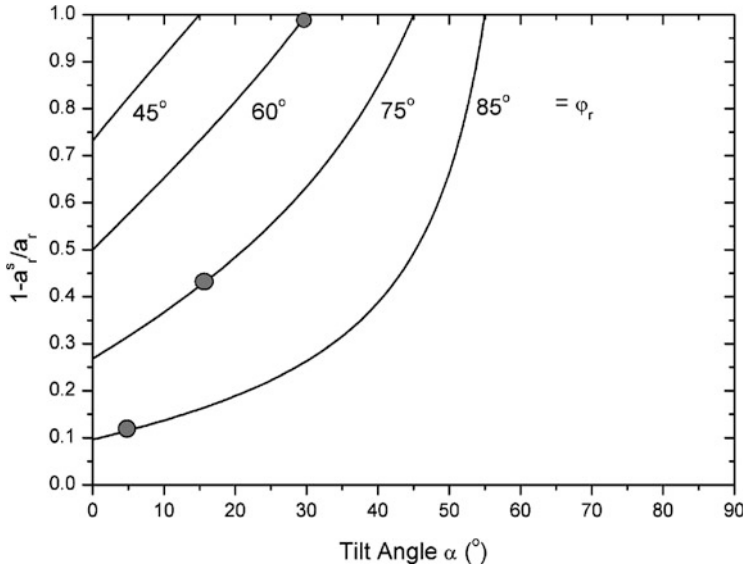


Fig. 5.38 Nonshadowed part of the *left* side as a function of sample tilt angle after (5.25), for the four roughness angles indicated in the figure. *Full circle* symbols mark the tilt angles when shadowing of the *right* side by the incident electron beam starts

corresponds to the incidence angle, where there is no roughness dependence because of the symmetric roughness angle effect (see Sect. 5.1.3). In contrast to XPS without shadowing (see Fig. 5.10), the shape of the angular dependence curve changes with roughness in AES.

Ad (b), shadowing of electron emission only: There is no shadowing for the incident electron beam in the range $0 < \alpha < 90 - \varphi_r$. It is evident from Fig. 5.8 that complete shadowing of the emitted electrons from the left side of the pyramid occurs for a roughness angle $\varphi_r > 90 - \phi_l$, when partial shadowing of the right side is decreasing with increasing α until $\alpha = \varphi_r - (90 - \phi_l)$. The areal fraction of the right side that contributes to electron emission, $1 - a_r^s/a_r$, is given by the ratio of the shadowed area, a_r^s , to the total area, a_r , from the geometry of Fig. 5.8:

$$1 - \frac{a_r^s}{a_r} = 1 + \frac{\cos(\phi_l - \alpha + \varphi_r)}{\cos(\phi_l - \alpha - \varphi_r)}. \quad (5.25)$$

Expression (5.25) is shown in Fig. 5.38 for $\phi_l = 60^\circ$ and several values of $\varphi_r > 30^\circ$. The full circles mark the values for $\alpha = 90 - \varphi_r$ when electron incidence shadowing starts and a corresponding decrease of electron emission. It is obvious that for high values of φ_r , i.e., for highly corrugated surfaces, for example, porous surfaces, the measured intensity becomes extremely low (e.g., $\varphi_r = 85^\circ$). For $0 < \varphi_r < 30^\circ$, no emission shadowing but only incidence shadowing exists above $\alpha > 90 - \varphi_r$. For

$30^\circ < \varphi_r < 60^\circ$, there is an interval of α values, $\varphi_r < \alpha < 90 - \varphi_r$, for which there is neither emission nor incidence shadowing.

Ad (c), shadowing of emission and excitation: With (5.25) and (5.23), the right side intensity with emission shadowing is given by

$$\frac{I(\alpha)}{I(0)} = \left[1 + \frac{\cos(\phi_I - \alpha + \varphi_r)}{\cos(\phi_I - \alpha - \varphi_r)} \right] \frac{\cos(\phi_I - \alpha + \varphi_r)}{\cos(\phi_I - \varphi_r)}. \quad (5.26)$$

Regarding the incidence shadowing for the left side of the pyramid roughness structure in Fig. 5.8, it is recognized that the incidence is the reverse of emission. Therefore, Figs. 5.9 and (5.7b) apply when taking α for θ . The result for the normalized intensity of the left side is

$$\frac{I(\alpha)}{I(0)} = \left[1 + \frac{\cos(\alpha + \varphi_r)}{\cos(\alpha - \varphi_r)} \right] \frac{\cos(\phi_I - \alpha + \varphi_r)}{\cos(\alpha + \varphi_r)}. \quad (5.27)$$

An illustration of the behavior of both sides after (5.26) and (5.27) is shown in Fig. 5.39 for $\varphi_r = 45^\circ$ as compared to no shadowing ($\alpha_r^s = 0$) and to a flat surface ($\varphi_r = 0^\circ$). For the right side (5.26), emission shadowing occurs until $\alpha = 15^\circ$ (full drawn line), when, for the left side (5.27), emission starts without shadowing

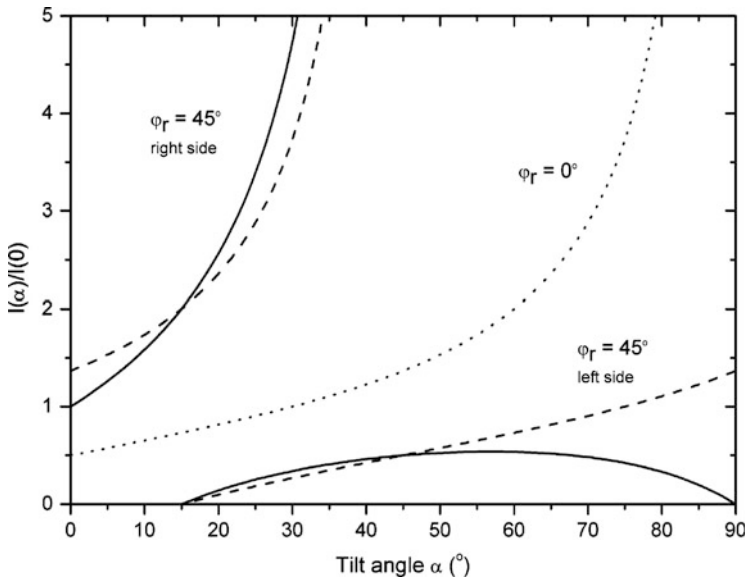


Fig. 5.39 Tilt angle dependence of the normalized AES intensity for both sides of the roughness model pyramid (Fig. 5.8) for roughness angle $\varphi_r = 45^\circ$, after (5.26) and (5.27). Full drawn lines are valid for shadowing at the right side for $0^\circ < \alpha < 15^\circ$ and at the left side for $45^\circ < \alpha < 90^\circ$. Dashed lines are valid for nonshadowing, i.e., for the right side above $\alpha = 15^\circ$ and for the left side for $15^\circ < \alpha < 45^\circ$. The dotted line shows the intensity for a flat surface ($\varphi_r = 0^\circ$) as in Fig. 5.23

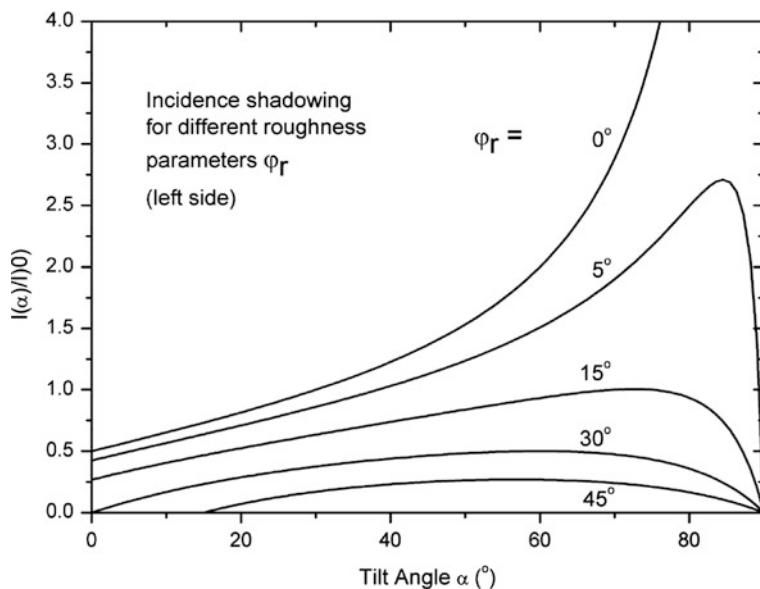


Fig. 5.40 Tilt angle (α) dependence of the normalized intensity, $I(\alpha)/I(0)$, after (5.27), showing the influence of incident electron-beam shadowing for different roughness parameters φ_r

(dashed line). Incidence shadowing for the right side starts at $\alpha = 45^\circ$ (full drawn line) and decreases the nonshadowed intensity (dashed line) until zero at $\alpha = 90^\circ$. Between $\alpha = 15^\circ$ and $\alpha = 45^\circ$, there is no shadowing. A problem for summation arises from the singular point at $\alpha = 45^\circ$ (intensity $\rightarrow \infty$ for 90° incidence angle).

Let us have a look at the incidence angle shadowing for different roughness angle φ_r after (5.27) depicted in Fig. 5.40. With increasing roughness, the intensity moves quickly down to considerably lower values. For low roughness angles, for example, $\varphi_r = 5^\circ$, the dependence of the intensity on α changes toward a shape suggested by the experimental results in Fig. 5.23, indicating residual roughness as a cause of the latter.

Restricting roughness considerations to moderate roughness angles, i.e., to the case of nonshadowing emission for $\varphi_r \leq 30^\circ$ (5.23), yields Fig. 5.41 which clearly reveals independence on roughness for $\alpha = 0^\circ$ and a moderate intensity increase of 3% for $\alpha = 15^\circ$ and of 13% for $\alpha = 30^\circ$ between $\varphi_r = 0^\circ$ and 30° .

Homogeneous Sample With Overlayer

Flat Surface: In AES, we can apply the same scheme as for AR-XPS by tilting the sample in front of the analyzer. However, the angular dependence is more complicated because of the excitation depth distribution function changes (1) with the electron-beam incidence angle α and (2) with the backscattering influence of the substrate on the overlayer. This gives rise to complications particularly for high excitation and emission angles and for relatively thick layers. Assuming very thin

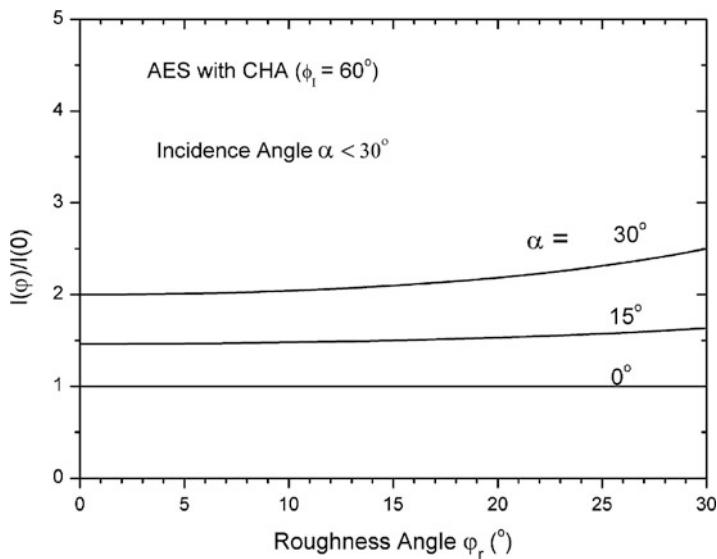


Fig. 5.41 Roughness angle (φ_r) dependence of the normalized intensity for the nonshadowed region ($\varphi_r \leq 30^\circ$) and electron incidence angles of 0° , 15° , and 30° , after (5.23)

layers ($d/\lambda < 2$) and $\lambda_{ov} = \lambda_{sub} = \lambda$, ignoring backscattering (correct for similar backscattering factors of substrate and overlayer and for incidence angles $< 45^\circ$ (see, e.g., (4.144) in Sect. 4.4.3 and Fig. 5.26), according to (5.10a) the AES signal intensity of an overlayer of thickness d as a function of the electron incidence angle, $I_{ov}(\alpha)$, is given by

$$I_{ov}(\alpha) = \frac{\cos(\Phi_I - \alpha)}{\cos \alpha} \left\{ 1 - \exp \left[-\frac{d}{\lambda \cos(\Phi_I - \alpha)} \right] \right\}, \quad (5.28a)$$

and for the substrate intensity, I_{sub} ,

$$I_{sub}(\alpha) = \frac{\cos(\Phi_I - \alpha)}{\cos \alpha} \exp \left[-\frac{d}{\lambda \cos(\Phi_I - \alpha)} \right], \quad (5.28b)$$

The ratio of (5.28a) and (5.28b) yields (normalized to $I(\alpha = 0)$)

$$\frac{I_{ov}(\alpha)}{I_{sub}(\alpha)} = \exp \left[\frac{d}{\lambda \cos(\Phi_I - \alpha)} \right] - 1. \quad (5.29)$$

Equation 5.29 is identical to (5.11b) for roughness zero ($\varphi_r = 0$) and when $\Phi_I - \alpha$ is replaced by the incidence angle θ . The result is presented in Fig. 5.42a. (Note that $I_{ov}^0/I_{sub}^0 = 1$ is assumed). Because α would be -30° for $\theta = 90^\circ$, $\theta > 60^\circ$ is not accessible for most instruments (e.g., JEOL JAMP 7830F).

The possible variation range for AR-AES by changing the incidence (=sample tilt) angle α after (5.29) is shown in Fig. 5.42b.

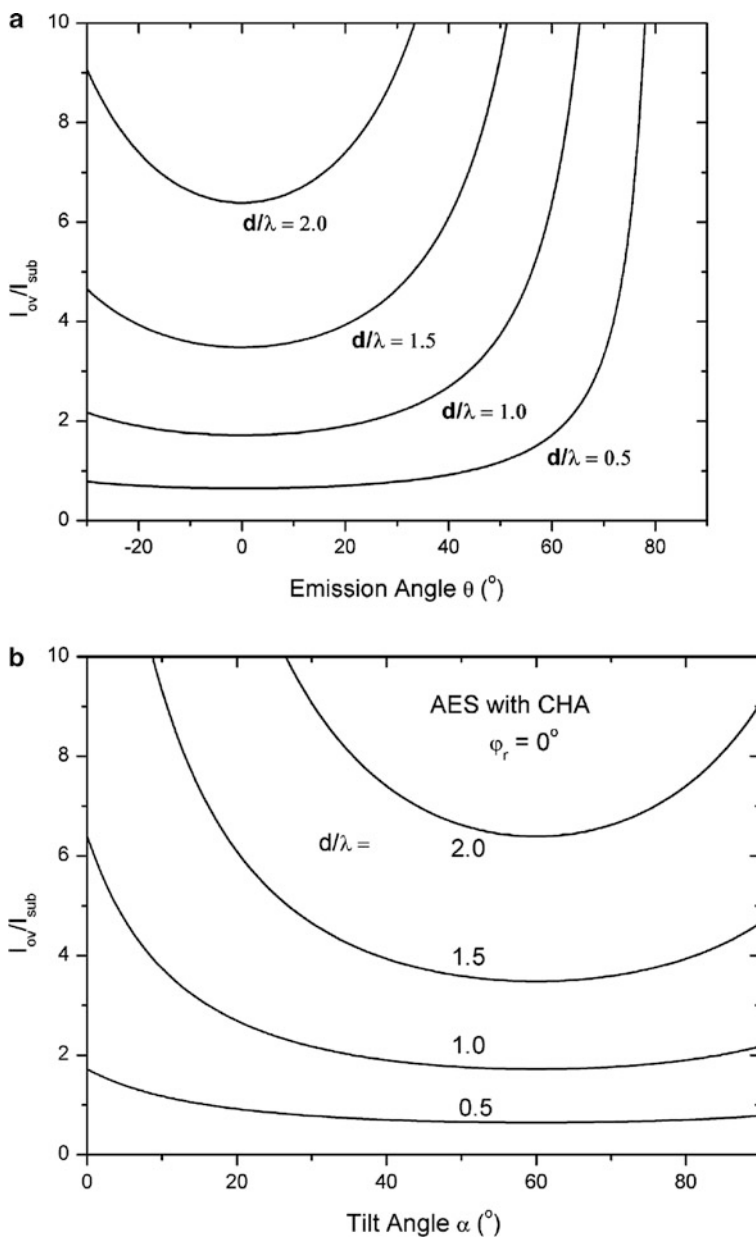


Fig. 5.42 Normalized AES intensity ratio overlayer/substrate, I_{ov}/I_{sub} , for a flat surface as a function of (a) the emission angle θ , and (b) the tilt angle α , according to (5.29), (for different values of d/λ , with $\theta = \phi_1 - \alpha$, and CHA angle $\phi_1 = 60^\circ$)

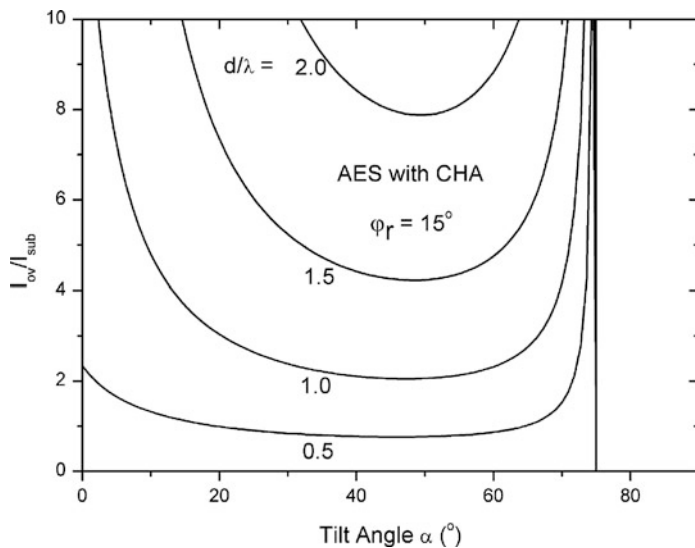


Fig. 5.43 Normalized AES intensity ratio overlayer/substrate, I_{ov}/I_{sub} , for a rough surface with roughness parameter $\varphi_r = 15^\circ$, and different values of d/λ , as a function of the tilt angle α , according to (5.30), with CHA angle $\phi_l = 60^\circ$. The limit for shadowing of the incident beam is at $\alpha = 90^\circ - \varphi_r = 75^\circ$

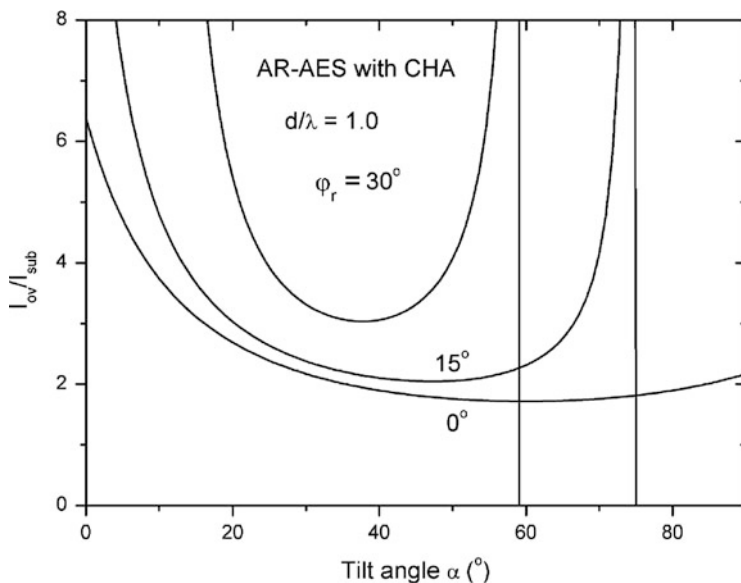


Fig. 5.44 Normalized AES intensity ratio overlayer/substrate, I_{ov}/I_{sub} , as a function of the tilt angle α , according to (5.30), for three roughness parameters $\varphi_r = 0^\circ$, 15° , and 30° , and $d/\lambda = 1$, with CHA angle $\phi_l = 60^\circ$. The limit for shadowing of the incident beam is at $\alpha = 90^\circ - \varphi_r$

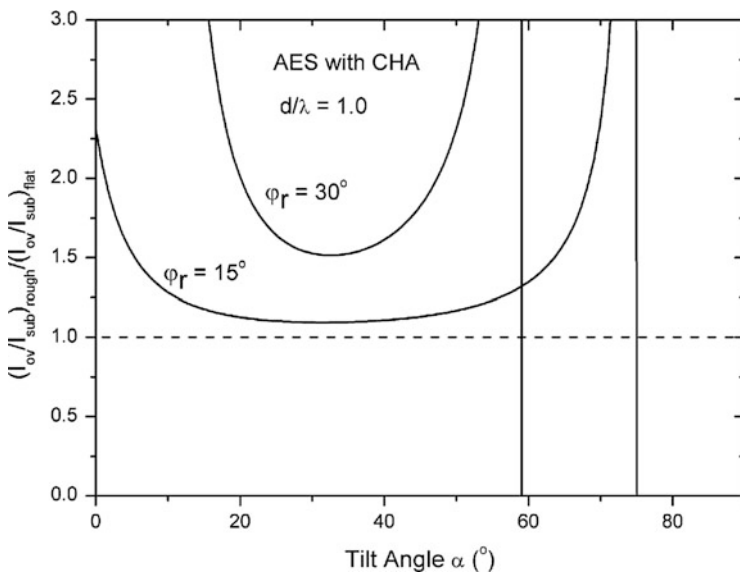


Fig. 5.45 Comparison of the intensity ratio $(I_{\text{ov}}/I_{\text{sub}})_{\text{rough}}/(I_{\text{ov}}/I_{\text{sub}})_{\text{flat}}$ for rough and flat surfaces as a function of the tilt angle α

Rough Surface: From (5.23), (5.24), (5.28) and (5.29) we get the overlayer/substrate intensity ratio as

$$\frac{I_{\text{ov}}(\alpha)}{I_{\text{sub}}(0)} = \frac{\cos \alpha}{\cos(\phi_{\text{I}} - \alpha)} \left\{ \frac{0.5 \cos(\phi_{\text{I}} - \alpha - \varphi_{\text{r}})}{\cos(\alpha + \varphi_{\text{r}})} \left\{ \exp \left[\frac{d}{\lambda \cos(\phi_{\text{I}} - \alpha - \varphi_{\text{r}})} \right] - 1 \right\} + \frac{0.5 \cos(\phi_{\text{I}} - \alpha + \varphi_{\text{r}})}{\cos(\alpha - \varphi_{\text{r}})} \left\{ \exp \left[\frac{d}{\lambda \cos(\phi_{\text{I}} - \alpha + \varphi_{\text{r}})} \right] - 1 \right\} \right\}. \quad (5.30)$$

For a roughness angle of $\varphi_{\text{r}} = 15^\circ$, (5.30) is shown in Fig. 5.43 for several relative layer thicknesses d/λ . The dependence of the intensity ratio $I_{\text{ov}}/I_{\text{sub}}$ on roughness for $d/\lambda = 1$ is indicated in Fig. 5.44.

Comparison of the intensity ratio for rough and flat surfaces, i.e., taking the ratio of the (5.30)–(5.29), provides an estimation of the deviation involved when ignoring roughness. This is shown in Fig. 5.45. As expected, the deviation increases with roughness. For moderate roughness ($\varphi_{\text{r}} < 15^\circ$), the deviation is minimal in the range $20^\circ < \alpha < 40^\circ$.

5.2.3.2 AES Using CMA

Homogeneous Sample Without Overlayer

For a flat surface, the tilt angle dependence of the AES intensity using a CMA is pointed out in Sect. 5.2.2. Since it is different from that of the CHA (compare, e.g., Figs. 5.23 and 5.34, the influence of roughness is expected to be different too.

For electron incidence normal to the macroscopic sample surface, $\alpha = 0^\circ$, the two-dimensional geometry of the CHA can be compared with the CMA with coaxial electron gun (see Sect. 5.2.2). Here, the instrumental emission angle is the CMA acceptance cone angle of $\phi_I = 42.3^\circ$, and the case of nonshadowing is obtained as above for a roughness angle of $\varphi_r \leq 90^\circ - 42.3^\circ = 47.7^\circ$. A simple three-dimensional picture of roughness is discussed by De Bernardes et al. [5.41]. These authors propose a triangular cone-shaped surface similar to Fig. 5.8 but made three dimensional by rotation around an axis in the picture plane through the top of the center pyramid. Because the acceptance cone of the CMA has a similar radial geometry, the two-dimensional case is valid for this special type of three-dimensional roughness. For normal electron incidence ($\alpha = 0$), it is obvious that because of the conical symmetry, there is practically no shadowing for a three-dimensional roughness below $\varphi_r \leq 47.7^\circ$. Above that angle, a shadowing effect similar to (5.26) and (5.27) occurs. As seen in Fig. 5.33, the emission intensity follows a cosine law with $\cos \theta_{av} = \cos(42.3^\circ) \times \cos \alpha$ for $\alpha \leq 47.7^\circ$. Assuming radial symmetry, we get for the left and right side of the roughness pyramid the same expression for emission but different expressions for the incidence. In analogy to (5.23), we may express the normalized intensity for AES with CMA and $\alpha, \varphi_r \leq 47.7^\circ$ as

$$\frac{I(\alpha)}{I(0)} = \frac{1}{2} \left[\cos(\arccos(\cos \theta_{av}) + \varphi_r) \left\{ \frac{1}{\cos(\alpha + \varphi_r)} + \frac{1}{\cos(\alpha - \varphi_r)} \right\} \right]. \quad (5.31)$$

With $\cos \theta_{av} = \cos(42.3^\circ) \times \cos \alpha$, (5.31) is plotted in Fig. 5.46 for roughness parameter values $\varphi_r = 0^\circ, 5^\circ, 15^\circ$, and 30° . It is obvious that for $\alpha = 0^\circ$, the roughness effect is zero (up to $\varphi_r = 47.7^\circ$), because of the compensation of the two cosine functions for emission and excitation in this range. However, for a tilt angle of $\alpha > 0^\circ$ this behavior changes and the effect of roughness increases with α . The practically linear intensity decrease with increasing roughness as depicted in Fig. 5.46 (from (5.31)) corresponds to experimental results given in Refs. [5.28, 5.41].

Because sample roughness or topographical features always mean different incidence angles and surroundings at different locations, surface topography affects AES analysis. The CMA analyzer averages over a range of directions, thus smoothing the topographical effect. However, the sidewall of a trough-shaped feature can only be studied when a small angular region, for example, a 10° -wide slit, is used for Auger electron detection as demonstrated by Hösler [5.42]. Excitation of neighboring sample features by backscattered electrons cause complications of qualitative and quantitative analysis, as elucidated by the thorough work of El Gomati et al. [5.43]. As demonstrated by Olson et al. [5.44], the AES line scan with primary voltage $E_p = 20$ keV across a TiN deposit on the protrusion of a steel sample in Fig. 5.47 is generally interpreted as a considerable amount of iron in TiN. For the same line scan with $E_p = 3$ keV, the distortional effect of backscattered electrons is drastically reduced (see Sect. 4.4.1 and Figs. 4.51, 4.53), and Fe in TiN is decreased to the noise level.

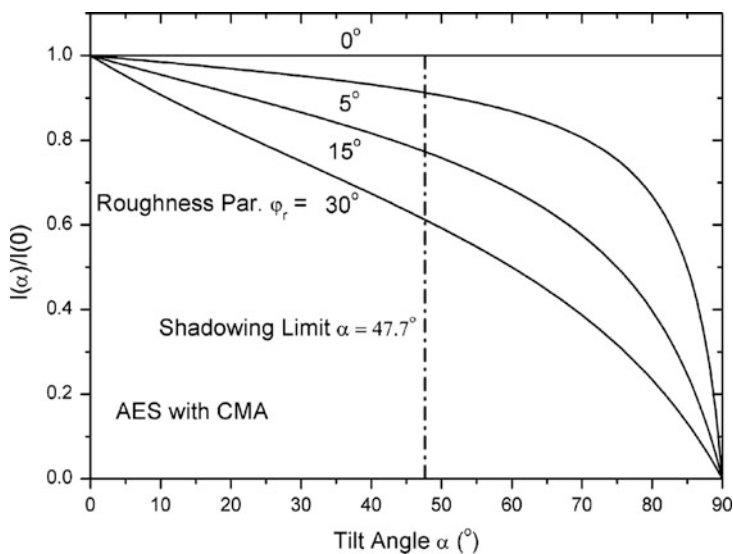


Fig. 5.46 Normalized intensity $I(\alpha)/I(0)$ for the case of nonshadowing after (5.28) as a function of the CMA tilt angle α for different roughness parameters $\varphi_r = 0^\circ, 5^\circ, 15^\circ$, and 30° . The lines are strictly valid only up to the limit of $\alpha = 47.7^\circ$ (see Fig. 5.9)

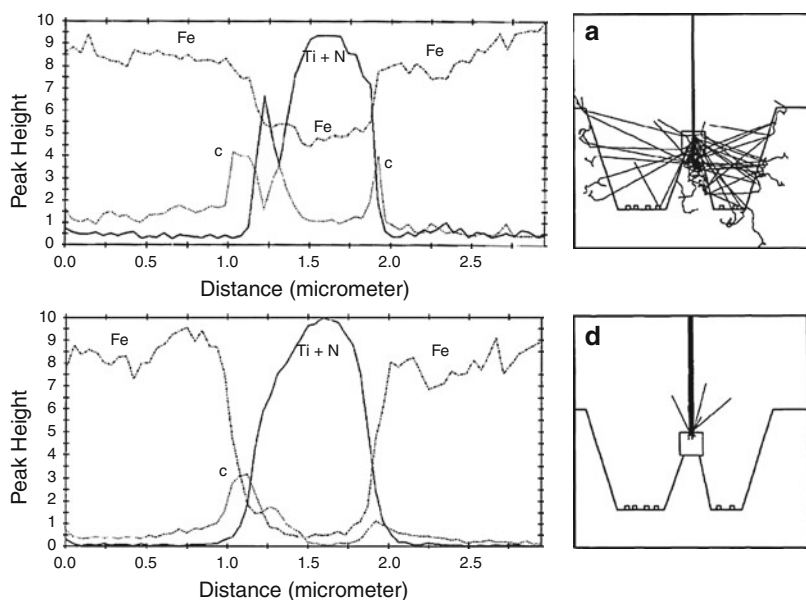


Fig. 5.47 Example of the influence of the primary energy, showing effect of backscattering (above, $E_p = 20$ keV, below $E_p = 3$ keV) in SAM analysis of a TiN deposit on a protrusion of a steel sample (left: line scan result, right: calculated electron trajectories) (Reproduced from R. R. Olson et al. [5.44], with permission of Elsevier B.V.)

Homogeneous Sample with Overlayer

Restricting the following considerations to the simple case of $\alpha \leq 47.7^\circ$ (in practice $\alpha \leq 50^\circ$), we adapt (5.28) and get in analogy to (5.10a) for the intensity of an overlayer with thickness d :

$$\frac{I_{ov}(\alpha)}{I_{ov}(0)} = \frac{1}{2} \left\{ \cos [\arccos(\cos 42.3 \cos \alpha) + \varphi_r] \left[\frac{1}{\cos(\alpha + \varphi_r)} + \frac{1}{\cos(\alpha - \varphi_r)} \right] \right\} \\ \times \left\{ 1 - \exp \left[-\frac{d}{\lambda_{ov,E(ov)} \cos [\arccos(\cos 42.3 \cos \alpha) + \varphi_r]} \right] \right\} \quad (5.32a)$$

In analogy to (5.10b), the intensity of the substrate is given by

$$\frac{I_{sub}(\alpha)}{I_{sub}(0)} = \frac{1}{2} \left\{ \cos [\arccos(\cos 42.3 \cos \alpha) + \varphi_r] \left[\frac{1}{\cos(\alpha + \varphi_r)} + \frac{1}{\cos(\alpha - \varphi_r)} \right] \right\} \\ \times \exp \left[-\frac{d}{\lambda_{ov,E(sub)} \cos [\arccos(\cos 42.3 \cos \alpha) + \varphi_r]} \right]. \quad (5.32b)$$

When taking the ratio of both intensities, the angle-dependent terms before the exponential terms cancel, and assuming $\lambda_{ov,E(ov)} = \lambda_{ov,E(sub)} = \lambda$ the expression simplifies to

$$\frac{I_{ov}(\alpha) I_{sub}(0)}{I_{ov}(0) I_{sub}(\alpha)} = \exp \left\{ \frac{d}{\lambda \cos [\arccos(\cos 42.3 \cos \alpha) + \varphi_r]} \right\} - 1. \quad (5.33)$$

Equations 5.32a and 5.32b are depicted in Fig. 5.48 for a flat surface ($\varphi_r = 0$) and for $d/\lambda = 1$ and 0.5. The dotted line with constant intensity is for substrate without overlayer, valid up to $\alpha = 47.7^\circ$ (nonshadowing). This limit applies for all plotted lines. For increasing layer thickness and higher tilt angle, the substrate intensity decreases strongly, while the layer intensity approaches the dotted line.

The layer/substrate intensity ratio is given by (5.33) and shown in Fig. 5.49 for a roughness angle of $\varphi_r = 15^\circ$ and for several values of d/λ . This ratio is frequently used in angle-resolved layer thickness determination because the instrumental property changes (e.g., transmission) cancel. For comparison, the lines for flat sample surface ($\varphi_r = 0^\circ$) for $d/\lambda = 0.5$ (dotted) and 1.0 (dashed) are also shown. According to Fig. 5.49, ratios larger than 10 (and below 0.1) will suffer from an intolerably high error. This fact favors restriction to tilt angles below 47.7° .

Let us have a look at the expected result for determination of d/λ if we ignore sample roughness. Equation 5.33 can be easily solved to give $(d/\lambda)_{app}$ for $\varphi_r = 0$ and for different roughness angles. For correct $d/\lambda = 1$, the result is plotted in Fig. 5.49 for different surface roughness.

Equations 5.32a and 5.32b are depicted in Fig. 5.48 for flat surfaces ($\varphi_r = 0$) and for $d/\lambda = 1$ and 0.5. The dotted line for constant intensity is for substrate without overlayer, valid up to $\alpha = 47.7^\circ$ (nonshadowing). This limit applies for all plotted lines. For increasing layer thickness and tilt angle, the substrate intensity decreases strongly, while the layer intensity approaches the dotted line.

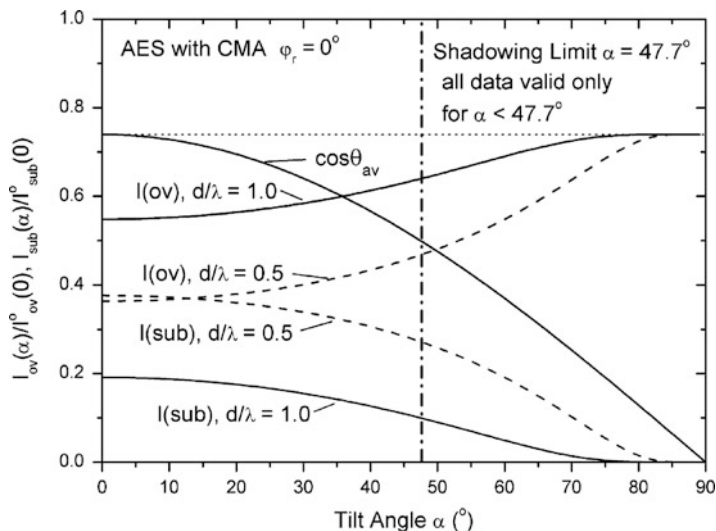


Fig. 5.48 Normalized intensities of overlayer ($I(ov) = I_{ov}(\alpha)/I_{ov}^0(0)$) and substrate ($I(sub) = I_{sub}(\alpha)/I_{sub}^0(0)$) for a flat surface ($\varphi_r = 0$) after (5.32a) and (5.32b), for $d/\lambda = 0.5$ (dashed lines) and 1.0 (solid lines). The horizontal dotted line is the limit for $d/\lambda \gg 1$ (bulk, see Fig. 5.32)

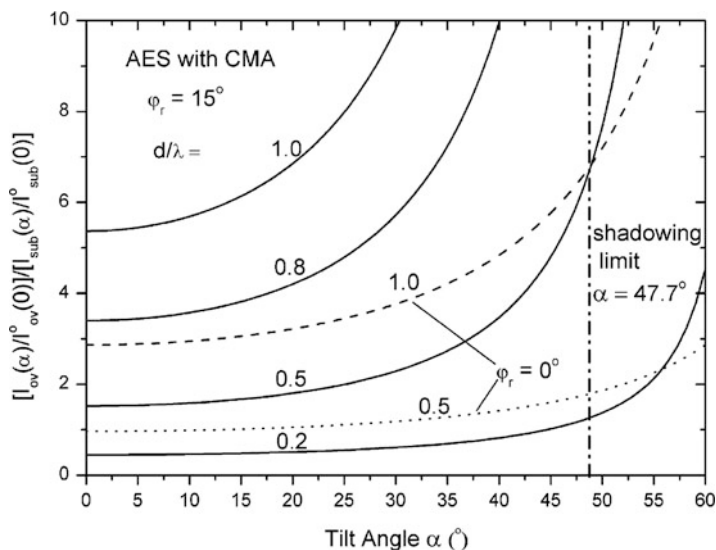


Fig. 5.49 Normalized intensity ratio $[I(\alpha)_{ov}/I(0)_{ov}]/[I(\alpha)_{sub}/I(0)_{sub}]$ of overlayer and substrate for the case of nonshadowing ($\alpha \leq 47.7^\circ$) after (5.33) as a function of the CMA tilt angle α , for roughness parameters $\varphi_r = 15^\circ$, different relative thickness values d/λ . For comparison, flat surface results are shown for $d/\lambda = 0.5$ (dotted line) and 1.0 (dashed line)

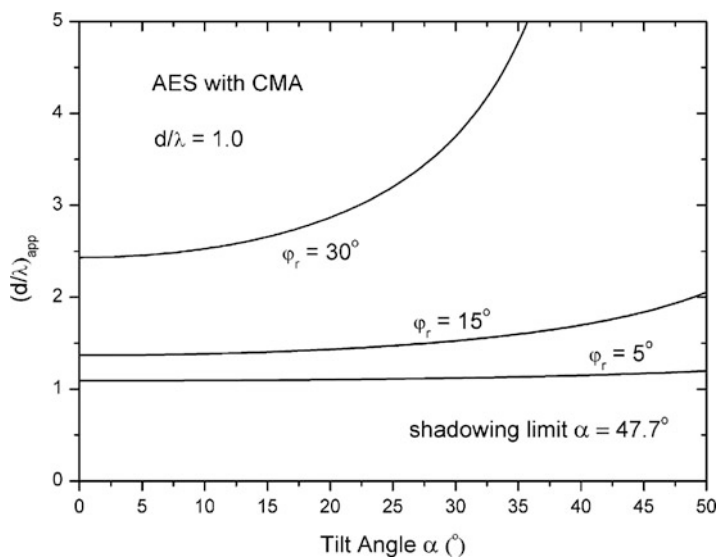


Fig. 5.50 Deviation of the thickness of an overlayer determined using the flat surface expression (5.33) for $\varphi_r = 0$, giving $(d/\lambda)_{\text{app}}$ instead of the assumed true $d/\lambda = 1$, for roughness angles $\varphi_r = 5^\circ$, 15° , and 30° . Note the restriction to $\alpha < 47.7^\circ$ for the nonshadowing case. The deviation increases monotonically with roughness and tilt angle (markedly different from the emission angle dependence in XPS (see Fig. 5.16))

The layer/substrate intensity ratio, given by (5.33), is usually used in angle-resolved layer thickness determination because of canceling of instrumental property changes (e.g., transmission) and is shown in Fig. 5.49 for a roughness angle of $\varphi_r = 15^\circ$. For comparison, the lines for flat sample surface ($\varphi_r = 0^\circ$) for $d/\lambda = 0.5$ (dotted) and 1.0 (dashed) are also shown. According to Fig. 5.47, ratios larger than 10 (and below 0.1) will suffer from an intolerably high error. This fact favors tilt angles below 47.7° .

Let us have a look at the expected result for determination of d/λ if we ignore sample roughness. Equation 5.33 can be easily solved to give $(d/\lambda)_{\text{app}}$ for $\varphi_r = 0$ and for different roughness angles. For correct $d/\lambda = 1$, the result is plotted in Fig. 5.50 for different surface roughness.

5.3 Summary and Conclusion

The measured XPS or AES intensity depends on the emission angle through variation of the electron escape depth. Different emission angles are chosen by sample tilt, by mechanical, or by electronic angle selection. The strong effect of the electron-beam incidence angle in AES, together with the angular dependence of electron backscattering, causes additional intensity changes. The result is an

intensity increase until a maximum at high incidence angles near 80° . Optimum peak-to-background ratios are obtained for the special techniques of total reflection XPS (TR-XPS) and of grazing incidence AES (GI-AES). Changing the escape depth by sample tilt results in the technique of determination of thickness and composition of thin layers (thickness smaller than five times the attenuation length) which is simplest and popular in XPS. Whereas the latter is almost exclusively performed with a concentric hemispherical analyzer (CHA), the cylindrical mirror analyzer (CMA) is additionally used in AES. Both analyzers give different tilt angle dependencies.

A practical means to minimize backscattering influence and topographical effects is using intensities normalized to background intensity $(P - B)/B$ (see Fig. 7.28). A simple way of describing surface roughness are pyramidal structures with a roughness angle equal to the mean slope angle from the average surface. With this model, the derived angular relations can be used to predict semiquantitative relations between intensity and roughness and its influence in layer thickness determination.

References

- 5.1. C.S. Fadley, J. Electron Spectrosc. Relat. Phenom. **5**, 725 (1974)
- 5.2. J. Zemek, Acta Phys. Slov. **50**, 577 (2000)
- 5.3. P.W. Palmberg, J. Vac. Sci. Technol. **12**, 379 (1975)
- 5.4. J.C. Rivière, *Surface Analytical Techniques* (Clarendon Press, Oxford, 1990)
- 5.5. J.M. Sanz, Ph.D. thesis, University of Stuttgart, Stuttgart, 1983
- 5.6. S. Hofmann, *Analisis* **9**, 181 (1981)
- 5.7. S. Hofmann, J.M. Sanz, Surf. Interface Anal. **6**, 75 (1984)
- 5.8. R. Frech, Ph.D. thesis, University of Stuttgart, Stuttgart, 1985
- 5.9. J. Steffen, S. Hofmann, Fres. Z. Anal. Chem. **329**, 250 (1987)
- 5.10. S. Hofmann, J.M. Sanz, J. Trace Microprobe Technol. **1**, 213 (1982–1983)
- 5.11. S. Hofmann, J.Y. Wang, Surf. Interface Anal. **39**, 45 (2007)
- 5.12. S. Hofmann, Depth Profiling, in *Practical Surface Analysis Vol. I, AES and XPS*, 2nd edn., ed. by D. Briggs, M.P. Seah (Wiley, Chichester, 1990), pp. 148–199
- 5.13. C.M. Theodorescu, D. Gravel, E. Ruehl, T.J. McAvoy, J. Choi, D. Pugmire, P. Pribil, J. Loos, P.A. Dowben, Rev. Sci. Instrum. **69**, 3805 (1998)
- 5.14. E. Kobayashi, J. Seo, A. Nambu, K. Mase, Surf. Sci. **601**, 3589 (2007)
- 5.15. J. Kawai, M. Takami, M. Fujinami, Y. Hasiguchi, S. Ayakawa, Y. Goshi, Spectrochim. Acta B **47**, 983 (1992)
- 5.16. T. Jach, E. Landree, Surf. Interface Anal. **31**, 768 (2001)
- 5.17. T. Jach, M.J. Chester, S.M. Thurgate, Rev. Sci. Instrum. **65**, 339 (1994)
- 5.18. Y. Iijima, K. Miyoshi, S. Saito, Surf. Interface Anal. **27**, 35 (1999)
- 5.19. M. Nagoshi, T. Kawano, N. Makiishi, Y. Baba, K. Kobayashi, Surf. Interface Anal. **40**, 738 (2008)
- 5.20. P.H. Holloway, J. Electron Spectrosc. Relat. Phenom. **7**, 215 (1975)
- 5.21. O.K.T. Wu, E.M. Butler, J. Vac. Sci. Technol. **20**, 453 (1982)
- 5.22. S. Hofmann, A. Zalar, Surf. Interface Anal. **10**, 7 (1987)
- 5.23. A. Zalar, S. Hofmann, Nucl. Instrum. Methods Phys. Res. B **18**, 655 (1987)
- 5.24. P.T. Dawson, S.A. Petrone, Surf. Interface Anal. **17**, 273 (1991)
- 5.25. W.S.M. Werner, Surf. Interface Anal. **23**, 696 (1995)
- 5.26. P.L.J. Gunter, J.W. Niemantsverdriet, Appl. Surf. Sci. **89**, 69 (1995)

- 5.27. P.L.J. Gunter, O.L.J. Gijzeman, J.W. Niemantsverdriet, *Appl. Surf. Sci.* **115**, 342 (1997)
- 5.28. T. Wöhner, G. Ecke, H. Rößler, S. Hofmann, *Surf. Interface Anal.* **26**, 1 (1998)
- 5.29. K. Vutova, G. Mladenov, T. Tanaka, K. Kawabata, *Surf. Interface Anal.* **30**, 552 (2000)
- 5.30. K. Vutova, G. Mladenov, T. Tanaka, K. Kawabata, *Vacuum* **62** 297 (2001)
- 5.31. K. Olejnik, J. Zemek, W.S.M. Werner, *Surf. Sci.* **595**, 212 (2005)
- 5.32. P. Kappen, K. Reihs, C. Seidel, M. Voetz, H. Fuchs, *Surf. Sci.* **465**, 40 (2000)
- 5.33. J. Zemek, *Anal. Sci.* **26**, 177 (2010).
- 5.34. K. Tsutsumi, Y. Nagasawa, T. Tazawa, *JEOL News E* **42**, 45 (2007)
- 5.35. A. Jablonski, C.J. Powell, *Surf. Sci.* **574**, 219 (2005)
- 5.36. A. Jablonski, C.J. Powell, S. Tanuma, *Surf. Interface Anal.* **37**, 861 (2005)
- 5.37. Z.J. Ding, W.S. Tan, Y.G. Li, *J. Appl. Phys.* **99**, 084903 (2006)
- 5.38. G.C. Smith, M.P. Seah *Surf. Interface Anal.* **14**, 823 (1989)
- 5.39. J. Cazaux, *Microsc. Microanal. Microstruct.* **3**, 271 (1992)
- 5.40. T. Bungo, Y. Mizuhara, T. Nagatomi, Y. Takai, *Jpn. J. Appl. Phys.* **42**, 7580 (2003)
- 5.41. L.S. De Bernardez, J. Ferron, E.C. Goldberg, R.H. Buitrago, *Surf. Sci.* **139**, 541 (1984)
- 5.42. W. Hösler, *Surf. Interface Anal.* **17**, 543 (1991)
- 5.43. M.M. El Gomati, M. Prutton, B. Lamb, C.G. Tuppen, *Surf. Interface Anal.* **11**, 251 (1988)
- 5.44. R.R. Olson, L.A. La Vanier, D.H. Narum, *Appl. Surf. Sci.* **70/71**, 266 (1993)
- 5.45. M. Mohai, I. Bertóti, *Surf. Interface Anal.* **36**, 805 (2004)

Chapter 6

Optimizing Certainty and the Detection Limit: Signal-to-Noise Ratio

6.1 Introduction and Definitions for Pulse-Counting Systems

Sensitivity, detection limit, and uncertainty are essential characteristic figures of any analytical method. They are ultimately limited by the signal-to-noise (S/N) ratio. For a given analytical task, the art of the analyst is to find the appropriate, optimum signal-to-noise (S/N) ratio within instrumental limits. Because of its importance and dependence on many parameters in AES and XPS, the S/N ratio is considered in detail in the following.

The accuracy of any measurement is limited by the total error, which can be separated into systematic errors and random errors. For example, in electron spectroscopies, systematic errors comprise erroneous energy scale or nonlinear intensity scale (such as multiplier dead time influence at higher count rates), wrong alignment of sample, etc. Systematic errors are deviations in one direction. Systematic errors can be principally avoided or at least diminished to negligible levels by careful setting up of the instrument and by using appropriate calibration and test procedures (see Sect. 8.4). In contrast, random errors are caused by statistical variations of a measured value which are summarized as “noise” and only detectable by a large number of repeated measurements. Since the number of events puts an ultimate limit to statistical relevance, the number of counts is a measure of the minimum random error in any pulse-counting system. The statistical error or uncertainty of each measurement in the latter case is usually defined by the standard deviation, σ , of the respective Gaussian distribution of the measured values. According to standard measurement statistics [6.1], quadratic values of independent variables such as σ , i.e., the variances, σ^2 , add up, as given by

$$\sigma_f^2 = \sum_{j=1}^n \left(\frac{\partial f}{\partial x_j} \right)^2 \sigma^2(x_j), \quad (6.1)$$

where σ_f is the standard deviation of the function $f(x_1, x_2, \dots, x_n)$ that consists of the independent variables x_n , and $\sigma(x_j)$ is the standard deviation of the variable x_j .

For the difference (or sum) of the uncertainty of two values, as for peak (x_1) and background (x_2), $f = x_1 - x_2$ and, after (6.1),

$$\sigma_f = \sqrt{\sigma^2(x_1) + \sigma^2(x_2)}. \quad (6.2)$$

Any measured signal contains a random error, usually called noise, often referred to as “any kind of unwanted signal that blurs the measurement” (definition in [6.2]).

The *relative uncertainty* of a measured signal value x is defined as $\sigma_R(x) = \sigma(x)/x$. The reciprocal value, $x/\sigma(x)$, is called the *signal-to-noise ratio*, S/N , in the case of many measurements in a usually short time (in analogy to acoustics). The value of S/N expresses how many times the signal exceeds the noise, and therefore determines the precision of quantification. If the signal represents that of a pure element, S/N determines its detection limit, i.e., its lowest detectable concentration. Thus, for a given set of experimental parameters, the attainable S/N ratio is a quality figure of an instrument. Usually, the detection limit is expressed by the 3σ confidence criterion [6.3]. This definition means the relative detection limit is $3 \times N/S$, if S is the signal intensity for the pure-element ($= I^0$) and matrix correction factors are ignored (see Sect. 4.4.3.2). Note that for a measured intensity, $S \pm \sigma$, there is a 68% probability that the true value lies within one standard deviation, a 95% probability within $S \pm 2\sigma$ and a 99.5% probability within $S \pm 3\sigma$.

Principally, there are two types of measurement systems: analog (current amplifying) and digital (pulse counting) ones. Today, electron spectrometry is generally performed with pulse-counting systems, which are considered first and extensively. In Sect. 6.3, analog systems are briefly summarized, with emphasis of those using voltage to frequency conversion to obtain digitized output data.

6.1.1 Definitions and Explanations

A number of articles define S/N in typical spectroscopic measurements in a slightly different way [6.3, 6.4, 6.5, 6.6]. Here, we refer to the original work of Koenig and Grant [6.4] and present a simple version for practical usage. For more detailed discussions, the reader is referred to [6.5, 6.7].

There are many sources of noise in an instrument, such as power supplies, electron multipliers, amplifiers, etc. In any measurement, the statistical shot noise of single-electron events is the theoretical limit of precision. For a sufficiently large number of events ($n > 10$), the Poisson statistics for counting can be approximated by a Gaussian distribution of the counts with an uncertainty equal to the standard deviation, σ , given by $\sigma = p^{1/2}$ if p is the total number of counts per channel [6.3, 6.4, 6.5]. Therefore, we can simply add counts from different sweeps to get the total uncertainty, because after (6.2) for n sweeps, $\sigma_n = (p_1 + p_2 + \dots + p_n)^{1/2}$.

If we neglect background counts, p is the signal and the signal-to-noise ratio is given by $p/p^{1/2} = p^{1/2}$ (see below for P/B considerations, Sect. 6.1.2). In electron spectroscopy, however, we have to consider the background counts that can be an appreciable part of the peak counts. In general, the signal intensity, I , used throughout this book is represented by any quantity which is a measure of the amount of a detected species (e.g., peak area, Auger peak-to-peak height). In this chapter, the signal intensity is conventionally denoted by S (in total counts for specified energy and time intervals), which is obtained when the background intensity B is subtracted from the peak intensity P ($S = P - B = I$). Note that the true background value under the peak cannot be measured but has to be interpolated from measurements on both sides of the peak, assuming a linear background or, more precisely, a suitable background function (see Sect. 4.4.1.1). As a reasonable approximation, the more conveniently accessible lowest intensity value at the high-energy side of the peak is frequently taken as a measure of the background. Usually, this corresponds to a value between 5 and 50 eV away from the peak, which is felt sufficiently precise for an estimation of the S/N ratio. Assuming a measured $N(E)$ peak with total counts P and the adjacent background at higher kinetic energy with total counts B for AES and XPS, as depicted in Fig. 6.1 for the Cu LMM Auger peak at 914 eV, $S = P - B$ is a measure of the signal intensity. The total statistical noise N consists of quadrature addition (cf. (6.2)) of peak and background noise, i.e., $N = [(P^{1/2})^2 + (B^{1/2})^2]^{1/2}$. Thus, the signal-to-noise ratio is given by

$$\frac{S}{N} = \frac{P - B}{\sqrt{P + B}} = \frac{S}{\sqrt{S + 2B}} \quad (6.3)$$

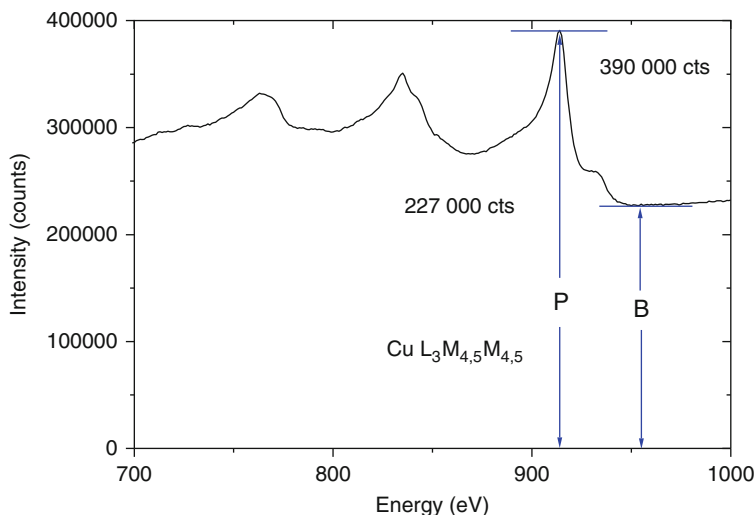


Fig. 6.1 Typical Auger spectra with the prominent Cu L₃M_{4,5}M_{4,5} (= L₃VV, 914 eV) Auger peak in the $E \times N(E)$ pulse-counting analyzer mode, showing the definition of peak (P) and background (B) intensity (given in total counts, cts), where the signal intensity is given by $S = P - B$. Note that we adopt the original definition by Koenig and Grant [6.4]

in accordance with the formulation by Koenig and Grant (equations (4) and (8) in [6.4]). In the following, we prefer the notation of these authors with peak (P) and background (B), because these values are directly measured in a spectrum (see Fig. 6.1). This definition, which is also used by Harrison and Hazell [6.7] and others, differs slightly from that of Seah and coworkers [6.5] where $P - B = S$ is defined as peak [6.3].

The S/N ratio determines the lower limit of the mean measurement error, i.e., the uncertainty that gives the error bar in quantification, and it is also a measure of the detection limit. Note that the relative uncertainty, σ_R , is given by

$$\sigma_R = \frac{N}{S} = \frac{\sqrt{P+B}}{P-B}. \quad (6.4)$$

Peak and background are usually measured by summing up the signal for several sweeps. If there are n sweeps with the single counts per sweep P_1 , B_1 , $P = nP_1$ and $B = nB_1$, and (6.4) reads

$$\frac{S}{N} = \frac{P_1 - B_1}{\sqrt{P_1 + B_1}} \sqrt{n}. \quad (6.5)$$

It is important to note that the signal-to-noise ratio increases only with the square root of the number of sweeps according to (6.5).

Equation 6.3 can be written as

$$\frac{S}{N} = K_1 \frac{P-B}{\sqrt{B}} \quad (6.6)$$

with

$$K_1 = \frac{1}{\sqrt{\frac{P}{B} + 1}}. \quad (6.7)$$

Very often, the noise contained in the signal is not taken into account. For the purpose of finding the detection limit and when comparing instrument performance, (6.6) with $K_1 = 1$ is frequently used in the respective literature [6.6,6.8,6.9] instead of the correct (6.7). As compared to (6.3), this means that the noise in the signal is neglected, resulting in too high S/N values. For example, considering small signals above a large background, as encountered near the detection limit, and as often found for AES peaks at higher energies (even at high elemental concentration, see Fig. 6.2), the peak intensity P approaches that of the background B , and according to (6.7), S/N is about a factor of $(1/2)^{1/2} = 0.71$ lower than that from (6.6) with $K_1 = 1$. For large peaks above a low background (typical for low-binding-energy peaks for high elemental concentration in XPS), this factor, for example, can become 0.25 for $P/B = 15$. Because there is no signal without noise, we use (6.3) for further considerations, in accordance with [6.3,6.4,6.5,6.7,6.10,6.11,6.12].

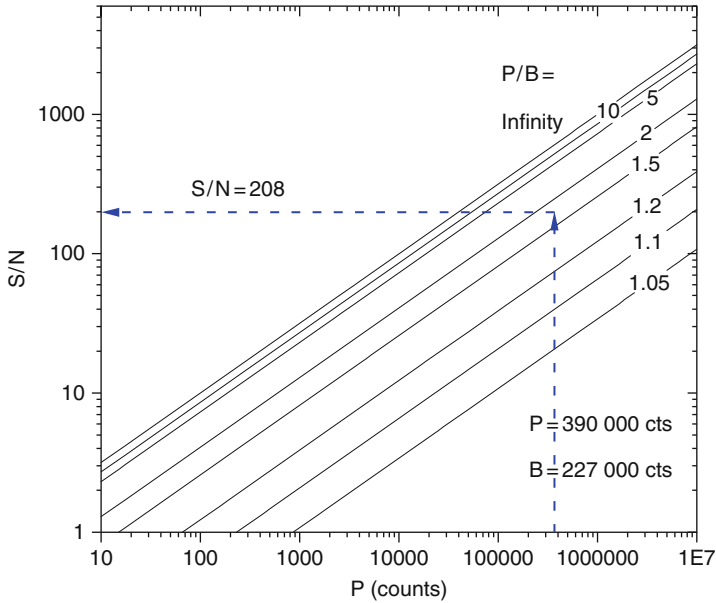


Fig. 6.2 Signal-to-noise (S/N) ratio as a function of the peak counts $P (=S + B)$ in double logarithmic plot for different P/B ratios, according to (6.8). Data from Fig. 6.1 to find $S/N = 208$ with $P/B = 1.72$ are indicated by dashed arrows. For high P/B values (exactly when P/B approaches infinity), $S/N = P^{1/2}$ and the upper limiting line is attained. The detection limit corresponds to a horizontal line through $S/N = 3$ (see Sect. 6.2.6)

A typical AES measurement (JEOL 7830F) of the Cu L_3 VV high-energy peak at 914 eV is shown in Fig. 6.1, measured for a clean Cu surface bombarded with 10 keV electrons, beam current 10 nA, 1 eV/step, and dwell time per step = 50 ms. The total counts are plotted as a function of the kinetic energy of the detected electrons. After 10 sweeps, the total counts are $P = 390000$ and $B = 227000$, and the corresponding S/N ratio after (6.3) is $(390000 - 227000)/(390000 + 227000)^{1/2} = 208$. (Taking only background noise into account, as in (6.6) with $K_1 = 1$, the S/N value would be 342.)

6.1.2 Role of Peak-to-Background (P/B) Ratio

Equation 6.3 can be rewritten to give S/N as a function of the peak-to-background ratio and the peak (6.8) or the background (6.10) intensity,

$$\frac{S}{N} = \frac{\left(\frac{P}{B} - 1\right) \sqrt{P}}{\sqrt{\left(\frac{P}{B} + 1\right) \frac{P}{B}}} \quad (6.8)$$

or, by taking squares and rearranging,

$$\frac{P}{\left(\frac{S}{N}\right)^2} = \frac{\left(\frac{P}{B} + 1\right)}{\left(\frac{P}{B} - 1\right)^2} \frac{P}{B}. \quad (6.9)$$

Likewise,

$$\frac{S}{N} = \frac{\left(\frac{P}{B} - 1\right) \sqrt{B}}{\sqrt{\left(\frac{P}{B} + 1\right)}}, \quad (6.10)$$

or, with P/B ratio and the signal intensity $(P-B)$,

$$\frac{S}{N} = \sqrt{\frac{\left(\frac{P}{B} - 1\right)}{\left(\frac{P}{B} + 1\right)}} (P - B). \quad (6.11)$$

Equations 6.8, 6.10, and 6.11 show that S/N is proportional to the square root of either the peak, the background, or the signal intensity, but with a proportionality constant depending on the P/B ratio. Figure 6.2 shows the total counts needed for the peak P to get a desired S/N ratio for a wide range of P/B ratios according to (6.9). As a consequence of the adding up of the noise in the peak and in the background, a low P/B ratio is associated with a low S/N even for high count rates. Increasing P/B increases S/N , and for high P/B ratios ($P/B > 10$), S/N approaches a maximum “saturation” value of $P^{1/2}$, since the vanishing background does not contribute any more to the total uncertainty.

The values for the measurement of the LMM peak of pure Cu depicted in Fig. 6.1, with $P = 390000$ and $P/B = 1.72$, are indicated in Fig. 6.2. As seen from (6.8), $S/N = 208$ and the corresponding uncertainty $\sigma = N/S = 0.005$, i.e., the detection limit ($= 3\sigma$, see above), is 1.5 at %Cu. If a S/N of 300 is desired, equivalent to an uncertainty of $\sigma = 0.33\%$ or a detection limit of 1 at %, the total peak counts after (6.8) should be about 800000. Note that for a 50% decrease in the uncertainty or detection limit, we need about twice the total counts and that means twice the measurement time. The detection limit of $S/N = 3$ [6.3] stems from the practical experience that the signal should be at least three times the noise to be reliably recognized as an existing signal with 99.5% confidence (3σ criterion). We can draw the detection limit line ($S/N = 3$) in Fig. 6.2. The strong influence of P/B on the detection limit is clearly recognized. Thus, Fig. 6.2 can be used to estimate the peak counts – and therefore the measurement time – necessary for a desired S/N ratio, if the P/B ratio is known.

As seen from Fig. 6.2 and according to (6.8), for high P/B , the dependence of S/N “saturates” with $S/N = P^{1/2}$. By reformulation of (6.8), the characteristic, dimensionless quantity $P/(S/N)^2$ is obtained (similar to the “intensity factor” F of Koenig and Grant [6.4] and Sherwood [6.12] as a function of the P/B ratio (6.9) and plotted on double logarithmic scale in Fig. 6.3). This diagram shows that for a given S/N ratio, the peak counts vary inversely with the P/B ratio. From the

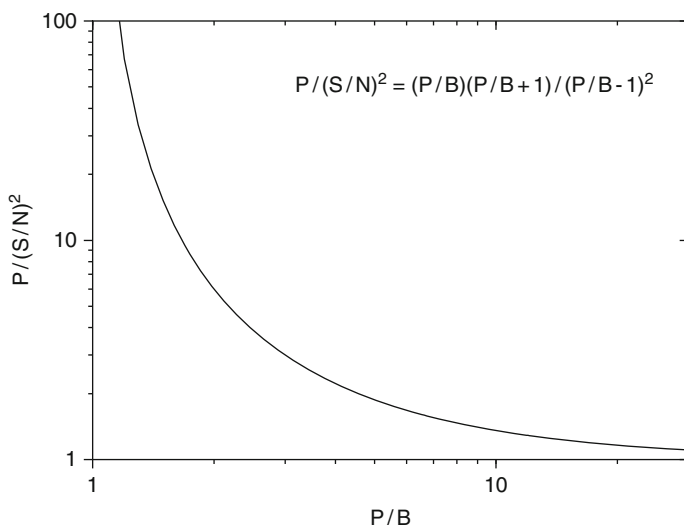


Fig. 6.3 Double logarithmic plot of (6.9) showing the dependence of the characteristic dimensionless quantity $P/(S/N)^2$ as a function of the peak-to-background ratio, P/B

P/B ratio of a given peak in a survey spectrum and a desired S/N ratio, the total counts P (proportional to measurement time) can be estimated. Two peaks with different P/B values can be directly compared with respect to the counts necessary for a given S/N ratio. For example, $P/B = 10$ or 2 correspond to a value of $P/(S/N)^2 = 1.36$ or 6.0, respectively. To obtain the same S/N ratio for both peaks, the peak with the lower P/B value has to be acquired with $6.0/1.36 = 4.4$ times more counts (i.e., the measurement time (per channel) has to be 4.4 times longer). Even for pure-element peaks, AES measurements usually show P/B ratios below 2 (see example Fig. 6.2). In contrast, P/B ratios are frequently of the order of 10 in XPS. Therefore, with respect to detection limit, AES can only compete with XPS by higher total counts (or higher count rate for comparable measurement time).

For quantitative analysis of a binary system with comparable sensitivity factors, it is clear that the component with minor concentration has a lower P/B value and therefore requires a much longer measurement time if the same S/N value for both peaks should be attained. Fortunately that is not necessary. Because the absolute value of uncertainty decreases with decreasing intensity, it is obvious that the minor component can be measured with a lower P/B ratio than the major component to contribute similarly to the total uncertainty. As shown in detail in Sect. 6.2.9, contrary to intuition (and to the conclusion that may be suggested by the P/B comparison made above using Fig. 6.3), a longer measurement time of the major peak is required to minimize the total error in quantification of elemental concentration.

6.2 Parameters Affecting P/B and Singal-to-Noise (S/N) Ratios

To obtain a high S/N ratio, a reasonably high P/B ratio is important in addition to a high count rate (see Figs. 6.2 and 6.3). Particularly in AES, with a high count rate but a large electron background, it is necessary to optimize the P/B ratio to obtain reasonably high S/N ratios. Whereas the magnitude and energy distribution of the electron background depend on the physics of electron–solid interaction, several instrumental and experimental parameters are decisive for peak, background, and P/B ratio. Both peak height and P/B ratio are affected by instrumental parameters such as the aperture angle or energy resolution (see Sects. 2.5 and 6.2.2). For CMA instruments, the latter parameters are usually fixed, whereas, in CHA instruments, at least the resolution and sometimes the aperture angle can be varied between given limits. As pointed out by Seah [6.13], scattering of high-energy electrons from the spectrometer electrodes increases the background. Today, it is effectively reduced by proper surface treatment and can sometimes be completely avoided (e.g., Prof. Keisuke Goto, Nagoya Institute of Technology, uses soot treatment of the outer electrode in his “metrological” CMA to greatly reduce electron scattering [6.30]). Increasing the X-ray source intensity in XPS or the primary beam current in AES increases both peak and background proportionally (at least for not-too-high count rates, see below) with no effect on the P/B ratio [6.5] (but S/N is increased owing to the higher count rates, see Fig. 6.2). Similarly, the electron emission angle does not change the P/B value. However, the electron-beam energy and, in particular, the electron-beam incidence angle affect both the count rate and the P/B ratio [6.5].

6.2.1 *Emission and Incidence Angle Dependencies of P/B and S/N for XPS and AES*

6.2.1.1 XPS (CHA)

The influence of emission and incidence angle on signal intensity for XPS with concentric hemispherical analyzer (CHA) is extensively presented in Chap. 5. Here, the focus is on the P/B and S/N ratios which are more important with respect to uncertainty than pure intensity.

In XPS, we may generally ignore the incidence angle dependence and obtain a cosine dependence on the emission angle (with a CHA) as shown in Fig. 5.3. This dependence is less pronounced for the S/N ratio, because after (6.8), for constant P/B values, S/N is proportional to $P^{1/2}$, as shown in Fig. 6.4 (upper curve).

6.2.1.2 AES (CHA and CMA)

In AES, the incidence angle of the primary electrons plays an important role in addition to the emission angle. While its effect on the measured intensity is given

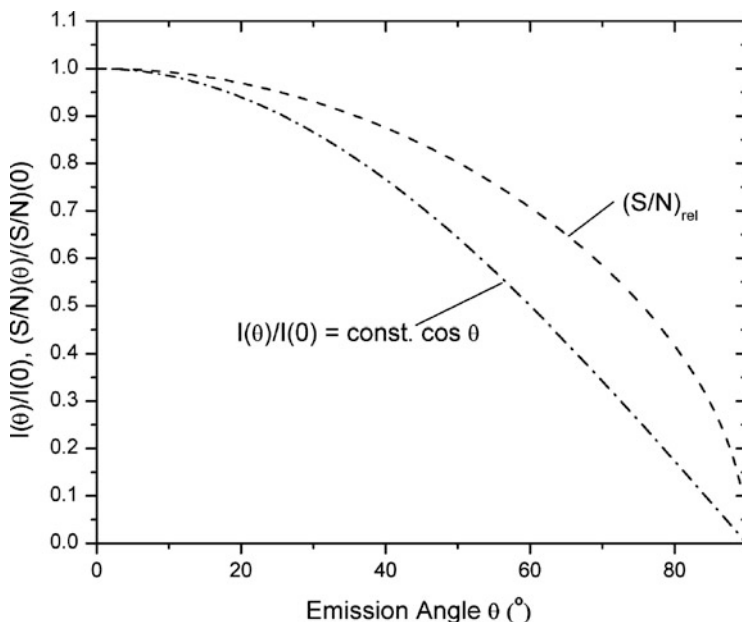


Fig. 6.4 Relative XPS signal intensity $I(\theta)/I(0)$, ($I = (P-B)$), and relative S/N ratio, $(S/N)_{\text{rel}} = (S/N)(\theta)/(S/N)(0)$ as a function of the emission angle θ , after (6.8) and (6.9)

in Sect. 5.2, the emphasis here is on the consequences for the P/B and S/N ratios. AES with concentric hemispherical analyzer (CHA) is considered first, and secondly the cylindrical mirror analyzer (CMA).

CHA

For CHA, the prediction of AES intensity dependence on the incidence angle is shown together with measured values for the Cu LMM peak in Fig. 5.23. Above $\alpha \cong 60^\circ$, the deviations of measured $P-B$ values from the prediction of simple theory are semiquantitatively explained by the combined influence of electron backscattering and residual surface roughness in Sect. 5.2.1 [6.14]. This explanation applies also for the P/B ratio shown in Fig. 5.25. Presumably because of lower surface roughness, higher $P-B$ values are obtained for the Si KLL peak on a silicon wafer depicted in Fig. 5.29.

With (6.11), the values in Figs. 5.23 and 5.25 can be combined to give the “measured” S/N ratio as a function of the beam incidence angle α shown in Fig. 6.5 for Si KLL. According to (6.11), the S/N ratio is proportional to the square root of $P-B$ for an approximately constant P/B ratio, that is below 50° (see Fig. 5.30), whereas at higher angles, P/B increases, i.e., the denominator in (6.3) tends to constancy and S/N is expected to be almost linear with $P-B$. With the dependence

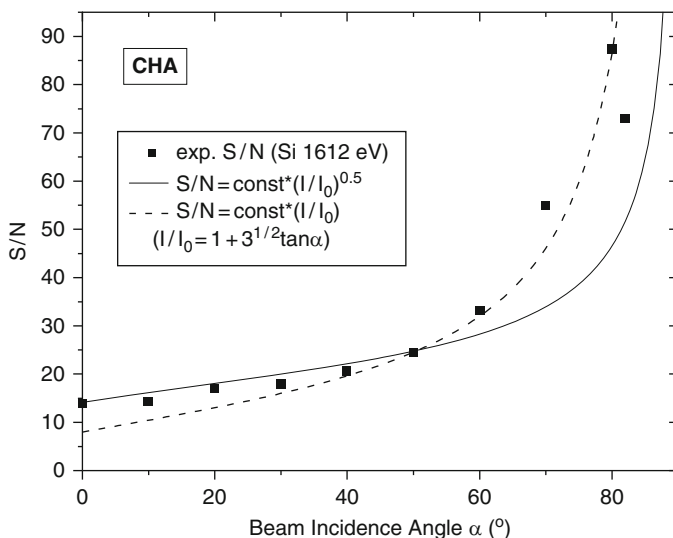


Fig. 6.5 Signal-to-noise (S/N) ratio for the Si KLL (1612 eV) Auger peak intensity as a function of the electron-beam incidence angle α for a CMA. Full points are from measured values of $P-B$ in Fig. 5.29 and of P/B in Fig. 5.30. Predictions of S/N are shown after (6.3) (dashed line) and (6.11) (solid line)

of $P-B = I$ on α described by (5.14), the fit given in Fig. 6.5 is obvious for the two regions as discussed above ($\alpha \leq 50^\circ$: $S/N \propto (I/I_0)^{1/2}$, $\alpha \geq 50^\circ$: $S/N \propto I/I_0$). Because the contribution of the backscattered electrons is much higher for the low-energy peaks, the peak and background values follow roughly the same dependence except for very high incidence angles, as seen in the P/B values for the Si 89 eV in Fig. 6.6, measured with the same conditions as the Si 1612 eV peak. The P/B value is fairly constant until $\alpha = 70^\circ$ and rises only to about 30% at 82° . That is the reason why good proportionality of S/N with $(I/I_0)^{1/2}$ is obtained over a wide range, as seen in Fig. 6.7, in contrast to Fig. 6.5.

According to Fig. 6.5, the S/N ratio for the Si 1612 eV Auger signal intensity increases from 14% at 0° to 90% at 80° , i.e., the relative uncertainty ($N/S = \sigma_{\text{rel}}$) decreases from 7% to 1.1%, more than a factor of six. The corresponding increase in detection sensitivity by grazing incidence AES has been used by Tsutsumi et al. [6.15] to determine contamination elements in the lubrication film on a hard disk as shown in Fig. 5.31.

CMA

For AES with a cylindrical mirror analyzer (CMA), predictions and measured values for the incidence angle dependence of the signal intensity are shown in Fig. 5.34 for Cu LMM (914 eV), and the measured P/B values in Fig. 5.35. Combining both data

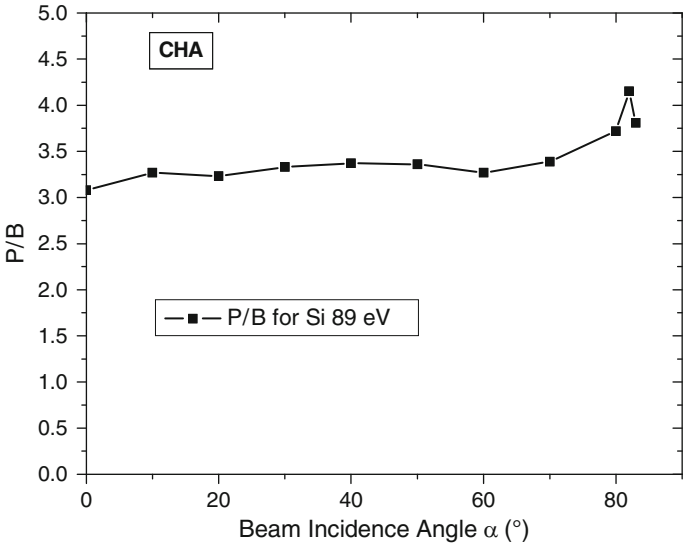


Fig. 6.6 P/B values for the low-energy Si LVV (89 eV) Auger peak as a function of the electron-beam incidence angle α

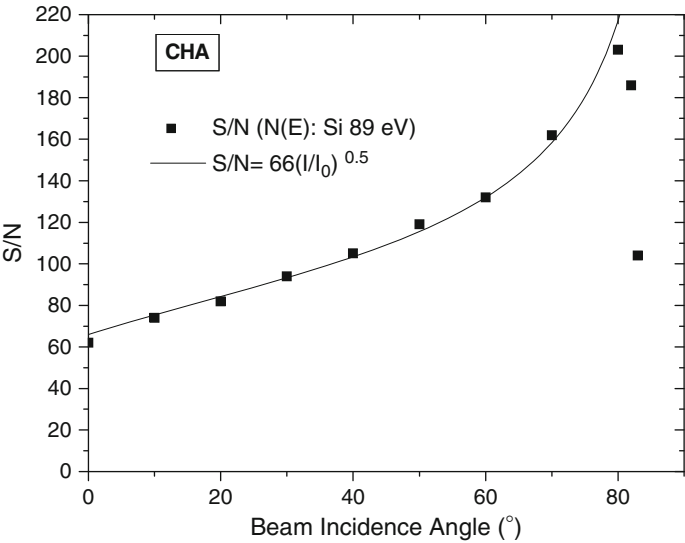


Fig. 6.7 Signal-to-noise (S/N) ratio of the low-energy Si LVV (89 eV) Auger peak as a function of the incidence angle α . Note the good agreement with (6.11). With intensity $I = (P-B)$ and $P/B = \text{const.}$, $S/N \propto (I/I_0)^{1/2}$ is obtained for a wide range until $\alpha = 80^\circ$

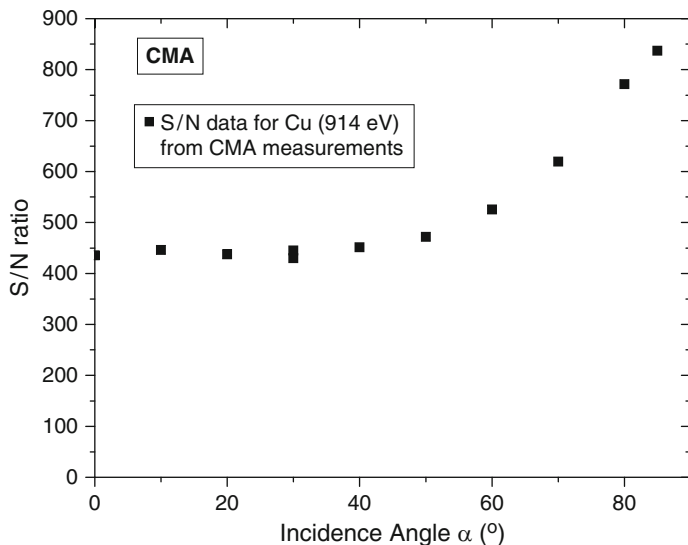


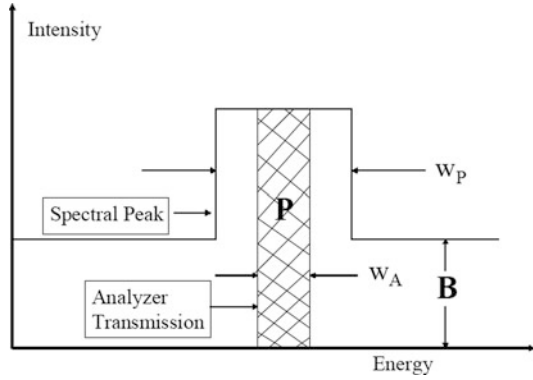
Fig. 6.8 Dependence of the signal-to-noise ratio, (S/N), of the Cu LMM (914 eV) Auger peak on the electron-beam incidence angle. Points are calculated with (6.11) using measured data from Figs. 5.34 and 5.35

sets, we get the signal-to-noise ratio, (S/N), with (6.11), plotted in Fig. 6.8. Like the peak intensity, S/N is practically constant up to 50° and then increases with the electron-beam incidence angle (or sample-tilt angle) until at glancing incidence (85°) about twice the lower angle value is obtained. Comparison of Fig. 6.5 with Fig. 6.8 shows the typical difference between both analyzers: While for comparable excitation conditions, at $\alpha = 0$, the S/N ratio is already higher for the CMA than for the CHA; the increase at $\alpha = 80^\circ$ is much less for the CMA than for the CHA (a factor of 2 compared to a factor of 6). Hence incidence angle and therefore sample tilt angle effects are less pronounced for the CMA, which in practice is an advantage when studying samples with rough or corrugated surfaces (see Sect. 5.2.3).

6.2.2 Analyzer Resolution

The energy resolution of the analyzer is one of the most important parameters influencing both the P/B and the S/N ratio. Within given limits, in CHA instruments, the analyzer resolution can be set by the operator (and in some CMA instruments, e.g., Physical Electronics (PHI) SAM 600). It is obvious that count rates are higher for a broader energy window, ΔE . However, beyond an optimum value, the S/N ratio is decreasing with increasing ΔE as shown below. Usually, the analyzer energy window is of Gaussian shape, while the signal intensity is of

Fig. 6.9 Influence of analyzer resolution (w_A) on transmitted intensities of peak (P) (with peak width w_P) and background (B), schematic for rectangular approximation



mixed Gaussian-Lorentzian or of asymmetric shape (see Sect. 3.2.7). The simplest approximation depicted in Fig. 6.9, a rectangular shaped peak with width, w_P , and a resolution of the analyzer given as the width of its (rectangular) resolution function, w_A , is assumed. We can easily calculate the P/B ratio and, using (6.10), the S/N ratio as a function of the ratio w_A/w_P . Two cases can be distinguished, depending on whether the analyzer resolution is smaller or larger than the natural peak width.

As seen in Fig. 6.9, for $w_A/w_P \leq 1$, P and B increase linear with w_A/w_P , and $P/B = P_0/B_0 = \text{const.}$ That means a square-root dependence of S/N on w_A/w_P after (6.10),

$$\frac{S}{N} = \frac{\left(\frac{P_0}{B_0} - 1\right)}{\sqrt{\left(\frac{P_0}{B_0} + 1\right)}} \sqrt{B_0 \frac{w_A}{w_P}}, \quad (6.12)$$

where P_0, B_0 is P, B for $w_A/w_P = 1$. For $w_A/w_P \geq 1$, we get

$$\frac{P}{B} = \frac{\left(\frac{P_0}{B_0} - 1\right)}{\frac{w_A}{w_P} + 1}, \quad (6.13)$$

or, normalized to $(P_0/B_0 - 1)$, $(P/B - 1)/(P_0/B_0 - 1) = 1/(w_A/w_P)$. With (6.13) in (6.12), we obtain

$$\frac{S}{N} = \frac{\left(\frac{P_0}{B_0} - 1\right) \sqrt{B_0}}{\sqrt{\left(\frac{P_0}{B_0} + 1 + 2 \frac{w_A}{w_P}\right)}}. \quad (6.14)$$

As an example, assuming $P_0/B_0 = 2$ and $B_0 = 10,000$ counts, Fig. 6.10 (upper curve) shows P/B and Fig. 6.11 (upper curve) shows S/N as a function of w_A/w_P , respectively, for the rectangular approximation of peak shape and analyzer resolution.

Of course, the edge in the relation $S/N = f(w_A/w_P)$ according to the upper curve in Fig. 6.10 is not realistic and a result of the coarse rectangular

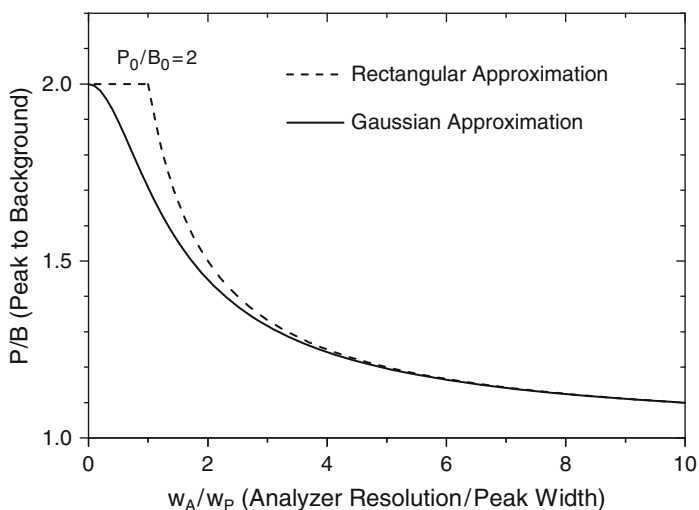


Fig. 6.10 Dependence of P/B on the ratio w_A/w_P for rectangular shape approximation (dashed line, cf. Fig. 6.9) and Gaussian shape approximation (solid line)

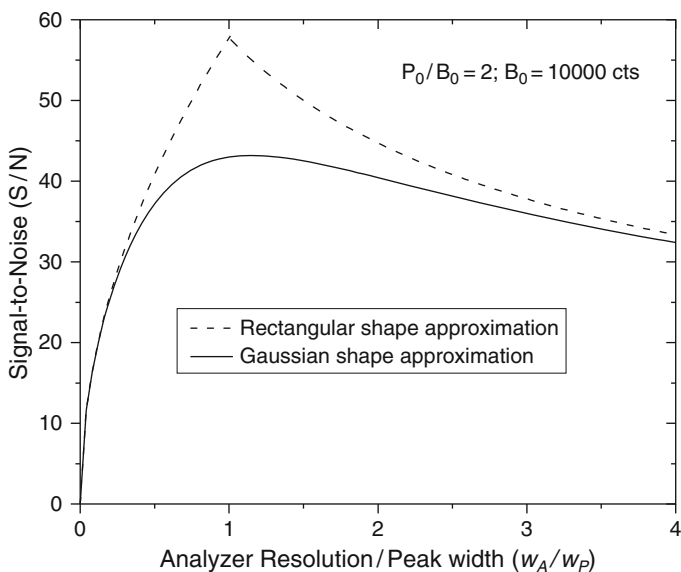


Fig. 6.11 Dependence of the S/N ratio on w_A/w_P for rectangular peak and resolution shape approximation (upper curve, according to Fig. 6.9 and (6.14)) and for Gaussian shape approximation (lower curve, according to (6.18))

approximation. To be more exact, for elemental XPS peaks in the $\Delta E = \text{const.}$ mode, a Gaussian–Lorentzian or Doniach–Sunjic shape should apply (see Sect. 3.1.7). For AES, the peak shape is even more complicated and has an additional asymmetry because of the E dependence in the $\Delta E/E = \text{const.}$ mode (see Sect. 2.5.1). The analyzer resolution depends on the instrument setup and is usually approximated by a Gaussian function. Therefore, a more reasonable approximation for consideration of the influence of the analyzer resolution on P/B on S/N is two Gaussian functions with the 2σ values ($\sigma = \text{standard deviation} \cong 0.87 \text{ FWHM}$) for analyzer and peak, w_A and w_P , respectively. For the folding of one Gaussian with a second one, it follows for the peak count rate

$$P = \frac{(P_0 - B_0)w_A}{\sqrt{w_A^2 + w_B^2}} + B_0 \frac{w_A}{w_P} \quad (6.15)$$

and for the background

$$B = B_0 \frac{w_A}{w_P}. \quad (6.16)$$

The P/B ratio is then given by

$$\frac{P}{B} = \frac{\left(\frac{P_0}{B_0} - 1\right)}{\sqrt{\left(\frac{w_A}{w_P}\right)^2 + 1}} + 1 \quad (6.17)$$

Figure 6.10 (lower curve) shows the plot of (6.13).

With (6.10), the S/N ratio is given by

$$\frac{S}{N} = \frac{\left(\frac{P_0}{B_0} - 1\right) \sqrt{\frac{w_A}{w_P} B_0}}{\left[\left(\frac{w_A}{w_P}\right)^2 + 1\right] \left[\left(\frac{w_A/w_P - 1}{(w_A/w_P)^2 - 1}\right) + 2\right]}. \quad (6.18)$$

The dependence of the S/N ratio on the ratio between analyzer energy width and Auger- or photoelectron peak width given by relation (6.18) is plotted in Fig. 6.11 (lower curve) for the conditions $P_0/B_0 = 2$, $B_0 = 10,000$ counts. For comparison, the prediction for rectangular instead of Gaussian approximation is also shown in Fig. 6.11 (upper curve). The true behavior is expected to be somewhere between both curves, but the lower one, i.e., the Gaussian approximation, appears to be more realistic.

It is clearly seen that the optimum condition for highest S/N ratio is achieved when the width of the analyzer resolution approximately matches the peak width ($w_A/w_P = 1$ for rectangular, $w_A/w_P = 1.15$ for Gaussian approximation). Setting the resolution to about two times the peak width results in a reduction of S/N of only 5%, whereas a setting to half the peak width results in a reduction of 14%.

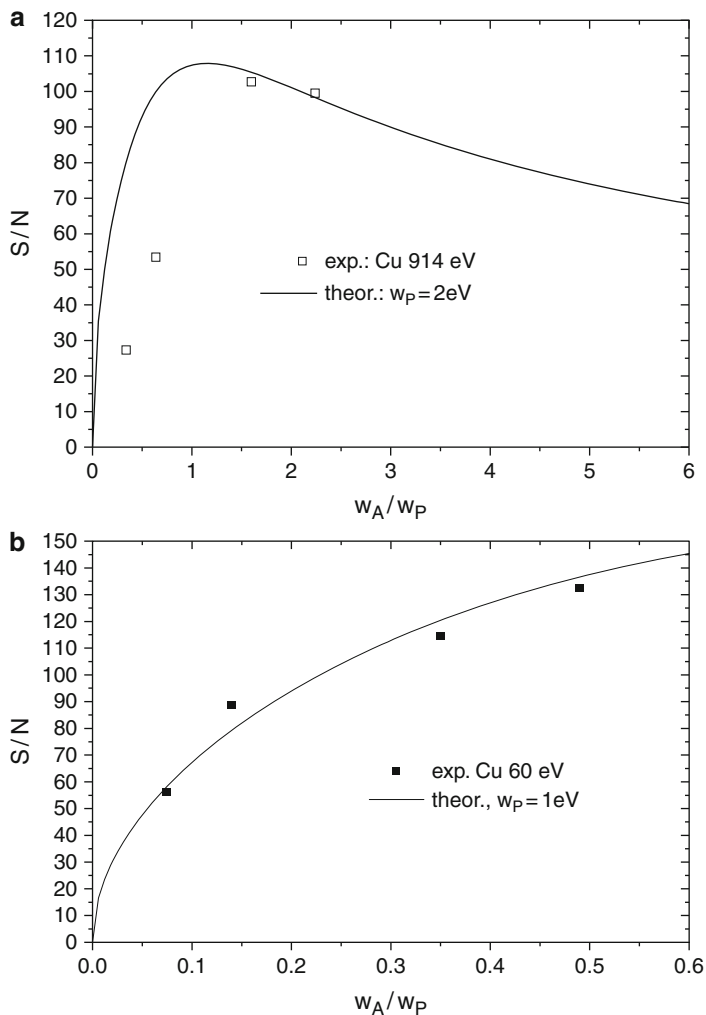


Fig. 6.12 Dependence of the S/N ratio on the relative analyzer resolution, w_A/w_P , according to (6.18) and comparison with measured values for (a) Cu LMM (914 eV) and (b) Cu MVV (60 eV) peak

Figure 6.12a illustrates the dependence for measured values on the Cu 914 eV peak (for the measurements, the FWHM of the elastic peak measured at 2000 eV was taken as an approximation for 2σ , with an error of 15%). Despite insufficient fit at lower resolution, the general trend according to (6.18) is reproduced. The fit appears better for the Cu 60 eV peak, as shown in Fig. 6.12b.

6.2.3 Surface Roughness

The effect of roughness on signal intensity is treated in detail in Sects. 5.1.4 (XPS) and 5.2.3 (AES). Whereas in XPS, a decreased intensity with respect to a flat surface is expected for increasing emission angles as in AES with CMA; AES with CHA may result even in some increase at lower angles but again a decrease at higher angles. For moderate roughness (e.g., mean roughness angle below 15° , see Fig. 5.37), the effect is usually less than 20% and therefore affects S/N rather moderately in comparison to flat surfaces.

6.2.4 Detector Efficiency and Scattered Electrons

Among the many other parameters that influence, the P/B ratio is the detection efficiency and its dependence on the count rate. At higher count rates (usually $> 10^6 \text{ s}^{-1}$), the dead time of the detector causes an approach to saturation with a gradual diminishing of the count rate [6.16, 6.17], thus lowering the P/B ratio.

High-energy electrons impinge on the negative-biased electrode of the spectrometer and are scattered from the outer hemisphere of a CHA or from the outer cylinder of a CMA. As a result, together with secondary electron emission, the background intensity is increased. Scattering at any obstacle in the electron beam, for example, at edges of slits and particularly on grids as used at the inner cylinder entrance of a CMA (see Fig. 2.12), further increases background. As a result, the P/B ratios of CMA instruments are usually lower than those of CHA instruments (see Table 6.1).

6.2.5 Excitation Intensity (Primary Beam Current) and Total Measurement Time per Channel

The measurement time, t , for gathering data in any energy channel is decisive for the total number of counts. With total measurement time t per channel (i.e., total time per step in the usual sweep over a certain energy range) and the peak count rate n_P and background count rate n_B , $P = n_P \times t$ and $B = n_B \times t$. For n measurements per channel (=per point), i.e., n sweeps over a part of a spectrum, $P = n_P \times t_s \times n$ and $B = n_B \times t_s \times n$, with t_s , the time per step, and (6.3) can be written as

$$\frac{S}{N} = \frac{(n_P - n_B)t}{\sqrt{(n_P + n_B)t}} = \sqrt{\frac{(n_P - n_B)}{(n_P + n_B)}}(n_P - n_B)t = \sqrt{\frac{\left(\frac{n_P}{n_B} - 1\right)}{\left(\frac{n_P}{n_B} + 1\right)}}(n_P - n_B)t. \quad (6.19)$$

Equation 6.19 means that the S/N ratio is proportional to the square root of the total measurement time: to improve the uncertainty, given by the noise, by a factor

of 2, we need to increase the total measurement time by a factor of 4. Of course that is also valid for the number of sweeps because $n \times t_s$ is the total measurement time (note that this analysis neglects the time needed to store data at the end of a sweep and to change the swept voltage).

Assuming that the output count rate (equivalent to the measured Auger or photoelectron current intensity I_A/e with e = elementary charge) is proportional to the primary-excitation photon intensity or electron current, I_p ,

$$I_A = (n_p - n_B) = K_I I_p, \quad (6.20)$$

and

$$K_I = \frac{(n_p - n_B)}{I_p} = \frac{(P - B)t}{I_p t}. \quad (6.21)$$

Thus, K_I is a figure of merit characterizing the output of a spectrometer for a given set of instrumental parameters (e.g., measured energy, resolution). For given Auger- or photoelectron spectra of a pure elemental sample, $K_I = Q_S(E) \times n_i(E)$, where $Q_S(E)$ is the spectrometer characteristic for given settings and $n_i(E)$ is the true spectrum emitted from sample i , as defined by Seah [6.18]. Since $Q_S(E)$ is another expression for the intensity–energy response function (IERF), $G(E)$, described in Sect. 4.3.2.1, K_I in the same manner consists of the total analyzer transmission, $T_A(E)$, and detector efficiency, $D(E)$ (see, e.g., (4.42)). More exactly, the etendue (product of analyzer transmission and analyzed area) has to be considered (see Sect. 4.3.2). Of course, $T_A(E)$ and $D(E)$ depend on the respective instrument and its settings and so does K_I . Since K_I does not take into account the S/N ratio, we define another figure of merit for this purpose, F_s . Introducing (6.20) and (6.21) in (6.19), and writing $n_p/n_B = P/B$, the S/N ratio is given by

$$\frac{S}{N} = \sqrt{\left(\frac{P}{B} - 1\right)} K_I I_p t = F_s \sqrt{I_p t}, \quad (6.22)$$

where the characteristic quantity F_s is expressed as

$$F_s = \frac{\left(\frac{S}{N}\right)}{\sqrt{I_p t}} = \sqrt{\left(\frac{P}{B} - 1\right)} K_I. \quad (6.23)$$

Note that $I_p t$ in (6.20), (6.22), and (6.23) has to be expressed in elementary charge numbers ($1 \text{ nA} = 6.25 \times 10^9$ counts). Equation 6.23 gives the characteristic function F_s as the square of the S/N ratio, connected with K_I by the P/B ratio of the respective instrument with given settings, and a given elemental sample peak, to the total primary intensity ($I_p t$). Thus, for a given peak of an elemental sample and a given set of experimental and instrumental parameters, F_s is a figure of merit for an instrument which takes into account the most important quantity S/N , normalized to the square root of the total amount of primary electrons or photons. For comparison of different instruments, (6.23) is very useful, when measurements

Table 6.1 Example of a comparison of essential characteristics of three AES instruments based on measurements of the Cu (914 eV) peak at 10 keV primary beam energy, and data acquisition with 1 eV/step, 1 s/step

I_p (nA)	α (o)	$\Delta E/E$ (%)	P/I (cps)	$(P-B)/I$ (cps)	$I_A (10^{-3} \text{ pA})$	$K_I = I_A / I_p (\text{pA} / \mu\text{A})$	P/B	S/N	$F_s (nAs)^{-1/2}$	$X_{Cu, min}$ (at%)
JEOL JAMP 7830F (CHA)										
1	0	0.68	44620	16540	2.65	2.7	1.59	61	61	5.0
10	0	0.68	438440	157740	25.2	2.5	1.56	186	58	1.6
100	0	0.68	4130040	1390820	222	2.2	1.51	532	53	0.6
10	60	0.68	1606700	661480	106	10.6	1.70	414	131	0.7
10	0	0.13	71080	35620	5.7	0.57	2.0	109	35	2.8
10	0	0.05	9700	4120	0.66	0.066	1.74	33	10	9.1
VG Microlab 350 (CHA)										
1	0	0.6	42897	16678	2.7	2.7	1.64	64	64	4.7
10	0	0.6	530742	203534	32.6	3.2	1.62	219	69	1.4
100	0	0.6	4742100	1724000	276	2.8	1.57	617	62	0.5
10	60	0.6	951952	407076	65.0	6.5	1.75	333	105	0.9
10	0	0.15	103109	51413	8.23	0.82	1.99	130	41	2.3
10	0	0.06	10954	5742	0.92	0.092	2.10	45	14	6.7
PHI 680 (CMA)										
1	0	0.39	311590	96113	15.4	15.4	1.45	133	133	2.3
10	0	0.39	2575265	889045	142	14.2	1.53	428	135	0.7
10	30	0.39	2521199	883039	141	14.1	1.54	433	137	0.7
10	60	0.39	2857600	111310	178	17.8	1.64	520	164	0.6

I_p (nA) is the primary electron-beam current, with incidence angle to the normal to the sample, α (o); $\Delta E/E$ (%) is the energy resolution of the analyzer; P is the peak; B the background and $P-B$ the signal intensity, all in counts (in 1-s measurement time per point); and I_A is the $P-B$ in (pA) ($I_A = (P-B) \times e$ with elementary charge $e = 1.6 \times 10^{-19}$ A s). The characteristic output figure of the instrument (see (6.21)) is $K_I = I_A / I_p$ (nA of AES current/ μ A of beam current); P/B is the peak-to-background and S/N is the signal-to-noise ratio, respectively; and F_s (nA s) $^{-1/2}$ is the detection efficiency or figure of merit of the respective spectrometer operated at the tabulated conditions. The last column shows the detection limit for Cu, $X_{Cu, min}$, in at % for $t = 1$ s according to (6.26) (note that test measurements were done in 1999)

are done with the same sample and peak and for the same energy/step and time/step parameters and number of sweeps (total measurement time). In XPS, besides the measured area, this comparison includes the X-ray excitation intensity which is fairly different and not easy to measure. In AES, the primary excitation is given by the primary beam current and energy which are easily determined.

An example of a comparison of the intensities obtained for the Cu LMM (914 eV) peak on a pure, sputter-cleaned Cu surface with three different AES spectrometers is shown in Table 6.1. It was done by the author and coworkers by courtesy of instrument manufacturers back in 1999, and therefore, the comparison is not relevant for instruments now available. However, the basic features are still relevant. As expected, the S/N ratios increase with electron incidence angle and with beam current. The increase with current is somewhat less than proportional to $(I_p t)^{1/2}$, as expected, for example, from (6.22), which is recognized by the slight decrease of F_s and may be explained by the influence of the dead time of the multiplier at high count rates [6.16] (see Table 6.1 and Fig. 6.21).

To understand the data compiled in Table 6.1, let us have a look at the basic quantitative AES equation (4.132) and the expression for $G(E_A)$ (4.133). The latter is a product of the spectrometer transmission, $T(E_A)$; the detector efficiency, $D(E_A)$; and the spatial acceptance angle of the instrument, $\Delta\Omega$. According to Seah and Hunt [6.5], for the L_3 core level of Cu, $\sigma(5 \text{ keV}) = 5 \times 10^{-24} \text{ m}^2$, $\rho \approx 1$, $r(E_A/E_p, 45^\circ) = 0.58$, $N = 8.5 \times 10^{28} \text{ m}^{-3}$, and $\lambda(E_A) = 1.35 \times 10^{-9} \text{ m}$. Taking into account that (4.131) represents the total Auger emission current in 4π space, the Auger electron emission from the surface forming the peak is only about 10–20% [6.18] (see (4.132), (4.133)), and we get

$$I_A = 10^{-5} I_p T(E_A) D(E_A) \frac{\Delta\Omega}{4\pi}. \quad (6.24)$$

With a typical value for the product of transmission, detector efficiency and angular acceptance of about 10% for a CHA, we see that, for the Cu 914 eV peak, ($L_3M_{4,5}M_{4,5}$ transition) the detected Auger electron current is

$$I_A \approx 10^{-6} I_p, \quad (6.25)$$

or about 1 pA (Auger peak)/ μA (primary beam). Indeed, the actually derived values of I_A from the count rates are of that order of magnitude, and $K_I = I_A/I_p \times 10^6$ is of the order of 1–15 for not too extreme conditions (see Table 6.1). The ratio K_I for a given elemental peak (usually Cu 914 eV) under well-specified measurement conditions (beam energy and incidence angle, eV/step and time/step) is a figure of merit of an instrument and is often specified as a guaranteed count rate by the manufacturer.

The comparison in Table 6.1 shows rather similar data for the two CHA instruments (JEOL JAMP 7830F and VG Microlab 350). In contrast, the CMA instrument (PHI 680) behaves quite differently. As expected, the K_I values are much higher, owing to the higher point transmission for the CMA. The S/N and

F_s values are also higher but less pronounced because of higher background count rates probably caused by the larger effect of scattered electrons in the CMA [6.19]. The dependence of F_s and S/N on the incidence angle is much reduced because of the cone-shaped acceptance geometry of the CMA (see Fig. 6.8 and Sect. 5.2.2).

The comparison in Table 6.1 was only done for one specified peak. The comparison will be somewhat different for peaks at different kinetic energies, because of the characteristic spectrometer function $Q_s(E)$ (IERF function called $G(E)$ here, see Sects. 4.4.2.2 and 4.4.3.2) [6.20]. This important quantity was extensively studied by Seah and coworkers with interlaboratory comparisons for AES [6.21] and XPS [6.22] instruments. Today, manufacturers provide the analyst with a database for the IERF.

6.2.6 Detection Limit

From the above calculations, it is clear that for given excitation conditions (e.g., photon flux and energy in XPS, primary-electron-beam current and energy in AES), the count rate for a specific peak and background depends on the overall performance of the instrument. Most interesting for the analyst is the detection limit, i.e., the lowest concentration of an element which can be reliably determined.

Adopting the usual 99.7% confidence limit, corresponding to three times the standard deviation (3σ) for the detection of the mole fraction, the detection limit of an element i is $X_{i,\min} = 3\sigma = 3 \times N/S$, if S/N is given for the pure-element peak [6.3] and matrix effects are ignored. With (6.23), it follows [6.8]

$$X_{i,\min} = \frac{3}{(S/N)} = \frac{3}{F_s \sqrt{I_p t}}. \quad (6.26)$$

The detection limit after (6.26) for $t = 1$ s dwell time per point is given in Table 6.1 for different instrument settings. It is recognized that the lowest detection limit is obtained with the CMA instrument, and for the CHA instruments, the lowest limit is for 60° incidence angle (it is expected to be slightly better at 80° , cf. Fig. 6.5).

The signal intensity is proportional to the elemental sensitivity, given by the parameters in the first term of (4.32). In practice, the relative elemental sensitivity factors S_i with respect to $S_{\text{Ag}(356\text{ eV})} = 1$ are used for quantification (see Sect. 4.4.3.2 and (4.44)). Since the above equations refer to Cu (914 eV), F_s has to be divided by the relative sensitivity factor of Cu (914 eV), S_{Cu} , to yield a generally applicable equation for elements with relative sensitivity factor S_i . The generalized detection limit for an element i , $X_{i,\min}$, is then

$$X_{i,\min} = \frac{3}{F_s \left(\frac{S_i}{S_{\text{Cu}}} \right) \sqrt{I_p t}}. \quad (6.27)$$

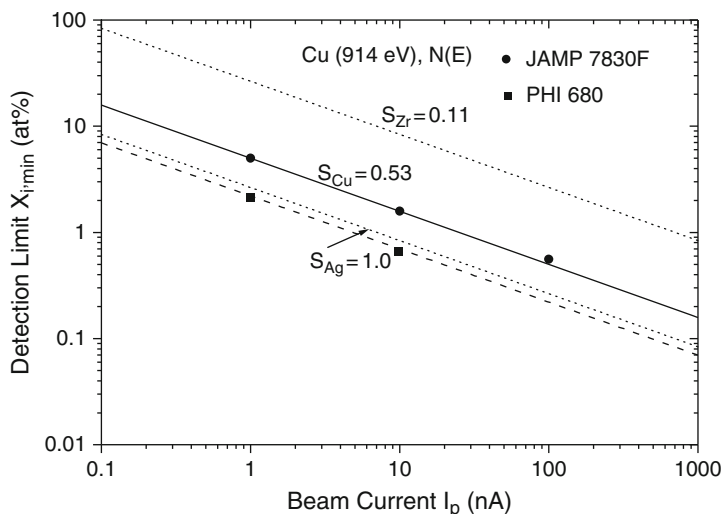


Fig. 6.13 Detection limit as a function of the primary-electron-beam current, shown for the Cu (914 eV) measured with the instruments JEOL JAMP 7830F (solid line) and PHI 680 (dashed line), after (6.13). Dotted lines for $S_{Ag} = 1$ and $S_{Zr} = 0.11$ are calculated from manufacturer's tables for the JAMP 7830F with respect to the measured value $S_{Cu} = 0.53$

Depending on the respective matrix, $X_{i,min}$ after (6.27) may vary by a factor usually between 1/2 and 2 which is obtained when taking into account the relative matrix correction factor (see Sect. 4.4.3.2). For the PHI SAM 680 instrument in Table 6.1, the instrumental efficiency factor F_s defined by (6.23) was determined to about $135 \text{ (nA s)}^{-1/2}$ for $(I_p t)^{1/2} = 10 \text{ nA s}$, giving a detection limit of $X_{Cu,min} = 0.7$ at % after (6.27). The detection limit as a function of the primary-electron-beam current is shown in Fig. 6.13 with $t = 1 \text{ s}$ per channel for Cu ($S_i/S_{Cu} = 1$). To calculate $X_{i,min}$ in (6.27) for other elements, we have to know the relative elemental sensitivity factors here for the peak height $S = P-B$ (see Fig. 6.1). While for valid quantification local measurements of elemental standards are recommended (see Chap. 4), for predictive estimates, we can use the relative sensitivity factors given by the manufacturer for the Auger peak height in $N(E)$ spectra and/or for Auger peak-to-peak heights for $d(N(E) \times E)/dE$ spectra. (In XPS, relative sensitivity factors are usually given in relative peak areas; see below.) For example, the JEOL JAMP 7830F manufacturer gives, with the parameters 10 keV, 0.5% energy resolution, 30° incidence angle, values $S_{Cu} = 0.53$ (914 eV) (relative to Ag sensitivity = 1), and $S_{Zr} = 0.11$ (147 eV), one of the lowest sensitivity factors. A parallel line can be drawn for any element by considering its relative sensitivity factor S_i in (6.27). According to the instruments figure of merit, F_s , the respective array of sensitivity lines is just parallel shifted to the one shown for Cu (914 eV) for the JEOL JAMP 7830F system and the PHI 680 system. As seen from Table 6.1 and Fig. 6.13, the respective values for VG Microlab 350 almost coincide with those for JEOL

(both CHA instruments), whereas the PHI 680 (with CMA) shows considerably better sensitivity for comparable excitation conditions.

The sensitivity for elemental analysis – as defined by the limit of detection – depends on the signal-to-noise ratio given by (6.23) and (6.26). It can be argued that by increasing the number of measurement channels while maintaining the time per channel (and subsequent smoothing), the noise is reduced and therefore the detection limit is improved [6.5]. However, this argument is only valid if the analyzer resolution is not in the optimum condition of being close (or somewhat larger than) the peak width (see Fig. 6.11 and discussion in Sect. 6.2.2). Expression (6.27) and Fig. 6.13 clearly demonstrate the importance of beam current and measurement time for the detection limit. However, their increase increases the risk of beam damage which establishes an ultimate limit (see Sect. 8.6)

Equations 6.19–6.23, 6.26, and 6.27 apply equally well for XPS too. However, the number of photons for the excitation in XPS is difficult to obtain. Therefore, the respective expressions for K_I or F_S are often related to the X-ray anode input power (in W), which of course includes another efficiency term characteristic for the instrument. With the highest possible input power, different instruments with equal settings can be directly compared. The detection limit for any spectrum is easily determined after (6.26). For example, the Mg survey spectrum shown in Fig. 3.2 yields for 1 s/step for the Mg 1 s peak $P = 22 \times 10^4$ counts and $B = 5 \times 10^4$ counts. With (6.3), this gives $S/N = 390$ and with (6.26) $X_{\text{Mg,min}} = 0.8$ at%. The most intense Mg KLL Auger peak with $P = 54 \times 10^4$ counts and $B = 2 \times 10^4$ counts yields $S/N = 695$ and $X_{\text{Mg,min}} = 0.4$ at%.

6.2.7 S/N Ratio and Uncertainty in Peak Measurements

With modern pulse counting, digital techniques, usually a spectrum is acquired in the direct mode, $N(E)$ or $E \times N(E)$. Using appropriate sensitivity factors, the peak-to-background (P/B) ratios used here can be directly taken as a measure of the elemental concentration, as, for example, proposed by Langeron et al. for AES [6.23]. Historically, the derivative spectra ($d[N(E) \times E]/dE$) were used in AES because of the analog technique that directly reproduced them by the second harmonic detection with a lock-in amplifier (see Sect. 3.2.2). Even today, the peak-to-peak height in the derivative Auger spectra is used as a quantitative measure of the concentration. In XPS, that approach has never been used mainly because of the lower background and therefore easier background subtraction. After background subtraction, the peak area is a measure of the elemental concentration (see Sect. 4.1).

In addition to the easiest intensity determination using the difference between peak and background counts ($P-B$), the use of peak area measurements (usually in XPS) and of derivative spectra (AES) has to be considered. Furthermore, the influence of data processing, for example, smoothing, is briefly discussed.

6.2.7.1 *S/N in Peak Area Measurements*

To determine the peak area, several data points along the peak's contour have to be acquired by summing up different counts in different channels ($N_i \times \Delta E$, where N_i are the counts at point i and ΔE is the energy step per point). Since we cannot measure the background counts under the peak, we have to define two points, one on the lower and one on the high-energy end of the peak, and interpolate with a suitable function (linear, Shirley, Tougaard background, see Sect. 4.1.1). In any case, that two points are used to calculate the background for all the background points in between; therefore, the errors in $P-B$ add up many times for the total intensity. Only if the background is very low, the error in the peak counts prevails. Smoothing cannot help, because the accuracy cannot be improved but it may introduce a systematic error considering peak shape and therefore the area [6.24]. Measuring more points in the background region and averaging ("background averaging" [6.7]) may lead to some improvement of the order of the square root of the averaged points. As discussed below, there is hardly a real gain of S/N by smoothing that has not its drawback in accuracy of intensities. Considering S/N for peak areas, we may in reasonable approximation look at the peak area as a summation over each of n data points, where the uncertainty is given by the square root of that sum and n times the two-point background average. This is equivalent to the uncertainty of a two-channel measurement with the total time $n \times t$, with t the dwell time per channel.

An elucidative and thorough consideration of uncertainties in peak area measurements is given by Harrison and Hazell [6.7]. Here, we adopt a simplified consideration, assuming a symmetric triangular peak shape with peak maximum counts P_m , and background counts B . If there are N measurements within the peak, each for an energy interval ΔE , then every peak element contributes as $(P_i - B) \times \Delta E$ to the signal area that is given by $(N/2) \times (P_m - B) \times \Delta E$. The noise "area" is $((N/2) \times P_m + N \times B)^{1/2} \times \Delta E$. Since ΔE cancels, the peak area signal to noise ratio, $(S/N)_{PA}$, is

$$\left(\frac{S}{N}\right)_{PA} = \frac{N}{2} \frac{P_m - B}{\sqrt{\frac{N}{2} P_m + NB}}. \quad (6.28)$$

Because P is increasing from zero to P_m but B is staying constant, the total influence of B is larger. A direct comparison with peak-height measurements is difficult because of the time needed for the measurement. If we take the same measurement time per channel, we need N times more total measurement time than for one peak to background measurement. Therefore, an increase of about a factor of $N^{1/2}$ is expected. In practice, always several points are measured for one peak. As an example, let us assume $P_m = 20000$ and $B = 10000$ counts and 5 points within the peak ($N = 5$). According to (6.3), we obtain $S/N(\text{peak height}) = 58$, and after (6.28), we get $S/N(\text{peak area}) = 79$, which is about 30% higher. However, taking the total measurement time for one channel combination (peak and background), we get ($N = 5$) five times more counts and more, i.e.,

$S/N(\text{peak height}, 5 \times t) = 58 \times 5^{1/2} = 177$. Taking into account the true background as an average between that on the low- and high-energy side of a peak, Harrison and Hazell find an even larger influence of the background on the uncertainty of peak area measurements.

6.2.7.2 S/N and Derivative Spectra

Spectra in the derivative or differential mode can be obtained either by the analog mode, i.e., by sinusoidal modulation of the continuous sweep of the analyzed energy, or in the digital pulse-counting mode, i.e., by computer differentiation of the direct spectrum. In the first case, the signal as a function of the peak-to-peak modulation voltage is complex, and the S/N ratio depends on the modulation voltage and time constant and is complicated to estimate theoretically [6.25]. According to Seah and Hunt [6.5], it can be a factor of three lower than for pulse counting and is, in any case, less than in the direct mode. Since differentiation “roughens” the direct spectrum, for an appropriate time constant, the noise is usually seen in the background of a measured differential spectrum (see, e.g., Figs. 6.14 and 6.15) with computer-differentiated signal. Then, the average or root-mean-square (rms) noise can be estimated by eye (or derived from the maximum by division with $2^{1/2}$ (by adding up the positive and negative deviations in quadrature)). Since the signal intensity is given by the Auger peak-to-peak height (APPH) (Fig. 6.14), the average noise of the background, σ_{dif} , is assumed to apply for both the positive and negative signal excursion, and by adding up in quadrature, according to (6.2), $(S/N)_{\text{dif}}$ is given by

$$\left(\frac{S}{N}\right)_{\text{dif}} = \frac{\text{APPH}}{\sqrt{2}\sigma_{\text{dif}}}, \quad (6.29)$$

and compared with the peak-to-peak height of the Auger line to obtain S/N or the uncertainty of the data.

For instruments operating in the pulse-counting mode, differential spectra can be obtained by computer differentiation. The most simple way is to subtract the counts in one channel (n_2) from that of another channel (n_1) separated by their energy difference ΔE on the kinetic energy scale, and divide the result by ΔE ($dN(E)/dE \approx (n_1 - n_2)/\Delta E$). Visualizing a triangular direct peak with $n_1(\rightarrow P)$ on top and $n_2(\rightarrow B)$ at background level, we see that $S/N = (n_1 - n_2)/(n_1 + n_2)^{1/2}$ corresponds to (6.2), and therefore, we have the same signal-to-noise ratio as for the direct spectrum. Considering another limiting case of many points in the peak area, n_1 approaches n_2 and we end up with an S/N value that is about $2^{1/2}$ times smaller than the former value, with the general case somewhere in between. A better signal-to-noise value may be obtained with the Savitzky–Golay method that combines differentiation with smoothing. Anthony and Seah [6.26] give a S/N ratio of 89% of that of the direct mode for the Cu (914 eV) peak for a 5-point Savitzky–Golay differentiation. As an example, Fig. 6.14 shows the differential of the $N(E)$ spectrum in Fig. 6.1, and Fig. 6.15 shows the magnified

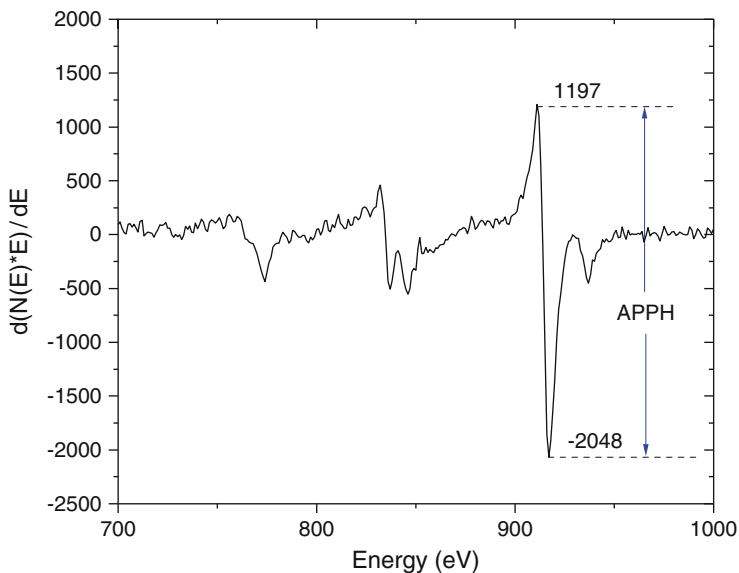


Fig. 6.14 Derivative spectrum of the Cu LMM (914 eV) Auger peak shown in Fig. 6.1 (5 point Savitzky–Golay differentiation), with $\text{APPH} = 3245$ a.u.

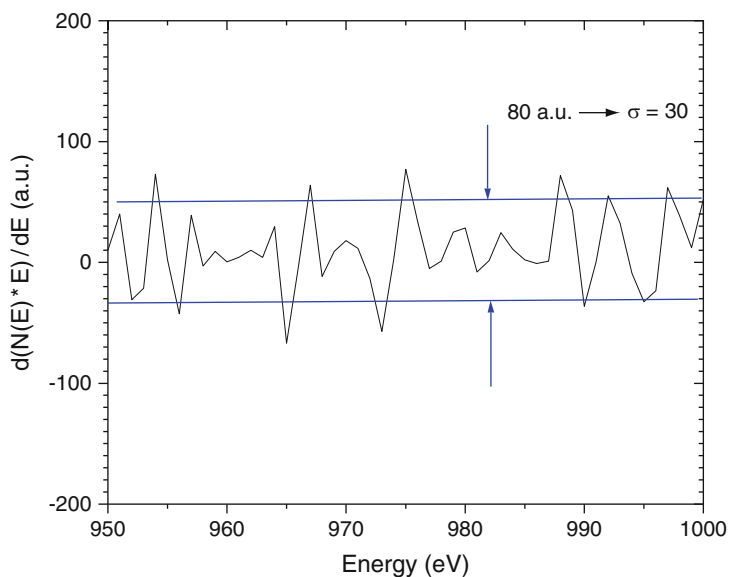


Fig. 6.15 Magnified background signal from Fig. 6.14 between 950 and 1000 eV. The maximum deviation is indicated, resulting in a mean uncertainty of $\sigma_{\text{dif}} = \pm 80 / (2 \times 2^{1/2}) = \pm 30$ a.u.

background with the operator's estimate of the maximum, "peak-to-peak" noise. Frequently, the experimentalist takes the APPH value divided by this value to get $S/N = 41$ for the example here. However, a more reasonable value is obtained when using the rms value σ of the noise. For a Gaussian distribution, the maximum noise with about 10% rejection of outlying data is 2.56σ [6.5], i.e., $\sigma = 31$ in Fig. 6.15. With that value in (6.29), we get $S/N = 3,245/(21/2\sigma) = 74$. This is almost a factor of 3 lower than the S/N for the direct spectrum, calculated from the P/B ratio [6.5]. Apparently, we can improve S/N further by smoothing. However, so-called improvement of S/N by smoothing has to be considered carefully. Smoothing can be considered as extracting the average of a measured value, therefore introducing inevitably a loss of information (e.g., small peaks are no more recognized) [6.12, 6.18] (see next paragraph).

6.2.7.3 S/N and Smoothing

Data manipulation by smoothing is generally applied in AES and XPS, particularly for noisy spectra to clearly reveal the peak shape that may be blurred by the noise [6.5–6.26]. Because smoothing is basically a convolution process, information is generally lost. This is obvious when smoothing is done by simple linear averaging between measured points that may wipe out fine features [6.25].

Because of the advantage of additional information from many measurement channels, smoothing clearly improves S/N as compared to the type of two-channel measurement discussed above. Basically, we need only two channels for an S/N figure of a peak, P and B . If we use more channels within the peak with the same time per channel, the total measurement time increases. For example, assuming a rectangular approximation as in Fig. 6.9, a 9-point smooth using nine channels within the peak would increase the measurement time by a factor of nine. Compared to one channel, the improvement in S/N ($\cong 9^{1/2}$) is a factor of 3. However, if we measure one channel with the energy width of the peak with the total measurement time of the nine channels, we get the same S/N improvement. Indeed, as shown by Evans and Hiorns [6.27], a Gaussian smoothing function operates like an increased spectrometer (energy) slit width, very similar to the discussion in Sect. 6.2.2 on the influence of analyzer resolution on S/N ratio. Obviously, by smoothing, we can gain in S/N ratio at the expense of loss of information, i.e., small spectral features are smeared out. Because this is anyway the risk in the optimized one-channel per peak measurement example above, it has been argued [6.5, 6.26] that it is generally better to measure with more than the minimum necessary channels and employ smoothing afterward, particularly since today Savitzky–Golay smoothing routines are part of any instrumental software. A most detrimental effect of extended smoothing is peak-shape distortion, notably the decrease of the original peak height [6.10].

In general, it is recommended to work with unsmoothed data as far as peak fitting, deconvolution, or peak synthesis procedures are concerned (see Sects. 3.1.7 and 4.4.1.2) [6.24]. Smoothing should be used carefully and only with the number

of points for smoothing given by the number of measurement channels within the FWHM of a spectral peak to be smoothed. Of course, any data manipulation should be disclosed in detail.

Smoothing will help to better recognize the most important spectral data. However, some detailed information, for example, small peaks in the vicinity of a larger peak, may be lost. A comparison of Savitzky–Golay and other smoothing algorithms is considered in detail by Gilmore and Seah [6.28]. Seah and Dench [6.10] conclude with the general warning that “the computer manipulation of spectral data can produce an output which appears to have a significantly greater certainty that is actually warranted by the statistical (scatter of) spectral data available.”

6.2.8 *S/N in Multichannel Detection*

Advanced instruments use multichannel detection as a convenient means to obtain parallel detection of a part of the spectrum (see schematic drawing in Fig. 2.15). Usually, several channeltrons in a row are placed in the dispersion plane at the exit of a hemispherical analyzer [6.29]. For example, the JEOL JAMP 7830F Auger spectrometer has seven channeltrons with one in the center (0), three to the left (+1, +2, +3), and three to the right (−1, −2, −3). There are three modes of operation: “Single,” “Sum,” and “Multichannel.” Each channeltron can be separately set in operation (“Single”) and acquires data in an energy channel that is separated from the adjacent one by an energy that depends on the analyzer resolution settings. For example, in the abovementioned instrument in the M5 mode (nominal energy resolution 0.39%), the addition of the single channels +3 and −3 in the “Sum” mode gives the two Cu LMM spectra in Fig. 6.16 that are shifted apart by 34 eV around the 914 eV peak by ± 17 eV. That means, the energy shift is about $34/7 = 4.9$ eV/channel corresponding to about 0.5% resolution in mode M5. The “Sum” of all seven channels together gives the spectrum in Fig. 6.17 with FWHM = 37 eV, roughly the distance of the channels that are widest separated. The “Sum” mode with two adjacent channels gives a slightly broader peak with a round top that is useful in elemental mapping because it is rigid against topographical effects that may influence the peak position. In the multichannel mode, the energy shift is corrected, and the channel counts add up to the final count rate, as seen in Fig. 6.18. If all seven channeltrons operate with the same efficiency, the count rate should increase linearly with the number of the channels. According to (6.19), in this case, the total $(S/N)_{\text{tot}}$ is expected to increase with the square root of the number of the channels, n_c , if $(S/N)_j$ is the signal-to-noise ratio for each single channel [6.29], as shown in Fig. 6.19,

$$\left(\frac{S}{N}\right)_{\text{tot}} = \left(\frac{S}{N}\right)_j \sqrt{n_c}. \quad (6.30)$$

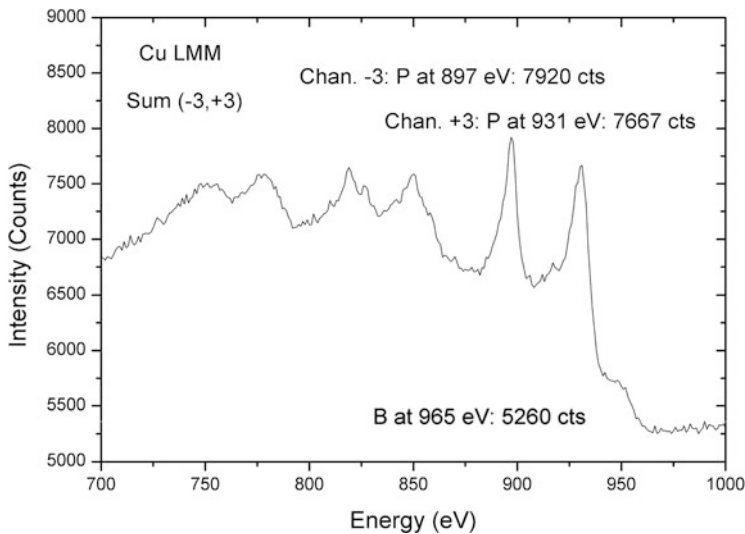


Fig. 6.16 “Sum” mode data acquisition of the Cu LMM peak with two channels -3 , $+3$ in the “M5” resolution mode, separated by 34 eV (914 ± 17 eV) (JEOL JAMP 7830F instrument)

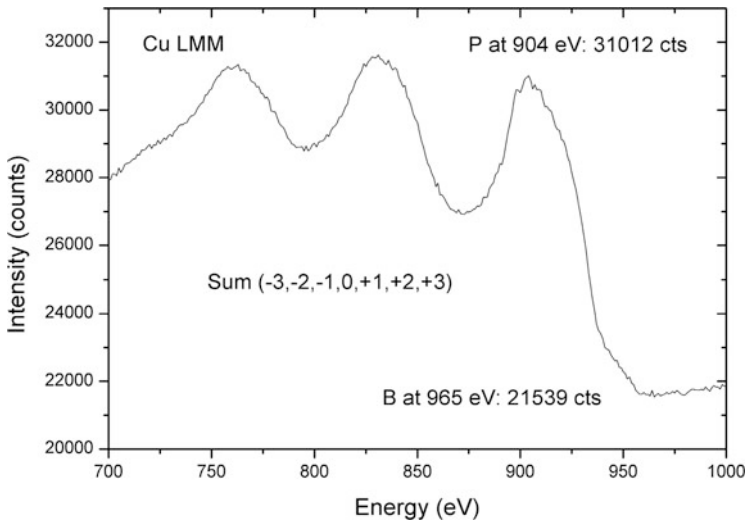


Fig. 6.17 “Sum” mode data acquisition of the Cu LMM peaks with all seven single channels in simultaneous operation, therefore the peak width is broadened to about 34 eV (JEOL JAMP 7830F instrument)

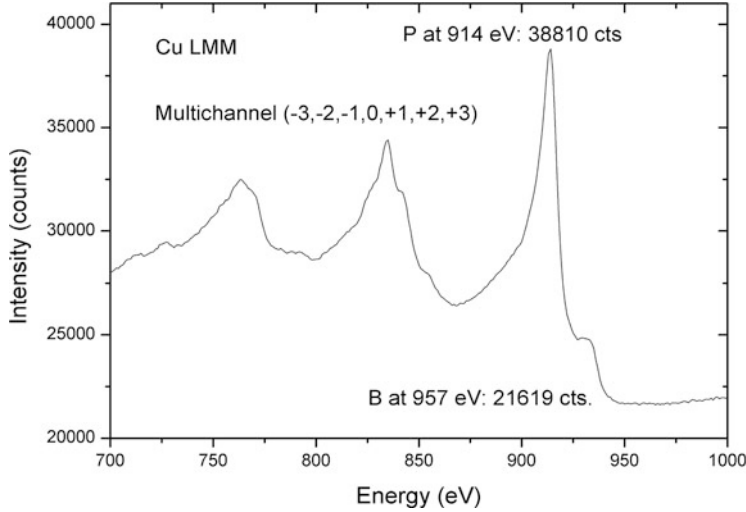


Fig. 6.18 “Multichannel” data acquisition mode of the Cu LMM peaks with correction of the energy shift in the “Sum” mode. Total peak intensity is the sum of all single peaks (JEOL JAMP 7830F instrument)

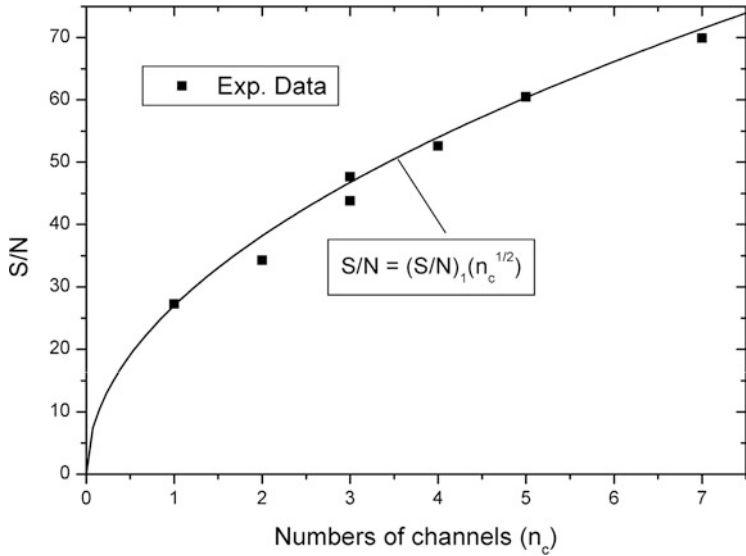


Fig. 6.19 Total S/N ratio as a function of the number of channeltrons ($n_c = 1 \dots 7$) of a multichannel detector. Measured points are for Cu LMM Auger peak, measured with a JEOL 7830F instrument. Solid line represents theoretical curve for a linear superposition of the counts with $(S/N)_1$ the average counts for a single channeltron

6.2.9 Uncertainty in Quantified Data and Strategy for Data Acquisition

While S/N ratios for a specified Auger peak (such as Cu LMM) are useful for testing instrumental performance and settings, applied surface analysis involves multielement analysis in a most efficient way with respect to the analytical aim and an adequate uncertainty of the result. Therefore, we have to deal with uncertainty in peak-intensity ratios and their effect on uncertainty of elemental concentrations limited by S/N ratios.

Ab initio quantification without standards (e.g., after (4.41)) requires knowledge of all relevant sample and instrument parameters that are generally not known. An absolute elemental sensitivity factor, S_A , is defined that gives a direct relation between the measured intensity, I_A , to the number of A atoms per unit volume, N_A , to the excitation intensity, I_p , with [6.18],

$$I_A = I_p S_A N_A. \quad (6.31)$$

The easiest way to find the concentration ratio of two elements in a multicomponent sample, X_1 , X_2 , is to correct the ratio of measured signal intensities I_1 , I_2 (total counts for peak heights, peak areas, or Auger peak-to-peak heights) with the respective relative elemental sensitivity factors, S_1 , S_2 ,

$$\frac{X_1}{X_2} = \frac{I_1/S_1}{I_2/S_2}. \quad (6.32)$$

Assuming sensitivity factors with no random error, the relative uncertainty, σ_{Ri} , of X_i is $\sigma_{Ri} = \sigma_i(I_i)/I_i$ because the sensitivity factors cancel out. Since the random errors of nominator and denominator add up in quadrature ((6.1) and (6.2)) to yield the total relative uncertainty of the mole fraction ratio,

$$\sigma_R \left(\frac{X_1}{X_2} \right) = \sqrt{\sigma_{R1}^2(I_1) + \sigma_{R2}^2(I_2)}. \quad (6.33)$$

The relative uncertainties σ_{R1} , σ_{R2} of I_1 , I_2 are given by the respective $1/(S/N)$ values after (6.4). Equation 6.32 shows that the higher uncertainty for a component always prevails, irrespective of the low uncertainty of the other [6.7].

The general quantification scheme (see (4.5)) assumes that all elements are detected, their peak intensities divided by the respective relative sensitivity factors S_i , the sum giving the total concentration of 100% or unity in the following calculations. The composition in mole fractions X_1 , X_2 , of elements 1 and 2 for a binary system, with abbreviation $I'_1 = I_1/S_1$, $I'_2 = I_2/S_2$ then given by

$$X_1 = \frac{I'_1}{I'_1 + I'_2} = \frac{I_1/S_1}{I_1/S_1 + I_2/S_2} \quad (6.34a)$$

and

$$X_2 = \frac{I'_2}{I'_1 + I'_2} = \frac{I_2/S_2}{I_1/S_1 + I_2/S_2}. \quad (6.34b)$$

Equations 6.34a and 6.34b mean that the uncertainty in the concentrations X_1 and X_2 is determined by the error in I_1 and I_2 . Following the treatment of Harrison and Hazell [6.7], with (6.1), we get for the absolute uncertainty σ in X_1 ,

$$\sigma^2(X_1) = \left(\frac{\partial X_1}{\partial I'_1} \right)^2 \sigma^2(I'_1) + \left(\frac{\partial X_1}{\partial I'_2} \right)^2 \sigma^2(I'_2). \quad (6.35)$$

With (6.34a) in (6.35), after differentiation and taking the square root, we get

$$\sigma(X_1) = \frac{1}{(I'_1 + I'_2)^2} \sqrt{I_2'^2 \sigma^2(I'_1) + I_1'^2 \sigma^2(I'_2)}. \quad (6.36)$$

Changing absolute uncertainties to relative uncertainties via $\sigma_R(I'_1) = \sigma(I'_1)/I'_1$ and $\sigma_R(I'_2) = \sigma(I'_2)/I'_2$, (6.36) gives

$$\sigma(X_1) = \frac{I'_1 I'_2}{(I'_1 + I'_2)^2} \sqrt{\sigma_R^2(I'_1) + \sigma_R^2(I'_2)}, \quad (6.37)$$

and with (6.34a) and (6.34b), we get

$$\sigma(X_1) = X_1 X_2 \sqrt{\sigma_R^2(I_1) + \sigma_R^2(I_2)}, \quad (6.38)$$

where $\sigma_R(I_1)$, $\sigma_R(I_2)$ refer now to measured intensities because the sensitivity factors cancel for relative intensity uncertainties. Taking the relative uncertainty in the mole fraction X_1 , $\sigma_R(X_1) = \sigma(X_1)/X_1$, (6.38) gives

$$\sigma(X_1) = X_2 \sqrt{\sigma_R^2(I_1) + \sigma_R^2(I_2)}, \quad (6.39a)$$

and similarly for X_2 ,

$$\sigma(X_2) = X_1 \sqrt{\sigma_R^2(I_1) + \sigma_R^2(I_2)}. \quad (6.39b)$$

It is obvious that, according to (6.38), (6.39a), and (6.39b), the absolute uncertainties of X_1 and X_2 have to be equal, but not the relative uncertainties.

Since uncertainties are given by the inverse S/N ratios, according to (6.4), the σ values in (6.39a) and (6.39b) can be expressed as

$$\sigma_R(I_1) = \frac{1}{\left(\frac{S}{N}\right)_1} = \left[\frac{\sqrt{P_1 + B_1}}{(P_1 - B_1)\sqrt{n_1}} \right] \quad (6.40a)$$

and likewise

$$\sigma_R(I_2) = \frac{1}{\left(\frac{S}{N}\right)_2} = \left[\frac{\sqrt{P_2 + B_2}}{(P_2 - B_2)\sqrt{n_2}} \right], \quad (6.40b)$$

with P_1 and P_2 the peak counts and B_1 and B_2 the background counts for element 1 and 2 for one sweep, respectively, and n_1 , n_2 are the number of sweeps for each element. Introduction of (6.40a) and (6.40b) in (6.39a) and (6.39b) gives for the relative uncertainties $\sigma_R(X_1)$, $\sigma_R(X_2)$ in concentrations X_1 , X_2 ,

$$\sigma_R(X_1) = X_2 \sqrt{\frac{P_1 + B_1}{(P_1 - B_1)^2 n_1} + \frac{P_2 + B_2}{(P_2 - B_2)^2 n_2}} \quad (6.41a)$$

and

$$\sigma_R(X_2) = X_1 \sqrt{\frac{P_1 + B_1}{(P_1 - B_1)^2 n_1} + \frac{P_2 + B_2}{(P_2 - B_2)^2 n_2}}. \quad (6.41b)$$

Equations 6.41a and 6.41b show the interdependence of the number of sweeps n_1 and n_2 that is the key to estimate the minimum data acquisition time for a required uncertainty. For example, let us consider a situation where element 1 is present with 90 at % and element 2 with 10 at %. Let us assume the following measured data for one sweep:

$$\begin{aligned} X_1 &= 0.9 (= 90\%) & X_2 &= 0.1 (= 10\%) \\ P_1 &= 200 \text{ counts/sweep} & P_2 &= 20 \text{ counts/sweep} \\ B_1 &= 100 \text{ counts/sweep} & B_2 &= 10 \text{ counts/sweep} \end{aligned}$$

According to (6.40a) and (6.40b), with the above values, we get $\sigma_R(I_1) = 0.1732/n_1^{1/2}$. That means, for one sweep ($n_1 = 1$), $\sigma_R(I_1) = 17.3\%$. For $\sigma_R(I_1) = 10\%$, three sweeps are necessary. Because $\sigma_R(I_2) = 0.548/n_2^{1/2}$, $n_2 = 30$ sweeps are required to arrive at $\sigma_R(I_2) = 10\%$. This corresponds to what we might have guessed intuitively. Since $\sigma_R(I_1)$ and $\sigma_R(I_2)$ influence each other for the uncertainty in the concentrations, we may add them up in quadrature and get $2^{1/2} \times 0.1$ or 7.1% for each single uncertainty. This means twice the number of sweeps for each element, i.e., 6 sweeps for X_1 and 60 sweeps for X_2 , with a total number of 66 sweeps. However, when we allow for different relative uncertainties for X_1 and X_2 , we can find a strategy that provides the minimum amount of sweeps for a required uncertainty in X_2 .

By rearranging Eq. 6.41b, we get

$$n_2 = \frac{(P_2 + B_2)}{(P_2 - B_2)^2} \frac{1}{\frac{\sigma_R^2(X_2)}{X_1^2} - \frac{(P_1 + B_1)}{(P_1 - B_1)^2} \cdot \frac{1}{n_1}}. \quad (6.42)$$

Addition of n_1 on both sides gives the total number of sweeps as a function of the number of sweeps for the more abundant element. For a required relative uncertainty

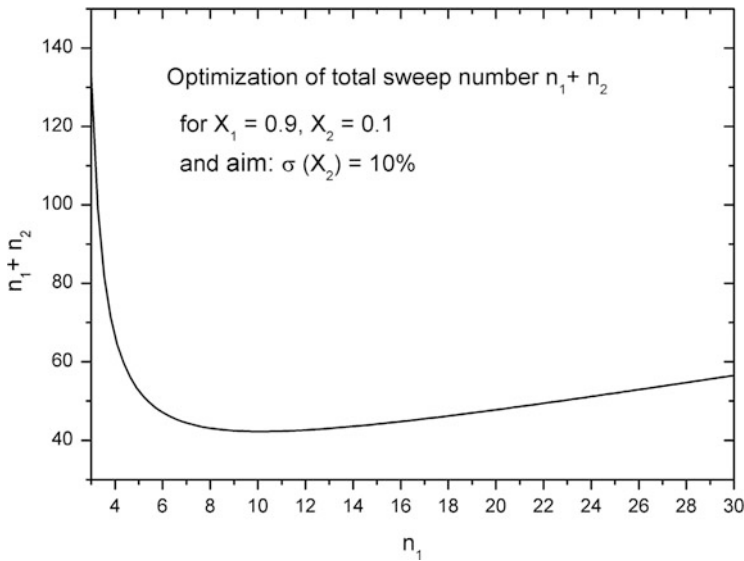


Fig. 6.20 For a binary system with major element $X_1 = 0.9$ and minor element $X_2 = 0.1$, a requested uncertainty of $\sigma(X_2) = 10\%$, the minimum after (6.46) with the data given in the text gives the minimal number of sweeps: for $n_1 = 10$, $n_1 + n_2 = 43$, i.e., $n_2 = 33$

of 10% ($\sigma_R(X_2) = 0.1$), $X_1 = 0.9$ and with the peak and background values of X_1 and X_2 values given above, (6.42) yields

$$n_1 + n_2 = \frac{30}{1.23 - \frac{3}{n_1}} + n_1. \quad (6.43)$$

Equation 6.43 is depicted in Fig. 6.20. It is recognized that the function has a minimum at $n_1 + n_2 = 43$ sweeps in total, with $n_1 = 10$ and $n_2 = 33$. This yields $\sigma_R(X_2) = 9.9\%$ and $\sigma_R(X_1) = 1.1\%$. What is against an intuitive approach is the fact that, according to Fig. 6.20, for a required uncertainty, the total number of sweeps and therefore the acquisition time decreases when the number of sweeps for the major element is increased. If an insufficient number of sweeps for that element is collected, for example, if $n_1 = 4$, it will take $n_1 + n_2 = 67$, i.e., an increase of more than 50% in acquisition time, to obtain $\sigma_R(X_2) = 10\%$.

In conclusion, (6.42) can be used to find the optimum strategy for data acquisition. At first, from a first sweep, we can take the peak and background data for the two elements, get a rough estimate of the concentrations by using relative elemental sensitivity factors, for example, after (6.34a) and (6.34b), and assume a required value $\sigma_R(X_2)$ for the uncertainty of the minor element. Then, the minimum of total sweeps can be found either by plotting (6.42) in the way of Fig. 6.20 or directly by differentiation after n_1 .

As shown by Harrison and Hazell [6.7], in case of several (n) elements, (6.38) can be generalized to give

$$\sigma_R(X_i) = \sqrt{(1 - X_i)^2 \sigma_R^2(I_i) + \sum_{j \neq i}^n X_j^2 \sigma_R^2(I_j)}, \quad (6.44)$$

with $\sigma_R(I_i)$ values given by (6.40a) and (6.40b). Equation 6.44 shows that, even when an element is not detected or when it is neglected in data evaluation, the respective error increases that of the elements taken into account.

6.3 *S/N* Ratio for Analog Systems

There are different reasons to work in the analog mode: Practically, all instruments built until 1980 (and some auxiliary equipment) were not computerized, and therefore, they were working in the analog, current amplifying mode. The second reason is that high count rates lead to nonlinear relations between true and measured counts because of multiplier dead time, and therefore, the multiplier has to be operated in the current amplification mode in case of too-high count rates [6.24]. Then, the output is digitized by a voltage/frequency (V/f) converter. Another reason is the aim to avoid additional sources of noise (and errors), for example, of multipliers, as done in the metrological CMA by Goto et al. [6.30]. Goto's instrument works with a Faraday cup combined with a linear current amplifier to display the data on an x - y recorder or to store them after V/f conversion.

Seah and Hunt [6.5] consider in detail the relation between different analog and digital measurements with respect to S/N ratios. If the mean gain of the multiplier-amplifier is g_0 (and setting the detector efficiency to unity), the count rate in the interval t is n_p , and the signal intensity (S) is $n_p \times t \times g_0$. Since the variance of g_0 is g_0^2 , the noise (N), given by the sum of the variances of peak and background uncertainties of the electron input current and of the gain, giving

$$N^2 = n_p t g_0^2 + n_B t g_0^2. \quad (6.45)$$

Thus, for $n_p \approx n_B$,

$$\frac{S}{N} = \sqrt{\frac{n_p t}{2}} = \sqrt{\frac{I_A t}{2e}}, \quad (6.46)$$

with the signal current of A, I_A (in A) and the elementary charge e (in As).

Equation 6.46 is valid for a fixed time interval t , as in the V/f conversion mode of a digital instrument. In current-measurement systems, the counts are damped with an exponential decay time τ , and S/N is approximately given by [6.5]

$$\frac{S}{N} = \sqrt{n_p \tau} = \sqrt{\frac{I_A}{e}} \tau. \quad (6.47)$$

It is obvious that the time constant τ has a similar effect on current measurement as computer smoothing has on pulse-count data. If the time constant is larger than the time necessary to sweep through a considerably changing signal intensity, the shape of the spectrum is distorted. As a rule of thumb, the time constant should match the resolved energy interval for a sweep with that time. For example, if the change in 1 eV should be resolved without changing the signal shape, for a sweep of 1 eV/s, a time constant of ≤ 1 s is appropriate.

Since generally the gain of amplifiers is not known, the S/N value has to be determined from the data (whether in direct or differential mode) in the manner described in Sect. 6.2.7. If there is only a chart recorder available, a change of the magnification by a factor of 10 in the background region will show the scatter from a straight line and the peak-to-peak noise can be estimated by eye, rejecting about 5–10% of the most extreme points. After having drawn the two respective lines (see Fig. 6.15), the rms noise ($=\sigma$) is about 1/3 of the distance of the lines [6.5].

For high count rates (e.g., $>10^6$ cps), the dead time of the multiplier causes an apparent reduction of the count rate. Therefore, current measurement is used that is converted to a count rate by a voltage-to-frequency (V/f) converter [6.5, 6.6]. However, the pulses from a V/f converter no longer correspond to single-electron events and therefore (6.3) is not valid here, and the rms background noise for V/f data has to be measured directly. (Of course, this can be done in pulse-counting systems, too.) Note that – in contrast to (6.3) where the rms background noise corresponds to the square root of B – the directly measured noise includes other noise sources as well (see Fig. 6.21). A simple procedure for the background measurement of the Cu LMM (914 eV) peak of a pure sputter cleaned Cu surface is, for example, given in the technical specifications of the PHI 700 instrument [6.6]: Measurement should be done at 0.2 eV steps with 1 s total dwell time (e.g., 50 ms per point times 20 sweeps), and the region between 961 and 975 eV is used to determine the rms noise of the background. To achieve this, the data (number n) are fitted to a second-order polynomial of the form $f(E) = AE^2 + BE + C$ (this takes into account a slight background curvature with energy). If the value of the fit at energy I is f_i , and the measured data value in the energy channel is d_i , then the rms noise is given by the least squares deviation [6.6]

$$N(B) = \sqrt{\frac{1}{n} \sum_{i=1}^n (d_i - f_i)^2}. \quad (6.48)$$

When only the background noise $N(B)$ is considered, as done in a PHI technical note [6.6], $S/N = (P-B)/N(B)$ with S the Cu signal counts ($P-B$) at the peak maximum (about 918 eV). As discussed in Sect. 6.1.1, it is more realistic to take additionally into account the noise in the signal. Taking the noise proportional to the square root of the signal intensity, $N(S) = (P/B)^{1/2} \times N(B)$, then the total

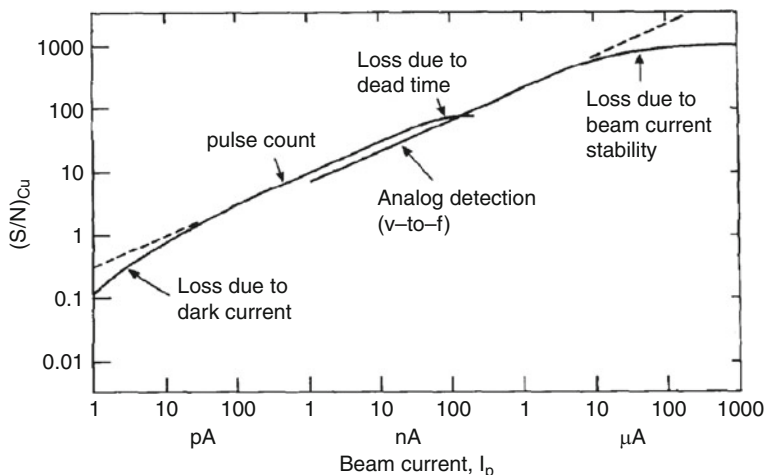


Fig. 6.21 Typical dependence of the signal-to-noise ratio, $(S/N)_{Cu}$ on the primary beam current, I_p , for pulse counting and analog detection, for the Cu LMM (914 eV) Auger peak ($I_p \propto I_A$ in (6.46), (6.47)), with 60 ms channel dwell time. The square root dependence of counting statistics is limited by additional noise sources indicated in the figure (Reproduced with permission of Elsevier B.V. from M.P. Seah and P.J. Cumpson [6.29]. Crown Copyright 1993.)

noise is the square root of $N(B)^2 + N(S)^2$, giving

$$N = N(B) \sqrt{\frac{P}{B} + 1} \text{ and } \frac{S}{N} = \frac{(P - B)}{N(B) \sqrt{\frac{P}{B} + 1}}. \quad (6.49)$$

Note that if $N(B)$ is defined by $B^{1/2}$, (6.49) is identical with (6.10). A simple computing facility is needed to do the fit of (6.48) (a convenient software is provided with PHI instruments).

A detailed consideration of S/N comparison in different analog and digital systems (including beam blanking techniques) can be found in Refs. [6.5,6.18,6.29]. Figure 6.21 shows a comparison of the signal-to-noise ratio of pulse-counting and analog detection methods for the Cu LMM peak as a function of the primary beam current after Seah and Cumpson [6.29]. Deviations lowering the square-root dependence predicted by (6.47) are caused by additional sources of noise such as intrinsic noise at low beam current (“dark current”), multiplier dead time, or voltage/current supply stability at high beam current.

References

- 6.1. E. Rabinovicz, *An Introduction to Experimentation* (Addison-Wesley Publ. Comp., Reading, 1970)
- 6.2. ISO 18115, *Surface Chemical Analysis – Vocabulary* (International Organization for Standardization, Geneva, 2001)

- 6.3. J. Cazaux, *Surf. Sci.* **140**, 85 (1984)
- 6.4. M.F. Koenig, J.T. Grant, *Surf. Interface Anal.* **7**, 217 (1985)
- 6.5. M.P. Seah, C.P. Hunt, *Rev. Sci. Instrum.* **59**, 217 (1988)
- 6.6. *Physical Electronics Techn. Bulletin*, No. 9501 (1995)
- 6.7. K. Harrison, L.B. Hazell, *Surf. Interface Anal.* **18**, 368 (1992)
- 6.8. S. Hofmann, *Mikrochim. Acta* **I**, 321 (1987)
- 6.9. S. Clough, *PHI Techn. Bull.* **1983**
- 6.10. M.P. Seah, W.A. Dench, *J. Electron Spectr.* **48**, 43 (1989)
- 6.11. M.P. Seah, *Surf. Interface Anal.* **2**, 222 (1980)
- 6.12. P.M.A. Sherwood, Data Analysis in XPS and AES, in *Practical Surface Analysis, Vol. 1: AES and XPS*, 2nd edn., ed. by D. Briggs, M.P. Seah (Wiley, Chichester, 1990), pp. 555–586.
- 6.13. M.P. Seah, *Surf. Interface Anal.* **20**, 865 (1993)
- 6.14. Z.J. Ding, W.S. Tan, Y.G. Li, *J. Appl. Phys.* **99**, 084903 (2006)
- 6.15. K. Tsutsumi, Y. Nagasawa, T. Tazawa, *JEOL News E* **42**, 45 (2007)
- 6.16. M.P. Seah, I.S. Gilmore, S.J. Spencer, *J. Electron Spectrosc. Relat. Phenom.* **104**, 73 (1999)
- 6.17. ISO 21270, *Surface Chemical Analysis – X-ray Photoelectron and Auger Electron Spectrometers – Linearity of Intensity Scale* (International Organization for Standardization, Geneva, 2003)
- 6.18. P.J. Cumpson, M.P. Seah, *Surf. Interface Anal.* **18**, 361 (1992)
- 6.19. M.P. Seah, *Surf. Interface Anal.* **20**, 876 (1993)
- 6.20. M.P. Seah, G.C. Smith, *Surf. Interface Anal.* **15**, 751 (1990)
- 6.21. M.P. Seah, G.C. Smith, *Surf. Interface Anal.* **17**, 855 (1991)
- 6.22. M.P. Seah, *Surf. Interface Anal.* **20**, 243 (1993)
- 6.23. J.P. Langeron, L. Minel, J.L. Vignes, S. Bouquet, F. Pellerin, G. Lorang, P. Ailloud, J. Le Hericy, *Surface Sci.* **138**, 610 (1984)
- 6.24. P.J. Cumpson, M.P. Seah, *Surf. Interface Anal.* **18**, (1992) 345.
- 6.25. M.P. Seah, W.A. Dench, B. Gale, T.E. Groves, *J. Phys. E Sci. Instrum.* **21**, 351 (1988)
- 6.26. M. Anthony, M.P. Seah, *J. Electron Spectrosc.* **32**, 73 (1983)
- 6.27. S. Evans, G. Hiorns, *Surf Interface Anal.* **8**, 71 (1986)
- 6.28. I.S. Gilmore, M.P. Seah, *Appl. Surf. Sci.* **93**, 273 (1996)
- 6.29. M.P. Seah, P.J. Cumpson, *J. Electron Spectrosc. Relat. Phenom.* **61**, 291 (1993)
- 6.30. K. Goto, N. Sakibara, Y. Takeichi, Y. Numata, Y. Sakai, *Surf. Interface Anal.* **22**, 75 (1994)

Chapter 7

Quantitative Compositional Depth Profiling

Any quantitative surface analysis has to be based on knowledge of the in-depth distribution of composition (Sects. 4.3.3 and 4.4.3). Obtaining information on the latter is the main purpose of any depth profiling method. There are two different approaches: nondestructive and destructive depth profiling. Whereas nondestructive methods (such as angle-resolved XPS, Sect. 7.2.1) give indirect composition – depth information, the destructive method of sputter depth profiling has the great advantage of immediately presenting an image of the in-depth distribution of composition (with more or less obvious distortions). Because of their relatively moderate matrix effects, AES and XPS in combination with argon ion bombardment have become the most popular tool for depth profiling of major components in thin films, with a clear preference of AES depth profiling as explained in Sect. 7.1.6.

Any method of depth profiling does not yield an exact image, but at best, a somewhat broadened image of the in-depth distribution of composition, which is roughly characterized by the value of the depth resolution. Understanding the parameters that determine the latter is the basis of optimized depth profiling. The normalized intensity as a function of depth can be described by a convolution of the true in-depth distribution of an elemental concentration by a depth resolution function, the mathematical form of which is determined by the physical mechanisms that cause profile blurring. Therefore, deconvolution and profile reconstruction are the main tasks in quantitative evaluation of depth profiles.

This chapter gives an overview of the main destructive and nondestructive profiling techniques, with special emphasis on sputter depth profiling (SDP) as the most important technique in many applications and on recent advances in quantification of measured profiles by the so-called MRI model (Sect. 7.1.8). Reviews on SDP are given in Refs. [7.1–7.8].

7.1 Sputter Depth Profiling

In the context of depth profiling, sputtering means bombardment of a surface with energetic primary particles (usually ions between 0.1 and 5 keV kinetic energy) that causes surface erosion by emission of secondary particles from the sample. With increasing sputtering time, layers beneath the original surface are subsequently exposed to surface analysis. Thus, there are two ways to obtain the in-depth distribution of composition as a function of the sputtered depth: either by analysis of the sputtered matter, as in SIMS and SNMS (see Sect. 10.4.3), or by analysis of the remaining surface, as in AES, XPS, and ISS [7.3]. These two types of methods are markedly different with respect to elemental composition and sensitivity, dynamic range, information depth, etc. The sputtering process itself, however, is independent of the analysis method and should therefore be considered as a separate physical process. Sputtering can be accomplished by removing atoms mainly from the first monolayer of a solid [7.9, 7.10]. Therefore, a depth resolution in the monolayer range should in principle be achievable. However, sputtering does not occur by an ideal layer-by-layer removal but is the result of a complex ion beam – sample interaction process. This process introduces a variety of distortional effects in the original morphology and composition of samples, which are the cause of the generally observed profile broadening and shape changes [7.1–7.3].

Progress in understanding the main physical processes and parameters involved in sputter erosion, as well as its implications in specific surface analysis methods, has led to a general framework of optimized profiling conditions for the achievement of high depth resolution. However, quantitative theories of depth profiling are still limited to special, simple cases.

7.1.1 Instrumentation and Experimental Setup

Instrumentation for depth profiling with AES or XPS requires a source of energetic ions impinging on the sample surface and subsequent analysis of the residual surface after a given sputtering time. In modern instruments, the ion gun is a differentially pumped device capable of producing a well-focused beam with an energy typically in the 0.5 – 5 keV range and with $x - y$ deflection plates to provide beam alignment and raster over an area of up to several mm (see Sect. 2.4). Most instruments have a possibility of azimuthal sample rotation (in the sample plane), which is necessary for high-resolution profiles of metallic samples [7.1, 7.3] (see Sect. 7.1.9.2).

The basic procedure of depth profiling consists of recording the intensity of element-specific peaks detected with the electron analyzer as a function of the sputtering time. For constant ion energy and beam current density, the latter is proportional to the sputtered depth if the sputtering rate does not change with time.

The following three steps are necessary for setting up depth profiling experiments: (a) ion beam current adjustment at a specific ion beam energy (accelerating voltage) and incidence angle, (b) ion beam irradiation position adjustment

(center point), and (c) ion beam scanning parameters adjustment (scanning width and direction). Reference specimens, for example, $\text{Ta}_2\text{O}_5/\text{Ta}$ with known oxide layer thickness, are frequently used to optimize the adjustments mentioned above [7.1–7.4]. Details on the use of reference samples in-depth profiling are given in two ISO documents [7.11–7.14].

The ion beam current density is generally optimized for useful beam current and minimum beam spot size. The maximum ion beam current is obtained by adjusting the ion beam intensity, mainly through the emission current, voltage, and focus of the gun. The minimum ion beam spot size is obtained by focusing the beam while observing an ion-induced secondary electron image. Typical ion gun conditions are 1 μA specimen current measured at the biased specimen at 10 mA emission current and 3 keV beam energy, focused into a spot of diameter of the order of 50 μm and rastered over a $1 \times 1 \text{ mm}^2$ area. The ion beam center point should be adjusted to coincide with the center of the electron beam (AES) or X-ray (XPS)-induced secondary electron image. This can be done simply by using a Faraday cup placed at the normal sample position. The incidence angle, defined with respect to the normal to the specimen surface, and the beam energy, should be chosen with regard to specific aspects of the particular specimen. A high beam energy and/or low incidence angle results in a high etching rate and is preferable for rough samples (see Sect. 7.1.4). For flat, smooth sample surfaces, low beam energy and/or high incidence angle results in high depth resolution but low sputtering rate. Because the current density varies across the static ion beam diameter, there will always be crater-edge effects (see Sect. 7.1.9) [7.12]. These effects can be minimized by making the ion beam scan area significantly larger (e.g., 10 times) than the analyzed area. Typical crater sizes in AES are of the order of 1 mm^2 . For conventional XPS, this is not enough for reasonable resolution. However, modern small-spot XPS instruments with analyzed area less than 100 μm can also give well-resolved depth profiles with scanned area of 1 mm^2 .

It is essential that the ion beam parameters are constant with time to ensure a constant sputtering rate. A thermostatically stabilized argon leak valve has been found useful to ensure this condition.

There are two possible modes of data acquisition and sputtering, the continuous mode and the discontinuous mode. In the continuous mode, data are recorded continuously during ion beam sputtering. This mode enables fast data acquisition. Furthermore, if the background pressure in the system is not sufficiently low, problems with surface contamination can be avoided. One disadvantage of this mode is a decrease of the signal-to-noise ratio, mainly caused by an increase of ion-induced secondary electrons. A further disadvantage is that Auger electrons are emitted from atoms and clusters which have just been removed from the surface. These particles are in a different chemical environment compared to the surface and bulk atoms. This fact often results in shifts and/or changes of the shapes of the corresponding Auger-electron and photoelectron peaks [7.15]. Furthermore, the profile may be blurred by additional emission from outside the analyzed area, particularly from the crater edge [7.16].

To overcome the abovementioned disadvantages, the discontinuous mode is usually performed. In this mode, sputtering and data acquisition steps are alternating, i.e., sputtering is stopped before data acquisition and vice versa. A prerequisite of this mode is that the residual pressure in the vacuum system is sufficiently low to avoid surface contamination during data acquisition (see Sect. 2.1).

Before the start of depth profiling, a careful check whether the (focused) ion beam is impinging in the center of the analyzed area is necessary. For example, this can be done in AES by monitoring the secondary electron signal while sputtering through a thin silicon dioxide layer. In XPS, a marker is frequently used. For example, the focused ion beam is impinging on a thin film (usually 30 nm thickness) of Ta₂O₅ on Ta with a marker, for example, consisting of grid-shaped scratches. After visual inspection, the ion gun spot can be directed with the x-y plate voltages and tested again until matching with the analyzed area center (or with the impinging photon beam in small-spot XPS) is achieved. The ion gun parameters (argon pressure, emission current, raster size, and voltage) and the incidence angle (sample tilt) should have values for which previously the sputtering rate for a Ta₂O₅/Ta reference sample of known thickness was obtained [7.13, 7.14]. This helps to estimate the depth scale and to choose an appropriate sputtering cycle time with respect to the measurement “resolution” required. For example, if 100 data points for a total profile are required, and an estimated (Ta₂O₅) sputtering rate is 4 nm/min, a total profiling depth of 100 nm with 1 nm per data point means a sputtering cycle time of 15 s. With 5 nm per data point, 75 s sputtering cycle time would be adequate and yields 100 points for 500 nm sputtered thickness. Note that in the first case, the data acquisition cycle for several peaks with an appropriate number of sweeps usually takes more time than the sputtering cycle. It has been found helpful to run a few Ta₂O₅/Ta samples of known thickness (BCR reference samples [7.17, 7.18] or secondary standards), for example, 30 nm, with several well-defined ion gun settings and sample tilt parameters in order to have a fairly reproducible sputtering rate. Fortunately, the sputtering rate for Ta₂O₅ is close to that of Ni, Fe, Cr (less than 20% deviation at 45° incidence angle) (Table 7.1).

Modern AES/XPS sputter depth analysis systems are equipped with a sample rotation facility that helps to improve the depth resolution (Sects. 7.1.3 and 7.1.6). Sputtering at a fixed ion incidence angle (particularly in the vicinity of 30–45°, see Fig. 7.1) will lead to a very high surface roughness in polycrystalline metallic materials and therefore to a degraded depth resolution (Sect. 7.1.6). Special alignment procedures are necessary if the specimen is rotated (Sect. 7.1.9). To ensure an identical analyzed spot during measurement, the area for analysis has to be placed as close as possible to the rotation center of the specimen holder. Any clips on the top of the specimen should be far enough away from the area of interest so they do not mask the ion beam at any angle. When the specimen is in the analysis position, the central position can be quickly established by turning the azimuthal gear manually. The SEM image then rotates, and the axis of rotation can be estimated. Having found the axis of rotation, it is important to set up the velocity and number of steps

Table 7.1 Sputtering yield (atoms/ion) of selected elements for Ar⁺ ions with 1 keV energy and 45° incidence angle, reproduced from Ref. [7.19]. Sputtering rate ratios of oxides were adapted from Ref. [7.26] and referred to Ta₂O₅ instead of SiO₂, and they were connected with sputtering yield values after expression (7.4b)

Element or oxide	Sputtering yield [1 keV] (atoms/ion)	$M/(n\rho)(\text{cm}^3/\text{g-atom})$	Sputtering rate ratio to Ta ₂ O ₅ (1keV)
⁶ C	0.98	5.21	0.31
¹² Mg	4.90	14.0	4.5
¹³ Al	2.71	10.0	1.8
¹⁴ Si	1.63	12.0	1.3
²² Ti	1.55	10.55	1.1
²⁴ Cr	2.77	7.23	1.3
²⁶ Fe	2.81	7.08	1.3
²⁷ Co	3.00	6.62	1.3
²⁸ Ni	3.08	6.60	1.3
²⁹ Cu	4.00	7.09	1.9
³¹ Ga	3.57	11.43	2.7
³² Ge	2.32	13.65	2.1
³³ As	10.0	13.07	8.6
⁴¹ Nb	1.65	10.48	1.2
⁴² Mo	2.15	9.39	1.3
⁴⁶ Pd	4.62	8.87	2.7
⁴⁷ Ag	5.77	10.27	3.9
⁴⁹ In	4.56	15.70	4.7
⁷² Hf	1.75	13.40	1.5
⁷³ Ta	1.60	10.87	1.1
⁷⁴ W	1.62	9.53	1.0
⁷⁸ Pt	2.80	9.10	1.7
⁷⁹ Au	4.19	10.21	2.8
⁸² Pb	4.94	18.23	5.9
⁸³ Bi	5.39	21.43	7.5
Al ₂ O ₃	1.8	5.13	0.62, (0.57)
SiO ₂	2.7	7.58	1.35
TiO ₂	1.8	6.30	0.73
Cr ₂ O ₃	2.0	5.83	0.72, (0.72)
Fe ₂ O ₃	2.0	6.10	0.82, (0.82)
Fe ₃ O ₄	2.5	6.39	(1.03)
ZnO	3.0	7.25	1.41
CeO ₂	1.4	7.50	0.70
HfO ₂	1.5	7.25	0.72
ITO ^{*)}	2.54	7.68	1.41
Ta ₂ O ₅	1.97	7.70	1.00

Data in parenthesis are from Ref.[7.25]

*)In–Sn oxide

on the rotation controller to achieve a whole number of rotations in the time given for one sputter cycle. In practice, the condition $u_{\min}/\dot{z} > 1 \text{ nm}^{-1}$ should be fulfilled, where $u_{\min}$ is the minimum speed of rotation (1/min) and $\dot{z}$ is the sputtering rate in nm/min (see Sect. 7.1.9.2).

7.1.2 Basic Quantification of Composition and Sputtered Depth

Common to all sputter depth profiling work are the following considerations: the finally required result is the in-depth distribution of elemental composition, i.e., the concentration, X , as a function of depth z , $X(z)$, is the required result. The raw data, however, consist of the elemental signal intensity, I , as a function of the sputtering time, t , $I(t)$ [7.1–7.4]. Therefore, the following three fundamental tasks have to be carried out:

1. Conversion of the measured sputtering time into sputtered depth, $z = f(t)$
2. Conversion of the measured signal intensities to concentrations, $X = f(I)$
3. Assessment of the depth resolution (Δz) (and, if possible, the depth resolution function which is necessary for advanced quantification, see Sects. 7.1.7 and 7.1.8)

A quality figure of any depth profile is the depth resolution, which characterizes the deviation of the measured profile shape from the exact shape of the original in-depth distribution. The main causes of this deviation are compositional and topographical changes in the surface region brought about by ion beam/sample interactions, which limit the accuracy of a measured profile. The latter determines the resolved depth, usually called depth resolution Δz .

It should be noted that the above three tasks are closely coupled and can only be separated in a first-order approximation. From a conceptual viewpoint, most desirable is a quantitative deconvolution, i.e., a mathematical procedure which is able to directly convert the measured profile into a quantified in-depth distribution of composition. In favorable cases, this can be done by a transfer function, generally called depth resolution function (DRF), which will be explained in Sect. 7.1.8. However, the basic task of estimation of the (average) sputtering rate has to be done before as explained in the following.

7.1.2.1 Conversion of Sputtering Time to Sputtered Depth

The primary result of a depth profiling experiment is a sputtering timescale instead of the requested depth scale. The key parameter for the conversion of sputtering time t into sputtered depth z is the instantaneous sputtering rate $dz/dt = \dot{z}$. Assuming a constant primary ion current density, the sputtering time is proportional to the aerial

dose density of the bombarding ions. The sputtered depth $z(t_1)$ at sputtering time t_1 is determined by

$$z(t_1) = \int_0^{t_1} \dot{z}(t) dt, \quad (7.1)$$

with the sputtering rate $\dot{z}$ given by

$$\dot{z} = \frac{j_I Y_M}{eN}, \quad (7.2)$$

with the primary ion current density j_I (A/m²), the elementary charge e (1.6×10^{-19} A s), the total sputtering yield Y_M (atoms/ion), and the atomic density N (atoms/m³). Knowledge of N , measurement of j_I (e.g., with a Faraday cup), and taking Y_M from literature data [7.19, 7.20], gives $\dot{z}$. Assuming constant Y_M and N , the sputtering rate $\dot{z}$ is constant, and

$$z = \dot{z}t \quad (7.3)$$

provides a direct conversion of sputtering time to depth. Because most often Y_M and j_I and sometimes even N are not available with adequate accuracy, it is customary to use experimental methods for determination of the sputtered depth z_1 obtained after a certain sputtering time t_1 and determine the sputter rate $\dot{z} = z_1/t_1$ after (7.3). Different methods of sputtered depth measurement are summarized in ISO/TC 201 technical reports [7.12, 7.14]. Frequently, the sputter crater depth is measured by mechanical stylus techniques [7.21] or by optical interference microscopy [7.22]. The accuracy obtained with both techniques is about 10 nm [7.14]. Systematic errors may occur due to oxide layer formation at the crater bottom when the sample is brought up to air, or possible swelling of the surface layer when reactive ion bombardment is employed, for example, with oxygen ions [7.23]. Because it assumes a constant erosion rate, crater depth measurement is most appropriate for low concentration dopant profile analysis in a uniform matrix, for example, SIMS profiles of B in Si. For layered structures with different sputtering rate for each layer, it is better to measure the thickness of the respective layers by an independent method such as TEM or SEM and, in that way, determine z_1 and compare it with the sputtering t_1 needed to sputter through the respective layer. A more indirect method is sputtering through a thin metallic or oxide layer of known thickness and composition (most often Ta₂O₅/Ta of which reference samples are available [7.17, 7.18]) and then give the depth in Ta₂O₅ depth equivalents or find the correct value by multiplying with the sputtering rate ratio to the material under study [7.13, 7.14]. For example, if the sputtering rate of sample m is $\dot{z}(m)$ and the sputtering time for a given sample feature is $t(m)$, and that for the reference Ta₂O₅ sample is $t(\text{Ta}_2\text{O}_5)$ and the sputtering rate is $\dot{z}(\text{Ta}_2\text{O}_5)$, the depth scale for m , $z(m)$, is given by [7.14]

$$z(m) = z(\text{Ta}_2\text{O}_5) \frac{t(m)}{t(\text{Ta}_2\text{O}_5)} \frac{\dot{z}(m)}{\dot{z}(\text{Ta}_2\text{O}_5)}. \quad (7.4a)$$

Calculated sputtering yields for the elements can be found, for example, in [7.19] based on semiempirical equations [7.20] and for oxides in [7.24–7.26]. Sputtering yields of a few selected elements and oxides bombarded with 1-keV Ar^+ ions incident at 45° are compiled in Table 7.1. Since the relative sputtering rate after (7.4a) is most important in-depth profiling, it is additionally given in Table 7.1. According to (7.2), the ratio of sputtering rates of two elements or compounds A and B and their sputtering yields (atoms/ion) are connected with the atomic density N_A, N_B by

$$\frac{\dot{z}_A}{\dot{z}_B} = \frac{Y_A N_B}{Y_B N_A} = \frac{Y_A (\rho_B n_B / M_B)}{Y_B (\rho_A n_A / M_A)} = \frac{Y_A a_A^3}{Y_B a_B^3}, \quad (7.4b)$$

where $\rho_{A,B}$, $M_{A,B}$, $n_{A,B}$, and $a_{A,B}$ are the density, mole mass, number of atoms per mole, and atomic distance of element A and B, respectively. The sputtering rate ratio is practically independent of ion energy (between 0.5 and 5 keV) and of the ion incidence angle below 50° [7.24, 7.27]. However, absolute sputtering rates increase approximately with the square root of the energy up to 5 keV [7.13, 7.17, 7.26, 7.28, 7.29].

All the mentioned methods of depth scale determination only give an average sputtering rate. However, the instantaneous sputtering rate usually depends on composition. In particular, when sputter profiling through an interface, more elaborate methods of determination of the instantaneous sputtering rate $\dot{z}(t)$ have to be employed. Experimentally, this can be done, for example, by in situ laser interferometry [7.30], by X-ray emission analysis of a residual film overlayer [7.31], or by determination of the mass of the sputtered material [7.32].

In general, in situ monitoring methods of $\dot{z}(t)$ are not available, and the instantaneous sputtering rate can only be estimated, for example, by assuming a linear dependence on composition [7.5, 7.4]. For two components A, B, with known sputtering rates $\dot{z}_A$ and $\dot{z}_B$, this means

$$\dot{z}(t) = \dot{z}_A X_A + \dot{z}_B X_B, \quad (7.5)$$

where X_A, X_B are the mole fractions of components A and B at sputtering time t .

Inserting (7.5) in (7.3) yields conversion of sputtering time to sputtered depth [7.33–7.35]. An example of such a conversion is shown in [7.31] for Ni/Cr multilayer samples profiled with 1 keV N_2^+ ions, where $\dot{z}_{\text{Ni}}/\dot{z}_{\text{Cr}} \approx 3$. Of course, the linear correction after (7.5) is only a first-order approximation, and deviations are expected particularly if sputtering-induced changes of surface binding energies and of topography occur. In Ta/Si multilayer profiling with AES, (7.4) with a sputter rate ratio of about 1:4 was successfully applied to model the measured profile [7.33], although an unexplained shoulder in the profile was later shown to be caused by a slowing down of the sputter rate owing to pronounced sputtering-induced formation of TaSi_2 in the vicinity of stoichiometric altered layer composition [7.36, 7.37]. A theoretical modeling is available within the more sophisticated MRI model for depth profile quantification outlined in Sect. 7.1.8.4 (Fig. 7.24a, b).

An elegant method particularly useful in AES is the estimation of the depth scale by using two Auger signals of the same element but with large difference in

kinetic energy. In a steep gradient, the result is a mutual shift of both profiles of the order of the difference in the attenuation length values which provides a sputtering time/depth scale conversion with fairly good approximation (see below, Fig. 7.2).

7.1.2.2 Intensity/Composition/Depth Scale Relation

Quantitative AES and XPS of homogeneous concentration distributions are fairly well established and are given in Chap 4. Depth profiling of alloys with variations in composition may include concentration-dependent matrix effects which are often neglected (Sects. 4.3.2 and 4.4.2). More difficult is quantitative analysis when chemical compounds are subject to sputter depth profiling. In this case, the elemental peak is shifted (XPS) and/or changes shape (AES). In XPS, where usually the peak area is determined, this poses no major problem because the total elemental intensity is measured and can be later decomposed into compounds (see, e.g., Chap. 3, Fig. 3.3). In contrast, the usual peak-to-peak height determination in AES may cause considerable errors because of the strong sensitivity of the differentiated signal to small changes in peak shape. Only for a few elements when, for example, the peaks of element and oxide are well separated (e.g., Al, Si, Sn), a separate analysis is straight forward. When both peaks overlap, a remedy can be overmodulation [7.38] or increased smoothing. A special method proposed by Bauer [7.39] can also be applied. A powerful method for quantitative extraction of chemical information is decomposition of a profile in principal components, for example, by least squares fitting of standard profiles or by factor analysis (Sects. 4.1.4 and 9.3).

A principal problem encountered in sputter depth profiling of compounds is ion-beam-induced decomposition [7.40, 7.41] or compound formation [7.36, 7.37], which changes the original compound and may give way to profile misinterpretation. Because these effects are usually limited within the range of strong defect formation, a signal from the undistorted compound below the altered layer can be detected which is representative for the compound before it is distorted by the impinging ions (e.g., the Ta^{5+} signal representing undistorted Ta_2O_5 in Fig. 3.3).

Inhomogeneous distribution on the monolayer scale, as induced by ion-surface interaction, presents a number of problems which will be treated in detail in Sect. 7.1.8 (MRI model). In the following, we will focus on the effect of the electron escape depth on the measurement of concentration gradients.

Escape Depth Correction

The information depth is limited by the electron escape depth $\lambda^e = \lambda \cos \theta$, with λ the effective attenuation length (EAL, see Sect. 4.2.2), and θ the electron emission angle. Therefore, a surface layer of thickness 5λ gives 99% of the Auger or photoelectron intensity (see (4.17) for $d = 5\lambda$). The resolved depth is improved by using signals with low kinetic energy, as directly observed in AES depth profiling

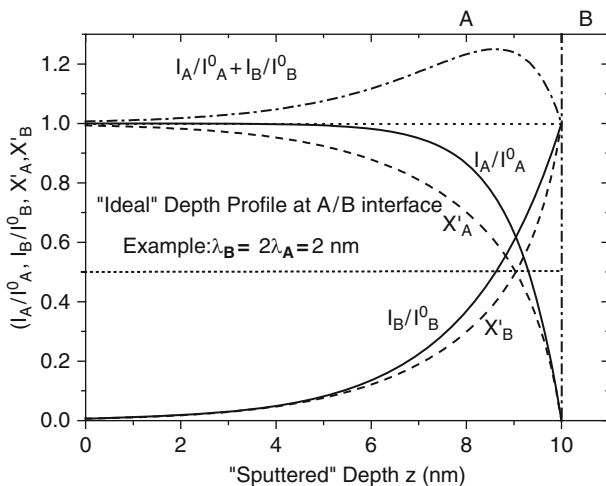


Fig. 7.1 “Ideal” sputter depth profile (neglecting roughness and atomic mixing effects) of the normalized intensities I_A^0/I_A^0 , I_B^0/I_B^0 (solid lines) at an A/B interface at $z_1 = 10$ nm for different electron escape depths $\lambda_B = 2\lambda_A = 2$ nm. Neglecting the escape depth correction (7.7), the apparent concentrations $X'_A \neq I_A/I_A^0$, $X'_B \neq I_B/I_B^0$, given by (7.11a) and (7.13) (dashed lines), are no more exponential functions. The deviation is given by $(I_A/I_A^0 + I_B/I_B^0)$ (dash-dotted line). Note the mutual shift of I_A and I_B of 0.7 nm at 50% intensity according to (7.9, 7.10)

of elements such as Al with low and high-energy peaks [7.42]. We may interpret the measured signal as being an average value for a thickness of 5λ , or we can go a step further and try to deconvolute the measured signal with the knowledge of λ . As shown in Sect. 4.3.3, the intensity of a thin layer follows from the basic equation (4.39) and is represented by (4.86) (see Fig. 7.1). For $z_1 = 0$ (the instantaneous surface), the contribution of a very thin layer of A with mole fraction X_A , $d(I_A/I_A^0)$ (normalized to I_A^0), with thickness $dz \ll \lambda^e$ (with the electron escape depth $\lambda^e = \lambda \cos \theta$), the exponential function can be approximated by a linear relation, and we obtain

$$d\left(\frac{I_A}{I_A^0}\right) = X_A \left[1 - \exp\left(-\frac{dz}{\lambda_A^e}\right) \right] = -X_A \frac{dz}{\lambda_A^e} \quad (7.6)$$

Of course, this contribution has to be added to the normalized signal intensity at $z_1 = 0$. For all progressing z values in the profile, (7.6) should be valid, and therefore, we may write for the relation between X_A and the instantaneous normalized intensity at any point z in the profile

$$X_A(z) = \left(\frac{I_A}{I_A^0}\right)_z - \frac{d}{dz} \left(\frac{I_A}{I_A^0}\right) \lambda_A^e \quad (7.7)$$

Indeed, (7.7) is a solution of the integral equation (4.39) as already pointed out by Iwasaki and Nakamura [7.43]. It has been shown in many examples [7.31, 7.44, 7.45, 7.46] that (7.7) can be successfully used to correct for the electron escape depth

influence on the total broadening of the profile. However, because other important effects like roughness and atomic mixing (Sect. 7.1.6) (as well as matrix correction factors, see Sect. 4.3.5) are ignored, (7.7) cannot expect to give a valid quantification if the escape depth effect is not preponderant [7.3]. To work with (7.7), we need already knowledge of the depth scale, i.e., the sputtering rate $\dot{z}$. Because $dz = \dot{z}dt$ and the concentration always have to be positive, $X_A(z) > 0$, a maximum gradient of the measured intensity sputtering time profile follows from (7.7) which defines a lower limit of the sputtering rate,

$$\dot{z} \geq \frac{\lambda_A^e}{I_A} \left| \frac{dI_A}{dt} \right|_{\max}. \quad (7.8)$$

Equation 7.8 has found to be useful in estimations of the sputtering rate of a sample with unknown thickness and composition. Because the normalizing sensitivity factor I_A^0 cancels, the tangent dI_A/dt can be taken directly at any point I_A of the measured profile where the slope is at maximum (usually at the beginning when the native oxide and contamination layer decreases rapidly or at a sharp interface) (Fig. 7.2).

Sputtering Rate from Escape Depth Shift

According to (7.7), the deviation between $X_A(z)$ and $(I_A/I_A^0)(z)$ depends on the slope of the measured profile: $X_A(z)$ is lower for a positive and higher for a negative gradient. (For a plateau region, there is no difference.) This fact generates a shift of the measured profile to lower depths with respect to the original composition distribution (see, e.g., Fig. 4.3 in [7.2], Figs. 7.21, 7.2, and 7.33). Because this shift depends on the value of λ , a profile measured for an element with two different λ values (e.g., AES LVV and KLL spectra of Al, Si, MVV and LMM of Cu, and Ni) offers a possibility to determine the sputtering rate. When two profiles of the same element, acquired with λ_1 and λ_2 at an A/B interface, are normalized to the same plateau value I_B^0 , we get for the shift of the 50% value of the normalized intensity with respect to the interface at z_1 ,

$$\frac{I_B}{I_B^0} = \frac{1}{2} = \exp\left(-\frac{z_1 - z}{\lambda_1^e}\right), \quad (7.9)$$

as depicted in Fig. 7.2. The shift of the 50% value for λ_1 is given by $z_1 - z(\lambda_1^e) = \lambda_1^e \times \ln 2$, and similarly that for λ_2^e , $z_1 - z(\lambda_2^e) = \lambda_2^e \times \ln 2$. Since $[z(\lambda_1^e) - z(\lambda_2^e)]_{50\%}$ is the mutual shift of both normalized intensities, the depth scale can be transformed to the sputtering timescale (t) with (7.3). Comparison of the timescale location for the two measured profiles, $t(\lambda_1^e)$, $t(\lambda_2^e)$, yields the mean sputtering rate according to

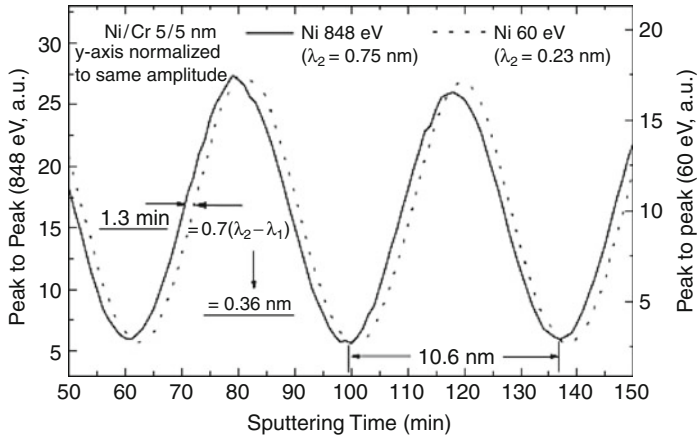


Fig. 7.2 Mutual shift of the high (848 eV, in figure, $\lambda_2 = \lambda_2^e = 0.75$ nm) and low (60 eV), $\lambda_1(\text{figure}) = \lambda_1^e = 0.23$ nm energy Ni Auger peaks measured during sputter depth profiling (1 keV Ar^+ , 75° inc. angle) of a Ni/Cr multilayer with 5 nm thickness per single layer (From Ref. [7.51])

$$\dot{z} = \frac{[x(\lambda_1^e) - z(\lambda_2^e)]_{50\%}}{[t(\lambda_1^e) - t(\lambda_2^e)]_{50\%}} = \frac{\lambda_2^e - \lambda_1^e}{[t(\lambda_1^e) - t(\lambda_2^e)]_{50\%}} \ln 2 = \frac{0.7(\lambda_2^e - \lambda_1^e)}{[t(\lambda_1^e) - t(\lambda_2^e)]_{50\%}}. \quad (7.10)$$

Many elements (e.g., Si, Al, Cu, Ni, Fe, Cr, Ta, Nb, W) possess low and high Auger energy peaks with similar sensitivity [4.21] (see, e.g., Fig. 4.5b). These peaks have different electron attenuation lengths λ_1 , λ_2 , and therefore, different electron escape depths $\lambda_{1,2}^e = \lambda_{1,2} \cos \theta$. The corresponding profiles are mutually shifted by a characteristic length of $\Delta\lambda^e = 0.7(\lambda_2^e - \lambda_1^e)$ [7.4, 7.47–7.50], if the influence of the atomic mixing can be ignored (cf. MRI-model, Fig. 7.36). An application of (7.10) is shown in Fig. 7.2 [7.51], where the AES depth profile of the low- and high-energy peak of Ni (MVV 60 eV and LMM 848 eV) is shown for a Ni/Cr multilayer structure consisting of 5 double layers of Ni and Cr, with each elemental layer being 5 nm thick (double layer = 10 nm thickness) [7.51]. These peaks have different electron attenuation lengths, $\lambda_2 = 1.01$ and $\lambda_1 = 0.30$ nm [7.4], respectively, corresponding to an electron escape depth of $\lambda_2^e = 0.747$ nm and $\lambda_1^e = 0.225$ nm or a CMA oriented perpendicular to the sample surface, where $\theta = 42.3^\circ$. The corresponding profiles are mutually shifted by $\Delta\lambda^e = 0.7(0.75 - 0.23) = 0.36$ nm. As seen in Fig. 7.2, the mutual shift of the profiles (normalized to the same amplitude) on the sputtering timescale is about 1.3 min. Thus, the average sputtering rate is equal to $0.36 \text{ nm}/1.3 \text{ min} = 0.28 \text{ nm/min}$. The double-layer thickness, corresponding to 38-min sputtering time (Fig. 7.2), is obtained as 10.5 nm, close to the nominal thickness of 10 nm. It should be emphasized that this intrinsic method of sputtered depth determination is not a high-precision method, but because of its simplicity – without the necessity of additional methods – it provides a valuable way to estimate

the sputtering rate in case of unknown samples. Whereas the roughness influence is rather small and can usually be neglected, the influence of the mixing length modifies the shift [7.42, 7.49].

It is evident from (7.7) and the shift of the profiles in Figs. 7.1 and 7.2 that the naive, simple quantification of profiles with sensitivity factors and (4.23) for homogeneous composition will only be consistent if the λ values for each element in the profile are the same, which is rarely the case (see Chap. 4). Therefore, we have to expect different elemental profiles, with the 50% value of the intensity of the elements of a binary system at different locations [7.47]. The usual normalization procedures cause an error that can be estimated as follows.

Provided matrix effects are negligible, the “ideal sputtering” depth profiles for a layer of A on B (with different escape depths λ_A^e, λ_B^e) near the interface A/B are shown as normalized intensities ($I_A/I_A^0, I_B/I_B^0$) versus depth z in Fig. 7.1. It is immediately seen that the basic equation for homogeneous quantification, $X_A/X_B = (I_A/I_A^0)/(I_B/I_B^0)$ (cf. (4.22)) loses its meaning, but at any z value, the normalized intensity ratio is representative for the remaining thickness d of layer A on B, $(I_A/I_A^0)/(I_B/I_B^0) = f(d)$ as shown in (4.58). The usual normalization formula for quantification, based on homogeneous alloy composition, gives a characteristic deviation from the shape of the measured intensity profile if $\lambda_A^e \neq \lambda_B^e$, because $I_A/I_A^0 + I_B/I_B^0 = X_A + X_B \geq 1 \geq$ dash-dot line in Fig. 7.1). Replacing d in (4.58) by $(z_1 - z)$ and applying (4.23) gives for the apparent mole fractions X'_A, X'_B ,

$$X'_A = \frac{\frac{I_A}{I_A^0}}{\frac{I_A}{I_A^0} + \frac{I_B}{I_B^0}} = \frac{1 - \exp\left(-\frac{z_1 - z}{\lambda_A^e}\right)}{1 - \exp\left(-\frac{z_1 - z}{\lambda_A^e}\right) + \exp\left(-\frac{z_1 - z}{\lambda_B^e}\right)} \quad (7.11a)$$

and

$$X'_B = \frac{\frac{I_B}{I_B^0}}{\frac{I_A}{I_A^0} + \frac{I_B}{I_B^0}} = \frac{1 - \exp\left(-\frac{z_1 - z}{\lambda_B^e}\right)}{1 - \exp\left(-\frac{z_1 - z}{\lambda_A^e}\right) + \exp\left(-\frac{z_1 - z}{\lambda_B^e}\right)}. \quad (7.11b)$$

With the interface A/B located arbitrarily at $z_1 = 10$ nm depth and $\lambda_B^e = 2\lambda_A^e = 2$ nm, (7.11a) and (7.11b) are plotted as dashed lines in Fig. 7.1. Strictly speaking, the apparent mole fractions of A and B obtained in this way are only normalized intensities which can be considered as average concentrations within the depth resolution determined by the escape depth. However, because differently shifted profiles are compared, the original profile shape is altered as seen in Fig. 7.4. Almost any general quantification software, for example, Multipack[®], works in that way and may cause appreciable errors particularly in profiles where the difference in the attenuation lengths of the two elements is large. As evident from Fig. 7.1, errors of 20% are not uncommon. Therefore, if the escape depth values are not similar, only the measured single-component intensities (normalized with appropriate λ values and sensitivity factors) will result in correctly quantified depth profiles. The “true” composition profile can only be obtained after deconvolution, for example, for ideal sputtering conditions after (7.7), but there are more realistic approaches like that of the MRI model (Sect. 7.1.8). There, we will see that the effect of different escape

depths, λ_e will be blurred with increasing influence of atomic mixing and/or surface roughness (cf. Fig. 7.36). All the above equations (7.6)–(7.10), and (7.11a) and (7.11b) are valid for XPS and for AES when the backscattering factors of A and B at an A/B interface are equal. If A and B have different backscattering factors ($1 + r$), we have already seen in Sect. 4.4.1 that a backscattering correction is necessary. For this case, and for ideal later by layer depth profiling, the expected intensity – depth distribution – is identical to the one shown in Figs. 4.55 and 4.56 (Sect. 4.4.3). Applications to measured depth profiles are shown in Sect. 7.1.8.

After having performed the above presented first steps in profile quantification, it is obvious that the profile is broadened compared to the original in-depth distribution of composition. The deviation of both is described by the depth resolution.

7.1.2.3 Depth Profiling and Chemical Bonding

Quantification of the intensity in sputter depth profiles is usually based on elemental profiles without distortions by chemical-bonding effects, as usually experienced in-depth profiling of alloys. However, when, for example, a profile through an oxide layer on an alloy is acquired, a chemical shift is observed and the peak shape varies. Taking the peak area as elemental intensity, as in XPS, chemical shift has no effect on the intensity if compound decomposition and preferential sputtering of a component by ion beam bombardment are negligible. When using only Auger peak-to-peak heights (APPH) in AES depth profiling, the effect of chemical bonding on peak shape affects APPH [7.38, 7.52]. This change is frequently interpreted as concentration change. A remedy is to blur the effect of bonding by decreasing the energy resolution, for example, by overmodulation or a strong smoothing of the Auger signal, as shown by Pamler [7.38], or by peak area determination after background subtraction [7.39]. To resolve the bonding problem and to use the great potential of AES for chemical analysis (Chap. 3), Gaarenstroom [7.53] introduced factor analysis (FA) (see Sect. 9.3), which nowadays is routinely used to separate the different constituents of complex Auger spectra [7.54–7.56]. Other multivariate methods for curve fitting include, for example, linear least square fitting of principal component spectra and maximum entropy approach. A survey is given in Ref. [7.57].

In contrast to simple APPH depth profiling, profiling with respect to further application of curve fitting methods requires a large enough energy window to ensure the inclusion of complete signal information range before and after storage of the acquired data; one of the multivariate methods can be applied to the ensemble of spectra [7.54]. Classical examples of application of FA are differentiation between spectra characterizing oxide and elemental states. With FA, even hitherto unknown component spectra can be disclosed, as shown for chemisorption states in the course of low temperature oxidation of NiCrFe [7.54] (see Fig. 9.17). The application of linear least squares fitting (LLS) is much easier, when the standard spectra of each component are known. Frequently, these component spectra can be taken from different locations in the profile (e.g., pure oxide at the start of an oxide layer profile

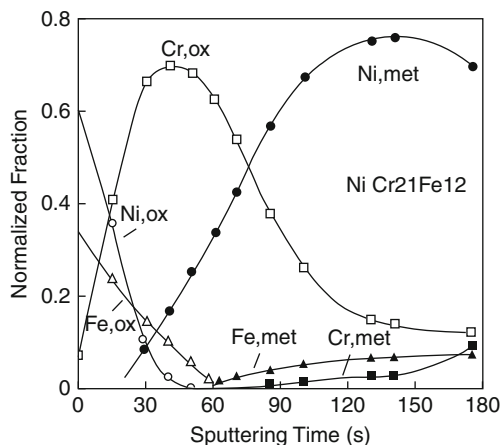


Fig. 7.3 Depth profile of the chemical composition of the alloy NiCr21Fe12 after exposure to 900 L oxygen at room temperature. Using linear least squares fitting (LLS), the normalized fractions of the metallic (Ni,met; Cr,met; Fe,met) and oxidic (Ni,ox; Cr,ox; Fe,ox) states of the $M_{2,3}VV$ Auger transition between 20 and 70 eV of the elements are plotted as a function of the sputtering time. According to the corresponding sputtering rate for Ta_2O_5 , the total sputtering time of 180 s corresponds to about 3 nm (From J. Steffen and S. Hofmann [7.58])

and pure metal at the end) [7.38]. An example is shown in Fig. 7.3 for the depth profile of a NiCrFe alloy, performed after exposure to 900 L (Langmuir) of oxygen at room temperature ($1\text{ L} = 10^{-6}\text{ Torr}\cdot\text{s}$) [7.38] (see also Fig. 9.6). Another example is the quantitative separation of Ti, TiN, and TiO_2 in the respective Ti spectra, where peak separation is difficult because of strong peak overlapping, particularly of the $N\text{ }KL_{2,3}L_{2,3}$ and the $Ti\text{ }L_{3}M_{2,3}M_{2,3}$ peaks [7.55, 7.56]. Figure 7.4a shows the conventional APPH depth profile of a nitrogen-implanted Ti sample [7.56], where the bonding state and quantification of Ti are left unclear. Only the O-510-eV peak gives an indication of a probable Ti oxide. Using LLS with the standard component spectra of Ti, TiN, and TiO_2 , shown in Fig. 7.4c, a clear separation of these components is possible and the component profiles are shown in Fig. 7.4b. The formation of a carbide layer at the interface C/Ti after annealing at 550°C has been disclosed by Swart et al. [7.59], using LLS with standard spectra of graphite and carbide. Whereas the usual APPH depth profile only indicates some strange cusp in the C profile (Fig. 7.5a), LLS fitting with the standard spectra (Fig. 7.5b) reveals a quantitative measure of the amount of graphite and carbide in the C/Ti interface (Fig. 7.5c). The carbide thickness obtained for different annealing temperatures enabled the determination of the C/Ti interdiffusion constant [7.59].

Special care has to be taken not to confuse the original compound with sputtering-induced changes of chemical bonding (see Sect. 7.1.4). For example, transition metal oxides show ion-bombardment-induced reduction by preferential sputtering of oxygen, whereas SiO_2 and Al_2O_3 sputter congruent (see Fig. 7.14). A method to test if there is a sputtering-induced altered layer is, for example, angle-resolved depth profiling of the layer structure (see Sect. 7.2.1).

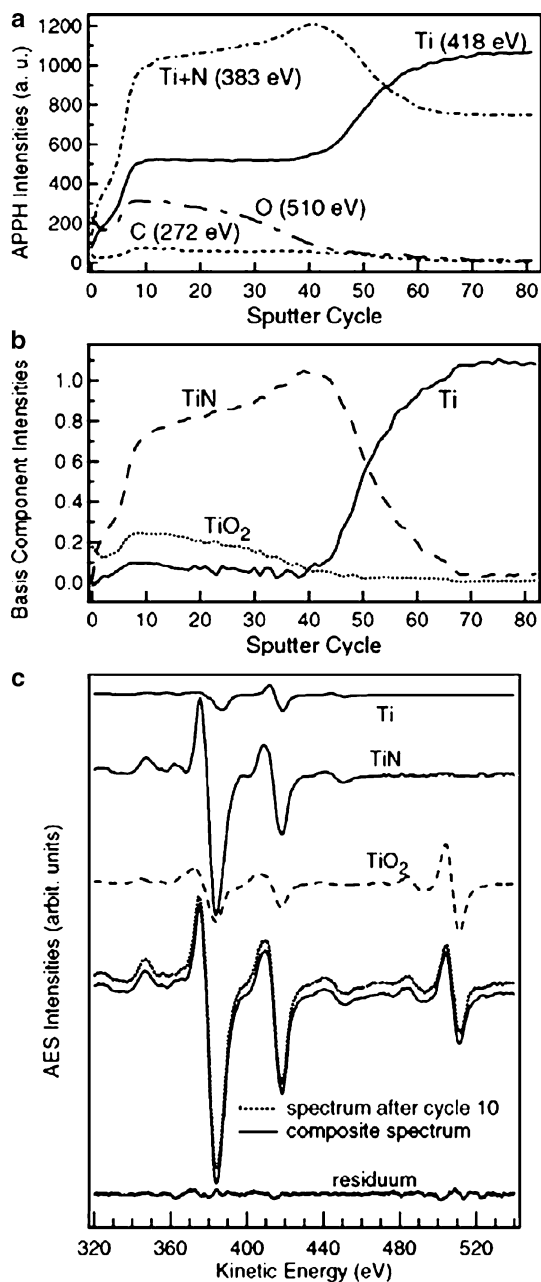


Fig. 7.4 Sputter depth profiles of a Ti sample implanted with nitrogen: (a) conventional APPH depth profile with Ti-N peak overlap at 383 eV; (b) composition depth profile obtained by LLS fitting with principal component spectra of Ti, TiN, and TiO₂. (c) LLS fitting of the spectra in (a) obtained after sputter cycle 10, with the external standards of Ti, TiN, and TiO₂ used as component spectra. The residuum and basis spectra are also shown (Reproduced from J. Kovac, T. Bogataj and A. Zalar [7.56], with permission of J. Wiley & Sons Ltd.)

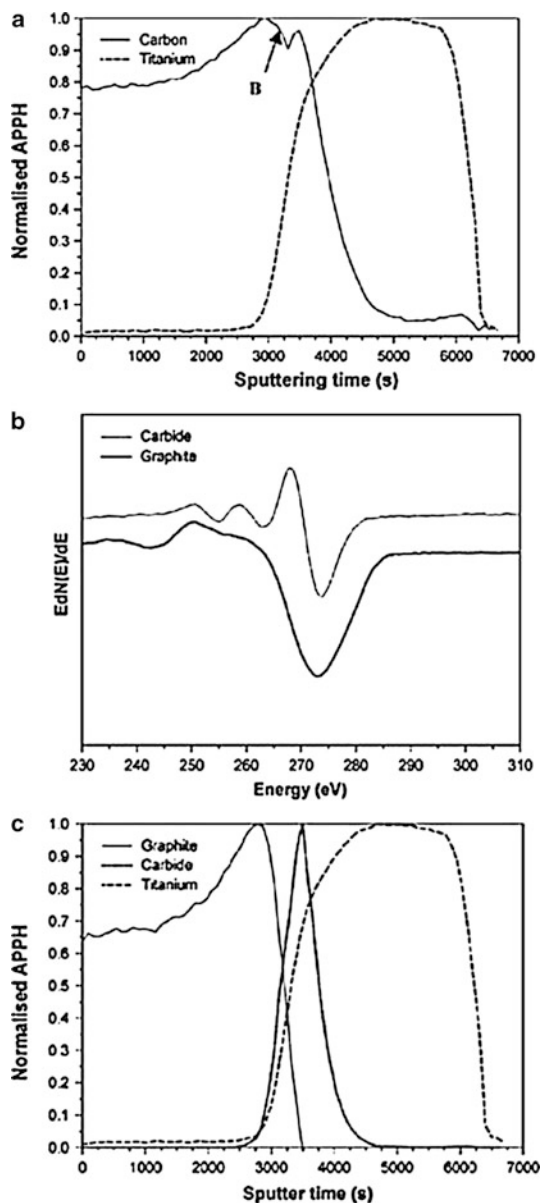


Fig. 7.5 (a) APPH depth profile of C on Ti (normalized to maximum peak intensity) of a Ti layer of 202 nm thickness on an oxidized Si wafer, covered with a 230-nm-thick C layer, after annealing for 121 min at 550°C. The cusp near point B indicates a peak shape change of the carbon signal; (b) differential Auger standard spectra for C in graphite and in TiC; (c) depth profile as in (a) but resolved for graphite and titanium carbide contents at the C/Ti interface, by using LLS with the standard spectra given in (b). The marked increase of the graphite signal before the interface is caused by electron backscattering from Ti, as quantitatively explained in Fig. 7.30 (Reproduced from H.C. Swart et al. [7.59], with permission of Elsevier B.V.)

7.1.3 Depth Resolution: Definition and Measurement

7.1.3.1 Definition of Δz

The depth resolution is given by a characteristic length Δz within which the details of in-depth compositional distribution are not resolved. Therefore, it is a useful quality figure of any depth profile: the smaller Δz , the better resolved is the profile and vice versa. To ensure comparison of profiles with respect to Δz , a quantitative measure has to be defined [7.60], as adopted by IUPAC [7.61], ISO TC 201 [7.62], and ASTM E42 [7.63]. The latter document states that “depth resolution is the depth range over which a signal increases (or decreases) by a specified amount when profiling an ideally sharp interface between two media. By convention, the depth resolution corresponds to the distance over which a 16–84% (or 84–16%) change in signal is measured.” This measurement prescription is schematically depicted in Fig. 7.6.

In case of a Gaussian depth resolution function (see Fig. 7.6 and Sect. 7.1.5), the sharp interface profile is broadened into an error function, and the depth resolution is given by $\Delta z = 2\sigma$, with σ the standard deviation of the Gaussian. Other definitions sometimes used can be easily converted to the 2σ definition in case of error-function-like profiles [7.2]. For example, $\Delta z(90 - 10\%) = 2.56\sigma$, the full width at half maximum of the Gaussian, $\Delta z(\text{FWHM}) = 2.35\sigma$, and the inverse maximum slope $\Delta z(dz/dI)$ (extrapolated to 0% and 100%) = 2.36σ [7.2, 7.64]. If the depth resolution function is non-Gaussian, the measured profile is asymmetric, and the $\Delta z(84-16\%)$ definition loses its simple meaning. For example, if only the electron escape depth λ^e contributes to Δz , $\Delta z_\lambda(84 - 16\%) \approx 1.67\lambda^e$ [7.48, 7.65] for an exponential resolution function with the characteristic length λ^e (Fig. 7.3) (see Sect. 7.1.8).

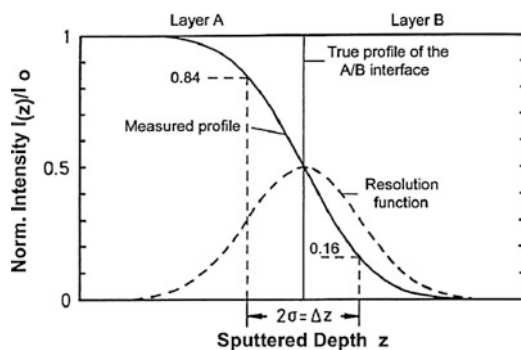


Fig. 7.6 Schematic broadening of the profile at a sharp interface and definition of the depth resolution, $\Delta z(84-16\%)$. For a Gaussian resolution function (dashed line, the derivative of the error function), $\Delta z = 2\sigma$, with σ = the standard deviation. For other definitions, see text and [7.2, 7.8, 7.64]

In general, a Gaussian depth resolution function is only a first-order approximation of the measured function. However, it has the advantage that only one parameter, Δz , is necessary for its description. Therefore, it is customary to work with a Gaussian approximation if the required precision is sufficient, for example, for comparison with other work or when comparing different contributions to depth resolution (see Sect. 7.1.5).

Usually, single-layer standard reference samples of 30-nm-thick Ta₂O₅ on Ta [7.17, 7.18] are used to test the optimum instrumental setup. A value of $\Delta z \leq 2$ nm for 1–3 keV Ar⁺ ions should be obtained [7.17] (Sect. 7.1.1).

7.1.3.2 Depth Resolution Values Derived from Layer Structures

Well-defined depth resolution values cannot only be obtained at sharp interfaces (or on monolayer markers or so-called delta layers, see Sects. 7.1.7, 7.1.8, Fig. 7.31), but also from thicker “sandwich” layers (Fig. 7.7b) and from multilayers (Fig. 7.7c). In case of a sandwich layer with thickness d , the measured profile can be described by a superposition of the two respective error functions at each interface, increasing on the left and decreasing on the right side (Fig. 7.10b) [7.3, 7.5, 7.8, 7.64, 7.66]. Then, the normalized peak intensity I_s/I_0 in Fig. 7.7b is a measure of the depth resolution according to the relation [7.64]

$$\frac{I_s}{I_0} = \operatorname{erf}\left(\frac{d}{\sqrt{2}\Delta z}\right), \quad (7.12)$$

where I_s is the measured intensity of the maximum and I_0 is the intensity of a thick layer ($d \geq 5\lambda$) used as depth resolution quantification standard (not necessarily an elemental standard intensity I^0 as discussed later and in Chap. 4). Equation 7.12 directly gives a relation between the limit of detection and the ratio $\Delta z/d$. For example, a minimum detectable I_s/I_0 of 0.05, slightly above the noise in routine AES depth profiling, gives $\Delta z/d = 15$, which means that detection of a monoatomic layer ($d = 0.25$ nm) requires $\Delta z \leq 4$ nm. In the limiting case $\Delta z = 4$ nm, a distinction between a full monolayer and a lower concentration spread out over several monolayers thickness would be impossible without deconvolution by knowledge of the resolution function (see Sect. 7.1.8, Fig. 7.37) [7.8, 7.67].

Multilayers are especially advantageous for determination of the depth dependence of depth resolution (Fig. 7.7c). The fundamental equations for the determination of depth resolution values from single- and multilayer sandwich structures are derived in [7.2, 7.65], summarized in [7.66], and critically reconsidered in [7.64]. As visualized in Fig. 7.8, the measured intensity of component A of a multilayer sandwich structure (e.g., A/B/A/B/A/...) is represented by positive contributions from interfaces 1', 3' ..., and 2, 5 and by negative contributions from interfaces 4', 2' ..., and 1, 3, ... For the sputter depth profile with constant single-layer thickness d , the general relation for the normalized maximum intensity, $I_{\max}/I_0$, and Δz is given by [7.2, 7.66]

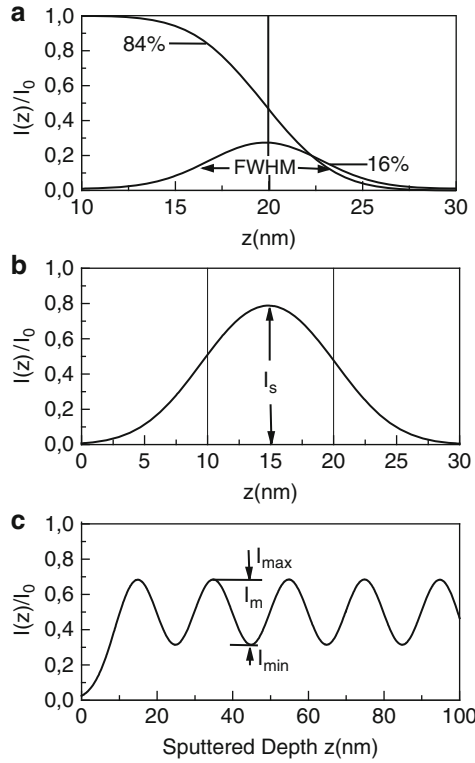


Fig. 7.7 Depth resolution concepts (details see text): (a) definition at a sharp interface: $\Delta z = 2\sigma = (84\% - 16\%)I_0$; (b) single-layer depth profile: normalized maximum value I_s/I_0 ; (c) multilayer depth profile: normalized amplitude I_m/I_0 (From S. Hofmann [7.64])

$$\frac{I_{\max}}{I_0} = \frac{1}{2} \sum_{k=-M}^{k=+M} \left[\operatorname{erf} \left(\sqrt{2} \frac{(2k+0.5)d}{\Delta z(2k+0.5)} \right) - \operatorname{erf} \left(\sqrt{2} \frac{(2k-0.5)d}{\Delta z(2k-0.5)} \right) \right], \quad (7.13)$$

where k denotes the interface number on both sides ($-M \dots +M$) of the considered layer with $I_{\max}/I_0$. According to Fig. 7.8, the normalized amplitude of the multilayer profile, $(I_{\max} - I_{\min})/I_0$, is given by $I_m = 2(I_{\max}/I_0) - 1$. With that, and assuming the same Δz for the next neighbors, (7.13) can be approximately expressed as [7.2, 7.64]

$$\frac{I_m}{I_0} = 2 \left[\operatorname{erf} \left(\frac{d}{\sqrt{2}\Delta z} \right) - \operatorname{erf} \left(\frac{3d}{\sqrt{2}\Delta z} \right) + \operatorname{erf} \left(\frac{5d}{\sqrt{2}\Delta z} \right) \mp \dots \right] - 1. \quad (7.14)$$

Diagrams of (7.12)–(7.14) are shown in Fig. 7.9. In case of a single layer or a multilayer with constant single-layer thickness d , the steep interface measurement

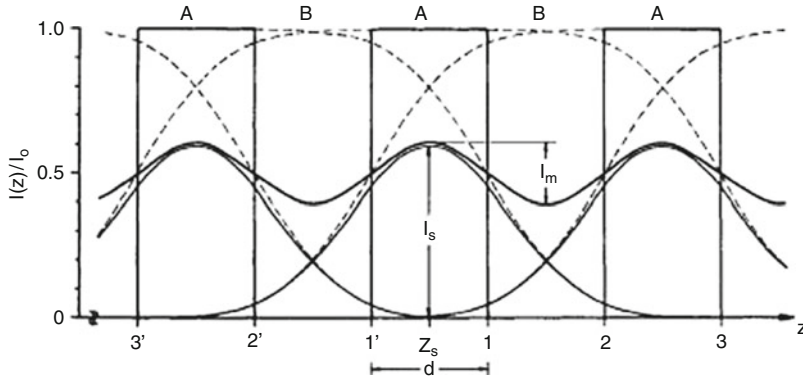


Fig. 7.8 Schematic diagram of a multilayer structure A/B/A/B... with single-layer thickness d , showing the “measured” sputtering profile of element A (dark-drawn curve) composed by error functions (dashed lines) around each interface ($3'$, $2'$, $1'$, 1 , 2 , 3) and the corresponding sputtering profiles of each single-sandwich layer (light drawn curve). The intensity of a single layer is $I_s = I_{\max}$, and $I_m = I_{\max} - I_{\min}$ obtained by overlapping of adjacent layers (From S. Hofmann [7.66])

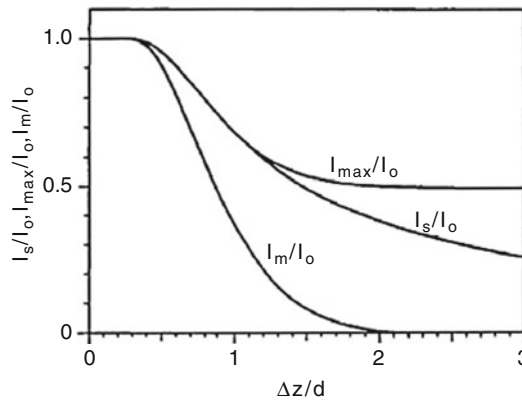


Fig. 7.9 Normalized maximum intensities of a single-sandwich layer, I_s/I_0 , and of a multilayer, $I_{\max}/I_0$, and the “amplitude” of a multilayer, I_m/I_0 , as a function of the ratio $\Delta z/d$, with single-layer thickness d , according to (7.12) and (7.13) and Figs. 7.7 and 7.8. Note that (7.14) and Fig. 7.9 only apply if roughness determines depth resolutions. For preponderant atomic mixing, slightly different equations apply as described in Ref. [7.64]

of Δz as in Fig. 7.7a applies for $\Delta z/d < 0.4(I_s/I_0 = 1)$. For $\Delta z/d > 0.4$, the single-layer evaluation is given by (7.12) and the multilayer amplitude by (7.14) [7.66]. Taking into account only the next adjacent interfaces (i.e., the second term in (7.14) and taking unity for the third term) results in the following expression,

$$\frac{I_m}{I_0} = 1 - 2 \left[\operatorname{erf} \left(\frac{3d}{\sqrt{2}\Delta z} \right) - \operatorname{erf} \left(\frac{d}{\sqrt{2}\Delta z} \right) \right]. \quad (7.15)$$

Equation 7.15 has frequently been used for the determination of the depth dependence of Δz in sputter profiling of Ni/Cr multilayer samples as a function of Ar^+ ion energy and incidence angle and of surface roughness [7.2–7.8, 7.16, 7.66]. The error in the approximate expression is less than 1% of I_0 for $0 < \Delta z/d < 1.7(I_m/I_0 = 0.04)$. For a single-sandwich layer (7.12), Δz is determined for a location at the maximum between the adjacent interfaces and therefore represents a mean value of the adjacent interfaces. In contrast, for a multilayer (7.14), the value of Δz corresponds to the respective interface. The ultimate limit of resolving a multilayer structure is attained for $\Delta z/d \geq 2$, when $I_m/I_0 = 0$ [7.66], as evident from Fig. 7.12. An extension of (7.13) to the generalized case of multilayers with different thickness of layers adjacent to d_0 , that is a sequence of $\dots d'_2/d'_1/d_0/d_1/d_2/\dots$ and the respective interface resolutions $\Delta z'_3, \Delta z'_2, \Delta z'_1, \Delta z_1, \Delta z_2, \Delta z_3$ (see Fig. 1 in Ref. [7.66] or Fig. 7.11). Equation 7.13 is still valid for $k = 0$; for $k = l$, the term $(2k + 0.5)d$ must be replaced by $(2d_1 + 2d_2 + d_0)$, and for $k = -l$ by $(2d'_1 + d'_2 + d_0)$. In this approximation, the result for layer d_0 is

$$\left(\frac{I_{\max}}{I_0}\right)_{d_0} = \frac{1}{2} \left[\begin{aligned} &\text{erf}\left(\frac{d_0}{\sqrt{2}\Delta z_1}\right) + \text{erf}\left(\frac{d_0}{\sqrt{2}\Delta z'_1}\right) + \text{erf}\left(\frac{d_0 + 2d_1 + 2d_2}{\sqrt{2}\Delta z_3}\right) \\ &-\text{erf}\left(\frac{d_0 + 2d_1}{\sqrt{2}\Delta z_2}\right) + \text{erf}\left(\frac{d_0 + 2d'_1 + 2d'_2}{\sqrt{2}\Delta z'_3}\right) - \text{erf}\left(\frac{d_0 + 2d'_1}{\sqrt{2}\Delta z'_2}\right) \end{aligned} \right]. \quad (7.16)$$

Multilayer structures for which the layer thicknesses of A and B are constant but different, ($d_A \neq d_B$), are a special case of (7.16) given by [7.2, 7.5]

$$\left(\frac{I_{\max}}{I_0}\right)_{d_0} = \frac{1}{2} \left[\begin{aligned} &\text{erf}\left(\frac{d_A}{\sqrt{2}\Delta z_1}\right) + \text{erf}\left(\frac{d_A}{\sqrt{2}\Delta z'_1}\right) + \text{erf}\left(\frac{3d_A + 2d_B}{\sqrt{2}\Delta z_3}\right) \\ &-\text{erf}\left(\frac{d_A + 2d_B}{\sqrt{2}\Delta z_2}\right) + \text{erf}\left(\frac{3d_A + 2d_B}{\sqrt{2}\Delta z'_3}\right) - \text{erf}\left(\frac{d_A + 2d_B}{\sqrt{2}\Delta z'_2}\right) \end{aligned} \right]. \quad (7.17)$$

Because (7.12)–(7.17) are implicit functions of $\Delta z/d$ (or $\Delta z_i/(xd_1 \dots yd_n)$), it is most convenient to take values of $\Delta z/d$ from diagrams such as Fig. 7.12 or tables after first assuming a constant Δz and then determining the exact Δz at the respective depth by regressive iteration procedures.

Sharp interface profiles are often asymmetric or skewed because of various physical processes responsible for their shape, as we have already seen (e.g., λ -effect on profiles, Fig. 7.1). However, the above equations can be used as a good approximation, even in the case of asymmetrical shapes of the measured profiles, with the advantage of being independent of changes in the sputtering rate from layer A to layer B . A thorough discussion of the influence of different resolution functions on the determination of $\Delta z/d$ after (7.14) is given in [7.64].

7.1.4 Factors Limiting Depth Resolution and Profile Accuracy

The large number of phenomena that cause a degradation of depth resolution can be roughly divided in three categories: instrumental factors, ion-beam-sample interactions, and special characteristics of the sample. The most important influences on the depth resolution are [7.2–7.6]:

1. *Instrumental Factors*: Nonuniform ion beam intensity in the analyzed area, impurities and neutrals in the ion beam, adsorption and contamination from the residual gas atmosphere, resputtering from instrument parts close to the analyzed surface, information depth and matrix dependence of the analysis method (e.g., backscattering effect in AES)
2. *Ion-Beam-Sample Interactions*: Atomic mixing in the collision cascade, primary ion and recoil implantation, ion-bombardment-induced surface topography, preferential sputtering, enhanced diffusion and segregation, new phase formation, decomposition of compounds, charging and electromigration in insulators
3. *Sample Characteristics*: Original surface roughness and topography, crystalline structure, defects, second phases, and compounds, low electrical and thermal conductivity

The above classification does not mean that the phenomena are independent, since all are connected with the sputtering process and the analysis method. However, it is customary to differentiate between them with respect to the dominant property or effect.

7.1.4.1 Instrumental Factors

Ion Gun Setup and Crater-Shape Effects

An appropriate setup of the instrument is a prerequisite to obtain a good depth resolution. Most important is optimum matching between the ion-etched area and the analyzed area [7.68]. This can be done by observing the sputtered crater of a focused ion beam on a SiO₂/Si layer (AES) or by electron X-ray (XPS)-induced secondary electron image. Using a Faraday cup placed at the normal sample position is another means to adjust the ion beam in the optimum position. A nonuniform ion beam intensity across the analyzed area means that the sample is eroded to different depths which contribute to the measured signal. The result is a characteristic contribution to depth resolution, Δz_1 , which increases proportionally to the sputtered depth z . For the case of a static ion beam of Gaussian intensity distribution with diameter (FWHM) d_i , Δz_1 depends on the mismatch distance b between the center of the ion and electron beam (in AES) of diameter d_e and is approximately given by [7.68]

$$\Delta z_1 = 4 \frac{d_e}{d_i^2} \left(\frac{d_e}{2} + b \right) z. \quad (7.18)$$

It is obvious that Δz_1 increases linearly with depth z . Therefore, Δz_1 plays a negligible role in profiling of very thin films (monolayer region) but is often the limiting factor at large sputtered depths, as demonstrated by results of Magee and Honig [7.69] with SIMS profiling of GaInAs/In layers [7.2, 7.5, 7.7] for thickness >400 nm. A depth-independent Δz at larger depth always means a negligible instrumental factor. Depth profiling of a Ta₂O₅/Ta sample of 100 nm thickness [7.18] is a good test of instrumental parameters. For optimized conditions, $\Delta z \leq 2$ nm should be achieved for Ar⁺ energies below 3 keV and incidence angles below 60° [7.17]. Then, the contribution of Δz_1 is $< 1\%$ which means a good instrumental adjustment. Equation 7.18 demonstrates the advantage of a small electron beam diameter in AES depth profiling ($d_e/d_1 < 0.01$) and the much worse situation in conventional XPS, where d_e is equivalent to the diameter of the analyzed area and $d_e/d_1 \approx 1$. Obviously, small-spot analysis XPS instruments are better suited for high-resolution depth profiles. In any case, the flatness of the crater bottom can be considerably improved when the ion beam is rastered across a certain area that can be adjusted continuously by usual ion guns up to typically 10 by 10 mm. Because of the current density distribution within an ion beam, there will always be some crater-edge effects, and these can be minimized by making the etching area (ion beam scan area) significantly larger (e.g., 10 times) than the area under analysis. Typical crater sizes in AES are of the order of 1 mm². Modern XPS instruments are able to define the analysis area sufficiently well (<100 μm) to work within the same parameters.

Rotation of the sample during AES profiling requires an especially careful matching between the rotation center, ion beam, and electron beam [7.70, 7.71] (see Sect. 7.1.9).

Surface Contamination

Adsorption of reactive gases (e.g., CO, H₂O, C_xH_y) from the residual gas atmosphere (see Sect. 2.1), neutrals and impurities in the ion beam, and redeposition of sputtered species are important instrumental factors that have to be minimized. Argon gas of highest purity (usually 6N) is required, and the base pressure before opening the Ar valve has to be in the UHV range ($<10^{-7}$ Pa). As demonstrated by Mathieu and Landolt [7.72], partial pressures of CH₄ above 10^{-5} Pa can severely alter AES depth profiles. For an ion gun operating at 5×10^{-3} Pa of argon in a closed, backfilled chamber, the contaminant gas is also ionized and implanted in the sample surface. These impurities in the primary ion beam can be considerably reduced by a differentially pumped ion gun which is generally used today. Neutrals in the ion beam are more difficult to avoid and may cause a “hole” at the spot of their impingement, because they are not deflected and scanned as the ions. Sometimes adjusting the center of the scan (and the analyzed area) away from the ion gun axis, but more reliable is usage of an ion gun with deflection plates that ensure a bent in the ion beam (see Fig. 2.10 in Sect. 2.4).

Redeposition of Sputtered Species

Another source of surface contamination is redeposition of sputtered species (e.g., due to resputtering at construction parts close to the sample surface and/or of parts of the sample surface inclined to the mean surface plane) [7.73, 7.74]. Therefore, this effect is particularly important in-depth profiling of samples with rough surfaces (see Fig. 7.37).

The influence of redeposition and resputtering on rough surfaces is demonstrated in Fig. 7.10 [7.74]. Figure 7.10a shows how a model roughness is simulated by two identical Ni/Cr multilayers on smooth Si substrates, mounted with different inclination angles. Both multilayers are simultaneously bombarded with ions from one direction. Two-point (selected area) depth profiling was used to simultaneously monitor the depth profiles of each analyzed area shown in Fig. 7.10b, c [7.74]. Because of the different sputtering rate in points Pt. 1 and Pt. 2, the Ni and Cr intensities are modified by mutual redeposition from each other until the sputter depth profile of the original layer is finished in the faster sputtering sample area of point Pt. 2 (for sputtering time = 67 min). For larger sputtering time, the Ni and Cr profiles in Pt. 1 are undistorted, because the sputtered area of Pt. 2 is already in pure silicon. However, a “ghost profile” caused by resputtering of redeposited matter from Pt. 1 appears in Pt. 2, as proven by the nearly identical time dependence. (The amount of redeposition is in the monolayer region but is exaggerated here due to normalization to 100 at%.)

Information Depth

The information depth in XPS and AES is of fundamental importance to depth profiling. It is determined by the escape depth, λ_i^e , of the measured Auger or photoelectrons of species i , given by the attenuation length λ_i and the emission angle θ , ($\lambda_i^e = \lambda_i \cos \theta$). The general effect of λ_i on quantitative depth profiling is explained for “ideal” depth profiling in Sect. 7.1.2. With respect to the definition of Δz (16–84%), the respective contribution is $\Delta z_\lambda = 1.67\lambda_i^e = 1.67\lambda_i \cos \theta$. Because usually λ_i is known from databases (see Chap. 4), Δz_λ can be rather well predicted for a given matrix. Since in an interfacial depth profile, the matrix usually changes, we have to expect a changing λ value [7.35, 7.75]. Principally, these changes can be taken into account by matrix effect correction factors as shown in Chap. 4, but they are relatively small and therefore of minor importance for profile shape alterations [7.35], as shown in detail in Sect. 7.1.8 (Fig. 7.29).

Backscattering Effect in AES Depth Profiling

The effect of backscattering in AES depth profiling is important at interfaces of materials with very different backscattering factors. A correction is difficult but possible as demonstrated in Sect. 7.1.8 (MRI model extension). The measured depth

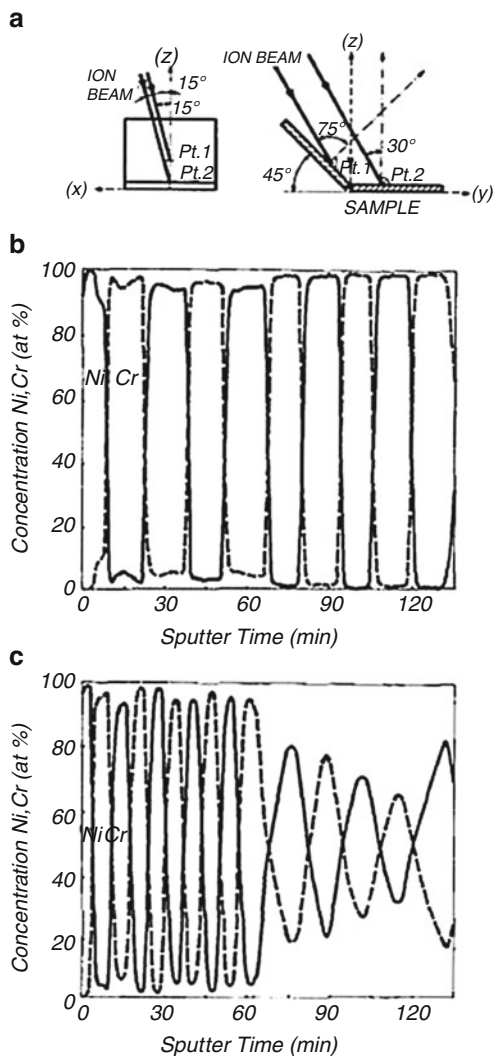


Fig. 7.10 Redeposition and resputtering: normalized AES sputter depth profiles of two identical Ni/Cr multilayers (10 layers of 30 nm thickness) differently inclined to the ion beam. **(a)** Arrangement of the two Ni/Cr multilayers, with points of AES analysis Pt.1 (ion incidence angle = 75°) and Pt.2 (ion incidence angle = 30°); **(b)** (=c in figure) AES analysis in Pt.1: mutual influence of the two parts but no redeposition (undistorted profile) from part of Pt.2 for sputtering time > 67 min; **(c)** (=d in figure) AES analysis in Pt. 2: distortions of profile for sputtering time < 67 min and “ghost” profile for sputtering time > 67 min due to redeposition from the profile in Pt.1 and resputtering (From A. Zalar and S. Hofmann [7.74])

resolution Δz at an A/B interface can even be improved by the backscattering effect (see, e.g., Sect. 4.4.3, Fig. 4.55).

7.1.4.2 Ion-Beam-Sample Interactions

Bombardment of a solid surface by energetic ions results in primary ion implantation as well as in energy and momentum transfer to the atoms of the sample [7.9, 7.10]. These fundamental interactions cause a number of complicated processes which inevitably lead to changes in surface composition and surface topography.

Atomic Mixing in the Collisional Cascade

Atomic mixing in the collisional cascade is based on complicated processes including recoil implantation, recoil-lattice atom collisions (cascade mixing) and defect generation (vacancies, interstitials, and agglomerates) [7.9, 7.10, 7.76]. Atomic mixing effectively redistributes the sample atoms within a certain range which is directly related to the projected ion range (R_p). It is inevitable in any sputter depth profiling experiment and determines the ultimate limit of depth resolution [7.77]. Numerous theoretical models have been developed to explain atomic mixing in terms of physicochemical characteristics of ion/sample interactions. Using diffusion-like equations for atomic transport, many authors have derived expressions for profile broadening [7.75, 7.78]. Andersen [7.75] derived a general relation of the contribution of atomic mixing to the depth resolution, Δz_m , which scales with the ion range and with the square root of the primary ion energy, $\Delta z_m \propto E_p^{1/2}$, and is frequently observed [7.31, 7.44]. For 1 keV Ar^+ ions and normal incidence, Andersen [7.75] predicts values of Δz_m between 2 nm (Ag, Pt) and 4 nm (Si), which are of the right order of magnitude. In sputter equilibrium, an altered layer of that dimension [7.40, 7.79, 7.80] is generated. In the simplest case, this layer is characterized by a complete homogeneous mixture of the sample constituents within the mixing zone length [7.24]. Any sputter depth profile is broadened with respect to the original depth distribution by roughly the width of the mixing zone [7.75].

Primary ion and recoil implantation are minor problems, because in AES and XPS, generally, noble gas ions (most often argon ions) are used for sputter depth profiling. Therefore, chemical reactions with the matrix are negligible, and the amount of argon retention usually is of the order of a few percent which causes practically no density change, in contrast to oxygen ion bombardment [7.23].

Preferential Sputtering

Preferential sputtering frequently changes the surface composition of alloys and compounds. In general, the emission of secondary particles of a multicomponent system subjected to sputter erosion is not proportional to the atomic concentration in the bulk. Due to different masses and surface binding energies, the sputtering yield

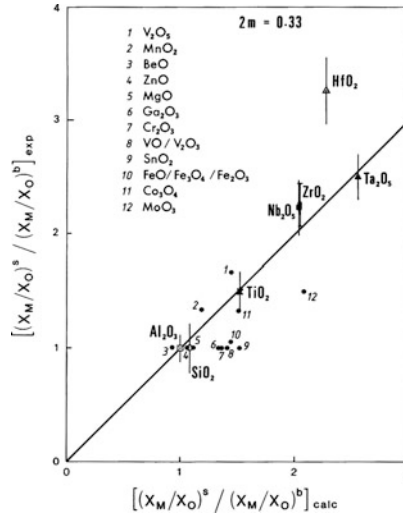


Fig. 7.11 Preferential sputtering of oxides. The experimentally determined ratio of surface composition of the altered surface layer during sputtering to that of the bulk oxide $[(X_M/X_O)^s / (X_M/X_O)^b]_{\text{exp}}$ is plotted against the predicted ratio $[(X_M/X_O)^s / (X_M/X_O)^b]_{\text{calc}}$ as calculated from (7.19) and (7.20) for various oxides indicated in the figure (From J.B. Malherbe et al. [7.81])

for different atoms differs. Preferential sputtering occurs for atoms with low mass and low surface binding energy and is described by Sigmund's [7.9, 7.10] relation for a binary system A, B as

$$\frac{Y_A}{Y_B} = \alpha_s \left(\frac{m_A}{m_B} \right)^{1-m} \frac{U_B}{U_A} \quad (7.19)$$

with Y_A , Y_B , m_A , m_B , and U_A , U_B the sputtering yields, atomic masses, and surface binding energies of A and B, respectively, α_s a constant and m a parameter of the order of 0.25. For several oxides, preferential sputtering of oxygen was quantitatively determined by Hofmann and Sanz [7.40, 7.41, 7.80] and compared with predictions after (7.19) by Malherbe et al. as shown in Fig. 7.11 [7.81]. As a rule, oxides of the heavier metals are expected to exhibit more pronounced preferential sputtering of oxygen than lighter metals.

Preferential sputtering of a component causes generation of an altered surface layer with different composition from the bulk [7.260]. For a homogeneous sample, a stationary state is attained (i.e., for $t \rightarrow \infty$ in (7.21)). Because of mass conservation, in the stationary state, the mean composition of the sputtered matter of a binary system A, B is equal to the bulk composition ratio X_A^b/X_B^b . With the respective sputtering yields Y_A , Y_B and the surface composition ratio X_A^s/X_B^s , the corresponding sputtered matter ratio is $(Y_A X_A^s)/(Y_B X_B^s)$, which gives the relation after Shimizu et al. [7.82],

$$\frac{X_A^s}{X_B^s} = \frac{Y_B}{Y_A} \frac{X_A^b}{X_B^b}. \quad (7.20)$$

Because the origin of sputtered particles is mainly confined to the first monolayer [7.10], (7.20) applies only for this layer. In the initial transient regime, an apparent concentration change is obtained even in a homogeneous sample [7.83, 7.27] (see Fig. 7.15). As shown by Ho et al. [7.27], the instantaneous mole fraction of component A, $X_A^s(t)$, of the altered layer of a homogeneous alloy with the bulk mole fraction, X_A^b , and that of the altered surface layer, X_A^s , for the stationary state ($t \rightarrow \infty$), is given by an exponential function with sputtering time t

$$X_A^s(t) = (X_A^b - X_A^s) \exp\left(-\frac{t}{\tau}\right) + X_A^s. \quad (7.21)$$

The parameter τ is the characteristic sputtering time for establishing the altered surface layer and is given by the sputtering depth scale equivalent $\dot{z}\tau$ of the order of magnitude of the mixing zone width w (usually $w \approx 2\dot{z}\tau$) [7.24, 7.84]. Preferential sputtering is a rather general phenomenon which has to be expected whenever the sputter yield of components differ (see Table 7.1)

Decomposition of Compounds

Decomposition of compounds during ion sputtering is frequently encountered if preferential sputtering of one component occurs and is accompanied by a change of the chemical state of the sample constituents in the altered layer. An example of the validity of (7.21) is given in Fig. 7.12 for the preferential sputtering of oxygen in Ta₂O₅ [7.41]. The exponential decay of the oxygen 1s signal in the XPS depth profile is clearly recognized in Fig. 7.12a. (The surface content X_A^s of oxygen is about 20% less than the bulk content X_A^b .) It is accompanied by a change of the chemical state of the sample constituents in the altered layer. Many oxides are reduced to lower oxidation states by ion bombardment (Fig. 7.11), as demonstrated as an example by the chemical-bonding-resolved sputter depth profile of a Ta₂O₅/Ta layer of 30 nm thickness in Fig. 7.12 [7.41]. The inset in Fig. 7.12a depicts the Ta4f XPS doublet peaks as a function of sputtering time. Deconvolution of the peaks with respect to the different valence states of tantalum [7.24] and evaluation of the peak areas yield quantification of the decomposition. This evaluation shows that the intensities of Ta⁴⁺, Ta²⁺, and Ta⁰ represent the suboxides TaO₂ and TaO and metallic Ta, respectively, in the altered layer, whereas the remaining Ta⁵⁺ is due to the contribution of the unchanged Ta₂O₅ beneath the oxygen-depleted layer. A dynamic equilibrium is established after the initial transient stage caused by preferential sputtering of oxygen. Correspondingly, the suboxides with lower valence of Ta arise until a plateau region is attained. The steady-state thickness of the altered layer is about 2.5 nm and can be disclosed by angle-resolved XPS (see Sect. 7.2.1).

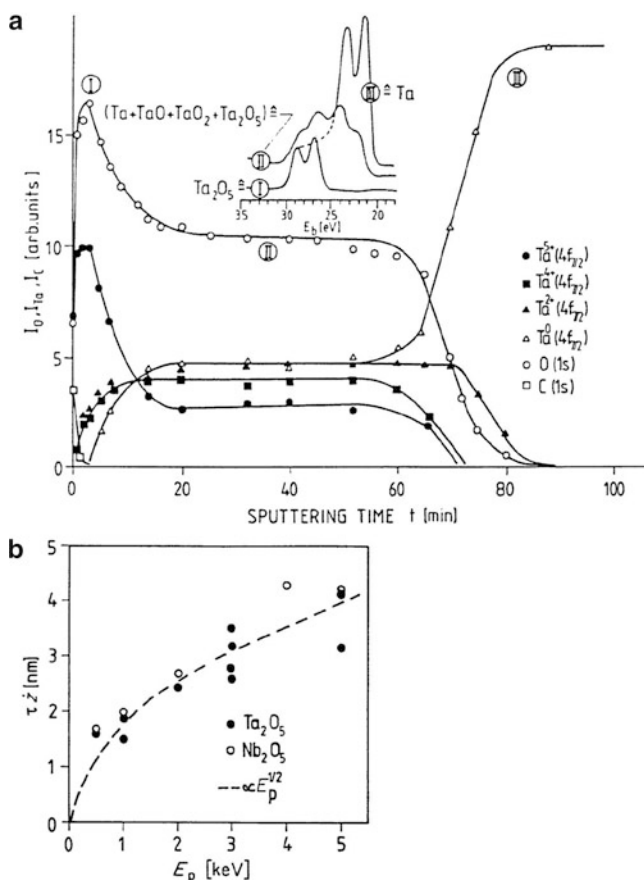


Fig. 7.12 Preferential sputtering of oxygen in sputter depth profiling of Ta₂O₅. (a) XPS sputter depth profile (with 3 keV Ar⁺ ions), showing intensity of O1s and Ta 4f with peak intensities decomposed according to its valence states: Ta⁵⁺ (Ta₂O₅), Ta⁴⁺ (TaO₂), Ta²⁺ (TaO), and metallic Ta⁰ (see *inset*). (b) Thickness of the transient layer τ_z in Ta₂O₅ and Nb₂O₅ as a function of the primary Ar⁺ ion energy (From J.M. Sanz and S. Hofmann [7.24])

The decay length τ_z is the equivalent of about two times the range of the primary argon ions and therefore energy dependent as seen in Fig. 7.12b. The transient surface concentration described by (7.21) distorts the intensity–sputtering time profile and therefore affects the profile shape, particularly at the beginning and at sharp interfaces. A characteristic asymmetry of measured profiles at interfaces is caused by the changing sputtering rate with composition, as discussed in Sect. 7.1.8 (see Fig. 7.27). Obviously, the most distortional effect of preferential sputtering is the generation of an apparent depth profile when there is no concentration gradient in the original profile, as in the beginning of the profile in Fig. 7.12a.

Radiation-Enhanced Diffusion and Segregation

Radiation-enhanced diffusion and segregation [7.3] is a consequence of defect generation in the atomic mixing zone [7.85, 7.86] and will generally change the measured profile. Because thermally activated diffusion depends on both time and temperature, an increased sample temperature should result in profile broadening. Consequently, cooling sometimes has the beneficial effect of leading to improved depth resolution [7.87]. In combination with strong surface segregation, the interplay between sputter removal and thermally activated transport from the bulk can be used to determine diffusion coefficient as demonstrated for solute O in Nb (Fig. 7.17) [7.24, 7.88]. For sufficiently high segregation enthalpy, diffusion is responsible for the measured profile width which increases with temperature. This effect is proportional to the ratio of bulk diffusivity, D , and sputtering rate, dz/dt , $D/(dz/dt)$, which enables the determination of D [7.88]. A marked influence of diffusion on depth profiles was reported by Yoshitake and Yoshihara [7.89, 7.90] for surface segregation of Ti on Nb during sputtering at room temperature and at elevated temperatures. Temperature dependence of the interfacial sputtering profile of Ag/Cu bilayers was demonstrated by Seah and Kuehlein [7.91].

Fine and coworkers [7.92, 7.94] studied in great detail segregation- and radiation-enhanced diffusion as disclosed by AES depth profiles of Ag/Ni multilayers. Here, the effect of $D/(dz/dt)$ results in a much sharper profile of the Ag layer when (dz/dt) is decreased and D is increased. This profile-steepening effect was modeled by Kelly and Miotello [7.93] and can be explained by the combined action of transport of Ag to the surface driven by both segregation and preferential sputtering and by the absence of interdiffusion between Ni and Ag because of their nonmixing behavior. In contrast, Ni/Cr multilayer profiles are broadened when sputtering takes place at elevated temperatures [7.24].

The importance of thermochemical material parameters in preferential sputtering and in radiation-enhanced diffusion and segregation is discussed by Kelly [7.95–7.97] and Kirschner [7.98]. According to Lam [7.85], three regimes with respect to the melting temperature T_m can be roughly distinguished. For low temperatures ($T < 0.2T_m$), nonthermal mixing prevails, and the diffusivity corresponds to that of the ballistic mixing calculations (see, e.g., [7.98]) and is confined within the mixing range. At increased temperatures ($0.2T_m < T < 0.6T_m$), radiation-induced defects can migrate, and the range of diffusional transport extends effectively beyond the mixing range. The concentration of thermally generated vacancies dominates at higher temperatures ($>0.6T_m$), and thermal diffusion may lead to profile broadening [7.28, 7.88] (Fig. 7.17). Of course, segregation is only important for systems showing sufficiently high segregation enthalpies [7.95]. Surface segregation kinetics principally causes outward diffusion of the segregant to the surface. Therefore, a characteristic minimum below the surface layer occurs as shown by Hofmann and Erlewein [7.99] for surface segregation of Sn in Cu. When diffusional transport to the surface is counterbalanced by surface sputtering, such profiles are obtained in steady state during alloy sputtering [7.100]. Using ion surface scattering (ISS), Swartzfager et al. [7.101] disclosed the Cu profile in a Cu–50%Ni alloy showing a

distinct minimum in the subsurface layer. Similar studies by Koshikawa and Goto [7.102] and by Shimizu [7.103] revealed that earlier conclusions of preferential sputtering in Cu–Ni alloys were based on a wrong interpretation of AES profiling data. Because of its typical information depth of several monolayers, the intensity of AES and XPS is a weighted average over the surface layer and the subsurface minimum (see, e.g., Sect. 4.3.3). Therefore, the apparent surface monolayer concentration obtained by the simple homogeneous concentration assumption is too low. Because the ISS intensity represents the composition of the first monolayer, a combination of AES or XPS with ISS has proved to disclose the near surface profile [7.104, 7.105]. Combined AES/ISS studies by Li et al. [7.83] in sputter depth profiling of a Cu–Pt alloy are shown in Fig. 7.13. The time-dependent establishment

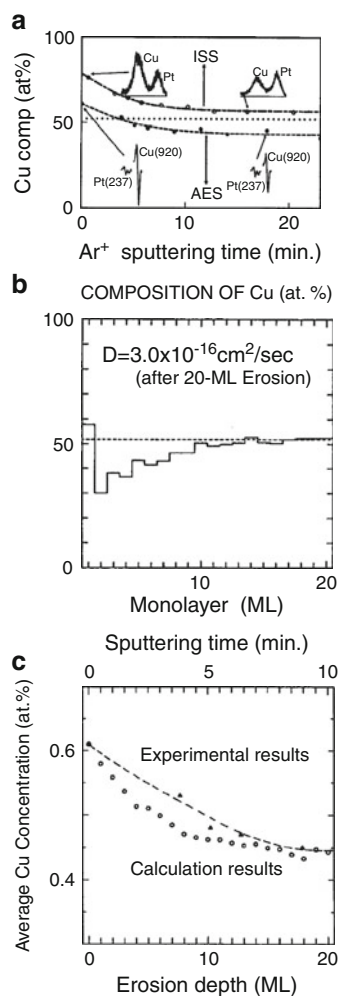


Fig. 7.13 Combined AES and ISS sputter depth profiling of a homogeneous Pt–52 at.% Cu alloy with 3 keV Ar⁺ ions. (a) Experimental results of the Cu concentration from AES and ISS (see Sect. 10.4.3) measurements; (b) Monte Carlo simulation of the steady-state depth distribution of composition; (c) comparison of the AES result in (a) with calculations of the average concentration applying (1) type formalism to profiles such as depicted in (b) for different times (Adapted from K. Min and R. Shimizu [7.106], with permission of J. Wiley & Sons Ltd.)

of a steady-state in-depth distribution is monitored by simultaneous AES and ISS in Fig. 7.13a, representing the typical difference between the ISS data (representing the first monolayer) and the AES data (representing an average over the first several monolayers, see Sect. 4.4.3). However, as shown in Fig. 7.13c, good agreement is obtained for the apparent, average composition when the AES intensity is calculated according to the altered layer structure depicted in Fig. 7.13b. Similar profiles were calculated by Reichel et al. [7.105] and compared with quantitative AES, XPS, and ISS. Because the decisive parameters for the steady-state profile are given by $D/(dz/dt)$ and the width of the mixing zone, a change of the ion energy and/or a change of the ion current density causes a change in the measured AES or XPS intensity. In practice, this fact can be used as a quick check whether preferential sputtering occurs.

Preferential sputtering in case of depth profiling at interfaces or steep concentration gradients is more complicated because no steady state is attained. However, the general effect is expected to be less pronounced, and profile modeling is possible assuming an average concentration in the mixing zone (see Sect. 7.1.8).

Electron and Photon Beam Effects in Depth Profiling

With the exception of highly focused synchrotron radiation, the photon flux of usual laboratory X-ray sources is too weak to cause major changes in-depth profiling. Focused electron beams in AES are more likely to cause distortions of sputter depth profiles by beam heating, charging of insulators, and decomposition of compounds. For example, electron-irradiation-stimulated desorption (ESD) of chlorine and oxygen is frequently observed [7.107–7.109] and can cause enhanced sputtering in the area of the electron beam impingement with a loss in-depth resolution as a consequence [7.110]. Since the effects of electron-beam-induced desorption and sputtering compete at the surface, the former effect is suppressed by lowering the electron beam current density (e.g., rastering) and/or increasing the ion beam current density [7.111]. (see Fig. 8.8)

In general, a high Ar^+ ion dose helps to overcome effects of charging in insulators during AES depth profiling [7.112]. Deeper deposited negative charge by energetic primary electrons may lead to electrotransport which changes the surface composition if there are mobile ions in the respective compound (e.g., Na^+ in glass) [7.113]. High sputtering rates and cooling the sample usually serves as a remedy.

In general, energy dissipation in the sample surface caused by X-ray irradiation and – with the exception of extreme cases – by ion sputtering is negligible. However, electron beam heating by a highly focused electron beam in AES can lead to a temperature increase of several hundred degrees, particularly in thin films on glass substrates [7.114, 7.115], which causes strong profile broadening due to bulk diffusion, segregation, and even evaporation. The temperature rise is kept small by lowering the electron beam current density. A test of the effect of electron beam heating on the depth profile can be made by sputtering the same sample with

different electron current densities [7.114, 7.116]. A survey of electron and photon beam effects is given in Sect. 8.6.

Sputtering-Induced Nano-Topography

Before attaining constant thickness, the mixing zone thickness gradually increases (the so-called transient state of sputtering) with approximately the square root of depth until a depth of about two times the ion range is attained, as shown by Tsai and Morabito [7.117]. A similar dependence is obtained by considering surface microroughening due to the statistical nature of the sputter erosion process [7.118–7.121].

According to Benninghoven [7.118], sputtering statistics lead to a depth-dependent probability of surface exposure and therefore to an increasing number of layers being analyzed that gives rise to a contribution $\Delta z_s = 2(az)^{1/2}$, with sputtered depth z and a being the monolayer thickness [7.60]. However, “roughening” by sputtering statistics is limited to a few atomic layers from the surface, because there are at least two processes that counteract the steady increase of surface roughness on the atomic scale and lead to a “saturation” at larger depth, namely, site-dependent sputtering probability [7.120] and surface diffusion [7.121] (see Sect. 7.1.7, SLS model). The first effect can be rationalized by different surface binding energies U_0 , depending on the geometric configuration, i.e., whether an atom occupies a position on top of a plane, or at a ledge, or within a flat part of the surface layer. Since the sputtering yield is inversely proportional to U_0 , the above model, after an initial increase with $z^{1/2}$, gives a depth-independent average surface roughness of the order of a few monolayers [7.120], which is determined by the difference of the respective site-dependent surface binding energies. In a similar manner, the surface diffusion model takes into account a surface-site-dependent atom mobility, i.e., a compensating exchange reaction of atoms on top of a plane with the vacancies in this plane which is inversely proportional to U_0 [7.120]. In summary, the contribution of Δz_s is rather small (of the order of a few monolayers at maximum) and therefore can generally neglect for thicker layers.

Topography Development at Larger Depth

Sputter depth profiling of polycrystalline metallic thin films frequently shows a depth-dependent depth resolution following approximately a $z^{1/2}$ relation at larger depth [7.48, 7.60, 7.122, 7.123], which can be attributed to the evolution of bombardment-induced topographical features, often in the shape of faceted, ripple-like or conical structures [7.124–7.128]. The main causes are the dependence of the sputtering yield on the ion incidence angle [7.123, 7.259] and on crystalline orientation [7.10]. Therefore, these effects are discussed in the next paragraph (sample characteristics).

7.1.4.3 Sample Characteristics

Accuracy and precision of sputter depth profiles are limited by a number of special sample characteristics relevant to depth profiling. Most important are original surface roughness and topography, crystalline structure and crystalline defects, chemical composition, and bonding (e.g., metal, alloy, semiconductor, compound, second phases), as well as electrical and thermal conductivity.

Original Surface Roughness

A large number of experiments have demonstrated that there is a substantial influence of an original surface roughness on the depth resolution [7.128–7.136]. This roughness contribution (Δz_r) was shown by Seah and Lea [7.135] to be proportional to the sputtered depth and increasing with the standard deviation of the angular distribution between differently inclined elements of a surface and the average surface plane, and with the deviation of the angular dependence of the sputtering yield from a cosine law (below 60°) [7.135]. The roughness contribution Δz_r is expected to increase with the ion incidence angle α_1 [7.135], because of increasing probability of shadowing of the ion beam as well as of redeposition (and resputtering). These phenomena are schematically visualized in Fig. 7.14. Similarly, depth resolution is degraded by increasing surface roughness, characterized by an (mean) inclination angle of the microplanes (see also Sect. 5.1.4).

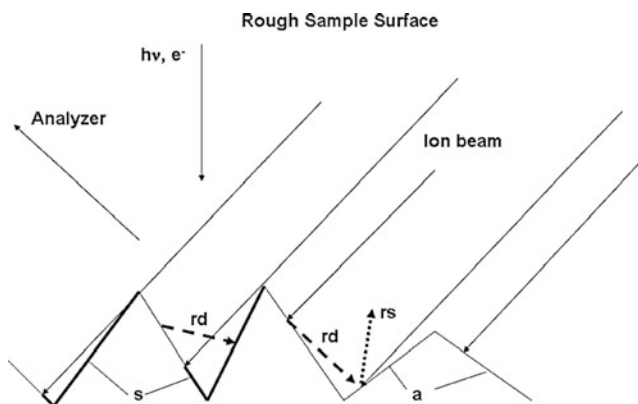


Fig. 7.14 Schematic explanation of shadowing (s , thick drawn lines (areas)), redeposition (rd), and resputtering (rs) at rough sample surfaces (compare also Fig. 7.10). For the geometry shown, the critical inclination angle of the surface structure to the average surface is $90 - \alpha_1$ (α_1 = ion beam incidence angle). Therefore, if the surface consists of structures similar to that on the right side of the picture, for areas (a), there is no shadowing, and sputter depth profiling is performed with considerably less distortions resulting in lower Δz (lower two curves in Fig. 7.15)

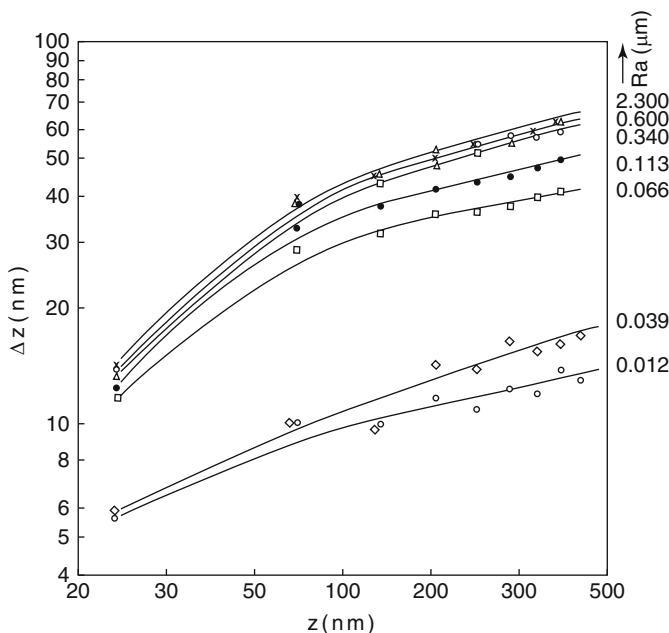


Fig. 7.15 Depth resolution Δz of multilayer Ni/Cr thin films of different roughness R_a , as a function of the sputtered depth z (1 keV Ar^+ , incidence angle 47°) (From A. Zalar and S. Hofmann [7.132])

Systematic studies using Ni/Cr multilayers with different roughness revealed that Δz_r depends mainly on the angular distribution of the inclination of different microplanes on a sample surface and much less on the mean, rms amplitude of roughness, R_a [7.132]. Figure 7.15 shows that the increase of the measured Δz at a given depth is most pronounced for the increase of roughness from $R_a = 0.039\mu\text{m}$ to $R_a = 0.066\mu\text{m}$ (increase by about a factor of 2) but almost vanishes from $R_a = 0.34\mu\text{m}$ to $R_a = 2.3\mu\text{m}$ (about a factor of 7). It has been demonstrated that for rough sample surfaces, the dominant causes of profile broadening are shadowing and redeposition (Fig. 7.14), which only depend on the inclination of neighboring planes [7.74]. With the sketch in Fig. 7.14, the experimental findings of Fig. 7.15 can be qualitatively explained. For lower roughness values R_a , when the distribution of microplane inclination angles to the average surface is below a critical value (given by the geometry of primary beam, ion beam, and direction to the analyzer), there is no shadowing (s) and negligible redeposition (rd) (regions (a) in Fig. 7.14). For higher R_a , the average inclination angle will increase and therefore redeposition (rd) in nonsputtered but analyzed parts of the surface (shadowing (s)) increases. However, the average inclination angle will be limited by the material stability and the grinding process, which may explain the rather small relative increase of Δz for $R_a > 0.34\mu\text{m}$. From Fig. 7.14, it is clear that shadowing and redeposition effects increase with the ion incidence angle and set a limit of the useful ion incidence angle to about $\alpha_i \leq 60^\circ$ for rough surfaces, above which the profile extensively

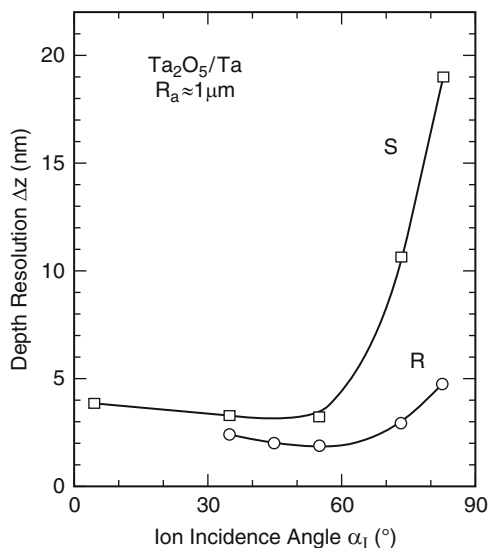


Fig. 7.16 Depth resolution as a function of the ion incidence angle for oxygen AES depth profiles of a $\text{Ta}_2\text{O}_5/\text{Ta}$ layer of 30 nm thickness obtained with 3 keV Ar^+ sputtering and a high surface roughness of $R_a \approx 1 \mu\text{m}$, for stationary (*S*) and rotating (*R*) sample with a rotation speed of $0.23 \text{ rev min}^{-1}$ (From S. Hofmann and A. Zalar [7.71])

broadens (cf. Fig. 7.16). In contrast to rough samples, smooth samples show an improved Δz with increasing α_1 (see Fig. 7.18), mainly caused by the decreasing mixing length. The strongly increasing Δz of sputter-depth-profiled $\text{Ta}_2\text{O}_5/\text{Ta}$ (30 nm thickness with about $1 \mu\text{m}$ surface roughness) for $\alpha_1 > 60^\circ$ in Fig. 7.16 (*S* for static (nonrotating) sample) is most probably caused by surface roughness. Multidirectional ion incidence, for example, by two ion guns [7.73, 7.137] or by sample rotation [7.138–7.142] are effective means to reduce shadowing and redeposition (see Sect. 7.1.9.2). The beneficial effect of these measures is demonstrated in Fig. 7.16, where the depth resolution is plotted as a function of the ion incidence angle with (*R*) and without (*S*) sample rotation. Details on depth profiling with sample rotation are given in Sect. 7.1.9.2, where Fig. 7.37 gives a schematic explanation of the principal effect of sample rotation during sputtering of rough surfaces.

Based on the angular distribution of microplanes and the respective sputtering yields, the depth dependence of Δz can be calculated for multilayers with smooth and rough surfaces using the concept of linear superposition of error functions [7.68, 7.143]. It has been shown that the geometry of a surface influences the development of surface topography during sputtering [7.74, 7.135–7.137]. Even in the case of a flat amorphous surface, the frequently observed cone formation under ion bombardment can be attributed to the dependence of the sputtering yield on the ion incidence angle [7.9, 7.20, 7.259].

Crystalline Structure and Orientation

Any local change of the local sputtering rate $\dot{z}$ within the analyzed area causes an increase of surface roughness with sputtered depth [7.130, 7.132]. In contrast to single-crystals and amorphous materials, polycrystalline metallic materials show such a behavior because of different $\dot{z}$ for the different grains [7.86]. Kojima et al. [7.144], Satori et al. [7.145], and Woehner et al. [7.143] demonstrated that the generally observed increase of Δz with depth z for sputtered metallic multilayers is directly related to sputter-induced roughness. Careful measurements on polycrystalline metallic layers show an excellent correlation of Δz with the root-mean-square (rms) roughness parameter R_p ($\Delta z = 2R_p = 2\sigma$) [7.143]. The depth dependence of the sputtering-induced roughness and therefore of Δz is mainly determined by the grain size relative to the sputtered depth z . For a large average grain size, $\bar{d} \geq z$, Δz is expected to increase linearly with z , as shown for Al evaporation layers on Si [7.143]. For a small grain size, $\bar{d} \ll z$, a random distribution of the locally different z is expected to result in a square root dependence with depth z [7.146]. In multilayers, any interface randomizes an originally linear increase of Δz , and $\Delta z \propto z^{1/2}$ is usually observed for Δz in Ni/Cr multilayer profiling [7.130, 7.131]. With $\Delta \dot{z}$ the standard deviation of $\dot{z}$ for different grains and the mean sputtering rate $\bar{\dot{z}}$, the crystallinity contribution Δz_c to the observed depth resolution can be described by [7.5, 7.88],

$$\Delta z_c = 2\sqrt{dz} \frac{\Delta \dot{z}}{\bar{\dot{z}}}. \quad (7.22)$$

The square root dependence of Δz_c on z (7.22) is frequently observed in unidirectionally profiling of sputter-deposited metallic multilayers [7.2, 7.60, 7.122]. An example is seen in Fig. 7.17 for the AES sputter profiling of Ni/Cr multilayers without rotation (S) performed by four different laboratories. In contrast, single crystals, amorphous materials, oxide layers, and semiconductors (which generally amorphize during Ar^+ ion sputtering) show a vanishing Δz_c because $\Delta \dot{z}$ in (7.22) is practically zero. Therefore, the total, measured Δz is constant with z , because the effect of atomic mixing, i.e., Δz_m , dominates. In polycrystalline metallic materials, multidirectional ion bombardment as obtained by sample rotation during sputtering effectively randomizes $\dot{z}$ for different grains which means $\Delta \dot{z} \rightarrow 0$ in (7.22). Therefore, $\Delta z_c \rightarrow 0$ and the total, measured Δz is independent on depth z . Fig. 7.17 shows a comparison of Δz obtained from an interlaboratory study of Ni/Cr multilayers, with sample rotation (R) and without sample rotation (S). Without rotation, the roughness increases with sputtering time and depth and roughly follows the square root dependence, $\Delta z_s \propto z^{1/2}$, as expected for randomized crystallite orientation dependence of the sputtering yield. This sputtering-induced roughness [7.143–7.145] can be minimized by sample rotation (Fig. 7.17, region marked with R) [7.147], which results in an average, constant, and significantly better depth resolution of about 6 nm over a sputter depth of 0.4 μm . Further details on the use of sample rotation in-depth profiling are presented in Sect. 7.1.9.2.

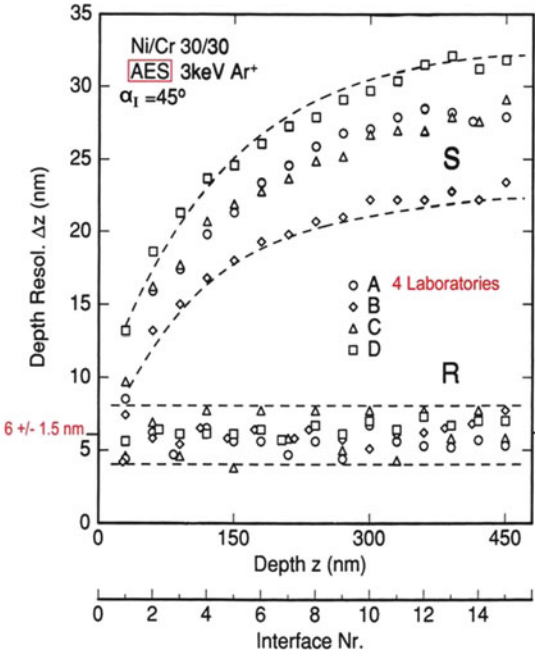


Fig. 7.17 Depth dependence of the depth resolution with (*R*) and without (*S*) sample rotation. AES analysis results of an interlaboratory study (A–D) on a Ni/Cr multilayer with 10 double layers of 30/30 nm thickness. Depth profiling with 3 keV Ar⁺ ions at 45° incidence angle (From S. Hofmann et al. [7.147])

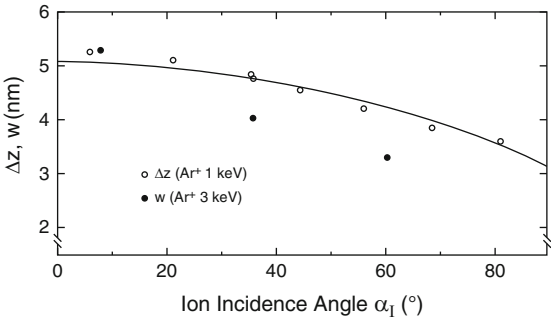


Fig. 7.18 Dependence of the depth resolution Δz on the ion incidence angle α_I for Ta/Si multilayers and for sputter depth profiling with 1 keV Ar⁺ ions (*open circles*) [7.148]. *Full points* indicate the mixing zone width, *w*, determined from TEM and STEM results [7.33] for 3 keV Ar⁺ sputtering of the same material (From S. Hofmann [7.3])

An example of the dependence of the measured Δz on the ion incidence angle in absence of the crystalline effect is shown in Fig. 7.18 for depth profiling results of Ta/Si multilayers [7.148]. (Although a small residual Δz_c of the Ta layers cannot be excluded, it is effectively counterbalanced by the amorphous Si layers.)

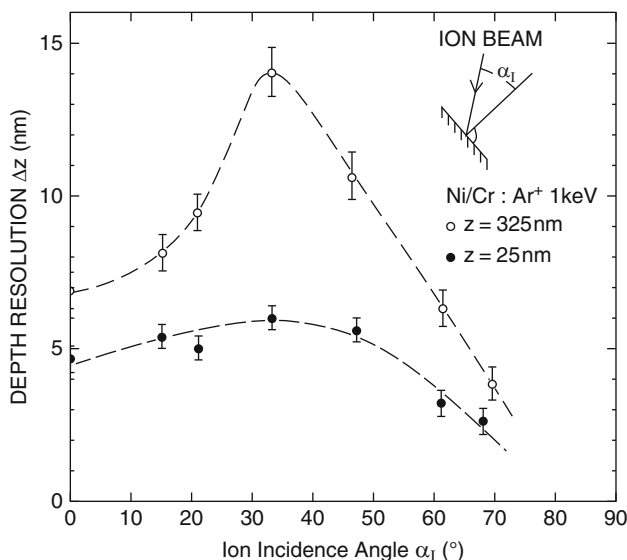


Fig. 7.19 Dependence of Δz on the ion incidence angle α_I for Ni/Cr multilayer samples with smooth surface and 1 keV Ar^+ ion sputtering. *Upper curve:* depth $z = 325$ nm, *lower curve:* $z = 25$ nm. (Note the marked difference to the results for Ta/Si shown in Fig. 7.18) (From A. Zalar and S. Hofmann [7.130])

The preponderant effect of atomic mixing is recognized by the monotonous, almost cosine-like dependence of Δz with α_I (in addition to a contribution of Δz of the original “interface width,” contribution, presumably from the observed “waviness” of the interface location of the deposited structure) (Fig. 7.18).

A theoretical explanation of the angular dependence of Δz for metallic layers was given by Pamler et al. [7.149] for their results on AES profiling of Al/Ti interfaces and was compared to Ni/Cr results by Höslér and Pamler [7.150]. The explanation is based on the lattice orientation dependence of the sputtering yield after Onderdelinden [7.151] by taking into account the strong $\langle 111 \rangle$ texture of sputter-deposited Al layers (and of Ni layers in Ni/Cr [7.150]). Single-crystal sputtering is described by the Lindhard’s theory of ion channeling [7.152]. Because channeled ions with long ranges are ineffective for sputtering, the sputtering yield depends mainly on the nonchanneled fraction of the incident ions, which is roughly proportional to the interatomic spacing in the respective lattice direction. Assuming a strong $\langle 111 \rangle$ texture, all the normally impinging primary ions ($\alpha_I = 0$) cause a sputtering yield close to $Y(111)$, and Δz in (7.22), and therefore, Δz_c are practically zero. Channeling takes place most effectively in the $\langle 110 \rangle$ direction which is 35.3° inclined to $\langle 111 \rangle$ and less pronounced in the $\langle 100 \rangle$ direction with 54.7° inclination angle (see Fig. 7.20). Due to their random orientation around the $\langle 111 \rangle$ axis, a substantial fraction of the grains are oriented in nonchanneling directions with a high sputtering yield approaching $Y(111)$. Therefore, the relative variation of the local sputtering rate $\Delta z/\bar{z}$ in (7.22) is at maximum for $\alpha_I = 35.3^\circ$ and less pronounced for $\alpha_I = 54.7^\circ$. For higher incidence angles ($\alpha_I > 60^\circ$), channeling

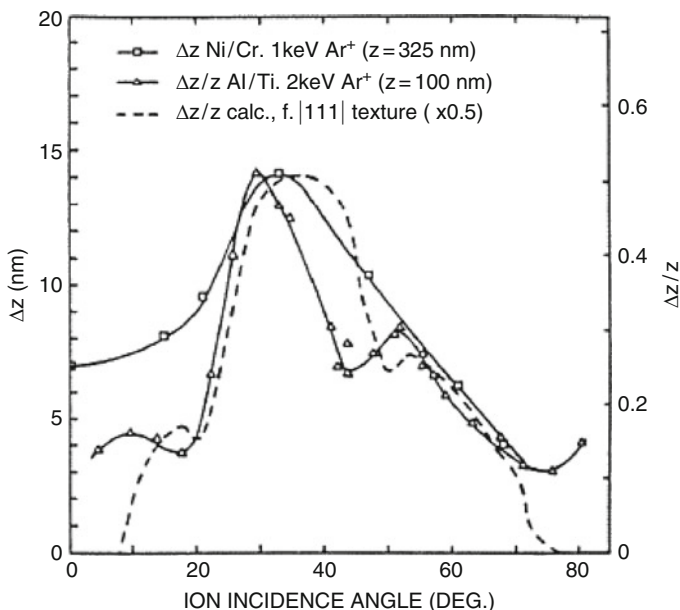


Fig. 7.20 Depth resolution Δz of Ni/Cr multilayers at depth $z = 325$ nm from Zalar and Hofmann [7.130] (open squares) and relative depth resolution $\Delta z/z$ of Al/Ti bilayers at $z = 100$ nm from Pamler et al. [7.149] (open triangles) as a function of the ion incidence angle. The broken curve shows $\Delta z/z$ calculated for an ideal [7.110] texture after Pamler et al. [7.149]. (All curves are normalized to the maximum value.) (From S. Hofmann [7.3])

does not lead to effective sputter yield reduction by channeling because even long ion range trajectories end near the surface, and $\Delta z/z$ is effectively reduced. The expected dependence of Δz_c calculated by Pamler et al. [7.149] is shown in Fig. 7.20 together with their results for 2 keV Ar^+ sputtering of (111) textured Al on Ti and with the data of Ni/Cr from Zalar and Hofmann [7.130]. Although the multilayer Ni/Cr with fcc/bcc lattice combination is somewhat more complicated, the basic features are similar and can be explained accordingly [7.150].

The effect of crystalline structure is efficiently reduced for amorphous samples or if the sample is amorphized by ion bombardment, as is usually the case in directionally bonded semiconductors and in oxides.

The difference of channeling and nonchanneling sputtering yields increases with the primary ion energy E_{PI} and so does Δz_c . The relation $\Delta z_c \propto E_{PI}$ is often found for medium incidence angles [7.5, 7.149], whereas at high incidence angles, Δz_c is practically independent on E_{PI} in accordance with the channeling model. The nonchanneled fraction in channeling directions increases with the atomic number of the primary ions [7.151]. This fact explains the frequently reported smaller Δz when using Xe^+ ion sputtering as compared to Ar^+ sputtering of metallic samples [7.153, 7.154]. This effect again is diminished at higher incidence angles [7.149]. In summary, a consistent model of surface roughening during depth profiling of metals caused by crystalline orientation exists which allows quantitative explanation of measured interface profiles, as shown by Wöhner et al. [7.143] for Al thin

films on Si substrates. Appropriate use of sample rotation in sputter depth profiling (see Sect. 7.1.9) serves to avoid the effect of crystallinity and, to a lesser degree, of original surface roughness.

7.1.5 Depth Dependence of Depth Resolution: Superposition of Different Contributions

The many different contributions to depth resolution described above superimpose on each other to yield the experimentally measured, total depth resolution. It is important to distinguish between depth-independent and depth-dependent contributions. Of course, the information depth contribution, Δz_λ , is strictly depth independent (but composition dependent). With the exception of the transient state until attainment of dynamic sputter equilibrium (usually a few monolayers, where the depth dependence of the sputtering statistics, Δz_s , usually applies [7.5, 7.120]), Δz_s and the mixing contribution, Δz_m , are depth independent. Only the contributions of sputtering-induced roughness (Δz_r) and of local variations of the ion beam intensity (Δz_l) increase with sputtered depth. Whereas Δz_l is always linearly dependent on the depth [7.2] (but can be principally avoided by careful adjustment and rastering of the ion beam), Δz_r shows a depth dependence that generally increases less than linear with depth and often follows a square root dependence (see Fig. 7.18, curves S). When Δz_r is made negligible, for example, by sample rotation (see Sect. (7.1.9) and Eqs. 7.15, and 7.23), it can be used to extract the different contributions to the measured Δz in test structures [7.6, 7.155].

The abovementioned contributions combine to the total, experimentally measured depth resolution Δz . Assuming that the different contributions Δz_j are independent of each other, their superposition is statistically at random, i.e., they add up in quadrature, and Δz is given by the square root of that sum [7.1–7.6, 7.48],

$$\Delta z = \sqrt{\Delta z_0^2 + \Delta z_s^2 + \Delta z_m^2 + \Delta z_\lambda^2 + \Delta z_r^2 + \Delta z_l^2 + \dots}, \quad (7.23)$$

where Δz_0 is the contribution of intrinsic surface roughness or interface width, Δz_s of surface roughening by sputtering statistics, Δz_m of atomic mixing, Δz_λ of information depth, Δz_r of ion-sputtering-induced roughening, and Δz_l of local variations of the ion beam intensity, respectively. If the original width of an *A/B* interface is characterized by Δz_0 , the measured or apparent interface width, Δz , is identical to the depth resolution if Δz_0 is zero or negligible with respect to the other contributions. Since a finite gradient in any original depth profile can be approximately described by a certain Δz_0 (e.g., according to the inverse slope definition, Sect. 7.1.3), (7.23) can be used to predict the necessity and the limitations of the deconvolution of a measured profile as discussed in [7.4, 7.5]. Although strictly valid only for Gaussian resolution functions (7.23) has proved to be very useful even in the case of other functions such as exponentials (as for the effect of mixing and information depth) (see Sect. 7.1.3). It should be kept in mind that due

to the adding up in quadrature, the contributions with lower Δz_j can be usually neglected when compared to a preponderant Δz_j (e.g., Δz_r for metals at larger sputtered depth).

During the past decades, considerable agreement has been achieved, and the main contributions to the depth resolution Δz are at least semiquantitatively understood. Consequently, conditions for optimized depth profiling have been established [7.1–7.7, 7.51].

7.1.6 Optimized Depth Profiling Conditions

Accuracy and precision of a measured profile are the basis of deconvolution and quantification. It is therefore essential to optimize profiling conditions with respect to high depth resolution (i.e., low Δz_j). This can be achieved by careful consideration of the effects of instrumental factors, ion-beam-sample interactions and sample characteristics as discussed in Sect. 7.1.3. General rules for optimized profile measurements are summarized in Table 7.2.

Table 7.2 Survey of optimized depth profiling conditions

Instrumental factors	Sample ambience	Low residual reactive gas pressure ($<10^{-8}$ Pa) “free” sample mount	
	Analyzing conditions	Sputtered area large against analyzed area Analyzed area centered in sputtered area Selection of low kinetic energy signal	
	Ion beam	Low beam energy (≤ 1 keV) Rastered and with constant intensity Large incidence angle for smooth sample ($>60^\circ$) Low incidence angle for rough sample ($<60^\circ$) High mass ion species (cluster ions) No impurities in ion beam (pure sputter gas) No neutrals in ion beam (beam deflection) Sample rotation and/or two differently inclined beams	
		Electron beam (AES)	Centered within sputtered area Fine-focused or small area rastering Low current density
			Photon beam (XPS)
		Sample characteristics	Smooth, polished surface Noncrystalline, no second phases Components with similar sputtering yields Good electrical and thermal conductivities Low interdiffusion, no Gibbsian segregation

7.1.6.1 Sample Ambience

To avoid contamination of the sample, in particular for alternative sputtering/data acquisition mode, a low residual pressure of reactive gases ($\text{UHV} < 10^{-8} \text{ Pa}$) is required (see Sect. 2.1). Resputtering and redeposition should be kept low by a “free” sample mount, with the sample placed on top of a holder and far away from construction parts which can be hit by the incident ion beam, by reflected ions or by sputtered matter.

7.1.6.2 Analyzing Conditions

Careful matching of the center area of sputtering with the analyzed spot, which should be small relative to the crater size [7.68], is a prerequisite. A flat crater bottom is generally achieved by constant, uniform ion beam intensity and by rastering across an area which is large against the analyzed area. Selecting AES or XPS signals of low kinetic energy ensures lowering of the information depth contribution to profile broadening in high-resolution depth profiling (see Fig. 7.21). Besides higher spatial resolution, this is another advantage of AES against XPS in sputter depth profiling, because in AES usually peaks at kinetic energy below 100 eV with typical electron escaped depth values of one atomic monolayer can be used resulting in an information depth contribution to depth resolution comparable to SIMS (see Sect. 10.4).

7.1.6.3 Ion Beam

Low ion beam energy ($\leq 1 \text{ keV}$), high mass ion species, and large ion incidence angles ($\alpha_i > 60^\circ$) ensure minimization of the influence of atomic mixing as well as ion-induced roughening on smooth sample surfaces. In contrast, rough sample surfaces require a lower ion beam incidence angle ($\alpha_i < 60^\circ$) to minimize shadowing and redeposition [7.74] (see Figs. 7.16 and 7.18). Avoiding impurities in the sputter ion gas supply and neutrals impinging in the analyzed spot (e.g., by beam deflection, see Sect. 2.4, Fig. 2.10) are indispensable for high-quality profiles.

Multidirectional ion incidence, for example, dual beam sputtering or the more effective sample rotation technique reduces original sample roughness effects and, in addition, minimize ion-induced roughening caused by different local sputtering rates, for example, by different crystallite orientations in polycrystalline metallic materials [7.132–7.136, 7.147, 7.149]. An example of the beneficial influence of sample rotation on depth resolution is shown in Fig. 7.17.

Optimized results using sample rotation mainly depend on a high-precision rotation axis [7.71], on careful adjustment of the analyzed area in the axis of rotation, and on an appropriate rotation speed. Even a small deviation from the rotation axis may cause artifacts that degrade depth resolution at larger depth. According to results by Sobue and Okuyama [7.141] and by Hofmann and Zalar [7.71], the minimum sputtering speed should not be lower than $u_{\min}/\dot{z} \geq 1 \text{ nm}$, with

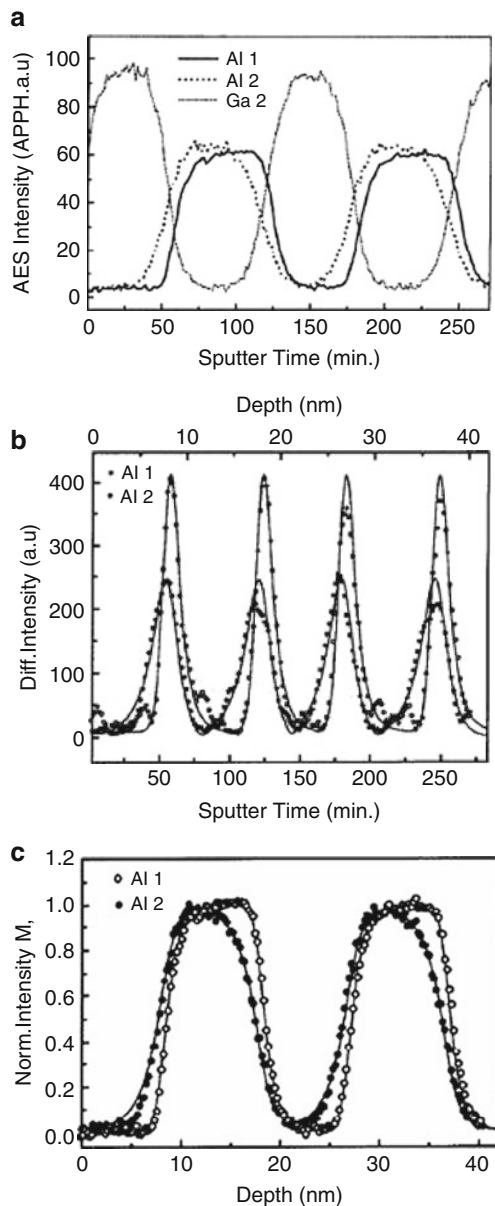


Fig. 7.21 (a) Measured sputter depth profile of the first four layers of a GaAs/AlAs (8.8/9.9 nm) multilayer using 0.6 keV Ar^+ ions with 80° incidence angle. The low-energy (Al 1: 68 eV) and high-energy (Al 2: 1396 eV) AES signal intensities are shown as a function of the sputtering time; (b) Depth resolution functions (DRFs) derived from the differentiated profiles in (a) (points) and calculated by the MRI model with the parameters $w = 1.0$ nm, $\sigma = 0.6$ nm, λ (Al 1) = 0.4 nm and λ (Al 2) = 1.7 nm (lines); (c) Profile simulation of (a) with the parameters in (b), assuming a rectangular distribution of Al with depth (From S. Hofmann [7.4])

the rotation speed $u_{\min}$ in revolutions per minute (rpm) and the sputtering rate $\dot{z}$ in nm/min. Details for sputter profiling with sample rotation are given in Sect. 7.1.9.2.

7.1.6.4 Sample Rotation (see Sect. 7.1.9.2)

7.1.6.5 Electron Beam (AES)

The electron beam in AES analysis has to be centered in the sputtered area to ensure analysis in a flat bottom area (Sects. 7.1.3 and 7.1.4). A fine-focused beam is optimal. However, a small raster (e.g., $5 \times 5 \mu\text{m}^2$) is helpful to keep the time-averaged flux or dose density low enough in view of detrimental electron beam effects (Sect. 8.6.1).

7.1.6.6 Photon Beam (XPS)

A fine-focused photon beam or a small-spot-analyzed area (centered within the sputtered area) is required for high-resolution XPS depth profiling (see Sect. 7.1.4, Instrumental factors (a)).

7.1.6.7 Sample Characteristics

Frequently, a challenge for the analyst, specific properties of a sample are most important for the profiling result. For example, constituents with strongly different sputtering yields unavoidably cause preferential sputtering that shows up in profile distortions, which often are increased by thermal and radiation-enhanced diffusion and segregation. The latter effects can at least partially be suppressed by cooling the sample and/or by using increased sputtering rates [7.85, 7.102]. Because all the above effects depend on sputtering rate and on ion energy, a quick check of their occurrence is possible by comparison of profiles measured with very different ion energies [7.105].

Crystallinity effects, particularly in metals, can be overcome by high ion incidence angle and by sample rotation. Charging of insulators during ion bombardment and analysis, electron-beam-induced heating, and desorption (see Sect. 8.6.1) in AES sputter profiling can cause severe distortions of the measured profile [7.110]. Most favorable conditions are met if the sample has an amorphous (or single crystalline) structure, a smooth surface, good electrical, and thermal conductivity, and if it consists of components with similar sputtering yields, negligible diffusivity and negligible segregation enthalpies. Therefore, it is not surprising that optimum profiles are most often reported for semiconductor materials and for amorphous oxide layers. Many papers have clearly demonstrated the validity of the general rules for optimization of depth resolution. Kajiwara and Kawai [7.156] reported the achievement of $\Delta z \cong 1.5 \text{ nm}$ in AES sputter profiling of GaAs/AlAs multilayers

with 200 eV Ar^+ ions at $\alpha_1 = 55^\circ$ using low-energy Auger transitions (As 32 eV, Ga 55 eV, Al 65 eV) with escape depths of about 0.5 nm.

Certified reference materials (CRMs) are useful for testing and optimizing a given instrument with respect to achievable depth resolution. A compilation of presently available CRMs with suppliers are shown in Table 7.3.

Table 7.3 Certified reference materials (CRMs) for depth profiling

Reference materials	Properties	Certification bodies	Certification methods
GaAs/AlAs superlattice	Alternate GaAs/AlAs layers on GaAs substrate (Each piece has its specified values) Certified: Thickness of 2nd AlAs: 22.44 ± 0.20 nm Thickness of 3rd GaAs: 23.23 ± 0.33 nm Thickness of 4th AlAs: 22.51 ± 0.29 nm	NIMC CRM 5201-a	X-ray reflectivity
Ta ₂ O ₅ /Ta multilayer	Alternate amorphous Ta ₂ O ₅ and polycrystalline Ta layers Certified thickness of: Ta ₂ O ₅ layer: $30 \text{ nm} \pm 2.5\%$ Ta layer: $30 \text{ nm} \pm 2.5\%$	KRISS 03–04–101	TEM
Ni/Cr multilayer	Alternate Cr/Ni layers on Si (total 8 layers) Certified thickness of: Cr layer: $38.2 \pm 2.3 \mu\text{g}/\text{cm}^2$; Ni layer: $58.8 \pm 3.5 \mu\text{g}/\text{cm}^2$ Uncertified thickness of: Cr layer: 53 nm; Ni layer: 66 nm	NIST SRM 2135	RBS; NRA (nuclear reaction analysis); ICP-AES; AES
Cr/CrO _x multilayer	Cr multilayer film separated with 2–3 nm oxide marker layers Certified total thickness of Cr layer: $175.3 \pm 6.4 \mu\text{g}/\text{cm}^2$ (Each layer thickness is $20.5\text{--}25.1 \mu\text{g}/\text{cm}^2$) Uncertified: Each layer thickness (29–35 nm)	NIST SRM 2136	Polarography; ICP-AES; AES

(continued)

Table 7.3 (continued)

Reference materials	Properties	Certification bodies	Certification methods
B-implanted Si	¹⁰ B implanted on ntype Si(100) Certified: Amount of implanted ¹⁰ B: (1.018 ± 0.035) × 10 ¹⁵ at/cm ² Uncertified: Concentration of ¹⁰ B with depth	NIST SRM 2137	NDP (neutron depth profiling)
SiO ₂ single layer	Thermal oxide film on Si (Thicknesses are between 10 and 200 nm) Certified: Refractive indexes, thicknesses	NIST SRM 2531–2536	Ellipsometry; (TEM lattice image for confirmation)
Ta ₂ O ₅ single layer	Anodic oxidation film on Ta Certified: (1.80 ± 0.04) × 10 ²¹ oxygen at/m ² (5.42 ± 0.10) × 10 ²¹ oxygen at/m ² Uncertified thickness: 32.2 nm; 97.0 nm	NPL/BCR CRM. 261	Collaboration of European Labs.; NRA, Optical Reflectometry, etc.

Courtesy of I. Kojima, NIMC

Certification bodies e-mail addresses: NIMC: National Institute for Materials and Chemicals, now: National Metrology Institute of Japan, AIST, e-mail: standard.material@sasj.gr.jp; KRISS: Korea Research Institute of Standards and Science (K.J. Kim, kjkim@kriss.re.kr); NIST: National Institute of Science and Technology, Gaithersburg, MD, USA (srminfo@nist.gov); NPL/BCR: National Physical Laboratory, Teddington, UK/BCR (jrc-irmm-rm-sales@ec.europa.eu).

In the preceding sections (Sects. 7.1.2–7.1.5), the basic principles of profile quantification were discussed. Important is estimation of the amount of profile broadening by the concept of depth resolution, which gives a figure of the degree of similarity between the measured profile and the original in-depth distribution of composition. In order to obtain the true original in-depth distribution, particularly in the nanometer regime, more advanced quantification methods have to be applied.

7.1.7 Modeling, Deconvolution, and Reconstruction of Depth Profiles

7.1.7.1 Depth Resolution and Depth Resolution Function

From a theoretical point of view, any depth profile – whether obtained destructively or nondestructively – can be theoretically described by convolution of the true in-depth distribution of elemental concentration, $X(z)$, by a depth resolution function

$g(z)$ [7.1, 7.3, 7.4, 7.38, 7.39, 7.42, 7.157]. In sputter depth profiling, the normalized intensity, $I(z)/I^0$ as a function of the sputtered depth z is given by

$$\frac{I(z)}{I^0} = \int_0^{\infty} X(z')g(z-z')dz', \quad (7.24)$$

where z' is the running depth parameter for which the composition is defined. The mathematical form of the depth resolution function (DRF), $g(z-z')$, under the convolution integral (7.24) is determined by the physical mechanism that causes profile degradation. Because the aim is to obtain $X(z')$ from measurements of $I(z)/I^0$, (7.24) establishes a so-called ill-posed problem, i.e., a direct deconvolution solving (7.24) for $X(z')$ gives a large scatter enhanced by insufficient data precision (low signal-to-noise ratio) [7.4, 7.131]. Very early, it was shown that usual mathematical approximation schemes tend to “roughen” the retrieved $X(z')$ curve [7.8, 7.158]. Studies by Gautier et al. [7.67] have also shown that due to noise limitations and a certain frequency limit in the transformation, a sharp edge in the original distribution cannot be retrieved [7.8]. Therefore, it is customary to assume $X(z')$, and to calculate in a “forward” manner – with a known $g(z-z')$ – the intensity $I(z)/I^0$ and perform this several times in a trial-and-error manner until optimum fit to the measured $I(z)/I^0$ is obtained [7.8, 7.158]. For this case, the final input $X(z')$ is the reconstructed profile and the solution of the task of quantitative depth profiling, as schematically shown in Fig. 7.22. Because I/I^0 is determined experimentally, the key to determine the in-depth distribution of composition is to find the appropriate depth resolution function (DRF). The latter has to be known, either by theoretical prediction or from direct measurements with appropriate reference samples with atomically flat interfaces [7.35, 7.144, 7.159–7.162]. Reference samples are necessary as calibration standards, for optimization procedures in-depth profiling, for testing theoretical models and predictions, and for experimental determination of the depth resolution function (DRF) (Fig. 7.22). In any case, exact knowledge of the DRF $g(z-z')$ is the key to accurate reconstruction of the original profile from the measured data. The convolution integral equation and the deconvolution of depth profiles were first established by Ho and Lewis [7.162], and the relation between deconvolution and “forward calculations” to reconstruct the original in-depth distribution was presented by Hofmann and Sanz [7.65]. Since then, many different approaches have been considered and applied to establish the DRF [7.35, 7.38, 7.42, 7.60, 7.163–7.172]. Most elaborate are approaches based on a dynamic TRIM (transport of ions in matter) code [7.173] (today SRIM), such as the one developed by Badheka et al. [7.163] for SIMS depth profiles. Menyhard and coworkers [7.166–7.168] and Kupris et al. [7.169] simulated depth profiles for arbitrary in-depth distributions, taking ion mixing into account on the basis of TRIM simulations. The authors determined the corresponding Auger

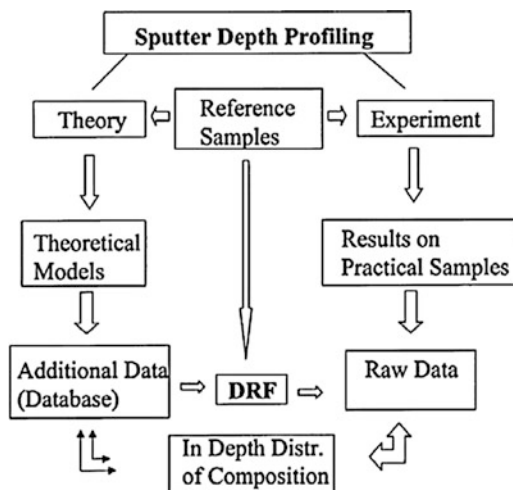


Fig. 7.22 Procedures necessary for accurate quantification of sputter depth profiles using the depth resolution function (DRF). Improved after T. Wagner et al. [7.1]

intensities by comparison with measured Auger depth profiles. These comparisons have shown that there are still some necessary parameters missing for the complete description of the DRF, such as meaningful incorporation of the information depth. Another approach, proposed by Fine et al. [7.172, 7.174, 7.175], is the description of a measured DRF by the logistic function. This function can then be used in (7.24) to fit the measured profile. However, because the logistic function is only a mathematical description, the connection of its parameters with physical quantities remains questionable. Nevertheless, such fits provide a convenient and objective representation of the measured profile shape and location and how they change for different sputtering conditions. Purely empirical approaches like the up- and downslope model of Dowsett and Barlow [7.170] are useful for mathematical representation of a delta-layer response function but still lack physical relevance for general profile quantification.

The depth resolution function of the MRI model can be experimentally determined and/or theoretically predicted, and any successful modeling of a measured profile is at the same time a confirmation of having used a correct depth resolution function [7.1–7.5, 7.171]. Experimentally, the depth resolution function $g(z - z')$ in (7.24) is obtained by profiling through an infinitesimal thin, so-called delta layer (in reality, one monolayer thickness most often used in SIMS [7.170]). Because of their lower dynamic range, in AES and XPS, the derivative, the depth profile of a step function concentration distribution – as used for the determination of Δz – provides the DRF. According to (7.24), differentiation of $I(z)/I^0$ gives

$$g(z - z') = \left| \frac{d[I(z)/I^0]}{dz} \right|, \quad (7.25)$$

as obvious in Fig. 7.6. High-accuracy AES depth profiles performed at GaAs/AlAs multilayers [7.42] are appropriate to derive the experimental resolution function after (7.25) [7.42, 7.159, 7.171], as shown in Fig. 7.21 together with the calculated resolution functions fitted with the MRI model (see Sect. 7.1.8). It is obvious that the narrower DRF corresponds to the better resolved profile with lower information depth (all). The observed mutual shift of the profiles can be used to estimate the depth scale (see Fig. 7.2).

Of the different approaches which were made to simulate or calculate depth profiles, two simple models have proved to be very useful for profile reconstruction and quantification, namely, the “sequential layer sputtering” (SLS) model [7.2, 7.5] and the “mixing-roughness-information-depth” (MRI) model [7.3, 7.42] which are considered below in more detail.

7.1.7.2 Depth Resolution Function of the SLS Model

At the beginning of a sputtering profile, the DRF quickly changes and is hardly predictable until the dynamic sputter equilibrium is attained. This is the region where the sequential layer sputtering (SLS) can be successfully applied. The SLS model is based on the monolayer sputtering approach introduced by Benninghoven [7.118] and was further developed in the seventies in order to describe the sputtering-induced roughness changes for the first few monolayers [7.60, 7.119]. It is quite obvious that as soon as a part of the first monolayer is removed by sputtering, the second layer is laid free and prone to sputter removal and so forth. Thus, sputtering statistics lead to surface roughening on the monolayer scale, and the remaining sequential layer composition follows a Poisson distribution, which gives an exponential for the first layer ($n = 1$), and gradually approaches a Gaussian for higher number of layers sputtered, and in accordance with many experiments, the depth resolution Δz increases with the square root of the sputtered depth. Additional implementation of the constant contribution of the electron escape depth correction (e.g., Fig. 7.1) establishes the SLS model. Although the SLS model is inaccurate by not taking into account the atomic mixing contribution, the latter gradually evolves in a similar fashion as SLS roughness, namely, with approximately a square root law with depth [7.117]. This similarity appears to be the reason that for the first few monolayers, the SLS model gives a fairly good profile description, whereas other approaches (like the MRI model) only consider the dynamic equilibrium of sputtering. (Recently, Wang et al. [7.256] introduced a variable mixing parameter in the MRI model to describe the initial transient stage in-depth profiling.)

As shown by Seah et al. [7.120], the SLS roughness term of the depth resolution function tends to approach a constant, depth-independent value of typically a few monolayers, depending on bonding differences with respect to surface atomic

positions. Introducing the information depth contribution by the exponential term (e.g., with λ^e , the Auger-electron escape depth (see Sect. 4.2.2)), the normalized (AES) intensity as a function of sputtered depth z is given by [7.8, 7.176, 7.177],

$$I(z) = I^0 \sum_{m=0}^M \sum_{n=1}^N X_{m+n}^0 \frac{z^{n-1}}{(n-1)!} \exp(-z) \exp\left(-\frac{m}{\lambda^e}\right), \quad (7.26)$$

with the depth scale z in atomic monolayers ($n = 1, 2, \dots$). The parameter I^0 is the normalization factor for the intensity of a monolayer, X_{m+n}^0 , is the molar fraction of the detected element in the unaltered layer $m + n$, followed by the Poisson distribution term representing the surface fraction of layer n at depth z , and the term $\exp(-m/\lambda^e)$ represents the AES or XPS intensity with electron escape depth λ^e at the instantaneous surface ($m = 0$) and below ($m > 0$). (Note the similarity of (7.24) and (7.26)). Equation 7.26 has been successfully applied in many in-depth distribution studies of thin surface layers [7.176–7.179] (see also Figs. 7.26, 7.28, and 7.29). Equation 7.26 can also be modified to include preferential sputtering of one component [7.179]. Typical applications of (7.26) for profile reconstruction are sputter depth profiles of thin segregation, oxide, and passive layers in corrosion as seen, for example, in Sect. 9.1.2, Fig. 9.6.

As a rule, for layer thicknesses beyond about 10 monolayers, the contribution of sputtering statistics to depth resolution (Δz_s) is only a few (2–3) monolayers and therefore usually negligible compared to the contributions of mixing and sputtering-induced roughening on a larger scale. In the latter case, sputter-induced roughening is given by a relation formally similar to (7.26) (but without the $-$ in that case – negligible correction term containing λ^e) with the Poisson function replaced by two depth-dependent Gaussians (representing high and low sputtering rates) as shown by Woehner et al. [7.143] in a remarkably quantitative description of interface profile broadening based on sputter-induced roughening of Al evaporation layers.

7.1.8 The MRI Model and Its Modifications

7.1.8.1 Fundamentals

The so-called mixing-roughness-information-depth (MRI) model for the depth resolution function which is based on physically well-defined parameters was developed in the late eighties by Hofmann and coworkers [7.5, 7.33, 7.148, 7.165, 7.180]. Starting with the simplified assumption of Liao et al. [7.181] of a complete, instantaneous zone of mixing with homogeneous concentration, a semiempirical model for the depth resolution function was established based on the following three fundamental profiling quantities: atomic mixing, surface roughness, and information depth (MRI model) [7.51, 7.182]. Atomic mixing is characterized by an exponential

term with the characteristic mixing length, w , surface roughness is taken into account by a Gaussian term with standard deviation, σ , and the information depth is represented by an exponential term with the characteristic electron escape depth $\lambda^e = \lambda \cos \theta$ defining the range of the analytical information (the information depth is usually defined as $3\lambda^e$ or $5\lambda^e$ [4.61], with larger depth being irrelevant in the integral over expression (7.27b) (see Sect. 4.2.2)). Thus, the DRF of the simple MRI model [7.42, 7.182] is basically represented by the following three components g_w , g_λ , and g_σ atomic mixing:

$$g_w = \frac{1}{w} \exp\left(-\frac{(z - z' + w)}{w}\right), \quad (7.27a)$$

information depth:

$$g_\lambda = \frac{1}{\lambda^e} \exp\left(-\frac{(z - z')}{\lambda^e}\right), \quad (7.27b)$$

surface roughness:

$$g_\sigma = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(z - z')^2}{2\sigma^2}\right), \quad (7.27c)$$

where z is the sputtered depth, z' denotes the position of the delta layer, w the atomic mixing length, σ the surface roughness, and λ^e the information depth parameter (escape depth $\lambda^e = \lambda \cos \theta$ with emission angle θ , see Sect. 4.2.2). With the above three partial resolution functions, the convolution integral (7.24) can be written as

$$\begin{aligned} \frac{I(z)}{I^0} &= \int_0^\infty X(z')g(z - z')dz' \\ &= \int_{-\infty}^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty X(z''')g_w(z'' - z')g_\lambda(z' - z'')g_\sigma(z - z')dz'dz''dz'''. \end{aligned} \quad (7.28)$$

Even for constant contributions to the depth resolution, the possibility of presenting the convolution integral (7.28) with the resolution function in the form of a convolution of the three components is only strictly valid if the latter do not physically interact, as, for example, g_λ and g_w [7.64]. Therefore, (7.14) is applied in sequence with g_w , g_λ , and g_σ from (7.27a) to (7.27c) [7.42].

The three parameters of the MRI model have a well-defined physical meaning. Therefore, the MRI model allows straightforward predictions and measurements, as summarized in Table 7.4. Other advantages are that it can be used equally well for profiles in SIMS, AES, XPS, GDOES, etc., where the basic sputtering process is the same, and that each of the parameters can be varied – and often measured. Independently, thus allowing a test of its validity. For example, in one experimental run, the depth resolution functions for the high- and low-energy Auger peaks of the same element can be described by only changing the information depth parameter but with the same mixing and roughness parameters (see, e.g., Fig. 7.21). In contrast

Table 7.4 Characterization of MRI model parameters by theory and experiment

	Theory	Experiment
Mixing length: w	SRIM [7.173] (for estimation of the mean ion range)	Angle-dependent XPS, AES
Roughness: σ	Surface roughness plus straggling contribution of w	Surface roughness: AFM Interface roughness: GIXRD*
Information depth: λ^e	Tanuma–Penn–Powell model (TPP-2M) and EAL databases	For example, elastic peak measurements, evaporation layers, thickness dependence, etc.

* Grazing incidence X-ray diffraction

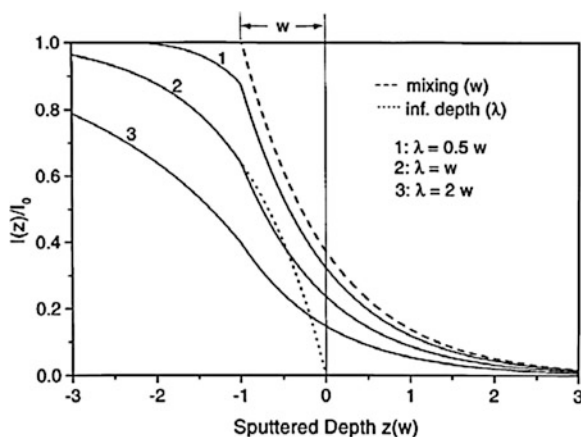


Fig. 7.23 Superposition of atomic mixing and information depth parameters in sputter profiling at an interface. The effect of complete atomic mixing (within mixing length w) on concentration distribution of A during sputter profiling (*dashed line*) and the additional effect of the information depth parameter, represented by the escape depth λ^e (called λ in the figure) in AES and XPS (with typical values of $\lambda^e = 0.5w$, w and $2w$) (*dotted line* for $\lambda^e = w$), combine to a nearly error-function-like profile (line 2) even for roughness $\sigma = 0$ (From S. Hofmann [7.64])

to purely empirical models [7.170], the observed shift of the half maximum value (or of the centroid) of the measured profile with respect to the original depth of the delta layer toward the surface is included in the MRI model and is a function of the three parameters [7.42] (see Figs. 7.23 and 7.36).

In the early days of depth profiling, Gaussian depth resolution functions were used as an adequate means for deconvolution because interfaces were shown to be broadened in an error-function-type profile [7.47, 7.60, 7.65, 7.122] and thin sandwich (delta) layers to be broadened in a Gaussian function type profile [7.47, 7.183]. At that time, some typical asymmetry toward larger depth was generally attributed to an additional forward recoil process, the so-called knock-on effect in sputtering. However, as demonstrated in Fig. 19 of Ref. [7.3], the old data [7.183] can be explained by homogeneous atomic mixing [7.184] which always yields an exponential tail (“trailing edge”), as schematically shown in Fig. 7.23.

The information depth contribution in sputter depth profiling using AES or XPS is characterized by an upward slope exponential function in front of a sandwich layer and a downward slope exponential function at the end (compare Fig. 7.1). The latter is shown in Fig. 7.21. Typically, the information depth contribution, characterized by the electron escape depth λ^e , is of similar size as the mixing length w (a few nm for escape depth of 1000 eV Auger electrons and for the mixing length of 2 keV Ar^+ ions). The depth resolution function resulting from the superposition of the two contributions, given by (7.27a) and (7.27b), is fairly symmetric, suggesting a Gaussian approximation, and in particular, curve 2 in Fig. 7.21 is error function like. Thus, even for vanishing roughness, it is not surprising that in AES- and XPS depth profiling of interfaces, error-function-like interface profiles are usually reported.

Based on appropriate assumptions for the three fundamental parameters of the MRI model, the depth resolution functions can be predicted according to the specific experimental conditions (see Table 7.4). However, because these parameters are either not known with sufficient accuracy and/or the simplifying assumptions of the model are not exactly met, a test of the model by appropriate reference materials with either monolayer structures or with sharp interfaces is useful to adjust the theoretical depth resolution function and to ensure high accuracy in applications. As an example, Fig. 7.21 shows the experimental determination of the DRF for AES depth profiles of the low-energy (68 eV) and high-energy (1396 eV) Al peaks in a GaAs/AlAs multilayer structure and the optimum fit of the theoretical DRF. According to (7.25), the absolute value of the differentiated, measured (and normalized) profile $I(z)/I^0$ gives the DRF. With the sputtering rate $dz/dt = 0.15 \text{ nm/min}$, the result of (7.25) applied to the measurements in Fig. 7.21a is shown in Fig. 7.21b by the open points. Comparison with DRFs (full-drawn lines, MRI with $w = 1.0$, $\sigma = 0.6$, $\lambda(\text{Al1}) = 0.4$, and $\lambda(\text{Al2}) = 1.7 \text{ nm}$) shows very good agreement. As seen by the large difference of the DRFs for which only λ differs by 1.3 nm (i.e., about 4.5 monolayers), an accuracy of about 1–2 monolayers is achieved. Such a difference in the original concentration depth distribution would be detected in the MRI fit of the measured profile (Fig. 7.21c). It is also recognized that the 4 interfaces can be fitted fairly well with the same DRF, only with slight adjustment of the normalized height.

7.1.8.2 Basic Parameters and Equations Representing the MRI Model

Atomic Mixing

The MRI model is based on the simplest approximation of atomic mixing to generate instantaneously a compositionally homogeneous zone of limited depth w by complete atomic redistribution [7.181]. Such a zone is built up after a certain sputtered depth (about twice the projected ion range [7.24]) and is then assumed to be constant with sputtered depth and of the order of the mean ion range. With the

additional assumption of a constant sputtering rate, the change of the concentration X_A of component A in matrix B with sputtered depth z is therefore given by [7.42]

$$\frac{dX_A}{dz} = \frac{1}{w} \left[X_{A,(z+w)}^0 - X_A(z) \right], \quad (7.29)$$

where $X_{A,(z+w)}^0$ is the original, unaltered concentration of A at a distance w in front of the instantaneous surface at z . For a sandwich layer structure B/A/B, with abrupt interfaces at z_1 (B/A) and z_2 (A/B), the solution of (7.20) for the interface B/A (the leading edge (L)) is

$$X_A^L = X_A^0 \left[1 - \exp \left(-\frac{z - z_1 + w}{w} \right) \right], \quad (7.30a)$$

and for the interface A/B (the trailing edge (T)) the solution is

$$X_A^T = X_A^L \exp \left(-\frac{z - z_2 + w}{w} \right). \quad (7.30b)$$

This corresponds to the DRF contribution of atomic mixing (7.27a).

Information Depth

In AES or XPS profiling, the information depth is larger than the first monolayer and has to be taken into account by the usual exponential function with the mean electron escape depth λ^e . According to (4.88a), for constant λ^e , a layer of thickness w contributes to the measured, normalized intensity I_A/I_A^0 for the trailing edge with

$$\left(\frac{I_A}{I_A^0} \right)_T = X_A^T \left[1 - \exp \left(-\frac{w}{\lambda^e} \right) \right]. \quad (7.31a)$$

For the leading edge, an additional contribution of the original layer of A beyond the distance $z + w$ from the surface has to be considered, i.e.,

$$\left(\frac{I_A}{I_A^0} \right)_L = X_A^L \left[1 - \exp \left(-\frac{w}{\lambda^e} \right) \right] + X_A^0 \exp \left(-\frac{w}{\lambda^e} \right) \left\{ 1 - \exp \left(-\frac{z_2 - z - w}{\lambda^e} \right) \right\}. \quad (7.31b)$$

Of course, the second term in (7.31b) is only valid for $z + w \leq z_2$.

Combination of the contribution of atomic mixing (7.30a) and of electron escape depth (7.31a) gives a measured intensity depth profile which resembles an error function if λ is of the order of w , as shown in Fig. 7.23. Further broadening is attributed to the contribution of a roughness term.

Roughness

For an infinitely thin layer of A, (7.30b) describes the mixing component of the DRF as an exponential broadening. Of course, there is always a certain broadening of the mixing zone edges and a certain roughness of the surface. In the simplest case, this roughness term can be approximated by an error-function-like distribution. It is taken into account by superposition of a normalized Gaussian broadening described by

$$X_A^b = \frac{1}{\sigma\sqrt{2\pi}} \int_{z-3\sigma}^{z+3\sigma} X_A^{L,T}(z') \exp\left[-\frac{(z-z')^2}{2\sigma^2}\right] dz', \quad (7.32)$$

with the standard deviation $\sigma(\Delta z_\sigma = 2\sigma)$. For the numerical calculation, the principal integral limits $-\infty$ and $+\infty$ are cut off at -3σ and $+3\sigma$ (0.3% error). As discussed in Ref. [7.185], the roughness parameter contains an additional term attributed to the range straggling related blurring of the mixing length.

Equations 7.30a, 7.30b, 7.31a, 7.31b, and 7.32 constitute the so-called MRI model for the quantification of sputter depth profiles in AES, XPS, and SIMS.

It should be emphasized that the simple functions for the partial contributions to the DRF given above in (7.27a, b) are strictly valid only for infinitesimal thin delta layers ($z_2 \rightarrow z_1$ in (7.30a) and (7.30b), and/or for $\lambda \ll w$, for which the second term in (7.31b) vanishes) [7.64]. In general, and particularly for $\lambda > w$, the information depth stretches into regions beyond the atomic mixing zone. Ignoring the effect of the combination of atomic mixing and information depth may cause errors in “naïve” profile quantification of up to 20% [7.3, 7.42, 7.64].

7.1.8.3 Advantages of the MRI model are:

- (a) The MRI model is based on physical parameters that can be predicted and/or measured (Table 7.4)
- (b) Experimental evaluation of the MRI parameters is enabled by fitting the results to measured profiles of well-defined reference samples
- (c) Through iterative improvement by experience, The MRI model gives clear guidelines for the optimization of depth profiling procedures (see Fig. 7.22)

A meaningful application of the MRI model has to consider critically the limitations of the basic model due to simplifications by ignoring frequently encountered effects. These include:

- (a) Nonlinear sputtering time/depth relation
- (b) Nonlinear relation between intensity and concentration
- (c) Restrictions by simplified definition of the parameters w , σ , λ^e in the MRI model

Some of these important effects can be taken into account to improve interpretation of experimental data by specific extensions and modifications.

7.1.8.4 Extensions and Modifications of the Basic MRI Model:

Nonlinear Sputtering Time/Depth Relation

Preferential sputtering of one of the main components of a sample is the main cause of a nonlinear change of the sputtering time/depth relation in concentration gradients because the sputtering rate depends on composition [7.3]. Although a precise correction can only be performed by monitoring the instantaneous sputtered depth during depth profiling, it was early demonstrated that introducing a linear dependence of the sputtering rate on composition serves as a first-order approximation of a correct time/depth relationship in case of preferential sputtering of a component [7.33].

In a binary system where the sputtering rates of the pure components A , B are $\dot{z}_A$ and $\dot{z}_B$, the linear approximation is

$$\dot{z} = \dot{z}_A X_A + \dot{z}_B X_B = \dot{z}_B \left[\left(\frac{\dot{z}_A}{\dot{z}_B} - 1 \right) X_A + 1 \right], \quad (7.33)$$

where $\dot{z}$ is the total sputtering rate which determines the sputtering time/depth relation.

With (7.33) and the sputtering rate ratio $r_s = \dot{z}_A/\dot{z}_B$, the basic mixing equation (7.29) can now be written in the sputtering timescale as

$$\frac{dX_A(t)}{dt} r_s = \frac{\dot{z}}{w} \left[X_{A,z+w}^0 - X_A(t) \frac{r_s}{(r_s - 1)X_A(t) + 1} \right]. \quad (7.34)$$

Normalized to the sputtering rate of the pure component B , the sputtering timescale in units of t_B is given by

$$t_B = \int_0^z \frac{dz}{\dot{z}_B [X_A(r_s - 1) + 1]}. \quad (7.35)$$

Introducing (7.34) and (7.35) in the MRI formalism yields the measured profile if the normalized intensity I/I^0 is plotted against the sputtering time.

As an example, Fig. 7.24a shows the measured AES depth profile of a Ta/Si multilayer (10 double layers), consisting of alternating 10.5-nm-thick Si layers and 7.5-nm-thick Ta layers, depth profiled with 3 keV Ar^+ ions at 81° incidence angle [7.33, 7.186]. It is immediately recognized that the apparent thickness of Ta is larger than that of Si, indicating preferential sputtering of Si. After having refined the MRI model with the preferential sputtering approximation according to (7.37), the full-drawn line in Fig. 7.24a demonstrates the good agreement between the measured and calculated profile, using the following MRI parameters: mixing

length $w = 2.6$ nm, roughness $\sigma = 1.1$ nm, information depth $\lambda = 0.4$ nm, and sputtering rate ratio $r_s(\text{Si}/\text{Ta}) = 3.5$ for the optimum fit. The sputtering rate ratio of 3.5 is in fairly good agreement with the ratio of 4.3 for 0.5 and of 2.9 for 3 keV Ar^+ ions, respectively, found earlier [7.37]. Figure 7.24b shows the change of the total sputtering rate (=the slope of the curve) as a function of the sputtering time according to (7.35). Qualitatively, the asymmetric profile of Si (and the corresponding one of Ta) can be understood by the retarded increase of Si owing to its preferential sputtering from the surface and the accelerated decrease when the delivery from the bulk through mixing does not supply enough Si. The good agreement between the quantification of the Si signal by the internal standard of pure Si of the first layer (Fig. 7.24a) is an indication that the assumption of perfect mixing is fulfilled. Otherwise, a gradient with a minimum before the first layer is expected. Because of the low attenuation length of the low-energy peaks of Si(92 eV) and Ta(179 eV), the first monolayer is practically representative for the measured intensity. The difference between Fig. 7.24a and b clearly demonstrates that the often reported replacement of the sputtering timescale by the sputtered depth is only valid if the sputtering rate ratio of the main components is close to unity. Although the linear relation between sputtering rate and composition is only a first-order approximation, this modification of the MRI model gives reasonable results.

Nonlinear Intensity/Concentration Relation

Nonlinear relationships between elemental intensity and concentration can if one or more of the important parameters are composition dependent as, for example, the sputtering rate, the mixing zone length, the electron escape depth in AES and XPS, the electron backscattering factor in AES, or the ionization probability in SIMS [7.187]. In a first-order approximation, these effects can be considered in the MRI model by introducing a linear concentration dependence of the respective parameters. Obviously, the expected effect of composition on the shape of profiles is most pronounced when sputtering through interfaces. Whereas the effect of sputtering rate changes by preferential sputtering and the according change of the shape of the measured depth profile was already discussed in the previous section, the changes of mixing length, attenuation length, and backscattering factor are briefly outlined below.

(a) *Change of Mixing Length with Composition:* Because the mixing length depends on the material, it will generally change when sputtering through an interface. In general, the change of w is neglected and an average mixing length (about the average ion range taken from TRIM code calculations) is frequently assumed for the calculation [7.188]. Because this is only an approximate value, the final w is found by trial and error in the vicinity of that value. A better approximation appears to be to consider the change of the parameter w through the interface A/B (of components A and B) by introducing a linear dependence on the composition [7.49]. However, the change is usually found small compared to the other parameters, and the simplification of an average w seems to be justified in most cases.

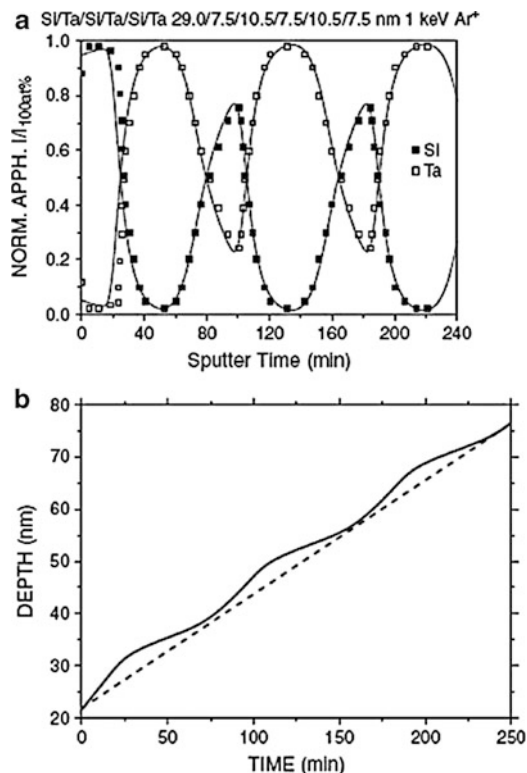


Fig. 7.24 (a) Measured AES sputter depth profile (*points*) MRI model calculation results (*lines*) of a multilayer of Ta/Si (7.5/10.5 nm) showing preferential sputtering of Si; (b) depth/time relation for the Ta/Si multilayer after (7.35) (From S. Hofmann and J.Y. Wang [7.186])

The biggest change in w is encountered in the beginning of sputtering, since w has to change from zero to its stationary state in dynamic sputter equilibrium. For this transient state, the SLS model appears to be more appropriate (see Sect. 7.1.7). The effect of changing w at the beginning of sputtering is presently explored [7.256].

(b) *Change of Electron Attenuation Length in AES and XPS with Composition:* Change of the electron escape depth with composition is obvious in AES depth profiling. Again, we may approximate that dependence by assuming a linear relation between the attenuation cross sections (represented by $1/\lambda$, [4.29]) and composition, i.e., [7.49, 7.182]:

$$\frac{1}{\lambda} = \frac{X_A}{\lambda_A} + \frac{X_B}{\lambda_B}. \quad (7.36)$$

Introducing (7.36) in the MRI model shows the influence of the change of λ^e ($=\lambda$ for emission angle $\theta = 0$) on a “sandwich” layer profile which is shown in Fig. 7.25 for increasing changes [7.182]. It is obvious that a remarkable profile alteration only occurs for rather high, unlikely changes of λ . In general, the profile shape is not much different for usual variations of the attenuation length. For example, when

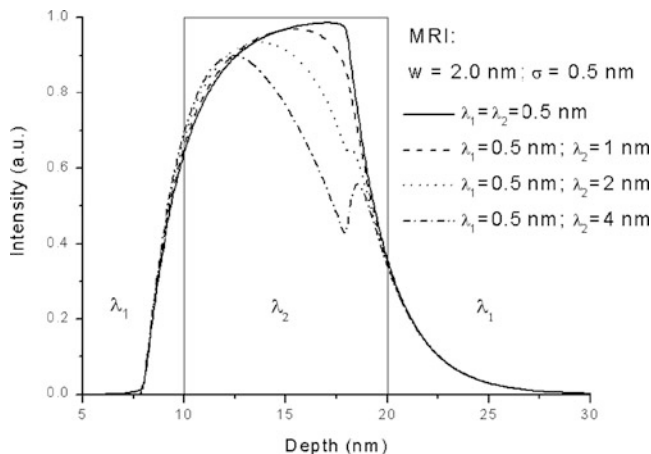


Fig. 7.25 Effect of the change of the mean electron escape depth λ^e (denoted λ in the *inset*) in AES and XPS profiling when sputtering through a sandwich layer with different escape depth. The result of MRI calculations is shown for different λ^e values given in the figure (From S. Hofmann [7.182])

sputtering through an Fe/Si interface, a nearly linear change of the inelastic mean free path of $\lambda_{\text{in}}(\text{Si } 1620 \text{ eV})$ was observed from 2.6 nm (pure Fe) to 3.5 nm (pure Si) [7.189], in accordance with (7.39).

(c) *Quantification of the Electron Backscattering Effect in AES Depth Profiling:* The most important nonlinear relation between intensity and concentration is caused by the backscattering factor in AES analysis of thin layers (Sect. 4.4.3). Most obvious is the change of the signal intensity with distance from an A/B interface when the backscattering factor A and B is very different [7.190, 7.191], as seen, for example, in Fig. 4.55 (Sect. 4.3.3) for ideal sputtering or evaporation. Recently, the backscattering effect was successfully implemented in the MRI model, as shown for single layers [7.190] and for multilayers [7.191]. Exact quantification of backscattering influence in the vicinity of interfaces requires difficult multiple scattering and energy loss calculations and is usually represented by sophisticated MC simulations [7.192]. However, a simple single-scattering approximation has proved useful in practice [7.190, 7.191, 7.193], as shown below. To describe the backscattering influence quantitatively, a new parameter, the “mean electron backscattering decay length” (MEBDL) $L_{B,A;C}$, was introduced [7.190, 7.191, 7.193], where A is the thin-film element measured in or on layer C , and B is the substrate. Thus, $L_{B,A;C}$ means the “MEBDL of (substrate) B on the AES intensity of element A in or on component C .” For a single layer of A on substrate B , we may assume for simplicity that the dependence with distance $z_0 - z$ from the interface (at depth z_0) is exponential [7.190, 7.191, 7.193]. Then the measured Auger intensity, I_A , is given by

$$I_A = I_A(\text{MRI}, R_{A,U(A)} = 1) R_{A,U(A)} \left[1 + \left(\frac{R_{B,U(A)}}{R_{A,U(A)}} - 1 \right) \exp \left(-\frac{z_0 - z}{L_{B,A;A}} \right) \right], \quad (7.37)$$

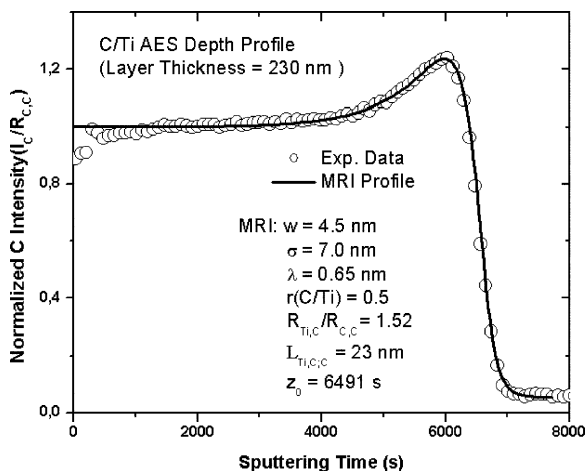


Fig. 7.26 AES depth profile (C 272 eV) of a 230-nm-thick C layer on Ti. *Open circles*: measured points [7.59], *line*: MRI quantification (parameters, see *inset*, λ denotes mean electron escape depth λ^e) with backscattering factor ratio $R_{\text{Ti,C}}/R_{\text{C,C}} = 1.52$ (From S. Hofmann and J.Y. Wang [7.190])

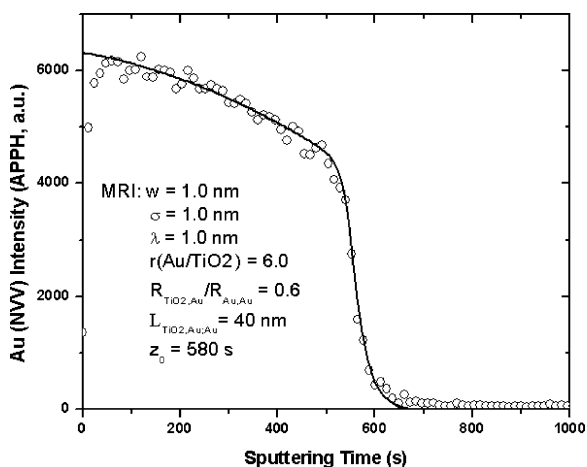


Fig. 7.27 AES depth profile (Au 68 eV) of an 80 nm Au film on $\text{TiO}_2/\text{Kapton}$, with backscattering factor ratio $R_{\text{TiO}_2,\text{Au}}/R_{\text{Au,Au}} = 0.6$. *Open circles* are measured data; *full-drawn line* shows MRI quantification with the parameters given in the *inset* (From S. Hofmann and J.Y. Wang [7.190])

where $I_A(\text{MRI}, R_{A,U(A)}) = 1$) denotes the intensity calculated with the MRI model for backscattering factor $R_{A,U(A)} = 1$, $R_{A,U(A)} = 1 + r_{A,U(A)}$, and $R_{B,U(A)} = 1 + r_{B,U(A)}$ the backscattering factor of A for $U(A)$ and of B for $U(A)$, respectively (see Sect. 4.4.1: The overvoltage $U(A) = E_p/E_{A,X}$ with primary beam energy E_p and ionization energy of electron level X of element A). The intensity according to (7.37) is introduced in the MRI model. The results for two typical depth profiles, one for a carbon thin film on Ti and the other for a gold thin film on

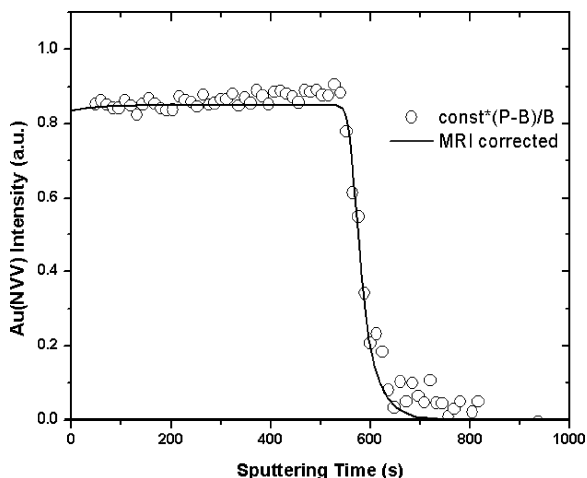


Fig. 7.28 Comparison of the exact, backscattering-corrected MRI profile of Au on TiO₂/Kapton in Fig. 27 (solid line) and the apparent experimentally “corrected” profile (open circles) (From S. Hofmann and J.Y. Wang [7.190])

a TiO₂/Kapton substrate, are shown in Figs. 7.26 and 7.27, respectively [7.190]. MRI parameters (w , σ , and λ^e), sputtering rate ratio $r(A/B)$, backscattering factor ratios ($R_{B,U(A)}/R_{A,U(A)}$), and MEBDL values ($L_{B,A;A}$) are given in the insets. As seen from (7.37) (see also Fig. 4.33), the intensity is increasing for the ratio $R_{B,U(A)}/R_{A,U(A)} = R_{Ti,C}/R_{C,C} > 1$ (Fig. 7.26) and decreasing for $R_{B,U(A)}/R_{A,U(A)} = R_{TiO_2,Au}/R_{Au,Au} < 1$ (Fig. 7.27). Owing to the fact that the background (B) varies approximately as the signal intensity (peak background, $P-B$) (see Sect. 6.1.1), normalization of the latter to the background, $(P-B)/B$, gives a fairly good experimental correction of the backscattering effect, as seen in Fig. 7.28 [7.190].

The above model description of the sputter depth profile analysis of a single layer on a substrate using AES can easily be extended to the case of multilayers A/B/A/B... by introducing an “effective backscattering factor” that depends on the layer thickness and of a more complicated definition of the MEBDL values, as in detail explained in [7.191]. An example is shown in Fig. 7.29 for the AES sputter-depth profile of a Ni/C multilayer on an Si substrate consisting of five layers of Ni (38 nm thickness) and of five layers of C (25 nm thickness) [7.193]. Figure 7.29a shows the measured profile of Ni together with the calculated MRI profile, and Fig. 7.29b shows the measured profile of C together with the MRI result, for optimized basic MRI and backscattering parameters ($R_{Ni,Ni}$, $R_{Ni,C}$, $R_{C,C}$, $R_{C,Ni}$, $R_{Si,C}$, and MEBDL values between 10 and 45 nm) [7.190]. It is interesting to note that the calculation correctly represents not only the shape of the individual profiles but also the decrease in absolute intensity due to the diminishing backscattering effect in the vicinity of the Si substrate. Because any profile can be approximately decomposed in a multilayer profile with zero interface width and varying composition, the multilayer model can be readily extended to general, multielemental depth profiles.

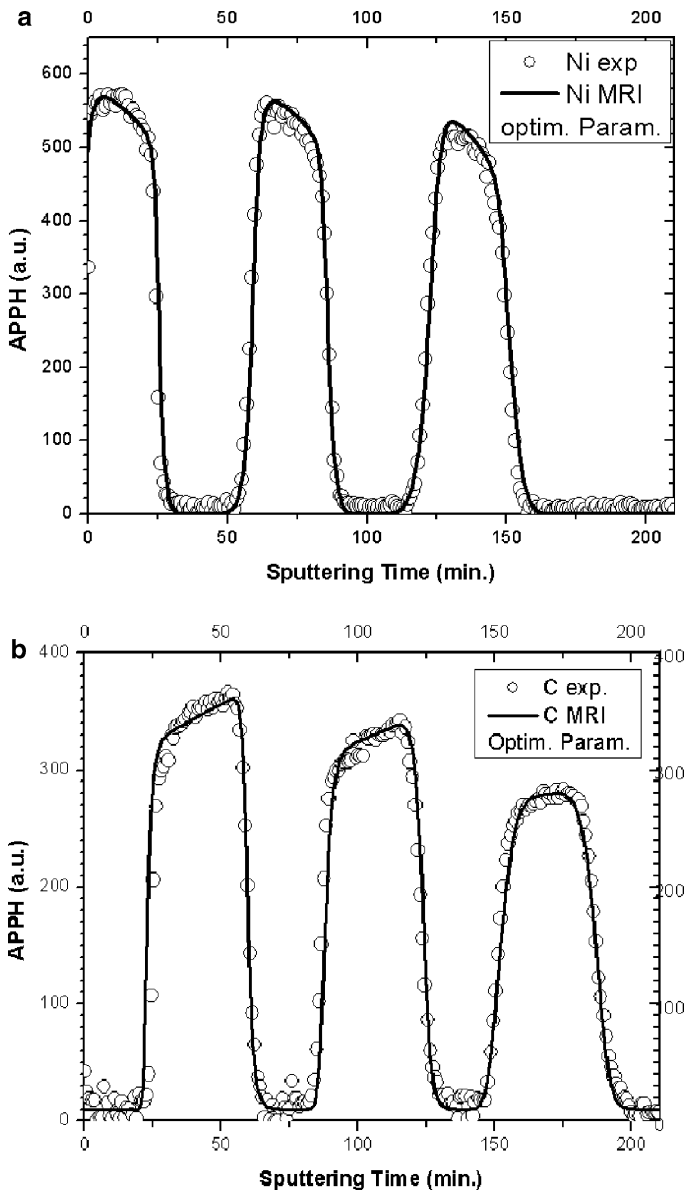


Fig. 7.29 MRI quantification including effective backscattering factor correction (*solid lines*) applied to measured AES sputter depth profiles (*open circles*) of a Ni/C (38/25 nm) multilayer on a Si substrate. **(a)** Ni (848 eV) profile; **(b)** C (272 eV) profile. For details see text and Ref. [7.191] (From S. Hofmann [7.193])

Restrictions by Simplified Definition of the Parameters w , σ , λ^e in the MRI Model

Although the MRI parameters w , σ , and λ^e are physically well defined, a cautious application is necessary in view of the simplifications on which the basic MRI model, including its extensions and modifications, is based.

Mixing Length Parameter w : Assuming complete mixing in a sharply defined range, w , is a considerable simplification. Nevertheless, at normal temperatures, the ion-bombardment-induced relocation of sample atoms in conjunction with vacancy production results in diffusional mixing that describes the real situation in most cases sufficiently well [7.76] and is in accordance with experimental evidence [7.3]. The usually measured exponential decay length in SIMS profiling is not only a measure of the parameter w but also an experimental proof of the above assumption [7.10]. Usually, w is of the order of the mean (projected) ion range, which is explicitly given as a result of any TRIM (SRIM) calculation [7.173], but the exact shape has to consider range straggling and the extent of relocation and vacancy generation. Therefore, the usual way is to estimate first a mixing length from TRIM and then adjusting it by trial-and-error methods with the other parameters. For example, in the MRI model, range straggling can be taken into account by a somewhat larger roughness parameter [7.4] (see below, (7.38)). Frequently, w can be measured directly in an interface profiling experiment by angle-resolved XPS or AES, as shown by Rar et al. [7.188] with AR-AES at the AlAs/GaAs interface of a multilayer structure (see Fig. 7.21) and depicted in Fig. 7.30.

In case of preferential sputtering, the apparent mixing length may change, and in conjunction with strong outward diffusion, the mixing zone will show a concentration gradient that has not been taken into account up to now. However, in principal, this effect can be taken into account by a change in the sensitivity factor by adjustment to a signal for constant concentration [7.100, 7.104, 7.105]. The mixing length will change with composition which can easily be taken into account but is generally negligible in interface profiling [7.193].

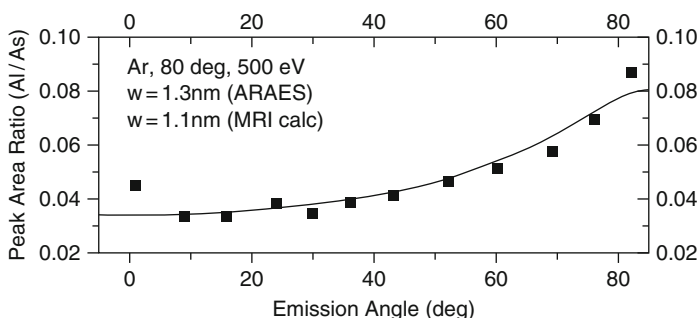


Fig. 7.30 Angle-resolved AES (AR-AES) applied to the mixing layer of an AlAs/GaAs interface. The full-drawn line is the fit of the measured points (full squares) according to (7.67b) in Sect. 7.2.1 resulting in $w = 1.3$ nm, in reasonable accordance to the value $w = 1.1$ nm used for optimum profile fit with the MRI model (Reproduced from A. Rar et al. [7.188])

Roughness Parameter σ : Although some models of sputtering-induced surface roughening exist [7.24, 7.125, 7.126, 7.142, 7.143, 7.194], there seems to be no generally accepted prediction of the depth dependence of surface morphology. Fortunately, surface roughness can easily be measured after depth profiling with atomic force microscopy (AFM). As shown in [7.142], for a dominating surface roughness influence, the rms roughness corresponds to the MRI parameter σ . However, the roughness to be considered in the MRI model consists of four different contributions: original surface (σ_0), interface roughness (σ_i), sputtering-induced surface topography (σ_s), and mixing length straggling (σ_w). Therefore, the roughness parameter is approximately given by [7.35]

$$\sigma = \sqrt{\sigma_0^2 + \sigma_i^2 + \sigma_s^2 + \sigma_w^2}. \quad (7.38)$$

In (7.38), only morphological parameters are considered. An apparent interface broadening given by a variation of the sputtering rate should be better included in the sample composition distribution to be reconstructed [7.195]. The different roughness parameters can be measured as follows: σ_0 by AFM before sputtering, and $\sigma_s(z)$ after stopping sputter profiling at a chosen depth z , and σ_i , for example, by grazing incidence X-ray reflectometry GIXR [7.195]. The contribution σ_w can be principally determined by profiling using angle-resolved AES or XPS (see Sect. 7.2.), but the error is usually too large for useful results. Therefore, we may only rely on TRIM/SRIM type calculations, from which about half the projected range seems to be a reasonable value for σ_w [7.173]. In summary, the MRI parameter σ is difficult to predict and to measure. Therefore, within estimated limits, this parameter can be varied for getting a good fit. AFM measurements, as seen from (7.38), give a lower limit. However, if surface roughness is preponderant, AFM results give an excellent description of the σ and therefore of the depth resolution 2σ [7.143]. Of course, change of the roughness parameter with depth can be easily included in the MRI model [7.196]. If AFM measurements show a non-Gaussian distribution of depth around the mean depth, the respective function can also be used as a DRF contribution in the MRI model.

Information Depth Parameter λ^e : In AES and XPS, the information depth is defined given by cutting off the negligible tail in the exponential function of the measured intensity versus depth, given by the value of λ^e (see Fig. 4.17 in Sect. 4.2.2). This somewhat arbitrary depth is defined as 3 or 5 times the escape depth λ^e of the Auger or photoelectrons [4.61], corresponding to 95% or 99% of the total intensity of a homogeneous sample. Cutting off the integral at $5\lambda^e$ is generally used in MRI calculations, keeping in mind that 63% of the information is already obtained within λ^e . For any experiment with emission angle θ , $\lambda^e = \lambda \cos \theta$, the effective attenuation length λ (EAL) (see [4.29]) is the relevant parameter, which unambiguously defines the information depth in the exponential approximation. As outlined in Chap. 4, the NIST database [4.21] is expected to give fairly reliable values. Therefore, in general, the parameter λ is looked upon as a fixed parameter in the MRI model that is not subject to fitting variations as are the other parameters, w and especially σ . Variation of λ with composition can be taken into account (see above, (7.36) and Fig. 7.25), but in general, it can be ignored [7.182].

7.1.8.5 Accuracy and Precision of MRI Applications

Accuracy and precision of profile reconstruction by the MRI model primarily depend on those of the measured profile, i.e., its signal-to-noise ratio, S/N (see Chap. 6). Even for high-precision AES or XPS depth profiles. The latter is rarely better than 100:1. Because thin layers (e.g., monolayers) are broadened by increasing width of the depth resolution function, it was early recognized [7.5, 7.197] that a layer with thickness d can only be detected if the minimum detectable intensity, I_s/I^0 , is given by (7.12), i.e., $(I_s/I^0)_{\min} = \text{erf}(d/\sqrt{2}\Delta z_{\max})$ (see Sect. 7.1.3). For $S/N = (I_s/I^0)_{\min} = 0.05$, this means that detection of a monolayer ($d = 0.3 \text{ nm}$) requires $\Delta z_{\max} \leq 4 \text{ nm}$. In the limiting case $\Delta z = 4 \text{ nm}$, a distinction between a full monolayer and a lower concentration spread out over several monolayers would be impossible even by deconvolution knowing the resolution function. High-resolution depth profiling therefore is a prerequisite for high-precision depth profile reconstruction. An example is given in Fig. 7.31 [7.182], which shows a nanolayer structure consisting of 3 layers of AlAs of various thickness in GaAs. The nominal deposition structure is (in monolayers (ML), 1 ML = 0.28 nm): 48 GaAs/1 AlAs/48 GaAs/4 AlAs/46 GaAs/20 AlAs/GaAs(bulk). (The sample is structurally characterized by atomic resolution TEM.)

In Fig. 7.31a, the AES depth profile of Al(68 eV) obtained by sputtering with 200 eV Ar^+ ions at 70° incidence angle is depicted. The fitting MRI parameters are shown in the figure. Because the bulk elemental intensity I^0 is just attained at the 20 nm AlAs layer, we can use that intensity as an internal standard with high accuracy. Considerable improvement is seen when the ion energy is further reduced to 100 eV, as shown in Fig. 7.31b. Because of the reduced sputtering rate, only the first two layers are profiled here. Quantification by MRI calculation shows an excellent fit with the parameters $w = 0.8 \text{ nm}$, $\sigma = 0.55 \text{ nm}$, $\lambda = 0.3 \text{ nm}$ ($\Delta z = 1.9 \text{ nm}$). In addition, Fig. 7.36c shows the result of an MRI calculation for 1.0 and for 1.2 ML at the first AlAs layer. In Fig. 7.36c, this layer is magnified to disclose the deviation between the MRI calculations for 1.2, 1.0, and 0.8 ML thickness and the experimental data. Obviously, 0.9 ML corresponds to the optimum value, with a maximum error of $\pm 0.2 \text{ ML}$ or, in terms of thickness, $0.28 \pm 0.06 \text{ nm}$. This is a remarkable accuracy that was already confirmed earlier with SIMS measurements on a different nanolayer of AlAs in GaAs [7.187].

The previous example demonstrates that in the disclosure of nanolayer structures, the experimental limits of accuracy and precision are of fundamental importance. Besides a high signal-to-noise figure, the highest possible depth resolution should be attained. Assuming as the physical limit for sputter depth profiling that each of the three MRI parameters is about 1 ML or 0.3 nm, we can simulate the intensity depth profiles that would be measured if there are two monolayers of the same element, separated by an increasing number of matrix monolayers. The result is shown in Fig. 7.32. With increasing separation, the two-layer structure is better resolved. Applying the Rayleigh criterion for resolution in optics, i.e., a 20% dip in between two adjacent maxima [7.159], we get a resolution of about 3 ML in between if the signal-to-noise ratio is better than 10:1. Because the MRI

evaluation is highly shape sensitive, already 2 ML in between could be reliably disclosed (Fig. 7.32). With a signal-to-noise figure of about 100:1, we could even differentiate the case of two layers being adjacent, i.e., a single layer of 2 ML thickness, from that of two layers with one ML in between. Maxima of two monolayers of different elements are easier to distinguish. Thus, two monolayers, one consisting of N and the other of S with a 2 ML distance in between ($n = 2$) could be fully separated with an excellent depth resolution of 0.9 nm, as shown in a GDOES study by Shimizu et al. [7.187] and quantified with the MRI model in Ref. [7.35].

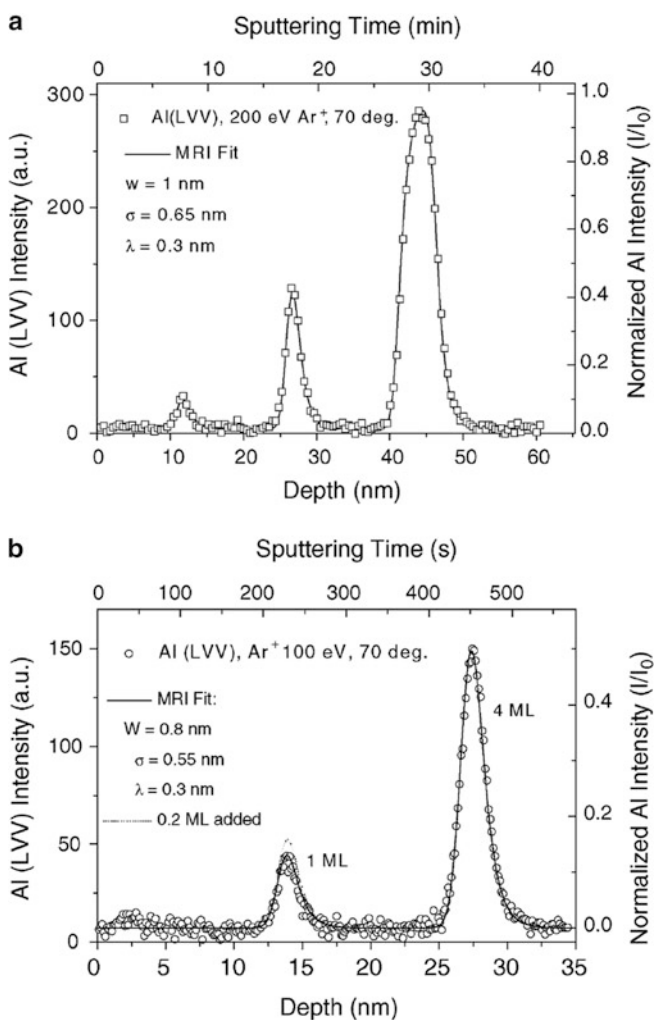


Fig. 7.31 (continued)

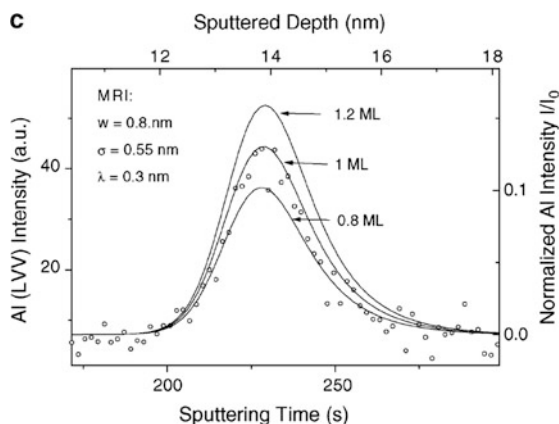


Fig. 7.31 (continued) (a) AES depth profile of three nanolayers of AlAs in GaAs (1 and 4 and 20 ML thick, 1 ML = 0.28 nm) obtained by sputtering with Ar^+ ions of 200 eV energy and 70° incidence angle. The Al LVV (68 eV) signal intensity (APPH) is plotted as a function of sputtering time and of depth (*open squares*). The *full line* shows the MRI-fitted calculation result with the parameters given in the figure; (b) as in (a), but sputtering with Ar^+ ions of 100 eV energy and the MRI calculation assuming 1.2 ML to illustrate the accuracy achieved; (c) as in (b), but magnified and with an additional MRI calculation based on 0.8 ML. It is clearly seen that the most probable layer thickness is 0.9 ML, with about 0.2 ML as a mean scatter of the measured data. Therefore, the more accurate value is 0.9 ± 0.2 ML (From S. Hofmann [7.182])

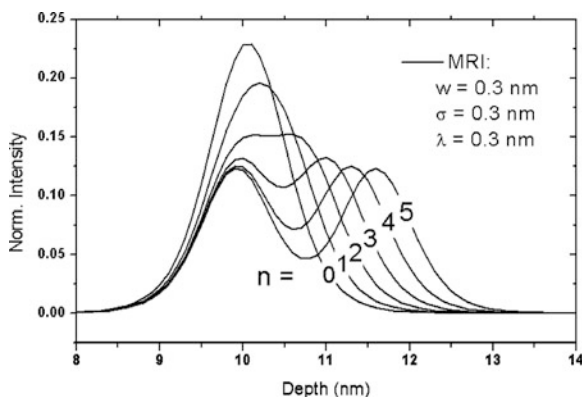


Fig. 7.32 Depth profile of two adjacent monolayers of the same element calculated by the MRI model for increasing distance of the monolayers, n (=numbers of ML in between) (1 ML = 0.3 nm) (From S. Hofmann, J. Schubert [7.159])

7.1.8.6 Some Typical Applications of the MRI Model

Since the MRI model applies for sputter depth profiling irrespective of the analysis technique, whether it is AES, XPS, SIMS, GDOES, etc. [7.35, 7.185], many applications to SIMS depth profiles have been reported [7.198, 7.199, 7.200, 7.201, 7.202]. Applications using depth profiling with AES and XPS include depth profiling

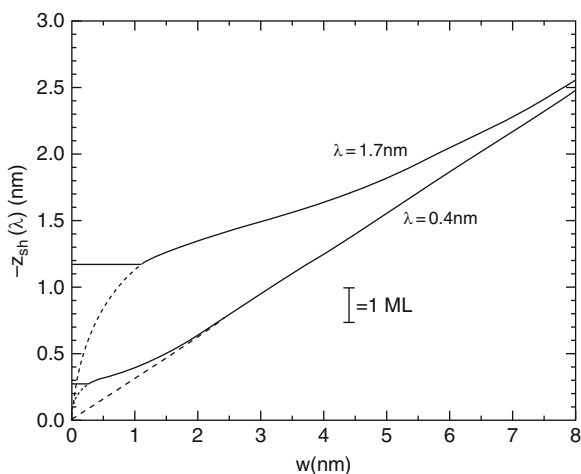


Fig. 7.33 Shift of the 50% maximum intensity with respect to the original interface location, $-z_{\text{sh}}$, as a function of the mixing length w , for $\lambda^e = \lambda = 0.4$ and 1.7 nm. For $w < 0.7\lambda^e$, only λ^e determines the shift after (7.9) in Sect. 7.2.1.1 (From S. Hofmann and J.Y. Wang [7.49])

studies in multilayers of transition metals [7.203], determination of concentration gradients [7.171, 7.204, 7.205], and quantitative comparison of AES and SIMS depth profiling studies [7.187], revealing the capabilities and limitations of techniques. In general, the MRI model gives valuable guidance for optimizing depth profiling parameters [7.1, 7.206]. A few typical applications of the MRI model are summarized in the following.

Estimation of the Depth Scale in Sputter Depth Profiling: One of the key tasks in quantitative depth profiling is determination of the sputtered depth (see Sect. 7.1.2). Sputter depth profiling combined with AES (and XPS) offers the possibility to estimate the depth scale from measured interface profiles, if the high- and the low-energy peak of an element are simultaneously monitored in the same profile [7.36, 7.51] (see Fig. 7.2). While the simple relation (7.10) (Sect. 7.1.2) is strictly valid only for negligible influence of mixing and roughness parameters, their mutual influence is disclosed by the MRI model [7.49]. Figure 7.33 shows the influence of atomic mixing on the 50% profile shift at a sharp interface for two different mean electron escape depth values.

Diffusion in Thin-Film Nanostructures: The MRI model offers an elegant possibility to study diffusion at the interfaces of nanostructures [7.51, 7.205]. Because diffusion basically causes a Gaussian broadening of any thin layer, any change of the roughness parameter σ in the MRI model can be directly attributed to diffusion by the well-known random walk relation $\sigma^2 = 2Dt$ with D the diffusion constant and t the annealing time. From two profiling measurements, one of the original sample and one of the annealed sample, with the MRI fitting parameters w , λ^e , σ , only the σ parameter should be different (σ_0 and σ_T , respectively), and the interdiffusion constant D_{eff} can be estimated from

$$D_{\text{eff}} = \frac{\sigma_{\text{Diff}}^2}{2t} = \frac{\sigma_1^2 - \sigma_0^2}{2t}. \tag{7.39}$$

An example is shown in Fig. 7.34 for interdiffusion in a Ge/Si layer structure [7.205]. The results of depth profiling and the corresponding MRI fitting for samples after deposition (at 300°C) and after annealing for $t = 30$ min at 700°C are presented

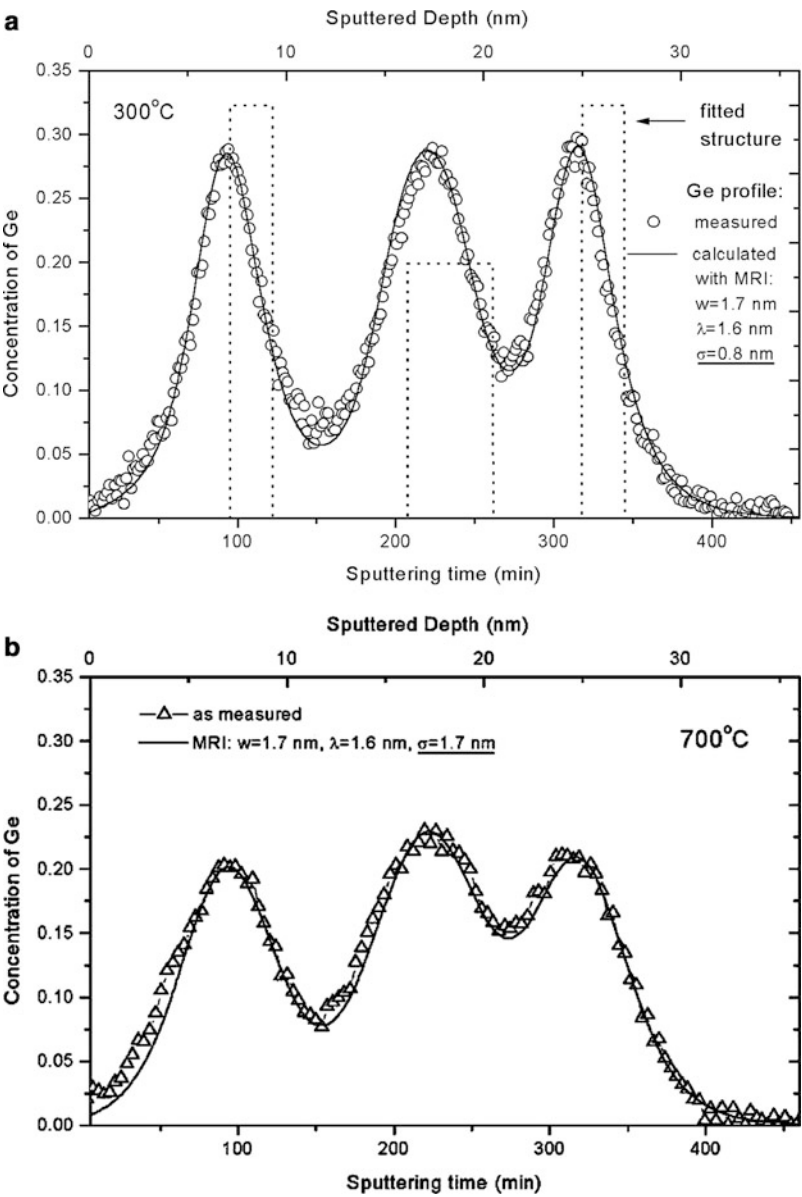


Fig. 7.34 (continued)

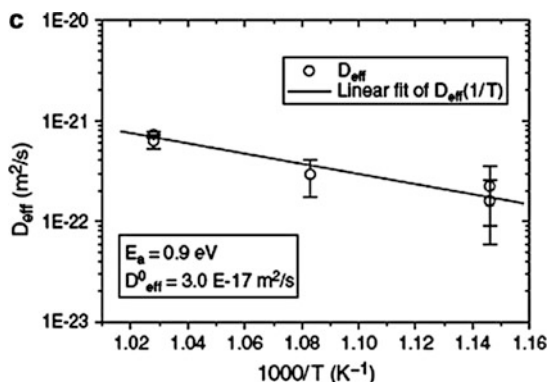


Fig. 7.34 (continued) (a) AES depth profile (1.5 keV ArC, 74° incidence) of a Ge layer structure in Si. The normalized Auger intensity (Ge LMM, 1147 eV) (*open circles*) is optimal, represented by the MRI model calculation (*solid line*) with the parameters given in the *inset*, based on the reconstructed Ge distribution (X/X^0) shown as the *dotted line*. (b) Depth profile of the same structure as in (a) with the same sputtering conditions after annealing at 700°C for 30 min. Note that by changing only the λ^e ($=\lambda$) parameter from 0.8 to 1.7 nm a good fit is obtained; (c) Arrhenius plot of the interdiffusion constant of Ge in Si obtained with (7.39) (Reproduced from V. Kesler and S. Hofmann [7.205])

in Figs. 7.34a and 7.34b, respectively. Figure 7.34b shows the broadening of the profile in Fig. 7.34a. The depth profile in Fig. 7.39b can be fitted by only changing the σ parameter in the MRI model from $\sigma_0 = 0.8$ nm (Fig. 7.39a, 300°C, as deposited) to $\sigma_T = 1.7$ nm for 700°C (Fig. 7.34b). The sputtering conditions and therefore the parameters w and λ^e ($=\lambda$ in the figure) are the same in both figures. With (7.39), the interdiffusion constant at 700°C is obtained as $D_{\text{eff}} = 6.3 \times 10^{-22} \text{ m}^2/\text{s}$. Figure 7.34c shows the Arrhenius plot after annealing at further temperatures for determination of the activation energy and the preexponential factor [7.51, 7.205]. A refined evaluation method which gives similar but more precise results is by first calculating the concentration depth profile of the annealed sample from the original layered structure by adopting a suitable diffusion model. This concentration profile is then convoluted with the resolution function by applying the MRI model, resulting in the quantified AES depth profile. Finally, the interdiffusion coefficient is obtained by fitting the calculated AES depth profile to the measured profile [7.1]. As demonstrated here, determination of diffusion lengths of the order of 1 nm is possible using the MRI model for evaluation, thus enabling measurements of diffusion constants as low as $10^{-22} \text{ m}^2/\text{s}$ for relatively short annealing times (30 min).

Prediction and Quantification of Depth Profile Improvement by EPES: Elastic peak electron spectroscopy (EPES) can be successfully used for depth profiling [7.166]. Since the backscattering cross section depends directly on the atomic number, taking – as a first-order approximation – the intensity of the elastically backscattered primary energy peak proportional to the composition in a binary system of elements A and B, this dependence can be used for the measurement of a depth profile through A/B interfaces [7.166, 7.207]. This approach opens a useful way to obtain a better depth resolution as compared to normal (medium or

high energy) AES peak measurement by choosing λ almost freely when selecting a specific primary energy, in contrast to the fixed Auger energy. In EPES depth profiling, the effective electron escape depth, $\lambda_{\text{eff}} \cos \theta_{\text{eff}}$, is composed of both the escape depth of the incoming primary electrons characterized by $\lambda_{\text{in}} \cos \alpha_{\text{in}}$ and of the escape depth of the emitted electrons, $\lambda_{\text{out}} \cos \theta_{\text{out}}$, both for the primary beam energy E_p (α is the electron incidence and θ the emission angle, respectively). Multiplying the according exponential decay functions (see, e.g., expression (4.88b) in Sect. 4.3.3) gives [7.207]

$$\exp\left(-\frac{z - z_1}{\lambda_{\text{eff}} \cos \theta_{\text{eff}}}\right) = \exp\left(-\frac{z - z_1}{\lambda_{\text{in}} \cos \alpha_{\text{in}}}\right) \exp\left(-\frac{z - z_1}{\lambda_{\text{out}} \cos \theta_{\text{out}}}\right) \quad (7.40)$$

with

$$\lambda_{\text{eff}} \cos \theta_{\text{eff}} = \frac{1}{\frac{1}{\lambda_{\text{in}} \cos \alpha_{\text{in}}} + \frac{1}{\lambda_{\text{out}} \cos \theta_{\text{out}}}}, \quad (7.41)$$

function of sputtering time and sputtered depth, together with the MRI fitting calculation. Fitting was performed with the following parameters: mixing length $w = 1.7$ nm, roughness parameter $\sigma = 0.8$ nm, and information depth parameter $\lambda^e = 1.6$ nm (with $\theta = 42^\circ$). Optimized fit for reconstruction of the (most simple) in-depth distribution in Fig. 7.35a shows a reduced Ge layer concentration (atomic fraction) of $X/X_0 = 0.6$ for layers 1 and 3 and $X/X_0 = 0.37$ for layer 2 [7.207]. Note that for AES, we can neglect λ_{in} in (7.41), because for the primary energy 10 keV in Si (with $\lambda = 2.2$ nm at 1147 eV) [7.207], $\lambda_{\text{in}} = 10.1$ nm $\gg \lambda_{\text{out}}$. Therefore, for the AES profile, only $\lambda_{\text{eff}} \cos \theta_{\text{eff}} = \lambda_{\text{out}} \cos \theta_{\text{out}} = \lambda_{\text{out}}^e (= 1.6$ nm, denoted λ in Fig. 7.35a) with $\theta_{\text{out}} = 42.3^\circ$ is considered.

Note that for different incidence and emission angle, θ , the escape depth is different even for the same energy (= equal attenuation length, λ), because $\lambda_{\text{in}}^e = \lambda \cos \alpha_{\text{in}}$ and $\lambda_{\text{out}}^e = \lambda \cos \theta_{\text{out}}$. An example of the depth resolution improvement by (7.40) and (7.41) is shown in Fig. 7.35 for a layer structure of Ge in Si [7.207]. The normalized Ge LMM (1145 eV) peak intensity is shown in Fig. 7.35a for the experimental sputtering conditions 1.5 keV Ar^+ ions, 74° ion incidence angle, as a Fig. 7.35b shows the elastic peak intensity at a peak energy of $E_p = 1000$ eV as a function of the sputtering time. It is obvious that Ge ($Z = 32$) has a higher elastic reflection cross section as compared to Si ($Z = 14$). Indeed, Fig. 7.35b is rather similar to the Ge LMM depth profile in Fig. 7.35a, but the depth resolution of the EPES profile is obviously higher, in spite of the approximately equal kinetic energy of the detected elastic peak (1000 eV) electrons as compared to the Ge (1147 eV) electrons. Evaluation of the EPES profile with the MRI model shows the parameters $w = 1.7$ nm (of course, this has to be the same as in Fig. 7.35a because of the same sputtering conditions), $\sigma = 0.6$ nm, (slightly readjusted from $\sigma = 0.8$ nm in Fig. 7.35a to give a somewhat better fit in view of the improved resolution, see Fig. 7.35b), and $\lambda_{\text{eff}} = 0.8$ nm. It follows that the effective escape depth change is responsible for the improved depth resolution in EPES depth profiling. According to (7.40) and (7.41), the effective escape depth of 0.8 nm can be explained as follows: for the primary beam with $E_p = 1.0$ keV, $\alpha_{\text{in}} = 0$ and the attenuation length $\lambda_{\text{out}}(1147 \text{ eV}) = 2.2$ nm at 1147 eV, we obtain $\lambda_{\text{in}}(1000 \text{ eV}) = \lambda_{\text{in}}^e = 2.0$ nm

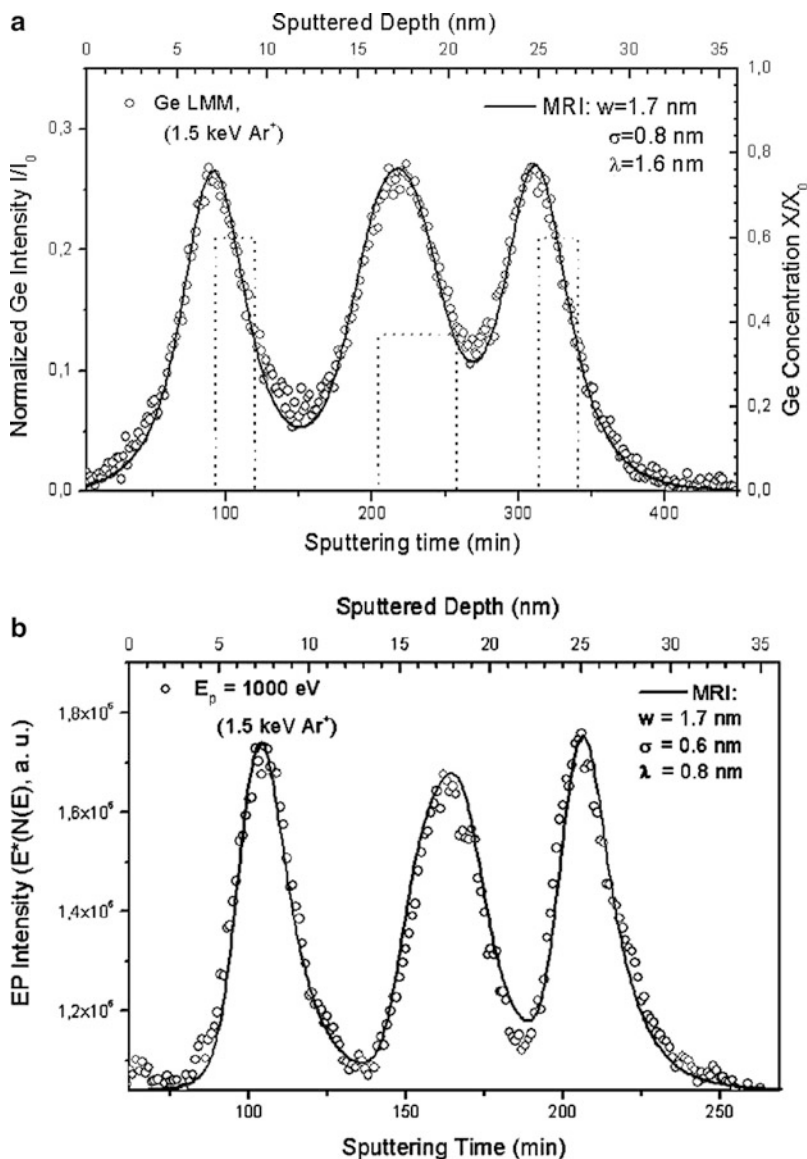


Fig. 7.35 AES sputter depth profile of a Ge/Si nanostructure (1–4–1 nm, 0.6–0.4–0.6 at%Ge) (open circles: measured data, line: MRI quantification for layer structure shown in upper picture as dotted line. MRI parameters see inset). (a) measurement using the Ge (1147 eV) peak; (b) measurement using EPES peak at $E_p = 1000 \text{ eV}$ (From V. Kesler and S. Hofmann [7.207])

and $\lambda_{\text{out}}^e = \lambda_{\text{out}} \cos 42.3^\circ = 1.45 \text{ nm}$ [7.207]. According to (7.41), $\lambda_{\text{in}}^e = 2.0 \text{ nm}$ and $\lambda_{\text{out}}^e = 1.45 \text{ nm}$ combine to $\lambda_{\text{eff}}^e = 0.84 \text{ nm}$. This value is in good agreement with the MRI best fit value of $\lambda^e = 0.8 \text{ nm}$ (see inset in Fig. 7.35b, where λ means λ^e). In summary, comparison of EPES- with AES depth profiling shows that the depth resolution function can be considerably improved in EPES depth profiling

by reducing the effective electron escape depth. A further advantage is the much better signal-to-noise figure (see Chap. 6) of the elastic peak, whereas a disadvantage is the limitation to strictly binary systems.

7.1.9 Special Sputter Depth Profiling Techniques

Besides the routinely employed general sputter profiling technique, there are some useful modifications which require special equipment and/or sample preparation. Most important are multiple-point depth profiling and sample rotation during sputtering. Although other destructive profiling methods, for example, beveling techniques like crater-edge profiling, angle lapping, and ball cratering in combination with SAM use sputtering mainly as an auxiliary method, they are also considered in the following.

7.1.9.1 Multiple-Point Depth Profiling

Small-spot XPS and in particular high-resolution scanning AES with programmable electron beam position offer the possibility of sequentially analyzing several preselected points on a surface after each sputtering cycle. With this method of “multiple-point depth profiling” [7.136] (often called “selected area depth profiling” [7.208, 7.209]), several profiles are obtained which represent different locations. In principle, a three-dimensional analysis is possible. In fact, because of the time necessary for each data point, only a reduction of the data acquisition time, as in the chemical imaging mode, is feasible. Usually, for a full analysis with reasonable signal-to-noise ratios, multiple-point depth profiling is reduced to two-point depth profiling [7.136, 7.208].

The main advantage of two-point depth profiling is the fact that depth profiles at different locations show the difference directly between the selected areas for identical sputtering conditions. For example, on rough or corrugated surfaces, specific microplanes can be selected which show different microroughness [7.136]. In polycrystalline samples, selection of single grains ensures a high depth resolution because of avoiding the polycrystalline effect of induced roughness in sputter depth profiling (Sect. 7.1.4) [7.136]. In oxidation studies on Ni_3Al , NiO particles were detected on an Al_2O_3 layer, and the depth profile analysis of both features was obtained by two-point sputtering [7.210]. Two-point sputter depth profiling was used to disclose the mechanisms of redeposition and resputtering. Figure 7.10 in Sect. 7.1.4 shows an example of simultaneous depth profiles on differently inclined sample surfaces.

In summary, multiple-point depth profiling is particularly useful when two or more distinct features at a surface are to be characterized by depth profiling and are directly compared.

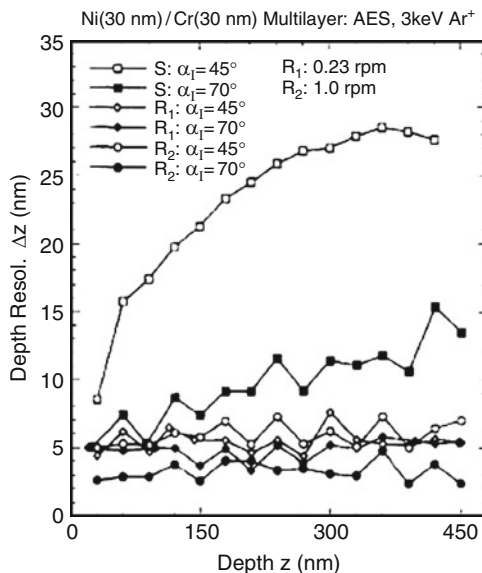


Fig. 7.36 Depth resolution Δz as a function of the sputtered depth z for a Ni (30 nm)/Cr(30 nm) multilayer (smooth surface). Sputtering with 3 keV Ar⁺ ions at two different incidence angles, with (R) and without (S) rotation, and at two different rotation speeds $R = 0.23$ and $1 \text{ rev} \cdot \text{min}^{-1}$ (From S. Hofmann and A. Zalar [7.71])

7.1.9.2 Sample Rotation During Sputter Depth Profiling

Usually, sputter depth profiling is done with an ion beam hitting the sample with an angle that is limited by the construction of the instrument with sometimes little possibilities of change (often only $40\text{--}50^\circ$ as in JEOL JAMP 9730). Higher incidence angles are often required for optimum depth profiling conditions on smooth sample surface (see Sect. 7.1.4). In that case, a wedge-shaped support for the sample holder can be used, which – by rotation of the holder – increases the incidence angle range from 40° to 83° [7.212]. In many cases, ion bombardment from one angle causes formation of surface morphologies such as ripples and cones or random roughness. Similar to a nonuniform ion current density distribution in the analyzed area, a contribution to depth resolution is expected that increases with depth (see Sect. 7.1.3) and therefore is the main reason for degradation of depth resolution with time. The effects of unidirectional ion bombardment can be overcome to some extent by the use of two ion guns at different incidence angles [7.136], as schematically depicted in Fig. 7.37 for the reduction of shadowing and redeposition effects. Most effective in reduction of sputter-induced roughening of the sample surface is sample rotation during sputter profiling, introduced by Zalar in 1985 [7.137]. A round-robin study of a Ni/Cr multilayer sample between four laboratories confirmed the attainment of a depth-independent and substantially improved depth resolution by sample rotation [7.146] (see Fig. 7.17). The main results are summarized below. Further details are found in [7.3, 7.5, 7.71].

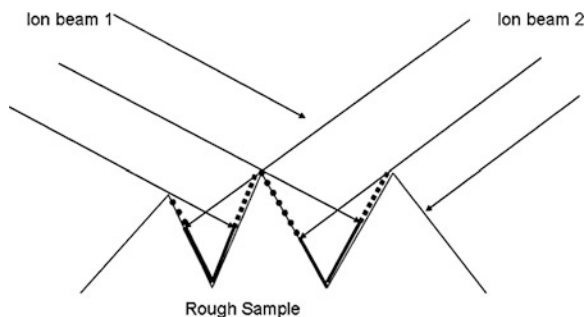


Fig. 7.37 Schematic view of a rough sample surface sputter profiled with two ion guns and of rotational depth profiling: shadowing of ion beam 1 is partially removed by ion beam 2 (*round pointed lines*) and vice versa (*square pointed lines*). However, a part of the sample surface in deeper troughs remains in the shadow of both ion beams (*thick full-drawn lines*). Similarly, sample rotation with one ion gun can be imagined viewing ion beam 2 as ion beam 1 after 180° rotation

The most important experimental conditions for sample rotation during sputter depth profiling are the ion beam incidence angle with respect to sample surface roughness and the speed of rotation. They are discussed in the following.

Smooth Sample Surfaces

For smooth sample surfaces, a high ion incidence angle reduces Δz in any case. At least two effects are of importance: (i) decrease of the atomic mixing zone length with the incidence angle [7.148], and (ii) reduction of the ion-beam-induced roughening due to the effect of crystalline orientation [7.130, 7.149]. The latter is preponderant for metallic layers. Very high values of the ion incidence angle ($>80^\circ$) may even lead to “polishing” effects at the sample surface during sputtering [7.212]. Studies of Henneberg et al. [7.213] on AES depth profiling of NiFe/Ta layers with and without sample rotation show a decrease of Δz with increasing incidence angle for both methods and practically a coincidence above 50° . An example of the depth dependence of Δz in AES depth profiling of Ni/Cr multilayers with and without sample rotation [7.71] is shown in Fig. 7.36 for the ion incidence angles for $\alpha_1 = 45^\circ$ and $\alpha_1 = 70^\circ$ and two different rotation speeds. In contrast to stationary samples, Δz is practically constant with z and the influence of θ_1 is much less pronounced for rotating samples, because the decrease of the mixing zone with θ_1 is much smaller than that of sputtering-induced roughening. For the lower rotation speed, the average value of Δz is 5.5 nm at $\alpha_1 = 45^\circ$ and 4.5 nm at $\alpha_1 = 70^\circ$, corresponding to the angular dependence of the mixing length. Increasing the rotation speed from 0.23 to 1 rpm at $\alpha_1 = \text{const.} = 70^\circ$ improves Δz from about 4.5 to 3 nm, obviously caused by a further reduction of the residual surface roughness (see below: rotation speed).

Rough Sample Surfaces

For samples with rough surfaces, stationary depth profiling causes an increase of Δz for an ion incidence angle above 60° [7.130], depending on the angular distribution of the microplanes. As visualized schematically in Fig. 7.37, the shadowing effect encountered in unidirectional sputtering is considerably reduced by two ion guns and/or sample rotation during sputtering. Two ion beams and a static sample decrease shadowing (and redeposition) by sputtering with ion beam 1 parts of areas shadowed by beam 2 and vice versa. More effective is sample rotation (with ion beam 1 only), since sample surface locations eventually come in position of ion beam 2 and in between get in a “trough” position where additional areas are sputtered. Below a critical angle, given by the average inclination angle of the surface microplanes, Δz is expected to decrease similar to smooth surfaces, but an increase of Δz is expected with higher α_1 , although less pronounced as compared to the stationary case. This behavior is seen in Fig. 7.16, where Δz is shown as a function of the ion incidence angle for the rough surface ($R_a \approx 1\mu\text{m}$) of a 30-nm-thick $\text{Ta}_2\text{O}_5/\text{Ta}$ anodic oxide layer [7.71], when AES depth profiling is done with and without sample rotation. As qualitatively explained by Fig. 7.37, depth resolution is considerably improved with sample rotation, although the critical angle around $\alpha_1 \approx 60^\circ$ is about the same for (*S*) and (*R*). It is remarkable that Δz is also improved for lower values of α_1 because those microplanes with a high inclination angle are at least partially sputtered during sample rotation, even if they cannot be reached by unidirectional ion bombardment of a stationary sample because of shadowing (see Fig. 7.37). Note that in contrast to Ni/Cr (Fig. 7.36), the effect of rotation is smaller in Ta_2O_5 because there is no crystalline effect in oxide profiling.

Rotation Speed

The speed of rotation obviously has to be above a lower critical value to ensure an improvement of Δz as compared to stationary conditions. For a homogeneous ion beam intensity, the effect of ion-beam-induced roughening is mainly due to the dependence of the sputtering rate on the orientation of different grains in the sample [7.143, 7.149, 7.150] (see Sect. 7.1.4, sample characteristics). The sputtering rate at maximum for nonchanneling $((dz/dt)_{\text{max}})$ and at minimum for channeling directions $((dz/dt)_{\text{min}})$. The dwell time Δt of the ion beam in the vicinity of a certain angular distribution $\Delta\phi_{\text{ch}}$ around a channeling direction is responsible for the growth of surface roughness in terms of a height difference causing a contribution Δz_{R} to the totally measured Δz . Therefore, the time-independent contribution Δz_{R} should be proportional to the difference $(dz/dt)_{\text{max}} - (dz/dt)_{\text{min}}$ and to $\Delta t/\Delta\phi_{\text{ch}}$. The latter is proportional to $1/u$, if u denotes the speed of rotation in revolutions per time unit (in general revolutions per minute, rpm), and Δz_{R} is given by

$$\Delta z_{\text{R}} = \left[\left(\frac{dz}{dt} \right)_{\text{max}} - \left(\frac{dz}{dt} \right)_{\text{min}} \right] \frac{\Delta t}{\Delta\phi_{\text{ch}}} = (k_{\text{R}}u)^{-n}. \quad (7.42)$$

The exponent n and the factor k_R depend on the details of roughness growth mechanism [7.214] and on the orientation distribution and is somewhere between 0.5 and 1 [7.86]. Of course, Δz_R does not depend on the absolute value of u but on the relative rotation speed with respect to the difference $(dz/dt)_{\max} - (dz/dt)_{\min}$. Because the latter decreases with the ion incidence angle, Δz_R decreases similarly (see Fig. 7.42). For high u , Δz_R is diminished until the measured, total Δz contains only other contributions Δz_j like the atomic mixing and information depth contributions according to (7.23) (see Sect. 7.1.5),

$$\Delta z = \sqrt{\Delta z_R^2 + \Delta z_j^2}. \quad (7.43)$$

A systematic study by Tanemura et al. [7.215] on the dependence of Δz on the rotation speed can be explained by (7.42) and (7.43). Their results for 1–3 keV Ar⁺ and Xe⁺ sputter profiling of Fe/Cu multilayers show that a limiting Δz_j of about 10 nm is attained at a useful, optimum rotation speed that depends on ion energy and mass through $(dz/dt)_{\max} - (dz/dt)_{\min}$ in (7.42).

According to (7.42), Δz_R approaches zero if the rotation speed is infinite. However, according to (7.43), additional contributions to the total Δz still exist, and its finite value (given at least by mixing length and information depth) suggests a lower limit of the useful, optimum rotation speed. For the latter, a rough estimation can be given assuming $n = 1$ in (7.43) and a dynamic equilibrium between growth and shrinkage per revolution. In general, $\Delta\phi_{\text{ch}}$ is less than 30° [7.150, 7.151]. Since for one revolution, we may have two times channeling directions or more (depending on the texture), we may assume twice the value corresponding to about 1/6 of the total revolution, giving a dwell time per revolution of $\Delta t / \Delta\phi_{\text{ch}} \approx 1 / (6u)$. Because the growth of roughness, given by $(dz/dt)_{\max} - (dz/dt)_{\min}$ in (7.42), cannot be higher than the (average) total sputtering rate, $(dz/dt)_{\text{av}}$, given by the depth/time relation of the profile, (7.42) simplifies to

$$u_{\min} = \frac{\left(\frac{dz}{dt}\right)_{\text{av}}}{6(\Delta z_R)_{\min}}. \quad (7.44)$$

The minimum tolerable rotation speed $u_{\min}$ depends on the other contributions after (7.43), with the limiting value of Δz_j given by the mixing and escape depth contributions. For the example shown in Fig. 7.36, the sputtering rate is about $(dz/dt)_{\text{av}} = 4.5$ nm/min for the Ni/Cr multilayer at $\alpha_1 = 70^\circ$. Assuming that the increase of the total Δz ($= 3$ nm for $R_2 = 1.0$ rpm) by Δz_R should be less than 10% (i.e., $= 2.7$ nm), according to (7.43), we obtain $(\Delta z_R)_{\min} = (3^2 - 2.7^2)^{1/2} = 1.3$ nm and, after (7.44), $u_{\min} = 0.6$ rpm. Experimentally (see Fig. 7.36), $u(R_2) = 1.0$ rpm was used, which gives a completely negligible value of $(\Delta z_R)_{\min} = 0.71$ nm. Lowering the rotation speed to $u(R_1) = 0.23$ rpm gives $(\Delta z_R)_{\min} = 3.3$ nm and with (7.43) (with $\Delta z_j = 2.7$ nm), $\Delta z = 4.3$, which is close to the experimentally determined value of 4.5 nm. For $\alpha_1 = 45^\circ$ (Fig. 7.36), Δz_j is larger and because

experimentally, $\Delta z = 5.5$ nm, a tolerable 10% lower value for Δz_j gives $(\Delta z_R)_{\min} = 2.4$ nm and accordingly $u_{\min} = 0.3$ rpm which is close to the lower rotation speed value of $u(R_1) = 0.23$ rpm. It is obvious that a higher rotation speed would further decrease the 10% deviation, but this would be beyond the measurement error of the total Δz .

In high-resolution depth profiling, we may generally assume that $(\Delta z_R)_{\min} = 1.0$ nm is an acceptable value, and as a rule of thumb, it follows that the minimum rotation speed in rpm is about 1/6 the sputtering rate in nm/min.

Limitations and Artifacts in Depth Profiling with Sample Rotation

Of course, sample rotation cannot overcome the fundamental ion-beam/sample interaction effects such as atomic mixing caused by the collisional cascade and the information depth of the respective elemental peak in AES or XPS. Only the effects of ion-bombardment-induced topography due to variations of the local sputtering rate will be affected. Furthermore, redeposition and shadowing in the case of originally rough sample surfaces will be diminished (see Figs. 7.21, 7.42). A detailed consideration of the influence of inhomogeneity of the ion beam intensity [7.71] shows that an additional, periodic contribution to the depth resolution, Δz_1 , occurs, which is given by

$$\Delta z_1 = \frac{\left(\frac{dz}{dt}\right)_1 - \left(\frac{dz}{dt}\right)_2}{\omega} \sin \omega t, \quad (7.45)$$

where $\omega = 2\pi u$ is the circular frequency and u is the rotation speed. The amplitude of Δz_1 is constant with sputtering time and similar to (7.42), with $(dz/dt)_1$ and $(dz/dt)_2$ denoting two different, extreme sputtering rates which are representative for the analyzed area but linearly dependent from the distance to the rotation axis. For quadratic dependence (or similar for higher-order dependence) on that distance, the periodic term with constant amplitude described by (7.45) is superposed by a term linearly depending on the sputtering time and leads to a nonvanishing degradation with depth [7.71]. Nevertheless, an improvement is obtained when comparing stationary sample conditions. A time-independent contribution and a smaller, time-dependent one was obtained in XPS depth profiling of Ni/Cr multilayers [7.147], where Δz was first observed to be constant with sputtering time but started to increase linearly with time after a sputtered depth above 180 nm. In AES, owing to the small analysis spot, the ion beam inhomogeneity effect is much less pronounced. However, for a considerable displacement between analysis spot and rotation axis, a periodic and a time-dependent contribution to the depth resolution is expected. This was demonstrated in a two-point-sputtering profile with AES on a Ni/Cr multilayer sample as shown in Fig. 7.38 [7.70]. The sputtered area was deliberately made asymmetric by rastering only in the x -direction and not at all in the y -direction. Analysis was performed with a focused electron beam of about

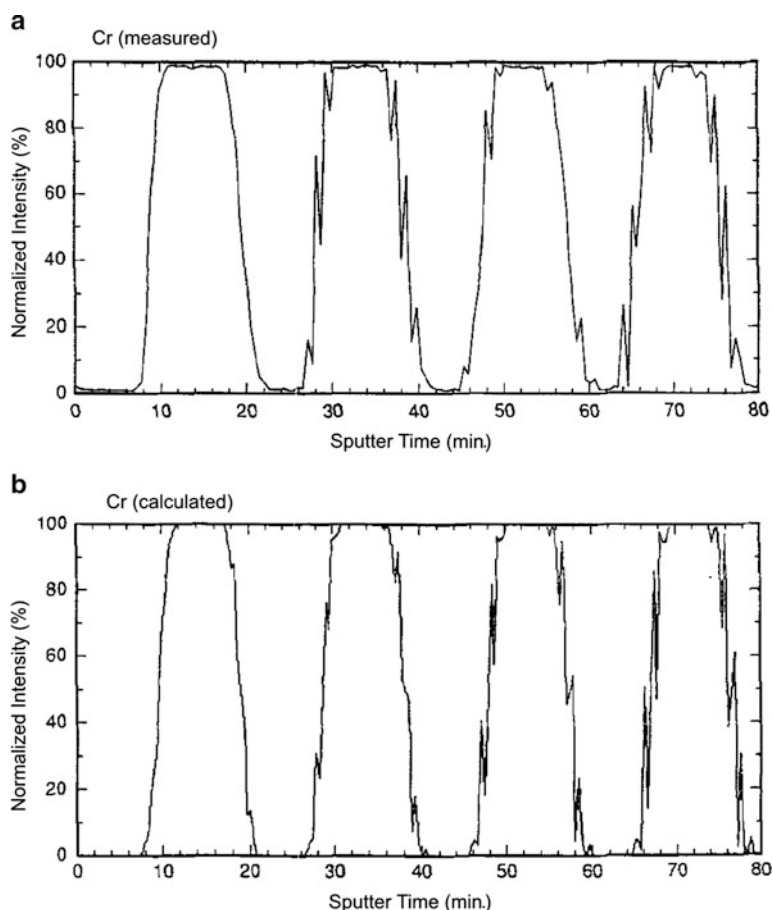


Fig. 7.38 (a) Chromium profile of the AES depth profile of a Ni/Cr multilayer (30 nm) until the fourth Cr layer. The periodic structure of the profile is deliberately generated by misalignment between analysis spot and rotation axis; (b) calculated Cr profile for explanation (From A. Zalar and S. Hofmann [7.70])

1 μm diameter with point 1 close to the rotation axis, where the ion beam was also centered. Point 2 was placed 400 μm away from point 1. Figure 7.38a shows the measured profile of the first 4 Cr layers obtained at point 2. The result of a calculation assuming the multilayer profile to be composed of a linear superposition of error functions is shown in Fig. 7.38b [7.70]. The similarity to the experimental profile supports the present approach to quantitative understanding of rotational depth profiling. Owing to the increasing amplitude of the periodic signal change, the profile and its depth resolution deteriorate with the sputtered depth.

It is interesting to note that the oscillatory term can be observed in a multilayer profile if there is any radial inhomogeneity in the analysis area, for example, by additional erosion of the sample by an intense primary electron beam. With the latter effect, Ericson [7.216] explained the observation of an oscillatory term in

rotational AES depth profiling of a GaAs/AlAs multilayer. A detailed discussion of the influence of sample rotation and ion beam rastering on depth resolution is presented by Shard and Seah [7.257].

Advantages of Depth Profiling with Sample Rotation

In summary, the advantages are:

1. Vanishing degradation of depth resolution with sputtered depth (increasing Δz with sputtering time) because in metals, crystalline-orientation-dependent sputtering rates cancel, and in semiconductors, ripple formation is suppressed.
2. Reduction of the original sample roughness influence on depth resolution because of diminished shadowing effects.
3. Reduction of the influence of inhomogeneity of the ion beam intensity on depth resolution. While the linear component of the ion beam intensity change in the plane of the sample practically vanishes, any nonlinear, for example, quadratic, component still increases Δz linearly with sputtering time, but the effect is considerably reduced.
4. Enhancement of the beneficial effect of increased ion incidence angle on depth resolution. The ion beam incidence angle is expected to be optimum at 70° for smooth sample surfaces and at about 45° for rough surfaces.
5. Improvement of depth resolution with increasing speed of rotation. As a rule of thumb, for a maximum tolerable contribution to Δz of about 1 nm, the minimum useful rotation speed in rotations per minute (rpm) is given by the sputtering rate in nm/min divided by 6.

7.1.9.3 Crater-Edge Profiling

In any sputter depth profiling experiment, there is a transition from zero to maximum sputtering rate at the crater edge, resulting in an according depth distribution. Thus, a line scan with high spatial resolution AES (or XPS) across the crater edge generates a compositional depth profile. This technique is called crater-edge profiling [7.36, 7.153, 7.217–7.225]. As schematically shown in Fig. 7.39 for a Gaussian ion beam intensity distribution, the slope α_m of the crater edge is fairly constant in the middle of the edge [7.218], and the “magnification factor,” $\tan \alpha_m$, determines the limiting depth resolution Δz_e given by the electron beam diameter d_e according to

$$\Delta z_e = d_e \tan \alpha_m. \quad (7.46)$$

High-resolution depth profiles have been frequently achieved by using crater-edge or bevel profiling [7.36, 7.154, 7.217–7.225]. Line scanning of an analyzing beam across a bevel of typically 10^{-2} to 10^{-4} degrees tilt angle reproduces an image of the depth distribution with a magnification factor of the reciprocal value, 10^2 to 10^4 . That means, for example, with a 1 μm beam diameter,

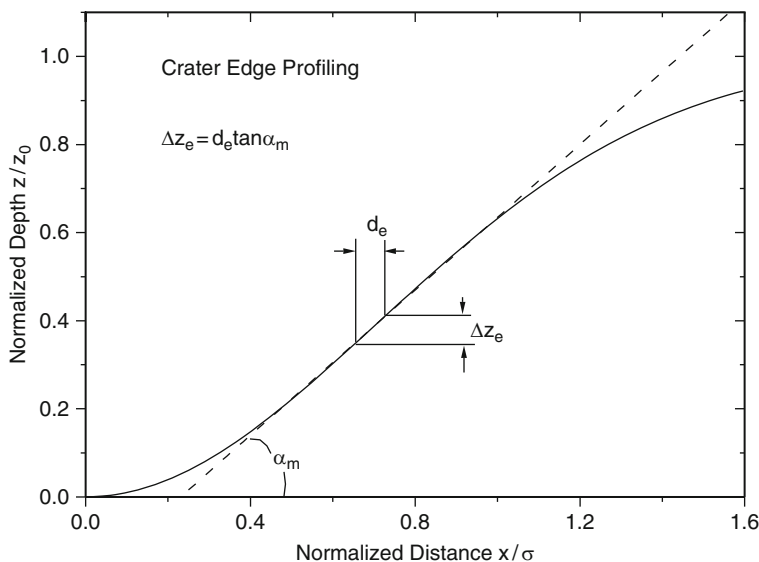


Fig. 7.39 Schematic view of the edge of a Gaussian-shaped crater used for crater-edge profiling [7.43]

the basic resolution is about 10 nm. However, crater-edge or bevel profiling is prone to similar distortions as direct sputter profiling [7.36] even when the bevel is generated, for example, by programmed mean ion beam current density steering during raster scanning [7.222, 7.225]. If contamination can be avoided, chemical beveling may give somehow better resolution [7.219], but it is limited to suitable materials.

An example of crater-edge profiling is shown in Fig. 7.40 [7.36]. A scanning electron microscopy (SEM) micrograph of the sputter depth profile of a Ta/Si multilayer of 18-nm-double-layer thickness, and 10 periods is shown in Fig. 7.40a. The inner dark region corresponds to the substrate, and the area of sputtering was 3 mm × 3 mm. The line scan of tantalum and silicon (Fig. 7.40b) demonstrates that the influence of preferential sputtering is still present in the crater-edge profile. Figure 7.40c schematically shows how the slope of the crater determines the apparent thickness of each layer. Taking a mean slope α_m , we would get the apparent thicknesses $d'_1(\text{Si}) = 6.8$ nm and $d'_2(\text{Ta}) = 13.2$ nm, whereas the correct thicknesses (obtained from a TEM micrograph) are $d_1(\text{Si}) = 10.5$ nm and $d_2(\text{Ta}) = 7.5$ nm as visualized by the different crater slopes for the Ta and Si regions, $\alpha_1(\text{Si}) > \alpha_2(\text{Ta})$. The apparent “hump” in the profile at about 70% of the Si signal is attributed to the sputtering-induced formation of TaSi_2 which decreases the sputtering rate [7.36].

A technique which uses a moving shutter in front of the ion beam to create a bevel with known and constant slope angle was developed by Procop et al. [7.225]. For further discussion of crater-edge and bevel profiling see, for example, [7.5].

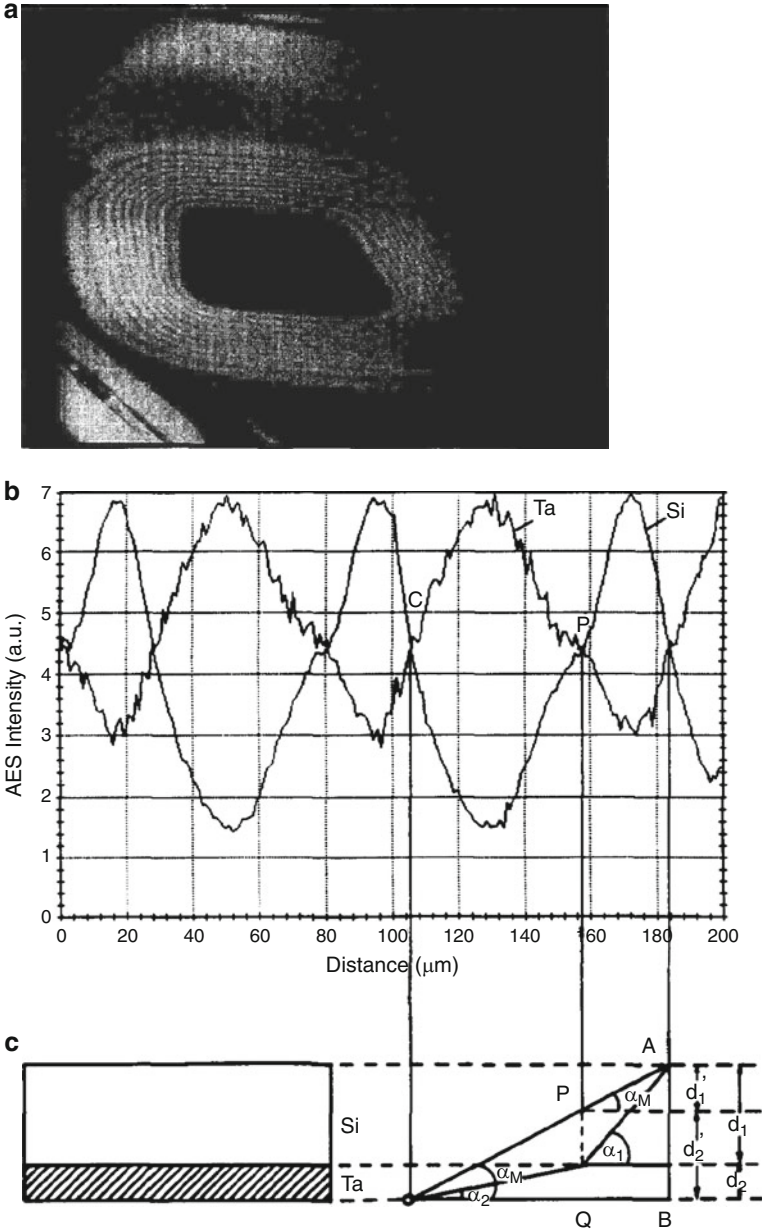


Fig. 7.40 Crater-edge profiling of a Ta/Si multilayer. (a) emission current SEM image showing the multilayer crater edge and the inner dark substrate region; (b) Auger peak-to-background signal line scan of tantalum and silicon along the sputtered crater edge in (a); (c) geometrical model of a sputtered crater edge to determine the true thickness of the layer (From B.R. Chakraborty and S. Hofmann [7.36])

7.1.9.4 Depth Profiling by Angle Lapping and Ball Cratering

For larger depths than those accessible by conventional sputter depth profiling (i.e., beyond a few microns) techniques, applying high ion current densities can be used, such as Glow Discharge Optical Emission Spectroscopy (GDOES, see Sect. 10.4.1.1), or focused ion beam sectioning (FIB) [4.18] followed by scanning AES (SAM). With the technique of “shave-off depth profiling”, FIB is used to remove the sample surface in a series of planes normal to the depth axis [7.258]. A simpler method to obtain a depth profile is a line scan over a cross section generated by mechanical abrasion. To get a magnification effect, angle lapping and ball cratering are usually applied in combination with scanning AES. For example, according to (7.46), with a 5.7° lapping angle, an instrumental depth resolution of about $0.1 d_e$ is obtained [7.226]. The advantage of this technique is that sputtering-induced effects are avoided. However, mechanical abrasion causes roughness, smearing of very soft constituents, and/or pulling out of hard phases, which often distorts the scanning profile. In special cases, chemical beveling is of advantage [7.219]. Some sputtering must be applied to get rid of surface contamination and oxidation. In conclusion, mechanical angle lapping is useful for thick layer profiles in the range of several micrometers [7.227].

The difficulty of a well-defined low bevel angle is avoided by ball cratering with a rotating steel ball according to Walls, Hall, and Sykes [7.228]. The geometry of the crater is a spherical segment with diameter D in the surface plane. Since the radius R of the ball is known (typically 1–3 cm), the depth d of the center of the crater is given by $D^2/8R$, and the lateral position of the electron beam on the spherical crater can be directly related to the depth. Assuming a perfectly smooth crater, the depth z is related to the distance x by which the electron beam is moved from the crater edge by [7.228],

$$z = d - R + \sqrt{R^2 - \left(\frac{D}{2} - x\right)^2}. \quad (7.47)$$

The limiting depth resolution Δz_{bc} of ball cratering is given by

$$\Delta z_{bc} = \left(\frac{d_e}{R}\right) \sqrt{2R(d - z)} + m, \quad (7.48)$$

where d_e is the diameter of the probing electron beam and m is an additional surface roughness term. In practice, the depth resolution is limited mainly by the surface roughness generated during the mechanical abrasion process. Equations (7.47, 7.48) show that the relative depth resolution $\Delta z_{bc}/z$ is improved for larger depths d [7.228]. Further considerations for the use of mechanical lapping and conventional AES sputter depth profiling with respect to optimum Δz as a function of total sputtered depth are given by Lea and Seah [7.227].

The advantage of ball cratering with respect to common angle lapping is its easy application without the need of a precise angle control and the fact that the slope, $\tan \alpha_m$, is extremely small near the crater bottom. Compared to conventional sputter

profiling and crater-edge profiling, a further advantage is that an absolute depth scale is established with a defined surface topography, despite the problems mentioned above. For lower depths ($<2(\mu\text{m})$), sputter profiling is a more sensitive technique than mechanical abrasion and inherently has a better absolute depth resolution.

7.2 Nondestructive Depth Profiling

Nondestructive depth profiling has become popular because of two main features as compared to destructive sputter depth profiling:

1. Negligible distortion of composition and chemical state of the sample
2. Inherent high depth resolution for the first few atomic layers

However, both items have to be critically considered, because (1) after longer exposure time, even with conventional XPS, chemical and compositional changes of the sample surface may occur (Sect. 7.1), and (2) the information is obtained as a convolution of the in-depth composition that is not a direct image (although more or less distorted) of the latter obtained by sputter depth profiling.

Basically, information about the compositional in-depth distribution can be obtained by variation of the probing depth (e.g., electron escape depth or excitation energy in XPS), or by additional information contained in the background.

7.2.1 Angle-Resolved XPS and AES

The electron escape depth, and therefore, the information depth of AES and XPS vary strongly with the emission angle of the detected electrons, as obvious from the general intensity equations (Sect. 4.3). Therefore, this dependence can be used for nondestructive-, angle-resolved depth profiling (AR-XPS and AR-AES). As pointed out by Hofmann and Sanz [7.65], these equations have the general shape of a Laplace function L of the real concentration distribution of component A, $X_A(z)$, which is an integral transformation with the conditions 0 for $z < 0$ and $\exp[-z/(\lambda_A \cos \theta)]$ for $z > 0$. Thus, the basic equation for the intensity I (see, e.g., (4.15)) can be expressed as

$$I \frac{1}{\lambda_A \cos \theta} = \text{const} \int_0^{\infty} X_A(z) \exp\left(-\frac{z}{\lambda_A \cos \theta}\right) dz = \text{const} L[X_A(z)], \quad (7.49a)$$

and $X_A(z)$ is determined by the inverse Laplace transformation L^{-1} according to

$$X_A(z) = \text{const} L^{-1} \left\{ I \frac{1}{\lambda_A \cos \theta} \right\}. \quad (7.49b)$$

Equations 7.49a and 7.49b are applicable for both XPS and AES. The basic problem of profile reconstruction is similar to that encountered in deconvolution of sputter depth profiles, namely, the inverse, “ill-conditioned” problem of finding the compositional profile from convoluted intensity information. Only for some special cases, the solution can be found in mathematical tables [7.65]. Applications for AR-XPS have been discussed by Bussing and Holloway [7.229] and by McCashin and Young [7.230].

As pointed out by Cumpson [7.158, 7.231], application of (7.49a) and (7.49b) is extremely sensitive to small errors in the measured peak intensities, i.e., to noise. Therefore, the depth resolution strongly depends on the signal-to-noise figure. The relative depth resolution $\Delta z/z$ is given by Cumpson as $0.81 < \Delta z/z < 1.35$ which is comparable to that of sputter depth profiling for the first few layers but is usually larger in vicinity of the limiting depth of about $3\lambda_i$ for AR-XPS. Although many sophisticated methods have been used to extract directly the depth profile from AR-XPS data such as regularization or maximum entropy approach, a “forward” calculation based on (7.49a) with an assumed layer model and least squares fitting has been proved useful in practice [7.58, 7.232, 7.233]. In general, most exact and useful results are obtained for the simplest case of determination of the thickness of a contamination, oxide, or evaporation layer on a substrate, as discussed in Sects. 4.3.3 (XPS) and 4.4.3 (AES). Often, additional information from sputter depth profiling helps to decide about layer structure assumptions.

In XPS instruments with a CHA, the experimental determination of the signal intensity versus emission angle is straightforward by tilting the sample, as already discussed by Fadley [7.234] and by Ebel and coworkers [7.235, 7.236]. Although in practice, some problems may arise with surface roughness (see Sect. 5.1.4). Furthermore, it is predicted that at emission angles above 60° , the attenuation length increases because of increasing influence of the angular dependence of elastic scattering (see Sect. 4.2.2), although no experimental evidence has been found studying ultrathin SiO_2 layers [7.237]. Mainly because of the additional influence of backscattering and of the incidence angle on the detected intensity (see Chap. 4), AR-AES is much less popular than AR-XPS. However, AR-AES is particularly useful, for example, for in situ determination of layer thickness in combination with sputter depth profiling, such as the mixing zone length (Fig. 7.30) [7.238].

In contrast to sample tilt, alternative methods for AR-XPS and AR-AES are the selection of the angle of the analyzer aperture, either sequentially, as in the double-pass CMA (see Sects. 2.5.1 and 4.3.2.6) or parallel as in some modern instruments (Thetaprobe, see Sect. 4.3.2.6). The advantage is that there is no physical variation of the angle between sample surface, excitation source, and analyzer. This means that distortional effects like alteration of the excitation intensity and/or variation of the analyzed spot location are avoided. With respect to AES, this method has the further advantage of constant incidence angle. In AR-XPS, however, because the angle ψ between the incident X-rays and the photoelectron emission angle changes with the latter, the asymmetry factor $W_A(\psi)$ has to be exactly known and taken into account (see Sect. 4.4.3.2). A further advantage of parallel angular aperture selection is that the angle-dependent information is available in any measurement.

7.2.1.1 Layer Structure Analysis

As with any convolution result, AR-XPS is particularly powerful and straightforward for the determination of the composition and thickness of thin layers [7.58, 7.231, 7.232, 7.233, 7.234, 7.235, 7.236]. The expected intensity can be described as a function of the emission angle, and the result can be compared with the experimentally found dependence. The relative thickness d/λ is found for optimum fit of both curves. In general, the signal intensity of any in-depth distribution of a species A , $I_A(\theta)/I_A^0(\theta)$ can be obtained from the contribution of a stack of atomic monolayers (in the best possible resolution) which is given by the general layer-by-layer equation (4.53, Chap. 4) of thin-film quantification. The intensity is the sum of all monolayer intensities with thickness d_{ML} below the surface,

$$\frac{I_A(\theta)}{I_A^0(\theta)} = \sum_{i=1}^N X_{A,i} \left\{ \exp \left[-\frac{(i-1)d_{ML}}{\lambda_A \cos \theta} \right] - \exp \left[-\frac{id_{ML}}{\lambda_A \cos \theta} \right] \right\}, \quad (7.50)$$

where $X_{A,i}$ is the mole fraction of species A in the i th layer from the surface. Here, the attenuation length λ_A is assumed independent of composition, layer thickness, and emission angle. The bulk standard intensity of A , $I_A^0(\theta)$, depends on instrumental parameters such as the emission angle θ , the asymmetry factor in XPS if the photon incidence angle is not 54.7° , and the possibility of excitation intensity variations when tilting the sample (see Sects. 5.1, 5.2).

Assuming constant composition in layers with thickness d_i , where $i = 1$ refers to the first layer at the surface, we may write alternatively to (7.50),

$$\frac{I_A(\theta)}{I_A^0(\theta)} = \sum_{i=1}^N X_{A,i} \left\{ \left[1 - \exp \left(-\frac{d_i}{\lambda_{A,i} \cos \theta} \right) \right] \exp \left[-\frac{d_{i-1}}{\lambda_{A,i-1} \cos \theta} \right] \right\} \quad (7.51)$$

Equation 7.51 means that only the layers $(i-1)$ above layer i attenuate the intensity from layer i . Considering the bulk as layer N with infinite thickness, $d_N \rightarrow \infty$, the expression in the first parenthesis is unity and for the contribution of the bulk we get

$$\left[\frac{I_A(\theta)}{I_A^0(\theta)} \right]_{\text{bulk}} = \sum_{i=1}^{N-1} X_{A,N} \exp \left[\frac{d_{N-1}}{\lambda_{A,i-1} \cos \theta} \right]. \quad (7.52)$$

As an example, let us consider the most important cases of one, two, and three layers on a substrate (bulk).

Let us consider a simple case of three layers (1,2,3) on a substrate (bulk) with mole fractions of A denoted by $X_{A,1}$, $X_{A,2}$, $X_{A,3}$, $X_{A,b}$ (subscript b denotes bulk). With (7.50) and (7.51), we obtain for the intensities from layer 1:

$$\frac{I_{A,1}(\theta)}{I_{A,m_1}^0(\theta)} = X_{A,1} \left\{ 1 - \exp \left[-\frac{d_1}{\lambda_{m_1,E(A)} \cos \theta} \right] \right\}, \quad (7.53a)$$

layer 2:

$$\frac{I_{A,2}(\theta)}{I_{A,m_2}^0(\theta)} = X_{A,2} \left\{ 1 - \exp \left[-\frac{d_2}{\lambda_{m_2,E(A)} \cos \theta} \right] \right\} \exp \left[-\frac{d_1}{\lambda_{m_1,E(A)} \cos \theta} \right], \quad (7.53b)$$

layer 3:

$$\begin{aligned} \frac{I_{A,3}(\theta)}{I_{A,m_3}^0(\theta)} &= X_{A,3} \left\{ 1 - \exp \left[-\frac{d_3}{\lambda_{m_3,E(A)} \cos \theta} \right] \right\} \\ &\times \exp \left[-\frac{d_2}{\lambda_{m_2,E(A)} \cos \theta} \right] \exp \left[-\frac{d_1}{\lambda_{m_1,E(A)} \cos \theta} \right], \end{aligned} \quad (7.53c)$$

and bulk:

$$\begin{aligned} \frac{I_{A,b}(\theta)}{I_{A,m_b}^0} &= X_{A,b} \left[-\frac{d_3}{\lambda_{m_3,E(A)} \cos \theta} \right] \\ &\times \exp \left[-\frac{d_2}{\lambda_{m_2,E(A)} \cos \theta} \right] \exp \left[-\frac{d_1}{\lambda_{m_1,E(A)} \cos \theta} \right]. \end{aligned} \quad (7.53d)$$

The indices m_1, m_2, m_3, m_b refer to the matrices in the respective layers for which the standard intensities (sensitivity factors) and attenuation lengths have to be corrected. For each angle θ , the totally measured intensity of A is then the sum of all contributions,

$$\frac{I_A}{I_{A,m}^0} = \frac{I_{A,1}}{I_{A,m_1}^0} + \frac{I_{A,2}}{I_{A,m_2}^0} + \frac{I_{A,3}}{I_{A,m_3}^0} + \frac{I_{A,b}}{I_{A,m_b}^0} \quad (7.54)$$

The above equations are valid for full coverage of each layer. (If we allow partial coverage of the first layer, the intensities change characteristically as shown below.)

For the simple case of two full layers ($d_3 = 0$) with $d_{A1} = d_{A2} = d_A$ and $X_{A,1} = X_{A,2} = 1$ on a substrate (Fig. 7.41a), and negligible matrix influence ($\lambda_{m1,E(A)} = \lambda_{m2,E(A)} = \lambda_{A,E(A)} = \lambda_{A,A}$), according to (7.53a,b), the intensities of A for layers 1 and 2 are given in Fig. 7.41b for two different values of $d/\lambda_{A,A}$. Depending on the analyzed area (cf. Fig. 5.1), the intensities will either not change or change with $\cos \theta$ or change in a way somehow in between. These difficulties can be avoided if the intensity of A is related to a bulk signal of species B, I_B , measured simultaneously with A. Because this signal of B is attenuated by the thickness of all layers of A, ΣN , for homogeneous concentration of B, according to (7.52), the intensity of B is given by

$$\frac{I_B(\theta)}{I_B^0(\theta)} = X_B \exp \left(-\frac{Nd_{ML}}{\lambda_{A,E(B)} \cos \theta} \right) \quad (7.55)$$

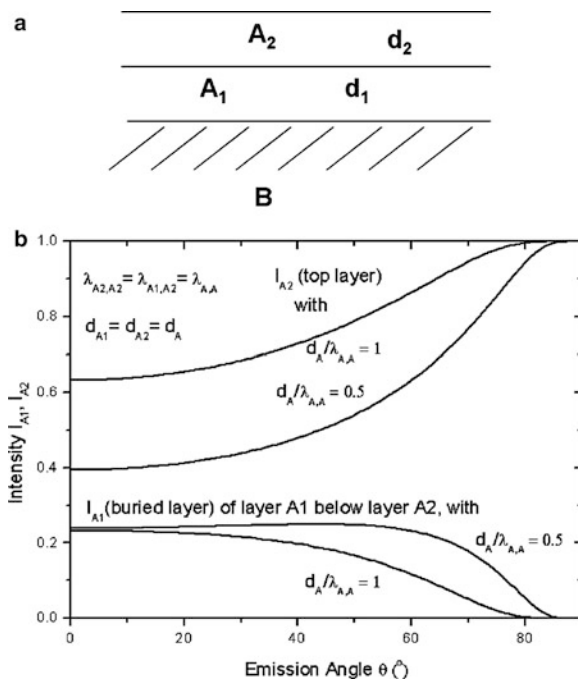


Fig. 7.41 (a) Scheme of two layers A₁, A₂ on top of substrate B; (b) Emission angle dependence of the normalized intensity of the top layer (component A₂) and of the layer beneath (component A₁) after (7.53a). The curves are for negligible cosine correction, i.e., when the acceptance area fully covers the analyzed spot. Otherwise both the intensities have to be corrected by a factor $\cos \theta$, which cancels when using intensity ratios (cf. (7.56)) (see also Sect. 4.3.3)

The ratio of equations (7.50) and (7.55) gives

$$\frac{I_A(\theta)I_B^0(\theta)}{I_B(\theta)I_A^0(\theta)} = \frac{\sum_{i=1}^N X_{A,i} \left\{ \exp \left[-\frac{(i-1)d_{ML}}{\lambda_{A,E(A)} \cos \theta} \right] - \exp \left[-\frac{id_{ML}}{\lambda_{A,E(A)} \cos \theta} \right] \right\}}{X_B \exp \left(-\frac{Nd_{ML}}{\lambda_{A,E(B)} \cos \theta} \right)} \quad (7.56)$$

Because the emission angle dependence of the bulk standard signal of A and B is assumed to be the same (provided that the asymmetry factor cancels, see Sect. 4.3.1), the ratio on the left side of (7.56) is equal to $(I_A(\theta)/I_B(\theta))/(I_A^0/I_B^0)$ and therefore does not change with any other intensity dependencies on θ (e.g., by analyzer acceptance or any variations caused by misalignment) except the escape depth dependence. Thus, I_B^0/I_A^0 is identical to the relative sensitivity factor $S_{B,A}$ defined in Sect. 4.3.2.2. Equation 7.56 can be further generalized for several layers with different thickness. In this way, a four layer structure of carbon contamination in different bonding states was analyzed by Seah et al. [7.239], who gave further approximations to perform such “stratification.”

The simplest case of (7.56) is that of a single-layer A on a substrate with composition B , i.e., $i = 1$, $N = 1$, giving

$$\frac{I_A(\theta)I_B^0}{I_B^0(\theta)I_A^0} = \frac{X_A \left[1 - \exp\left(-\frac{d_A}{\lambda_{A,E(A)} \cos \theta}\right) \right]}{X_B \exp\left(-\frac{d_A}{\lambda_{A,E(B)} \cos \theta}\right)} \quad (7.57)$$

If the kinetic energy is practically the same for A and B such as for a metal in different bonding states, $\lambda_{A,E(B)} = \lambda_{A,E(A)}$, (7.57) further simplifies to

$$\frac{I_A(\theta)I_B^0}{I_B(\theta)I_A^0} = \frac{X_A}{X_B} \left[\exp\left(\frac{d_A}{\lambda_{A,E(A)} \cos \theta}\right) - 1 \right]. \quad (7.58)$$

Equation 7.58 can be solved for d_A and gives

$$d_A = \lambda_{A,E(A)} \cos \theta \ln \left(\frac{I_A(\theta)I_B^0}{I_B(\theta)I_A^0} \frac{X_A}{X_B} + 1 \right), \quad (7.59)$$

which is identical to (4.90b) in Sect. 4.3.3.2 (for $E(B) \neq E(A)$, see Sect. 4.3.3.4).

Application of (7.59) requires knowledge of I_A^0/I_B^0 and of X_A/X_B [7.237]. However, if the intensity ratio in (7.58) is normalized to an angle θ_0 , we obtain for the emission angle dependence the following universal equation, which is independent of composition and of sensitivity factors:

$$\frac{I_A(\theta)I_B(\theta_0)}{I_B(\theta)I_A(\theta_0)} = \frac{\exp\left(\frac{d_A}{\lambda_{A,E(A)} \cos \theta}\right) - 1}{\exp\left(\frac{d_A}{\lambda_{A,E(A)} \cos \theta_0}\right) - 1}. \quad (7.60)$$

This transcendental equation is independent of the mole fractions X_A , X_B and can be solved for the relative thickness $d_A/\lambda_{A,E(A)}$ if the intensity is measured at least for two emission angles, and then the mole fraction ratio X_A/X_B is obtained from (7.57) and (7.58) if the relative sensitivity factor $S_{A,B} = I_A^0/I_B^0$ is known. For $\theta_0 = 0$, (7.60) is plotted in Fig. 7.42 for different values of $d_A/\lambda_{A,E(A)}$. Because of the square root dependence of the signal to noise ratio (S/N) on the intensity (see e.g. (6.33) in Sect. 6.2.9), the absolute uncertainty is given by the square root of the sum of nominator and denominator of (7.57). The relative error strongly increases with the layer thickness and with the emission angle because of the decreasing bulk signal [7.235]. For very thin layers, the error again increases because of the lower S/N ratio of the layer. For a typical total signal of 10000 counts ($S/N = 100$), the maximum uncertainty expected according to (7.57) (with $X_A/X_B = 1$, $\lambda_{A,E(A)} = \lambda_{A,E(B)}$) as a function of $d_A/\lambda_{A,E(A)}$ for three angles is shown in Fig. 7.43, similar to that obtained in the pioneering work of Ebel [7.235]. Depending on the angle, the minimum uncertainty is obtained for $d_A/\lambda_{A,E(A)}$ between 0.2 and 0.7.

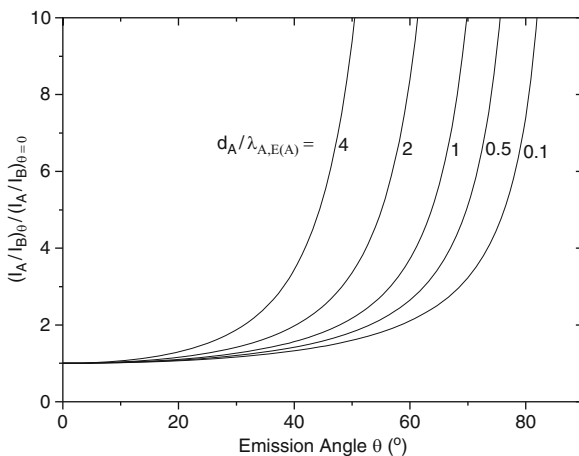


Fig. 7.42 Emission-angle-dependent intensity ratio I_A/I_B (normalized to $\theta_0 = 0$) for a surface layer of A with thickness d_A and substrate B , for different ratios $d_A/\lambda_{A,E(A)}$ after (7.60) (After Ref. [7.233])

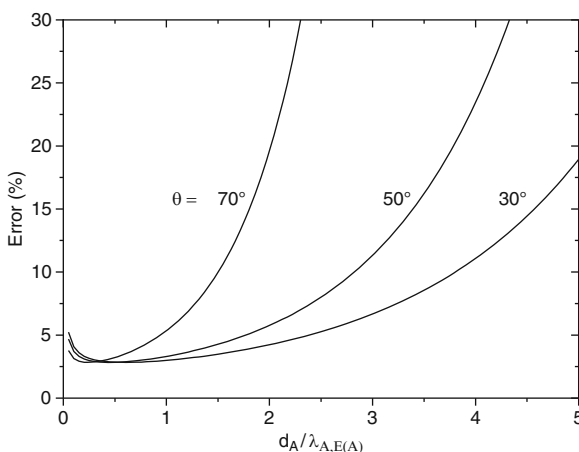


Fig. 7.43 Uncertainty (error) as a function of the relative layer thickness $d_A/\lambda_{A,E(A)}$. Determination after (7.57) for three different emission angles $\theta = 30^\circ, 50^\circ, 70^\circ$, assuming a typical total signal intensity of 10000 counts ($S/N = 100$), with $X_A/X_B = 1$, $\lambda_{A,E(A)} = \lambda_{A,E(B)}$

Above $d_A/\lambda_{A,E(A)} = 3$, the uncertainty is generally too high ($>10\%$ even for moderate emission angles) for useful quantitative results.

Figure 7.44 shows an early example of AR-XPS applied to a contamination layer on Nb_2O_5 [7.233]. A double-pass CMA with a rotational drum device with a fixed angle between the analyzer axis and the sample normal was used (angle $\alpha = 30^\circ$ in (5.4), see Fig. 5.4 in Sect. 5.1.2). The thickness of the contamination layer consisting of carbon and oxygen hydrides was determined using the C 1s and O 1s peaks. As shown in Fig. 7.44a, the O1s peak could be decomposed in

two peaks from oxide (binding energy $E_b = 530.8$ eV) and hydroxide (binding energy $E_b = 532.4$ eV). The hydroxide intensity increases with the emission angle and the oxide intensity decreases. Assuming that the pure oxide peak stems totally from Nb_2O_5 , the intensity (= peak area of the fitted Gaussians in Fig. 7.44a) ratio of oxygen in the hydroxide and oxygen in the oxide (open circles) is shown in Fig. 7.44b, together with the best fit of (7.60) with $\theta_0 = 12^\circ$. This is obtained for $1.1 < d_A/\lambda_{A,E(A)} < 1.7$, with a mean value of $d_A/\lambda_{A,E(A)} = 1.4 \pm 0.3$. The “true” thickness of the hydroxide layer, d_A , can only be derived if the attenuation length in the hydroxide layer is known. This is difficult because the exact layer composition is unknown. In Ref. [7.233], $\lambda_{A,E(A)}$ was assumed (after Seah and Dench [4.36]) to be 2.3 nm, which gives for the total thickness of the overlayer $d_A = 3.3 \pm 1.2$ nm. Additional information can be drawn from the intensity ratio of the C 1s peak (not shown in Fig. 7.44a) to the O 1s (hydroxide) peak as a function of the emission angle (Fig. 7.44b, full circles), which is constant over a wide range (Fig. 7.44b, dashed line). Since both peaks are of 1s type, the asymmetry term cancels (see Sect. 4.3.1.2) and the result indicates that carbon- and oxygen-hydrogen compounds are evenly distributed within the contamination layer on top of the niobium pentoxide. Using (7.58), the oxygen content of the contamination layer can be estimated. With $d_A/\lambda_{A,E(A)} = 1.45$, $X_B/X_A = 3.4 = X_O(\text{Nb}_2\text{O}_5)/X_O(\text{hydroxide})$ and $X_O(\text{Nb}_2\text{O}_5)/X_O = 0.71$ give $X_O(\text{hydroxide}) = 0.21$ (in molar fractions). A rough estimation of the carbon content can be made using the ratio $I_O(\text{hydroxide})/I_C$ (Fig. 7.44b), and the relative sensitivity factors for oxygen and carbon (for CMA) [7.233] give $X_C = 0.33$. This leaves $X_H = 0.46$ to get the total composition of the layer which is not unreasonable with respect to the expected hydrocarbon/water contamination. With this layer composition, an improved attenuation length can be estimated and the above calculation repeated to obtain better results. Of course, a more precise quantitative analysis should include well-defined standards. If the contamination layer only consists of hydrocarbons, the contamination layer thickness has to be estimated using the $I(\text{Cl}s)/I(\text{O}1s, \text{oxide})$ or $I(\text{Cl}s)/I(\text{Nb}3d)$ ratios with their respective attenuation lengths according (7.57) and assuming stoichiometric Nb_2O_5 . However, this procedure has to take into account the energy-dependent transmission function of the analyzer and the different asymmetry factors for the 1s and 3d levels (see Sect. 4.3.1).

Equation 7.60 can be rewritten in a more flexible form which is useful when considering a stack of several layers below, which reads

$$\begin{aligned} \frac{I_A(\theta)I_B(\theta_0)}{I_B(\theta)I_A(\theta_0)} &= \frac{\left[1 - \exp\left(-\frac{d_A}{\lambda_{A,E(A)} \cos \theta}\right)\right] \exp\left(-\frac{d_A}{\lambda_{A,E(A)} \cos \theta_0}\right)}{\left[1 - \exp\left(-\frac{d_A}{\lambda_{A,E(A)} \cos \theta_0}\right)\right] \exp\left(-\frac{d_A}{\lambda_{A,E(A)} \cos \theta}\right)} \\ &= \frac{\exp\left(1 - \frac{d_A}{\lambda_{A,E(A)} \cos \theta}\right)}{\exp\left(1 - \frac{d_A}{\lambda_{A,E(A)} \cos \theta_0}\right)} \exp\left[\frac{d_A}{\lambda_{A,E(A)} \left(\frac{1}{\cos \theta} - \frac{1}{\cos \theta_0}\right)}\right]. \end{aligned} \quad (7.61)$$

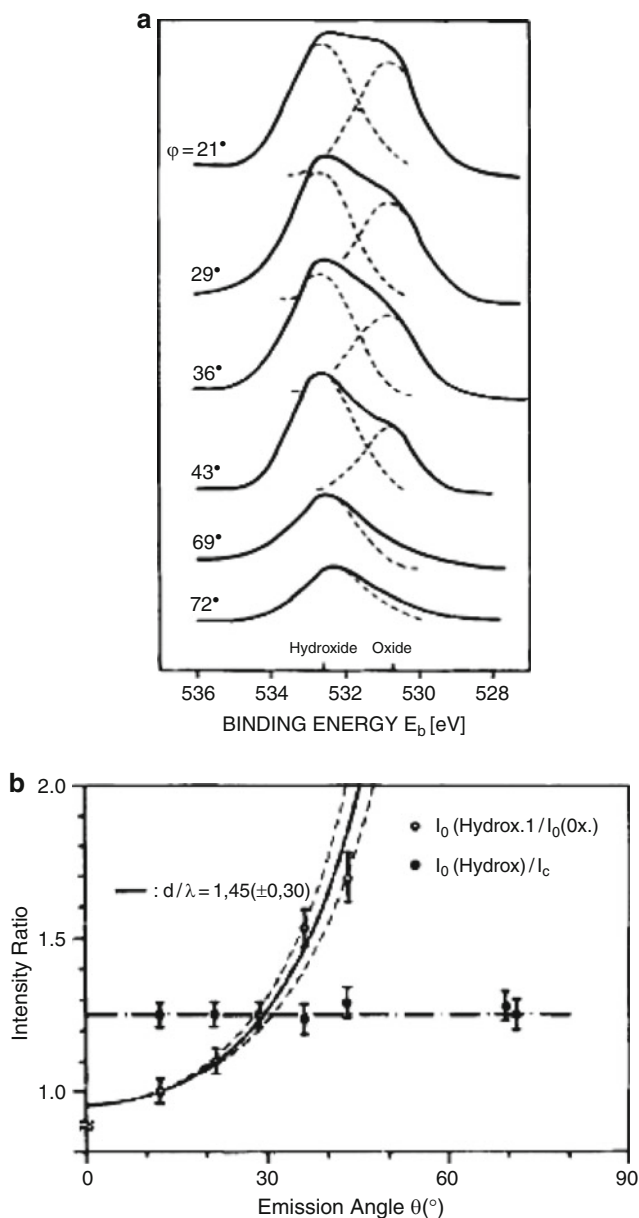


Fig. 7.44 AR-XPS of a contamination layer on Nb_2O_5 : (a) O 1s spectra for different emission angles θ . The dashed lines are fitted Gaussians (FWHM = 1.7 eV) for the hydroxide ($E_b = 532.4 \text{ eV}$) and metal oxide ($E_b = 530.8 \text{ eV}$). (b) Intensity ratios $I(\text{O1s,hydroxide})/I(\text{O1s,oxide})$ (exp. data: open circles) and $I(\text{O1s, hydroxide})/I(\text{C1s})$ (full circles) as a function of θ . The fitting line for d/λ was calculated after (7.60) (From S. Hofmann and J.M. Sanz [7.233])

Approximating the exponential equations in the first term of (7.61) by linear expressions (exact for $d_A/(\lambda_{A,E(A)} \cos \theta) \ll 1$), we get an explicit solution for the relative thickness of layer A ,

$$\frac{d_A}{\lambda_{A,E(A)}} = \frac{1}{\frac{1}{\cos \theta} - \frac{1}{\cos \theta_0}} \left[\ln \left(\frac{I_A(\theta) I_B(\theta_0)}{I_B(\theta) I_A^0(\theta_0)} \frac{X_A}{X_B} - \ln \left[\frac{1}{\cos \theta} - \frac{1}{\cos \theta_0} \right] \right) \right]. \quad (7.62)$$

Using the background intensity instead of the bulk intensity I_B and setting $\theta_0 = 0$, (7.62) was used by Seah et al. [7.239] to derive a more general expression in their stratification scheme. Because the background signal depends on many parameters and is less well defined, and because the linear approximation of the exponential function only holds for $d_A/\lambda_{A,A}/\cos \theta \ll 1$ (not valid for Fig. 7.44!), i.e., for very thin layers and relatively large attenuation lengths, the more exact equations (7.60) or (7.61) with implicit solutions are used here.

In practice, most important is a stack of two layers, for example, a contamination layer on an oxide layer [7.235] or different oxide layers in alloy oxidation [7.58]. Let us consider the layer structure shown in Fig. 7.41a, where a second layer, with intensity I_{A2} , mole fraction X_{A2} and thickness d_2 are placed on the first layer (I_{A1} , X_{A1} , d_{A1}) which was considered above. Let us assume we have already determined d_1 with (7.60) or (7.61) and X_{A1} with (7.58). For determination of the thickness d_2 , (7.61) has to be modified to take into account the attenuation of the bulk signal by layers 1 and 2, i.e., by the factor $\exp[-(d_1 + d_2)/(\lambda_{A,E(A)})]$, which gives

$$\frac{I_{A2}(\theta) I_B(\theta_0)}{I_B(\theta) I_{A2}(\theta_0)} = \frac{\left[1 - \exp \left(-\frac{d_2}{\lambda_{A,E(A)} \cos \theta} \right) \right] \exp \left(-\frac{d_1 + d_2}{\lambda_{A,E(A)} \cos \theta_0} \right)}{\left[1 - \exp \left(-\frac{d_2}{\lambda_{A,E(A)} \cos \theta_0} \right) \right] \exp \left(-\frac{d_1 + d_2}{\lambda_{A,E(A)} \cos \theta} \right)}. \quad (7.63)$$

Experimentally, the species $A1$ in layer d_1 next to the bulk can be immediately recognized because the intensity ratio (7.63) for two angles ($\theta > \theta_0$) is lowest for that layer. A diagram of (7.63) is shown in Fig. 7.45 for the predicted, normalized intensity ratio at the two emission angles $\theta = 60^\circ$ and $\theta_0 = 30^\circ$. Curves 1, 2, 3, and 4 show the relation for $d_2 = d_1$, $0.5d_1$, and $0.25d_1$, and for a single layer (I_{A1} for $d_2 = 0$). Because for the above assumption that $\lambda_{A1,E(A2)} = \lambda_{B,E(A2)}$, the intensities of $A1$ and B are similarly attenuated by layer $A2$, the ratio given by curve 1 is independent of d_2 but is valid for $I_{A1}/I_B(\theta/\theta_0)$. Therefore, this ratio serves to determine $d_1/\lambda_{A,E(A)}$ from the measured intensity ratio in Fig. 7.45. The point defined by the ratio I_{A2}/I_B and $d_1/\lambda_{A,E(A)}$ determines the thickness $d_2/\lambda_{A,E(A)}$. For example, if the intensity ratio $I_{A1}/I_B(\theta/\theta_0) = 2.5$ is experimentally obtained, curve 1 gives $d_1/\lambda_{A,E(A)} = 0.75$. If the experimentally determined value $I_{A2}/I_B(\text{norm}) = 4.0$, we see that d_2 is between curves 2 and 3, i.e., between 1 and $0.5d_1$. From (7.63), we obtain $d_2 = 0.73d_1$ and $d_2/\lambda_{A,E(A)} = 0.55$. In this way, using factor analysis to determine the oxide components after exposing a NiCr 23 alloy to 220 Langmuir ($1 \text{ Langmuir (L)} = 1 \times 10^{-6} \text{ Torr} \times \text{s} = 1.33 \times 10^{-4} \text{ Pa} \times \text{s}$) of oxygen, an NiO layer

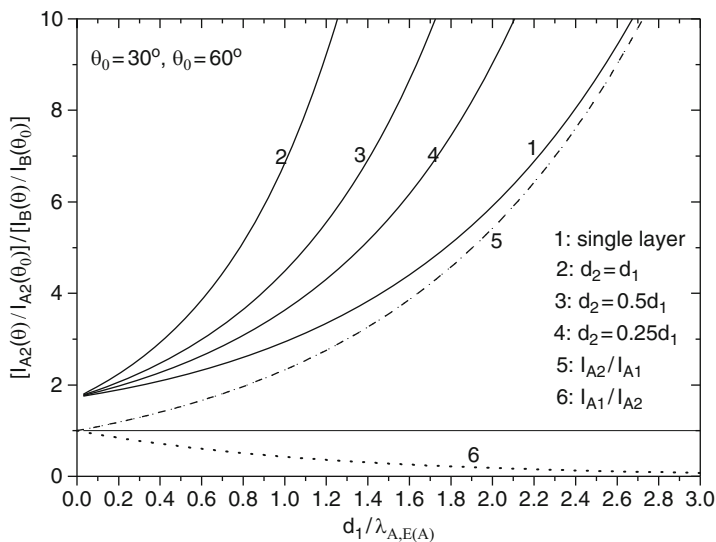


Fig. 7.45 Two layers A1, A2 on substrate B (Fig. 7.40a): ratio of the intensities of outer layer (A2) and bulk (B), $[I_{A2}(\theta)/I_{A2}(\theta_0)]/[I_B(\theta)/I_B(\theta_0)]$, for two different emission angles, $\theta_0 = 30^\circ$, $\theta = 60^\circ$, plotted against the relative layer thickness $d_1/\lambda_{A,E(A)}$, after (7.63). Line 1 is for a single layer on substrate B, lines 2, 3, 4 are for a double layer with 2: $d_2 = d_1$, 3: $d_2 = 0.5d_1$, 4: $d_2 = 0.25d_1$. Line 5 (dashed) is for the layer ratio $I_{A2}/I_{A1}(\theta/\theta_0)$ after (7.65) for $d_2 = d_1$, and line 6 (dotted) is the inverse function, $I_{A1}/I_{A2}(\theta/\theta_0)$

of 1.5 monolayer thickness above 3.5 monolayers of Cr_2O_3 could be determined by AR-XPS and the equations given above [7.58]. However, it has to be kept in mind that the equations given here are only valid for $\lambda_{A,E(A)} = \lambda_{A,E(B)}$, i.e., no matrix correction for different attenuation length and densities is included. While density correction is notoriously difficult, the attenuation length correction can be performed with the kinetic energy ratio approximation as shown in Sect. 4.3.3.4. Furthermore, different asymmetry factors have to be taken into account if the compared intensities are from different subshells and $\psi \neq 54.7^\circ$ (see Sect. 4.3.1).

Considering the ratio of the intensities of the species in both layers, i.e., the ratio of (7.63) and (7.61), the bulk signal contribution cancels and we get

$$\frac{I_{A2}(\theta)I_{A1}(\theta_0)}{I_{A1}(\theta)I_{A2}(\theta_0)} = \frac{\left[1 - \exp\left(-\frac{d_2}{\lambda_{A,E(A)} \cos \theta}\right)\right] \left[1 - \exp\left(-\frac{d_1}{\lambda_{A,E(A)} \cos \theta_0}\right)\right]}{\left[1 - \exp\left(-\frac{d_2}{\lambda_{A,E(A)} \cos \theta_0}\right)\right] \left[1 - \exp\left(-\frac{d_1}{\lambda_{A,E(A)} \cos \theta}\right)\right]} \times \frac{\exp\left(-\frac{d_2}{\lambda_{A,E(A)} \cos \theta_0}\right)}{\exp\left(-\frac{d_2}{\lambda_{A,E(A)} \cos \theta}\right)}. \quad (7.64)$$

For the case $d_1 = d_2 = d$, we obtain

$$\frac{I_{A2}(\theta)I_{A1}(\theta_0)}{I_{A1}(\theta)I_{A2}(\theta_0)} = \frac{\exp\left(-\frac{d}{\lambda_{A,E(A)} \cos \theta_0}\right)}{\exp\left(-\frac{d}{\lambda_{A,E(A)} \cos \theta}\right)} \quad (7.65)$$

The case of (7.65) is indicated as curve 5 in Fig. 7.45. The inverse ratio of (7.65), $I_{A1}/I_{A2}(\theta/\theta_0)$ is indicated as curve 6 which varies between 1 and zero. This demonstrates that for the dependence of the ratio for high (θ) to low angle (θ_0), we can immediately see whether the layer of species 1 is on top of species 2 or below (see also Fig. 7.41b). The two-layer model considered here can easily be extended to a third layer (or to more layers), if in (7.63) d_2 in the first exponential is replaced by the thickness of the third layer, d_3 , and d_3 are added to the sum in the second exponential function.

The angle dependence of any surface structure such as general roughness, islands, and spheres (powders) can be predicted (see Sect. 5.1.4), but care has to be taken not to overestimate the results, because the influence of the emission angle is generally reduced by surface structure, and different structures may cause rather similar angle dependencies.

7.2.1.2 Altered Surface Layers: Segregation, Atomic Mixing, and Preferential Sputtering

In principle, measurements at two emission angles are sufficient to determine layer thickness and composition, as shown in the previous section. However, measurements at several different angles showing the full angular intensity dependence increase the accuracy by fitting the predicted line to the data (see Fig. 7.44). The general relation for a layer on a substrate of a binary system A, B with different compositions in the surface layer, X_A^s, X_B^s , and in the bulk (substrate), X_A^b, X_B^b are given by (4.105) in Sect. 4.3.3.6,

$$\frac{I_A I_B^0}{I_B I_A^0} = \frac{X_A^s \left[1 - \exp\left(-\frac{d}{\lambda_{s,E(A)} \cos \theta}\right) \right] + X_A^b \exp\left(-\frac{d}{\lambda_{s,E(A)} \cos \theta}\right)}{X_B^s \left[1 - \exp\left(-\frac{d}{\lambda_{s,E(B)} \cos \theta}\right) \right] + X_B^b \exp\left(-\frac{d}{\lambda_{s,E(B)} \cos \theta}\right)}. \quad (7.66a)$$

With $X_B^s = 1 - X_A^s$ and $X_B^b = 1 - X_A^b$ and setting $\lambda_{s,E(A)} = \lambda_{s,E(B)} = \lambda_{A,E(A)}$, we get

$$\frac{I_A I_B^0}{I_A^0 I_B} = \frac{X_A^s + \frac{X_A^b}{\exp\left(\frac{d}{\lambda_{A,E(A)} \cos \theta}\right) - 1}}{1 - X_A^s + \frac{1 - X_A^b}{\exp\left(\frac{d}{\lambda_{A,E(A)} \cos \theta}\right) - 1}}. \quad (7.66b)$$

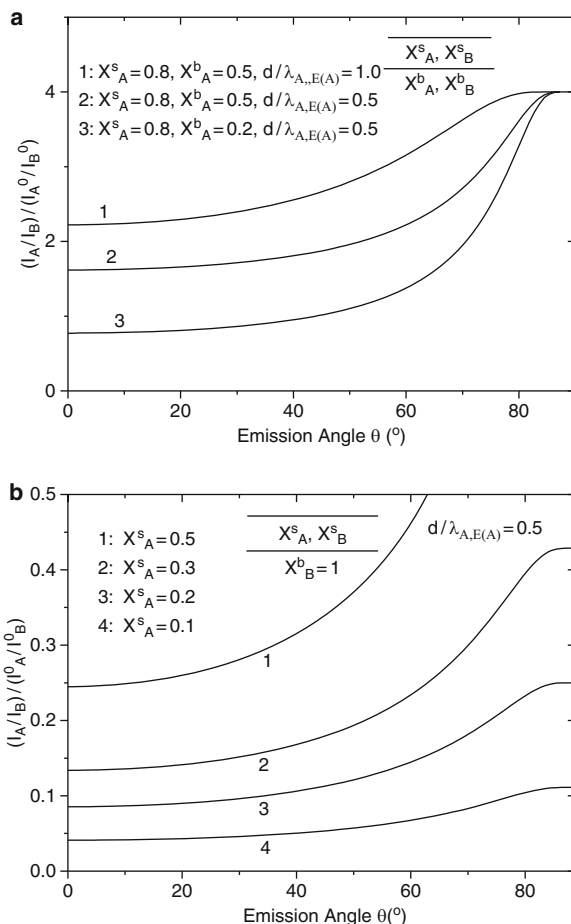


Fig. 7.46 Emission angle dependence of the normalized intensity ratio, $((I_A/I_B)/(I_B^0/I_A^0))$ of a binary system for the layer structure shown in the inset, after (7.66b), assuming **(a)** constant surface composition $X_A^s = 0.8$ and bulk composition $X_A^b = 0.5$, for $d/\lambda_{A,E(A)} = 1.0$ and 0.5 (curves 1 and 2) and for $X_A^b = 0.2$ (curve 3). Note that for very high emission angles, all curves merge into the surface layer composition ratio $X_A^s/X_B^s = X_A^s/(1 - X_A^s) = 4$; **(b)** constant bulk composition $X_B^b = 1, X_A^b = 0$, and different surface composition $X_A^s = 0.5, 0.3, 0.2$, and 0.1 (curves 1–4), for $d/\lambda_{A,E(A)} = 0.5$. Curve 4 is close to the case of mixing length determination by AR-AES in Fig. 7.30

As seen from (7.66a) and (7.66b), emission angle independence is only obtained for homogeneous composition, i.e., the surface and bulk compositions are equal. Therefore, a quick comparison of the intensity ratio at two angles already shows qualitatively whether there is a surface layer with altered composition as in segregation, preferential sputtering, or atomic mixing at surfaces. Usually, the bulk composition is known with sufficient accuracy, as well as the relative sensitivity factors. Then, for every surface layer composition, as there exists a value of $d/\lambda_{A,E(A)}$ that gives the best fit. An example is shown in Fig. 7.46a, where the angle

dependence of the normalized intensity ratio is shown for surface composition $X_A^s = 0.8$ and bulk composition $X_A^b = 0.5$, for $d/\lambda_{A,E(A)} = 1.0$ and 0.5 (curves 1 and 2) and for $X_A^b = 0.2$, $d/\lambda_{A,E(A)} = 0.5$ (curve 3). This type of relation is typical for segregation in alloys such as NiAl [7.240]. Using high- and low-energy peaks of the same element, both the composition and the layer thickness can be determined [7.2]. In surface segregation of constituents with low-bulk concentration (below 1at%, e.g., Sn in Cu [7.99], S in Cu [7.241], O in Nb [7.242], P and C in Fe [7.243]) (see Sect. 4.3.3), (7.66b), it can further be simplified by setting $X_A^b = 0$. The result is shown in Fig. 7.46b.

Another typical example is determination of the mixing zone length in-depth profiling at an interface (see Sect. 7.1.8), as performed by Rar et al. [7.238] with AR-AES at the AlAs/GaAs interface of a multilayer structure and depicted in Fig. 7.30. Profiling was stopped at the interface, and both the Al (1396 eV) and As (1227 eV) signals were measured. These signals have practically the same attenuation lengths ($\lambda_{m,E(As)} \cong \lambda_{m,E(Al)} \cong \lambda_{As,E(As)}$). In the region of decreasing Al signal, only the mixing zone contains Al (with mole fraction X_{Al}^s) together with As with X_{As}^s , whereas below the mixing zone, there is only As. Assuming constant concentration within the mixing zone, the ratio of the Al and As signal intensity, I_{Al}/I_{As} , is given by (7.66a) as

$$\frac{(I_{Al}/I_{As})}{(I_{Al}^0/I_{As}^0)} = \frac{\frac{X_{Al}^s}{X_{As}^s} \left[1 - \exp\left(-\frac{w}{\lambda_{As,E(As)} \cos \theta}\right) \right]}{\left(\frac{X_{As}^b}{X_{As}^s} - 1\right) \exp\left(-\frac{w}{\lambda_{As,E(As)} \cos \theta}\right) + 1}, \quad (7.67a)$$

where the surface layer thickness d corresponds to the atomic mixing length w , and $\lambda_{As,E(As)}$ is the Auger-electron attenuation length of As in As, and θ is the Auger-electron emission angle (to the normal to the surface). Because $X_{Al}^s/X_{As}^s < 1$, $X_{As}^s \approx X_{As}^b$ and the denominator in (7.67a) deviates by less than 10% from unity, (7.67a) can be approximated by

$$\frac{I_{Al}}{I_{As}} = K_1 \left[1 - \exp\left(-\frac{w}{\lambda_{As,E(As)} \cos \theta}\right) \right], \quad (7.67b)$$

with the constant factor $K_1 = (I_{Al}^0 X_{Al}^s)/(I_{As}^0 X_{As}^s) = \text{const.}$, consisting of the respective bulk elemental reference intensities or sensitivity factors and the constant mole fraction ratio of Al and As which are constant with θ . Thus, K_1 can be used as a fitting constant in angular dependence. As an example, Fig. 7.30 [7.238] shows the result of AR-AES from an interface of a depth profile obtained with 500 eV Ar^+ sputtering under 80° incidence angle. The full-drawn line corresponds to the best fit of the experimental data to (7.67b) which yields $w/\lambda_{As,E(As)} = 0.57$, and with $\lambda_{As,E(As)} = 2.3$ nm (see Sect. 4.2.2 and [4.37]) the mixing length value $w = 1.3$ nm is obtained. In addition, the inset in Fig. 7.30 shows the parameter $w = 1.1$ used for the MRI fit to the profile of this sample. Both values are in reasonable agreement.

The method of AR-XPS and AR-AES is fairly accurate for determination of layer thickness relative to the attenuation length. For disclosing more general in-depth

distribution profiles, special mathematical methods for profile determination from AR-XPS are often employed, such as regularization [7.244] and maximum entropy [7.245]. However, because these methods are rather sensitive to measurement errors, special care has to be taken in the interpretation of results [7.157, 7.231]. In any case, a conventional sputter depth profile or a high-resolution TEM cross-section image is highly recommended for comparison.

7.2.1.3 Fractional Surface Coverage

Frequently, surface coverage is incomplete, for example, when island formation occurs. The general case is presented in Sect. 4.3.3.5. For example, segregation layers of component A on substrate B with negligible A in the substrate, depicted in Fig. 4.27, can be described by (4.101). For coverage Θ_A of component A on substrate B , (4.101) gives for the measured, normalized intensity ratio

$$\frac{I_A I_B^0}{I_B I_A^0} = \frac{\Theta_A \left[1 - \exp \left(-\frac{d}{\lambda_{A,E(A)} \cos \theta} \right) \right]}{1 + \Theta_A \left[\exp \left(-\frac{d}{\lambda_{A,E(B)} \cos \theta} \right) - 1 \right]}. \quad (7.68)$$

Equation 7.68 is similar to (7.66b) for $X_A^b = 0$ and $X_A^s = \Theta_A$.

Extending the equations obtained in Sect. 4.3.3.5 and above for a two-layer structure with an incomplete coverage of the first layer (A2), the intensity of this layer is given – in analogy to Fig. 7.41a and to (7.53a–c) – by

$$1 - \Theta_{A2} + \Theta_{A2} \exp \left(-\frac{d_1}{\lambda_{A2,E(A1)} \cos \theta} \right) \quad (7.69)$$

for the next layer adjacent to the bulk (A1)

$$\begin{aligned} \frac{I_{A1}}{I_{A1}^0} &= X_{A1} \left[1 - \exp \left(-\frac{d_1}{\lambda_{A1,E(A1)} \cos \theta} \right) \right] \\ &\times \left\{ 1 - \Theta_{A2} + \Theta_{A2} \exp \left(-\frac{d_2}{\lambda_{A2,E(A1)} \cos \theta} \right) \right\}, \end{aligned} \quad (7.70)$$

and for the bulk intensity,

$$\begin{aligned} \frac{I_B}{I_B^0} &= \Theta_{A2} \exp \left(-\frac{d_1}{\lambda_{A1,E(B)} \cos \theta} - \frac{d_2}{\lambda_{A2,E(B)} \cos \theta} \right) \\ &+ (1 - \Theta_{A2}) \exp \left(-\frac{d_1}{\lambda_{A1,E(B)} \cos \theta} \right) \end{aligned} \quad (7.71)$$

As an example, the emission angle dependence of a 2-nm-thick layer of Al_2O_3 (A1) on Al (B), with a carbonaceous contamination layer (A2) on top with thickness 1 nm

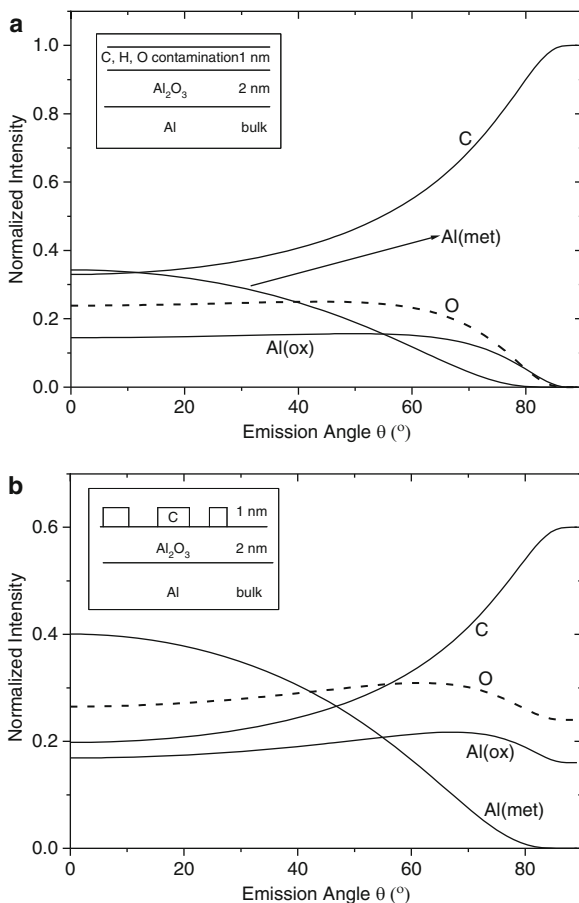


Fig. 7.47 Example of AR-XPS emission results predicted for an oxide layer of Al_2O_3 with 2 nm thickness on pure Al, (a) fully covered with a carbonaceous contamination layer of 1 nm thickness (see *inset*), (b) partially covered ($\Theta = 0.6$) with a carbonaceous contamination layer of 1 nm thickness (d_2) (see *inset*). Calculated with (7.69) for C intensity, with (7.70) for O and Al oxide peak intensities in Al_2O_3 (assumed for X_1), and (7.71) for the metallic Al peak intensity (see Fig. 3.7). Attenuation length values from Ref. [4.37] are: $\lambda_{C,E(C)} = 2.47$ nm, $\lambda_{Ox,E(Al)} = 2.79$ nm, $\lambda_{Ox,E(O)} = 2.35$ nm, $\lambda_{C,E(O)} = 2.1$ nm, $\lambda_{C,E(Al)} = 2.82$ nm

and full coverage ($\Theta_{A2} = 1$) is shown in Fig. 7.47a, with the respective attenuation length values for C, O, Al given in the inset. For comparison, the same structure but with $\Theta_{A2} = 0.6$ is shown in Fig. 7.47b. The main difference is obvious: Because of incomplete coverage, with the outer contamination layer, the intensities near $\Theta \rightarrow 90^\circ$ are not zero as for full coverage in Fig. 7.47a. For an island structure, such as in Fig. 7.47b, results at higher emission angle will be affected by inelastic scattering [7.261] and by shadowing effects as described in Sect. 5.1.4.

The emission dependencies in Fig. 7.47b are qualitatively in agreement with measured data of Oswald et al. [7.246] shown in Fig. 7.48. These authors give an algorithm for calculating layer structures and composition from AR-XPS [7.247].

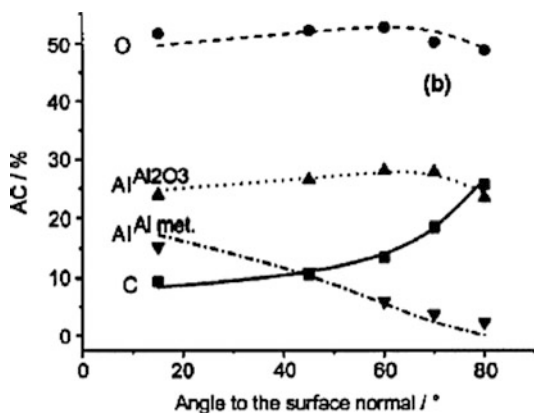


Fig. 7.48 AR-XPS results of an Al sample with native Al_2O_3 partially covered with a carbonaceous contamination layer similar to Fig. 7.47b, but with normalized intensities expressed as concentrations. Optimum fit parameters are for the C-containing layer $d_2(\text{C-O-H}) = 0.8$ nm, with coverage $\Theta = 0.6$ and $d_1(\text{Al}_2\text{O}_3) = 2.4$ nm (Reproduced from S. Oswald et al. [7.246], with permission of Elsevier B.V.)

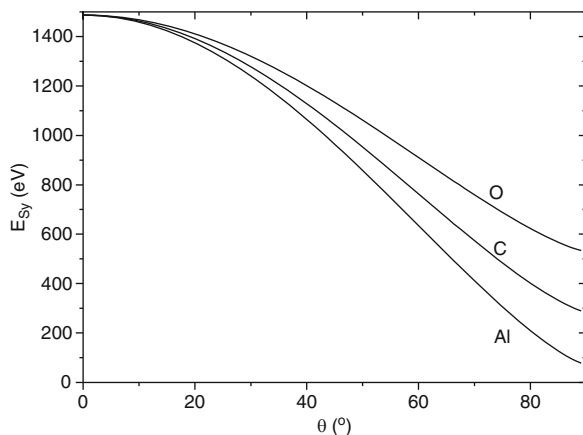
In conclusion, AR-XPS is well suited for analysis of thickness and composition of layer structures in the depth range of about 0–5 nm with smooth and laterally homogeneous surfaces. For samples with complicated structure and unknown compositional distribution, the interpretation of AR-XPS results gets complicated. A sputter depth profile is recommended to get a direct image of the in-depth distribution of composition. Rough surfaces (including fractional or island coverage on the nanometer scale) give additional complications which can only be partially overcome by appropriate model descriptions (see Sect. 5.1.4.3). An excellent review of AR-XPS is presented in the report of the 47th IUVESTA workshop on AR-XPS [7.248].

As compared to destructive depth profiling, the main advantage of angle-resolved electron spectroscopy is that the chemical-bonding state is practically unaffected, and that the depth scale in terms of the attenuation length is directly obtained. Main limitations are the rapidly degrading depth resolution with depth and the limitation to a maximum depth of about 3 times the attenuation length, which in practice means 5 nm or less, depending on the kinetic energy of the Auger- or photoelectrons.

7.2.2 Depth Profiling by Variation of the Excitation Energy

Another method of nondestructive depth profiling is offered by the dependence of the attenuation length λ on the kinetic energy of the emitted electrons. A useful estimation of the mean depth of origin of an Auger electron or photoelectron is possible through difference in intensity for low and high kinetic energy peaks of the same element (e.g., using (7.57), (7.58), (7.60) [7.2, 7.4]). For example, we can

Fig. 7.49 Relation between the change of the mean electron escape depth by the emission angle θ in AR-XPS and its equivalent by changing the synchrotron source energy E_{Sy} , after (7.45)



write (7.60) for a fixed angle (θ_0) and change $\lambda_A(E)$ with reference to $\lambda_A(E_0)$ and get for the determination of the layer thickness

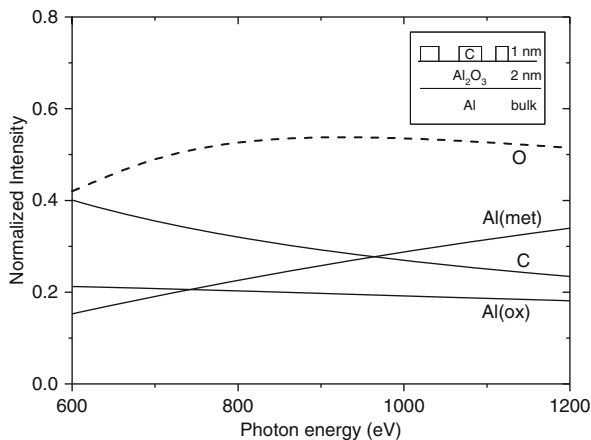
$$\left(\frac{I_A(E)}{I_A(E_0)} \right) / \left(\frac{I_B(E)}{I_B(E_0)} \right) = \frac{\exp\left(\frac{d_A}{\lambda_A(E) \cos \theta_0}\right) - 1}{\exp\left(\frac{d_A}{\lambda_A(E_0) \cos \theta_0}\right) - 1}. \quad (7.72)$$

The kinetic energy of Auger electrons is fixed, and often, two energies of the same element can be used in (7.72). Then, (7.60)–(7.65) apply for two attenuation length values instead of two emission angles. In contrast, the kinetic energy of photoelectrons varies with the energy of the photon source (see Chap. 3). Synchrotron radiation (see Sect. 2.2.4 and [2.8–2.12]) offers the possibility of continuously changing the photon energy and therefore the attenuation length of the photoelectrons. Extraction of the true elemental depth distribution follows the same principles as thin-film analysis by angle-resolved XPS. As seen, for example, in expressions (7.66b) and (7.70)–(7.72), the relative layer thickness can be varied either by $\lambda(E_{\text{kin}})$ or by $\cos \theta$. For constant emission angle θ_{Sy} for the synchrotron experiment and assuming an increase of λ with the kinetic energy with exponent 0.75 (see Sect. 4.2.2), the equivalent is given by

$$\left(\frac{E_{\text{Sy}} - E_b}{E_{\text{AlK}\alpha} E_b} \right)^{0.75} = \frac{\cos \theta}{\cos \theta_{\text{Sy}}}, \quad (7.73)$$

where E_b is the binding energy and E_{Sy} and $E_{\text{AlK}\alpha}$ the energy of the synchrotron and of the conventional Al K_{α} source, respectively. Equation (7.73) with $\theta_{\text{Sy}} = 0$ is depicted in Fig. 7.49. Replacing $\cos \theta$ in (7.66a)–(7.71) by (7.73), we obtain the synchrotron energy dependence of the structure of Fig. 7.47b shown in Fig. 7.50 in the energy range between 600 and 1200 eV. As obvious from Fig. 7.50, which resembles a mirror image of Fig. 7.47b, this energy range corresponds to a change of θ between 80° and 42° for the signal intensity of oxygen, 68° – 35° for that

Fig. 7.50 Photon energy dependence (E_{Sy} in Fig. 7.49) of the XPS peak intensities of oxygen, carbon and aluminum (in metal (Al(met)), and oxide (Al(ox)) bond) of the structure shown in the inset, equivalent to Fig. 7.47b



of carbon, and $61\text{--}32^\circ$ for that of aluminum. Synchrotron energies have to be above the threshold energy given by the binding energy of the studied core level (cf. (7.73)). The valence band is always accessible, and partial coverage studies can be performed as with emission-angle variations [7.249]. Compared to the conventional sample-tilting method, variable energy studies have the advantage that geometry and therefore analyzed area and excitation conditions do not change during the experiment. A further advantage is that sample roughness has a minor effect because the emission angle can be chosen normal to the macroscopic surface (in case of island nanostructures) or at about 40° where the average roughness effect on layer thickness determination is at minimum (see Sect. 5.1.4.3).

7.2.3 Depth Profiling Using Background Information (Peak-Shape Analysis)

Another nondestructive method to extract depth distribution from a measured spectrum is making use of the information contained in the background at the low kinetic energy side of photoelectron [4.7, 4.8] or Auger peaks [4.25]. The shape and intensity of the background depends directly on the number of scattering events the electrons have undergone until they reach the free surface, which is related to their depth of origin [7.248]. Thus, the shape of the complete peak (peak plus low-energy background) is used to obtain the in-depth distribution of composition. The method of XPS peak shape analysis (XPS-PSA) is often called Tougaard analysis after Sven Tougaard who proposed this method [4.7, 4.8, 7.250, 7.251]. Considering $F(E_0)$ as the primary spectrum of an element where it originates, the measured flux of electrons as a function of the energy is given by [4.8, 7.250]

$$J(E) = \int dE_0 F(E_0) \int c(z) G_K(E_0, \frac{z}{\cos \theta}, K(E) dE) dz, \quad (7.74)$$

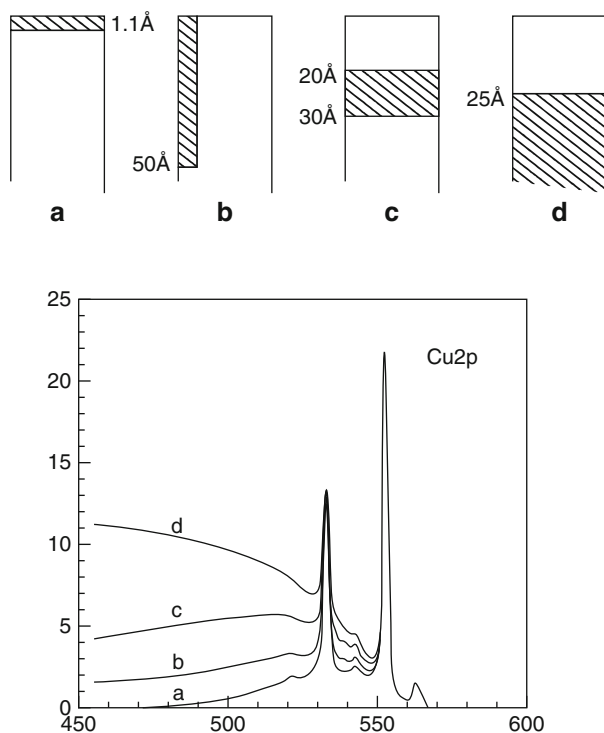


Fig. 7.51 Four different in-depth distributions (a,b,c,d) of copper in gold showing the same XPS Cu2p peak intensity but strongly different background intensities and shapes (a,b,c,d). Note that the layer thickness of 0.11 nm given in (a) corresponds to a coverage of about half a monolayer (with thickness 0.23 nm for Cu, compare Fig. 4.17) (Reprinted with permission from S. Tougaard [7.255]. Copyright (1996), American Vacuum Society)

where $c(z)$ is the number of atoms per unit volume at depth z and $G_K(E_0, z/\cos\theta, K(E)dE)$ is the probability that an electron has an energy in an interval dE at E after having traveled the path length $z/\cos\theta$. $K(E)$ is the differential inelastic scattering cross section which depends on the dielectric properties of the material where the electrons are traveling. This function can be obtained from energy loss spectroscopy measurements calculated from the dielectric description of the material or taken from universal background description (see Sect. 4.1.1).

If $F(E_0)$, λ and $K(E)$ in (7.74) are known; the shape and intensity of $J(E)$ are determined by the in-depth concentration distribution $c(z)$. Similar to all convolution integrals, direct deconvolution is difficult. Therefore, as in the MRI model of sputter depth profiling (see Sect. 7.1.8) a trial-and-error method is usually performed here: the peak shape $J(E)$ is calculated for an assumed concentration distribution, which is varied in the following calculation until a best match with the measured $J(E)$ is obtained. Tougaard [4.8] has developed quantitative expressions for the atomic excitation function for different types of in-depth distributions and has given an illustrative example reproduced in Fig. 7.56. The emitted “elastic” spectrum of the $\text{Cu}2p_{3/2}$ peak of copper in a gold matrix is the same for quite

different in-depth distributions of copper. However, both the corresponding intensity and the shape of the background in a region of about 100 eV below the kinetic energy of Cu 2p_{3/2} peak are quite different. The deeper the emitter element is located in the interior of the material, the higher is the intensity ratio of the background of inelastic scattered electrons to the elastic part. Figure 7.51 demonstrates the basis of quantitative XPS by peak shape analysis, provided by Tougaard as a software package called QuasesTM [7.252]. Promising steps have been made toward the analysis of nanostructures, because island height and coverage can be deduced from XPS peak shape analysis (PSA) [7.253, 7.254].

While Tougaard's peak shape analysis method is confined to a depth of $z < 5\lambda$ (i.e., the information depth), the depth resolution is given as $\Delta z = 1/3\lambda$ [7.250]. In principle, peak shape analysis is also possible for AES. But the background of electron excited spectra is strongly influenced by backscattering variations depending on details of composition changes with depth which can hardly be predicted, thus limiting its practical application.

7.3 Conclusion: Comparison of Nondestructive and Destructive Depth Profiling Methods

All nondestructive depth profiling methods are confined to a shallow surface layer of a few nanometer thickness ($<5\lambda_i$). Peak shape analysis is straightforward but requires measurement of the background 50–100 eV away from the peak, where no other peaks should overlap. Excitation energy-dependent methods with synchrotron radiation vary the escape depth in a way comparable to angle-resolved XPS but have the advantage of a reduced influence of surface roughness. AR-XPS is well suited for analysis of smooth and laterally homogeneous surfaces. Rough surfaces cause problems and can only be analyzed with some difficulties and with limited accuracy. For samples with completely unknown and/or with complicated compositional distribution, all nondestructive methods tend to give results with less certainty as compared to destructive methods like sputter depth profiling. At present, sputter depth profiling (with AES or XPS) is the only method where the raw data directly provide a semi-quantitative image of the in-depth distribution of composition, with no principal depth limitation of the analyzed depth and, if carefully optimized, with a subnanometer depth resolution. Combination with high resolution AES using multiple point or mapping data acquisition can provide a three dimensional analysis of nanostructures.

References

- 7.1. T. Wagner, J.Y. Wang, S. Hofmann, Sputter Depth Profiling in AES and XPS, in *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, ed. by D. Briggs, J.T. Grant (IM Publications, Chichester, 2003), pp. 619–649

- 7.2. S. Hofmann, Depth Profiling, in *Practical Surface Analysis, Vol. I, AES and XPS*, 2nd edn., ed. by D. Briggs, M.P. Seah (Wiley, Chichester, 1990), pp. 148–199
- 7.3. S. Hofmann, Rep. Prog. Phys. **61**, 827 (1998)
- 7.4. S. Hofmann, Surf. Interface Anal. **30**, 228 (2000)
- 7.5. S. Hofmann, Prog. Surf. Sci. **36**, 35 (1991)
- 7.6. S. Hofmann, Philos. Trans. R. Soc. Lond. A **362**, 55 (2004)
- 7.7. J.B. Malherbe, Crit. Rev. Solid State Mater. Sci. **19**, 55 (1993)
- 7.8. S. Hofmann, J.M. Sanz, Depth Resolution and Quantitative Evaluation of AES Sputtering Profiles, in *Thin Film and Depth Profile Analysis*, ed. by H. Oechsner (Springer, Berlin, 1984), pp. 141–158
- 7.9. P. Sigmund, Sputtering by Ion Bombardment: Theoretical Concepts, in *Sputtering by Particle Bombardment I*, ed. by R. Behrisch (Springer, Berlin, 1981), p. 9
- 7.10. K. Wittmaack, Surface and Depth Analysis Based on Sputtering, in *Sputtering by Particle Bombardment III*, ed. by R. Behrisch, K. Wittmaack (Springer, Berlin, 1991), pp. 161–190
- 7.11. K. Kajiwara, Surf. Interface Anal. **33**, 365 (2002)
- 7.12. ISO 14606, *Surface Chemical Analysis – Sputter Depth Profiling – Optimization Using Layered Systems as Reference Materials* (ISO, Geneva, 2000)
- 7.13. S. Hofmann, Surf. Interface Anal. **33**, 453 (2002)
- 7.14. ISO TR 15969, *Surface Chemical Analysis – Depth Profiling – Measurement of Sputtered Depth* (ISO, Geneva, 2001) ISO TR 22335, *Surface chemical analysis Depth profiling Measurement of sputtering rate: mesh-replica method using a mechanical stylus profilometer and X-ray photoelectron spectroscopy Determination of lateral resolution*
- 7.15. J.T. Grant, Ion Excited AES, in *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, ed. by D. Briggs, J.T. Grant (IM Publications, Chichester, 2003), pp. 763–774
- 7.16. A. Zalar, S. Hofmann, P. Panjan, V. Krasevec Thin Solid Films **220**, 191 (1992)
- 7.17. C.P. Hunt, M.P. Seah, Surf. Interface Anal. **5**, 199 (1983)
- 7.18. *Certified Reference Material, BCR No. 261* (NPL No. S7B83) BCR 1983, available from Joint Research Centre, Geel
- 7.19. *Sputtering Yields for Argon*, available from <http://www.npl.co.uk/nanoanalysis/sputtering/yields.html>
- 7.20. M.P. Seah, C.A. Clifford, F.M. Green, I.S. Gilmore, Surf. Interface Anal. **37**, 444 (2005)
- 7.21. D.S. Simons, The Depth Measurement of Craters Produced by SIMS-Results of a Stylus Profilometer Round-Robin Study, in *SIMS X*, ed. by A. Benninghoven, B. Hagenhoff, H.W. Werner (Wiley, Chichester, 1997), pp. 435–438
- 7.22. J.W. Guthrie, S. Blewer Rev. Sci. Instrum. **43**, 654 (1972)
- 7.23. M. Meuris, W. Vandervorst, J. Jackman J. Vac. Sci. Technol. A **9**, 1482 (1991)
- 7.24. J.M. Sanz, S. Hofmann, Surf. Interface Anal. **5**, 210 (1983)
- 7.25. H. Vieffhaus, K. Hennesen, M. Lucas, E.M. Miller-Lorenz, H.J. Grabke, Surf. Interface Anal. **21**, 665 (1994)
- 7.26. D.R. Baer, M.H. Engelhard, A.S. Lea, P. Nachimuthu, T.C. Droubay, J. Kim, B. Lee, C. Mathews, R.L. Opila, L.V. Saraf, W.F. Stickle, R.M. Wallace, B.S. Wright, J. Vac. Sci. Technol. A **28**, 1060 (2010)
- 7.27. P.S. Ho, J.E. Lewis, H.S. Wildman, J.K., Howard Surf. Sci. **57** 393 (1976)
- 7.28. R. Kirchheim, S. Hofmann, Surf. Sci. **83**, 296 (1979)
- 7.29. M.P. Seah, T.S. Nunney, J. Phys. D Appl. Phys. **43**, 253001 (2010)
- 7.30. J. Kempf, Surf. Interface Anal. **4**, 116 (1982)
- 7.31. J. Kirschner, H.W. Etzkorn, Appl. Surf. Sci. **3**, 251 (1979)
- 7.32. J.H. Thomas, S.P. Sharma, J. Vac. Sci. Technol. **14**, 1168 (1977)
- 7.33. S. Hofmann, W. Mader, Surf. Interface Anal. **15**, 794 (1990)
- 7.34. S. Hofmann, A. Zalar, Thin Solid Films **60**, 201 (1979)
- 7.35. S. Hofmann, J.Y. Wang, J. Surf. Anal. **13**, 142 (2006)
- 7.36. B.R. Chakraborty, S. Hofmann, Thin Solid Films **204**, 163 (1991)
- 7.37. S. Hofmann, M.G. Stepanova, Appl. Surf. Sci. **90**, 227 (1995)

- 7.38. W. Pamler, *Surf. Interface Anal.* **13**, 55 (1988)
- 7.39. H.E. Bauer, *Fres. J. Anal. Chem.* **353**, 450 (1995)
- 7.40. S. Hofmann, J.M. Sanz, *Mikrochim. Acta Suppl.* **10**, 135 (1983)
- 7.41. S. Hofmann, J.M. Sanz, *J. Trace Microprobe Technol.* **1**, 213 (1982–1983)
- 7.42. S. Hofmann, *Surf. Interface Anal.* **21**, 673 (1994)
- 7.43. H. Iwasaki, G. Nakamura, *Surf. Sci.* **57**, 779 (1976)
- 7.44. J.H. Thomas III, S. Hofmann, *Surf. Interface Anal.* **4**, 156 (1982)
- 7.45. S. Mischler, H.-J. Mathieu, D. Landolt, *Surf. Interface Anal.* **11**, 182 (1988)
- 7.46. I. Olefjord, P. Marcus, H.-J. Mathieu, S. Hofmann, AES Sputter Depth Profiling of a Thin Aluminium Oxide Layer, in *Proceedings of ECASIA 95*, ed. by H.J. Mathieu, B. Reichl, D. Briggs (Wiley, Chichester, 1996), pp. 188–191
- 7.47. S. Hofmann, *Mikrochim. Acta Suppl.* **8**, 109 (1979) 71
- 7.48. S. Hofmann, *Appl. Phys.* **13**, 205 (1977)
- 7.49. S. Hofmann, J.Y. Wang, *J. Surf. Anal.* **10**, 52 (2003)
- 7.50. S. Hofmann, *Vacuum* **48**, 607 (1997)
- 7.51. S. Hofmann, *Surf. Interface Anal.* **35**, 556 (2003)
- 7.52. T.W. Haas, J.T. Grant, G.J. Dooley III, *J. Appl. Phys.* **43**, 1853 (1972)
- 7.53. S.W. Gaarenstroom, *Appl. Surf. Sci.* **26**, 561 (1986)
- 7.54. S. Hofmann, J. Steffen, *Surf. Interface Anal.* **14**, 59 (1989)
- 7.55. T. Lang, A. Tschulik, H. Laimer, H. Stoeri, *Vacuum* **41**, 1703 (1990)
- 7.56. J. Kovac, T. Bogataj, A. Zalar, *Surf. Interface Anal.* **30**, 190 (2000)
- 7.57. W.F. Stickley, The Use of Chemometrics in AES and XPS Data Treatment, in *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, ed. by D. Briggs and J.T. Grant (IM Publications, Chichester, 2003), pp. 377–396
- 7.58. J. Steffen, S. Hofmann, *Surf. Interface Anal.* **11**, 617 (1988)
- 7.59. H.C. Swart, A.J. Jonker, C.H. Claassens, R. Chen, L.A. Venter, P. Ramoshebe, E. Wurth, J.J. Terblans, W.D. Roos, *Appl. Surf. Sci.* **205**, 231 (2003)
- 7.60. S. Hofmann, *Appl. Phys.* **9**, 59 (1976)
- 7.61. G.H. Morrison, K.C. Cheng, M. Grasserbauer, *Pure Appl. Chem.* **51**, 2243 (1979)
- 7.62. M.P. Seah, *Surf. Interface Anal.* **31**, 1048 (2001)
- 7.63. *ASTM E-42, Standard Terminology Relating to Surface Analysis*, E 673-91c, ASTM, Philadelphia (1992)
- 7.64. S. Hofmann, *Surf. Interface Anal.* **27**, 825 (1999)
- 7.65. S. Hofmann, J.M. Sanz, Deconvolution Procedures Applied to Depth Profiling, in *Proceedings of the 8th International Vacuum Congress, Cannes 1980, Vol. I, Thin Films*, ed. by F. Abeles, M. Croset (Société Française Du Vide, Paris, 1990), pp. 90–93
- 7.66. S. Hofmann, *Surf. Interface Anal.* **8**, 87 (1986)
- 7.67. B. Gautier, R. Prost, G. Prudon, J.C. Dupuy, *Surf. Interface Anal.* **24**, 733 (1996)
- 7.68. J.B. Malherbe, J.M. Sanz, S. Hofmann, *Surf. Interface Anal.* **3**, 235 (1981)
- 7.69. C.W. Magee, R.E. Honig, *Surf. Interface Anal.* **4**, 35 (1982)
- 7.70. A. Zalar, S. Hofmann, *Appl. Surf. Sci.* **68**, 361 (1993)
- 7.71. S. Hofmann, A. Zalar, *Surf. Interface Anal.* **21**, 304 (1994)
- 7.72. H.J. Mathieu, D. Landolt, *J. Microsc. Spectrosc. Electron.* **3**, 113 (1978)
- 7.73. S. Hofmann, A. Zalar, *Surf. Interface Anal.* **10**, 7 (1987)
- 7.74. A. Zalar, S. Hofmann, *Surf. Interface Anal.* **12**, 83 (1988)
- 7.75. H.H. Andersen, *Appl. Phys.* **18**, 131 (1979)
- 7.76. U. Littmark, W.O. Hofer, *Nucl. Instr. Meth.* **168**, 329 (1980)
- 7.77. S. Hofmann, *Appl. Surf. Sci.* **70/71**, 9 (1993)
- 7.78. G. Carter, R. Collins, D.A. Thompson, *Rad. Effects* **55**, 99 (1981)
- 7.79. J.W. Coburn, *J. Vac. Sci. Technol.* **13**, 1037 (1976)
- 7.80. S. Hofmann, J.M. Sanz, *Fres. Z. Anal. Chem.* **314**, 215 (1983)
- 7.81. J.B. Malherbe, S. Hofmann, J.M. Sanz, *Appl. Surf. Sci.* **27**, 355 (1986)
- 7.82. H. Shimizu, M. Ono, K. Nakayama, *Surf. Sci.* **36**, 817 (1973)
- 7.83. C. Li, T. Asahata, R. Shimizu, *J. Appl. Phys.* **77**, 3439 (1995)

- 7.84. H.J. Mathieu, D. Landolt, *Appl. Surf. Sci.* **10**, 100 (1982)
- 7.85. N.Q. Lam, *Surf. Interface Anal.* **12**, 65 (1988)
- 7.86. D. Marton, J. Fine, *Thin Solid Films* **185**, 79 (1990)
- 7.87. K. Ishikawa, S. Hamasaki, K. Goto, *Jpn. J. Appl. Phys.* **22**, 547 (1983)
- 7.88. S. Hofmann, *Mater. Sci. Eng.* **42**, 55 (1980)
- 7.89. M. Yoshitake, K. Yoshihara, *J. Surf. Anal.* **2**, 368 (1996)
- 7.90. M. Yoshitake, K. Yoshihara, *Vacuum* **51**, 369 (1998)
- 7.91. M.P. Seah, M. Kuehlein, *Surf. Sci.* **150**, 273 (1985)
- 7.92. D. Marton, J. Fine, G.P. Chambers, *Mater. Sci. Eng. A* **115**, 223 (1989)
- 7.93. R. Kelly, A. Miotello, *App. Phys. Lett.* **64**, 2649 (1994)
- 7.94. L. Tanovic, J. Fine, *Nucl. Instr. Meth. B* **67**, 491 (1992)
- 7.95. R. Kelly, *Surf. Interface Anal.* **7**, 1 (1985)
- 7.96. R. Kelly, *Nucl. Instr. Meth. in Phys. Res. B* **18**, 388 (1987)
- 7.97. R. Kelly, A. Miotello, *Nucl. Instr. Meth. Phys. Res. B* **122**, 374 (1997)
- 7.98. J. Kirschner, *Nucl. Instr. Meth. Phys. Res. B* **7/8**, 742 (1985)
- 7.99. S. Hofmann, J. Erlewein, *Surf. Sci.* **77**, 591 (1978)
- 7.100. P.S. Ho, *Surf. Sci.* **72**, 253 (1978)
- 7.101. D.G. Swartzfager, S.B. Ziemecki, M.J. Kelley, *J. Vac. Sci. Technol.* **19**, 185 (1981)
- 7.102. T. Koshikawa, K. Goto, *Nucl. Instr. Meth. Phys. Res. B* **18**, 504 (1982)
- 7.103. R. Shimizu, *Nucl. Instr. Meth. Phys. Res. B* **18**, 486 (1987)
- 7.104. G.N. van Wyck, J. duPlessis, E. Taglauer, *Surf. Sci.* **254**, 73 (1991)
- 7.105. F. Reichel, L.P.H. Jeurgens, E.J. Mittermeyer, *Phys. Rev. B* **73**, 024103 (2006)
- 7.106. K. Min, R. Shimizu, *Surf. Sci.* **341**, 241 (1995)
- 7.107. S. Thomas, *J. Appl. Phys.* **45**, 161 (1974)
- 7.108. C. LeGressus, D. Massignon, R. Sopizet, *Surf. Sci.* **68**, 338 (1977)
- 7.109. G.B. Hoflund, *Scann. Electron Microsc.* **IV**, 1391 (1985)
- 7.110. J. Ahn, C.R. Perleberg, D.L. Wilcox, J.W. Coburn, H.F. Winters, *J. Appl. Phys.* **46**, 4581 (1975)
- 7.111. M.P. Seah, C.P. Hunt, *Surf. Interface Anal.* **5**, 33 (1983)
- 7.112. S. Ichimura, H.E. Bauer, H. Seiler, S. Hofmann, *Surf. Interface Anal.* **14**, 250 (1989)
- 7.113. F. Ohuchi, M. Ogino, P.H. Holloway, C.G. Pantano, *Surf. Interface Anal.* **2**, 85 (1980)
- 7.114. S. Hofmann, A. Zalar, *Thin Solid Films* **56**, 337 (1979)
- 7.115. K. Roell, *Appl. Surf. Sci.* **5**, 388 (1980)
- 7.116. D.F. Mitchell, G.I. Sproule, *Surf. Sci.* **117**, 238 (1986)
- 7.117. J.C.C. Tsai, J.M. Morabito, *Surf. Sci.* **44**, 247 (1974)
- 7.118. A. Benninghoven, *Z. Phys.* **230**, 403 (1971)
- 7.119. R. Shimizu, *Appl. Phys.* **9**, 425 (1979)
- 7.120. M.P. Seah, J.M. Sanz, S. Hofmann, *Thin Solid Films* **81**, 239 (1981)
- 7.121. J. Erlewein, S. Hofmann, *Thin Solid Films* **69**, L39 (1980)
- 7.122. R.E. Honig, *Thin Solid Films* **39**, 3 (1976)
- 7.123. M.P. Seah, M.E. Jones, *Thin Solid Films* **115**, 203 (1984)
- 7.124. S. Morishita, M. Tanemura, Y. Fujimoto, F. Okuyama, *Appl. Phys. A* **46**, 313 (1988)
- 7.125. G.K. Wehner, *J. Vac. Sci. Technol. A* **3**, 1821 (1985)
- 7.126. G. Carter, *Nucl. Instr. Meth. Phys. Res. B* **115**, 440 (1996)
- 7.127. J.J. Vajo, R.E. Doty, E.H. Cirlin, *J. Vac. Sci. Technol. A* **14**, 2709 (1996)
- 7.128. J. Kovac, A. Zalar, B. Pracek, *Surf. Interface Anal.* **38**, 300 (2006)
- 7.129. D. Onderdelinden, *Appl. Phys. Lett.* **8**, 189 (1966)
- 7.130. A. Zalar, S. Hofmann, *Nucl. Instr. Meth. in Phys. Res. B* **18**, 655 (1987)
- 7.131. S. Hofmann, J. Erlewein, A. Zalar, *Thin Solid Films* **43**, 275 (1977)
- 7.132. A. Zalar, S. Hofmann, *Vacuum* **37**, 169 (1987)
- 7.133. A. Zalar, S. Hofmann, *J. Vac. Sci. Technol. A* **5**, 1209 (1987)
- 7.134. H.J. Mathieu, D.E. McClure, D. Landolt, *Thin Solid Films* **38**, 281 (1976)
- 7.135. M.P. Seah, C. Lea, *Thin Solid Films* **81**, 257 (1981)
- 7.136. A. Zalar, S. Hofmann, A. Zabkar, *Thin Solid Films* **131**, 149 (1985)

- 7.137. D.E. Sykes, D.D. Hall, R.E. Thurstans, J.M. Walls, Appl. Surf. Sci. **5**, 103 (1980)
- 7.138. A. Zalar, Thin Solid Films **124**, 223 (1985)
- 7.139. A. Zalar, Surf. Interface Anal. **9**, 41 (1986)
- 7.140. J.D. Geller, N. Veisfeld, Surf. Interface Anal. **14**, 95 (1989)
- 7.141. S. Sobue, F. Okuyama, J. Vac. Sci. Technol., A **8**, 785 (1990)
- 7.142. E.H. Cirlin, Y.T. Cheng, P. Ireland, B. Clemens, Surf. Interface Anal. **15**, 337 (1990)
- 7.143. T. Wöhner, G. Ecke, H. Rößler, S. Hofmann, Surf. Interface Anal. **26**, 1 (1998)
- 7.144. I. Kojima, N. Fukumoto, M. Kurahashi, J. Electron Spectrosc. Relat. Phenom. **50**, 19 (1990)
- 7.145. K. Satori, Y. Haga, R. Minatoya, M. Aoki, K. Kajiwar, J. Vac. Sci. Technol. A **15**, 478 (1997)
- 7.146. D. Marton, J. Fine, Thin Solid Films **151**, 433 (1987)
- 7.147. S. Hofmann, A. Zalar, E.H. Cirlin, J.J. Vajo, H.J. Mathieu, P. Panjan, Surf. Interface Anal. **20**, 621 (1993)
- 7.148. S. Hofmann, W. Hösler, R. von Criegen, Vacuum **41**, 1790 (1990)
- 7.149. W. Pamler, K. Wangemann, S. Kampermann, W. Hoesler, Nucl. Instr. Meth. Phys. Res. B **51**, 34 (1990)
- 7.150. W. Hösler, W. Pamler, Surf. Interface Anal. **20**, 609 (1993)
- 7.151. D. Onderdelinden, Can. J. Phys. **46**, 739 (1968)
- 7.152. J. Lindhard, Phys. Lett. **12**, 126 (1964)
- 7.153. D.F. Mitchell, G.I. Sproule, Surf. Sci. **177**, 238 (1984)
- 7.154. S. Sobue, N. Tanemura, F. Okuyama, Surf. Interface Anal. **14**, 451 (1989)
- 7.155. E.H. Cirlin, J.J. Vajo, T.C. Hasenberg, J. Vac. Sci. Technol. B **12**, 269 (1994)
- 7.156. K. Kajiwar, H. Kawai, Surf. Interface Anal. **15**, 433 (1990)
- 7.157. P.C. Zalm, Rep. Prog. Phys. **58**, 1321 (1995)
- 7.158. P. Cumpson, Angle-Resolved XPS, in *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, ed. by D. Briggs, J.T. Grant (IM Publications, Chichester, 2003), pp. 651–657
- 7.159. S. Hofmann, J. Schubert, J. Vac. Sci. Technol. A **16**, 1096 (1998)
- 7.160. K. Yoshihara, D.W. Moon, D. Fujita, K.J. Kim, K. Kajiwar, Surf. Interface Anal. **20**, 1061 (1993)
- 7.161. D.W. Moon, J.Y. Won, K.J. Kim, H.J. Kim, H.J. Kang, M. Petravic, Surf. Interface Anal. **29**, 362 (2000)
- 7.162. P.S. Ho, J.E. Lewis, Surf. Sci. **55**, 335 (1976)
- 7.163. R. Badheka, M. Wadsworth, D.G. Armour, J.A.v.d. Berg, J.B. Clegg, Surf. Interface Anal. **15**, 550 (1990)
- 7.164. S. Hofmann, J. Vac. Soc. Jpn. **33**, 721 (1990)
- 7.165. S. Hofmann, J. Vac. Sci. Technol. A **9**, 1466 (1991)
- 7.166. A. Konkol, M. Menyhard, Surf. Interface Anal. **25**, 699 (1997)
- 7.167. M. Menyhard, Micron **30**, 255 (1999)
- 7.168. M. Menyhard, Surf. Interface Anal. **26**, 1001 (1998)
- 7.169. G. Kupris, H. Roessler, H. Ecke, Fres. J. Anal. Chem. **353**, 307 (1995)
- 7.170. M.G. Dowsett, R.D. Barlow, Anal. Chim. Acta **297**, 253 (1994)
- 7.171. T. Kitada, T. Harada, S. Tanuma, Appl. Surf. Sci. **100/101**, 89 (1996)
- 7.172. W.H. Kirchhoff, G.P. Chambers, J. Fine, J. Vac. Sci. Technol. A **4**, 1666 (1986)
- 7.173. J.F. Ziegler, J.P. Biersack, M.D. Ziegler, *SRIM – The Stopping and Range of Ions in Matter* (SRIM Co., Liverpool, New York, 2008)
- 7.174. J. Fine, B. Navinsek, J. Vac. Sci. Technol. A **3**, 1408 (1985)
- 7.175. J. Fine, P.A. Lindfors, M.E. Gorman, R.L. Gerlach, B. Navinsek, D.F. Mitchell, G.P. Chambers, J. Vac. Sci. Technol. A **3**, 1413 (1985)
- 7.176. J.M. Sanz, S. Hofmann, Surf. Interface Anal. **6**, 78 (1984)
- 7.177. J.M. Sanz, S. Hofmann, Surf. Interface Anal. **8**, 147 (1986)
- 7.178. J. Steffen, S. Hofmann, Fres. Z. Anal. Chem. **333**, 408 (1989)
- 7.179. G. Lorang, F. Basile, Belo M. DaCunha, J.P. Langeron, Surf. Interface Anal. **12**, 424 (1988)
- 7.180. S. Hofmann, J. Vac. Sci. Technol. B **10**, 316 (1992)
- 7.181. Z.L. Liao, B.Y. Tsaur, J.W. Mayer, J. Vac. Sci. Technol. **16**, 121 (1979)

- 7.182. S. Hofmann, Appl. Surf. Sci. **241**, 113 (2005)
- 7.183. S. Hofmann, Composition Profile Broadening in the Sputtering of Thin Layers, in *Proceedings of the 7th International Vacuum Congress and 3rd International Conference on Solid Surfaces*, vol. III, ed. by A. Dobrozemsky et al. (Berger, Vienna, 1977), pp. 2613–2616
- 7.184. S. Hofmann, J. Korean Vac. Soc. **5**, 1 (1996)
- 7.185. S. Hofmann, Thin Solid Films **398–399**, 336 (2001)
- 7.186. S. Hofmann, J.Y. Wang, J. Surf. Anal. **9**, 306 (2002)
- 7.187. S. Hofmann, A. Rar, D.W. Moon, K. Yoshihara, J. Vac. Sci. Technol. A **19**, 1111 (2001)
- 7.188. A. Rar, S. Hofmann, K. Yoshihara, K. Kajiwar, J. Surf. Anal. **5**, 44 (1999)
- 7.189. P. Prieto, S. Hofmann, E. Elizalde, J.M. Sanz, Surf. Interface Anal. **36**, 1392 (2004)
- 7.190. S. Hofmann, J.Y. Wang, Surf. Interface Anal. **39**, 324 (2007)
- 7.191. S. Hofmann, J.Y. Wang, A. Zalar, Surf. Interface Anal. **39**, 787 (2007)
- 7.192. L. Zommer, A. Jablonski, K. Laszlo, M. Menyhard, J. Phys. D Appl. Phys. **41**, 155312 (2008)
- 7.193. S. Hofmann, J. Surf. Anal. **15**, 130 (2008)
- 7.194. R.M. Bradley, J.M. Harper, J. Vac. Sci. Technol. A **6**, 2390 (1998)
- 7.195. A. Rar, I. Kojima, D.W. Moon, S. Hofmann, Thin Solid Films **355–356**, 390 (1999)
- 7.196. J. Wang, S. Hofmann, A. Zalar, E.J. Mittemeijer, Thin Solid Films **444**, 120 (2003)
- 7.197. K. Shimizu, R. Payling, H. Habazaki, P. Skeldon, G.E. Thompson, J. Anal. At. Spectrom. **19**, 1 (2004)
- 7.198. T. Sekine, N. Ikee, Y. Nagasawa, Appl. Surf. Sci. **100/101**, 30 (1996)
- 7.199. S. Ootomo, H. Maruya, S. Seo, F. Iwase, Appl. Surf. Sci. **252**, 7275 (2006)
- 7.200. V. Barnier, O. Heintz, D.E. Roberts, R. Oltra, S. Costil, Surf. Interface Anal. **38**, 406 (2006)
- 7.201. A. Takano, Y. Homma, Y. Higashi, Appl. Surf. Sci. **203**, 294 (2003)
- 7.202. G.S. Lau, E.S. Tok, R. Liu, A.T.S. Wee, J. Zhang, Nucl. Instr. Meth. Phys. Res. B **215**, 76 (2004)
- 7.203. S. Baunack, S. Menzel, W. Bruckner, D. Elefant, Appl. Surf. Sci. **179**, 25 (2001)
- 7.204. D. Krueger, A. Penkov, Y. Yamamoto, A. Gryachko, B. Tillack, Appl. Surf. Sci. **224**, 51 (2004)
- 7.205. V. Kesler, S. Hofmann, J. Surf. Anal. **9**, 428 (2002)
- 7.206. S. Hofmann, A. Rar, Jpn. J. Appl. Phys. **37**, L758 (1998)
- 7.207. V. Kesler, S. Hofmann, Surf. Interface Anal. **33**, 635 (2002)
- 7.208. U. Scheithauer, Surf. Interface Anal. **39**, 39 (2007)
- 7.209. Z.M. Wang, J.Y. Wang, L.P.H. Jeurgens, E.J. Mittemeijer, Surf. Interface Anal. **40**, 427 (2007)
- 7.210. M. Haerig, S. Hofmann, Appl. Surf. Sci. **125**, 99 (1998)
- 7.211. T. Ogiwara, S. Tanuma, J. Surf. Anal. **15**, 246 (2009)
- 7.212. A. Barna, P.B. Barna, A. Zalar, Surf. Interface Anal. **12**, 144 (1988)
- 7.213. M.M. Henneberg, D.J. Pocker, M.A. Parker, Surf. Interface Anal. **19**, 55 (1992)
- 7.214. E.H. Cirlin, Thin Solid Films **220**, 197 (1992)
- 7.215. M. Tanemura, S. Aoyama, F. Okuyama, Surf. Interface Anal. **18**, 475 (1992)
- 7.216. R.E. Ericson, Surf. Interface Anal. **18**, 381 (1992)
- 7.217. A. Van Oostrom, Surface Sci. **89**, 615 (1979)
- 7.218. A. Zalar, S. Hofmann, Surf. Interface Anal. **2**, 183 (1980)
- 7.219. J.F. Bresse, Scann. Electron Microsc. **IV**, 1465 (1985)
- 7.220. L.L. Levenson, T.P. Massopust, J. Dick, M.C. Jaehnig, D. Griffith, Scann. Electron Microsc. **III**, 1087 (1985)
- 7.221. W.H. Gries, Surf. Interface Anal. **7**, 29 (1985)
- 7.222. D.K. Skinner, Surf. Interface Anal. **14**, 567 (1989)
- 7.223. R.L. Opila, M.A. Awal, E.H. Lee, R.M. Lum, J. Vac. Sci. Technol. A **7**, 1558 (1989)
- 7.224. X.Y. Wang, X.D. Cui, Z.B. Chen, E. Lambers, P.H. Holloway, J. Vac. Sci. Technol. A **8**, 2241 (1990)
- 7.225. M. Procop, A. Klein, I. Rechenberg, D. Krüger, Surf. Interface Anal. **25**, 458 (1997)

- 7.226. R.L. Moore, L. Salvati, G. Sundberg, V. Greenhut, J. Vac. Sci. Technol. A **3**, 2426 (1985)
- 7.227. C. Lea, M.P. Seah, Thin Solid Films **81**, 67 (1981)
- 7.228. J.M. Walls, D.D. Hall, D.E. Sykes, Surf. Interface Anal. **1**, 204 (1979)
- 7.229. T.D. Bussing, P.H. Holloway, J. Vac. Sci. Technol. A **3**, 1973 (1985)
- 7.230. P.C. McCashin, V. Young, Scann. Microsc. **1**, 1545 (1987)
- 7.231. P.J. Cumpson, J. Electron Spectrosc. Relat. Phenom. **73**, 25 (1995)
- 7.232. R.W. Paynter, Surf. Interface Anal. **3**, 186 (1981)
- 7.233. S. Hofmann, J.M. Sanz, Surf. Interface Anal. **6**, 75 (1984)
- 7.234. C.S. Fadley, Prog. Solid State Chem. **11**, 265 (1976)
- 7.235. M.F. Ebel, Surf. Interface Anal. **3**, 173 (1981)
- 7.236. M.F. Ebel, J. Wernisch, Surf. Interface Anal. **3**, 191 (1981)
- 7.237. M.P. Seah, J. Spencer, Surf. Interface Anal. **37**, 731 (2007)
- 7.238. A. Rar, S. Hofmann, K. Yoshihara, K. Kajiwar, Appl. Surf. Sci. **144/145**, 310 (1999)
- 7.239. M.P. Seah, J.H. Quiu, P.J. Cumpson, J.E. Castle, Surf. Interface Anal. **21**, 336 (1994)
- 7.240. P. Lejček, S. Hofmann, V. Paidar, Scr. Mater. **38**, 137 (1998)
- 7.241. R. Frech, Doctorate Dissertation, University of Stuttgart, Stuttgart, 1983
- 7.242. S. Hofmann, G. Blank, H. Schultz, Z. Metall. **67**, 189 (1976)
- 7.243. P. Lejček, S. Hofmann, Acta Metall. Mater. **39**, 2469 (1991)
- 7.244. R.W. Paynter, Surf. Interface Anal. **41**, 595 (2009)
- 7.245. G.C. Smith, A.K. Livesey, Surf. Interface Anal. **19**, 175 (1992)
- 7.246. S. Oswald, R. Reiche, M. Zier, S. Baunack, K. Wetzig, Appl. Surf. Sci. **252**, 3 (2005)
- 7.247. M. Kozłowska, R. Reiche, S. Oswald, H. Vinzelberg, R. Huebner, S. Oswald, K. Wetzig, Surf. Interface Anal. **36**, 1600 (2004)
- 7.248. A. Herrera-Gomez, Surf. Interface Anal. **41**, 840 (2009)
- 7.249. T.M. Owens, S. Suzer, M.M.B. Holl, J. Phys. Chem. **107**, 3177 (2003)
- 7.250. S. Tougaard, Quantification of Nano-structures by Electron Spectroscopy, in *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, ed. by D. Briggs, J.T. Grant (IM Publications, Chichester, 2003), pp. 295–343
- 7.251. M.C. Lopez-Santos, F. Yubero, J.P. Espinos, A.R. Gonzalez-Elipe, Anal. Bioanal. Chem. **396**, 2757 (2010)
- 7.252. S. Tougaard, *Quases (Ver.5), Software Package for Quantitative XPS/AES Surface Nanostructures by Peak Shape Analysis* (www.quases.com)
- 7.253. C. Mansilla, F. Yubero, M. Zier, R. Reiche, S. Oswald, J.P. Holgado, J.P. Espinos, A.R. Gonzalez-Elipe, Surf. Interface Anal. **38**, 510 (2006)
- 7.254. S. Hajati, S. Tougaard, Anal. Bioanal. Chem. **396**, 2741 (2010)
- 7.255. S. Tougaard, J. Vac. Sci. Technol. A **14**, 1415 (1996)
- 7.256. J.Y. Wang, Y. Liu, S. Hofmann, J. Kovac, Surf. Interface Anal. **44**, 569 (2012)
- 7.257. A.G. Shard, M.P. Seah, Surf. Interface Anal. **43**, 1430 (2011)
- 7.258. M. Nojima, M. Fujii, Y. Kakuhara, H. Tsuchiya, A. Kameyama, S. Yokogawa, M. Owari, Y. Nihei, Surf. Interface Anal. **43**, 621 (2011)
- 7.259. M.P. Seah, Surf. Interface Anal. **44**, 208 (2012)
- 7.260. C. Adelman, T. Conard, A. Franquet, B. Brijs, F. Munnik, S. Burgess, T. Witters, J. Meerschaut, J.A. Kittl, W. Vandervorst, S. Van Elshocht, J. Vac. Sci. Technol. A **30**, 041510 (2012)
- 7.261. S. Oswald, F. Oswald, Surf. Interface Anal. **44**, 1124 (2012)

Chapter 8

Practice of Surface and Interface Analysis with AES and XPS

To ensure optimum results of practical surface analysis studies, sample preparation, instrumental setup, and data acquisition have to be performed with care. Most important is avoidance of artifacts that may have a detrimental effect on the data, such as charging and beam effects. Any task begins with a precise identification of the problem and clarification of the question whether the task and the sample are compatible with surface analysis, and which result can be principally expected from the analytical study. Therefore, an analytical strategy is required.

8.1 Analytical Strategy

Development of an explicit strategy for solving a particular problem mainly serves to save time by finding the most efficient and therefore shortest way of problem solving with analysis. A suitable strategy depends on the problem to be solved and on the information about the sample. The latter item is particularly important in case of unexpected results. At any step, the already obtained results may cause a change in the adopted strategy. Following a proposal by Powell and Seah [8.1], the outline of a general strategy for the use of AES and XPS is given here as a sequence of typical decision steps as summarized in Table 8.1.

Practically, each item in the summary in Table 8.1 is treated in respective chapters or sections of this book. For example, Sect. 1.1.2 gives a survey of the kind of information that can principally be expected from surface analysis (items in Table 8.1). Sample properties, sample preparation, and mounting are described in Sects. 8.2 and 8.3, Chap. 2 on instrumentation covers most of items 6 and 7, Chaps. 3–7 include items 8–12, Sects. 3 and 4 on qualitative and quantitative analysis have identical headings with items 10 and 11, and there is a special chapter on quantitative depth profiling (Chap. 7).

Table 8.1 Typical sequence of steps in applications of AES and XPS for problem solving

1	Identification of the problem	– Questions that principally can be solved by AES and/or XPS
2	Sample properties	– Type of material (e.g., metal, insulator, organic matter) and previous treatments – Size, shape, morphology, and roughness – Inhomogeneities of structure and composition – Crystallinity (polycrystalline, single crystal (orientation), amorphous) – Electrical conductivity – Likelihood of electron- or photon-beam-induced damage
3	Development of a strategy	
4	Characterizations required	– Optical microscopy – Surface analysis (selection of techniques) – Bulk analysis – Other characterizations
5	Sample preparation and mounting	– <i>Ex situ</i> and in situ preparations and treatments – Mounting and alignment
6	Instrument setup and performance	– Selection of instrument parameters (e.g., mode of operation, apertures, operating voltages) – Instrument performance (e.g., energy resolution, spatial resolution, sensitivity) – Calibration of energy and intensity scales – Calibration of ion gun for sputter depth analysis
7	Acquisition of data	– Spectra (e.g., wide scan (survey) or narrow scan (peak), $E \times N(E)$ or $d[E \times N(E)]/dE$ data in AES) – Point analysis, line scan, or images (chemical mapping) – Angle-resolved spectra – Sputter depth profiles

(continued)

Table 8.1 (continued)

8	Data quality	– Signal-to-noise ratio – Signal-to-background ratio – Sample charging – Beam heating (AES) and damage
9	Data manipulation	– Smoothing – Background subtraction – Differentiation (AES) – Peak fitting – Factor analysis – Peak intensity determination – Topographic correction – Data presentation (e.g., depth profiles).
10	Qualitative analysis	– Elemental identification – Chemical state identification
11	Quantitative analysis	– Methodology and algorithms – Sensitivity factors – Matrix correction factors – Instrument correction factors – Deconvolution (e.g., in-depth distribution).
12	Quality of results	– Accuracy – Precision – Detection limits
13	Solution of problem or development of revised strategy	

Slightly modified after Powell and Seah [8.1]

8.2 Sample Properties

8.2.1 *Type of Material*

A prerequisite for a meaningful surface analysis is a stable surface with time. This means that analysis is restricted to solid surfaces, with negligible vacuum pressure at room temperature. Liquid surfaces can be studied using a cooled stage [8.2]. Inorganic matter, in particular metals and alloys, usually are easy to study with surface analysis because of their good electrical and thermal conductivity. In this respect, still tolerable are low band gap or doped semiconductors. Insulators may cause severe problems with respect to charging (see Sect. 8.5). Polymers are also difficult to study sometimes because of charging but most often because they tend to change their composition under electron or photon irradiation (see Sect. 8.6). The latter effect is particularly strong in biological matter, which often possesses an

intolerably high outgassing rate [8.3]. Usually, thermal effects caused, for example, by electron-beam radiation are negligible in bulk metals but increase for insulators and organic material. Knowledge of the history of previous treatments is necessary to prevent the vacuum chamber and the analyst from hazardous materials.

8.2.2 Size, Shape, Morphology, and Roughness

If size and shape of a sample do not fit to the instrument's stage, a specimen has to be cut out by mechanical means. Of course, the maximum size depends on the sample stage. Usually, $5 \times 10 \text{ mm}^2$ and thicknesses up to several mm are typical, but larger samples can be handled by special mounts, up to the diameter of the introduction flange. Irregular shapes can be handled by cutting off a part that will result in a flat bottom. Small samples can be mounted on a supportive sheet, for example, fixed with "liquid silver" or carbon, and powders can be pressed in a soft indium foil.

Compact bulk material with a smooth surface is most desirable. Surface analysis of materials with rough surfaces may be divided in two categories. The one with "macroscopic" roughness in the micrometer range or above, where frequently fairly smooth microplanes occur, can be studied with high-resolution AES (typically brittle fracture surfaces, see Sect. 9.1.4) or high-resolution XPS. The other category are surfaces with microroughness or nanoroughness where typically many differently oriented microplanes contribute to the signal. Quantitative analysis of the latter are the topic of Sects. 5.1.4 and 5.2.3. Usually, an emission angle close to the surface normal and an electron incidence angle in AES in adjacent direction are recommended. Surfaces with curvatures (e.g., ball-shaped (powder) particles or even bent thin sheets) establish similar problems. Porous surfaces are most detrimental to quantitative analysis. In general, the uncertainty of analysis is larger for rough surfaces. Depth profiling on rough surfaces results in a strong degradation of depth resolution with sputtered depth (see Sect. 7.1.4.3) that can at least partially be avoided by sample rotation (see Sect. 7.1.9). For further details on the influence of sample roughness on the results of surface analysis, see Sects. 5.1.4 and 5.2.3.

8.2.3 Inhomogeneous Structure and Composition

Amorphous materials are most desirable for quantitative surface analysis because there are no electron diffraction effects caused by atomic lattice structure (see Sects. 3.1.8 (XPS) and 3.2.5 (AES)). Fine-grained materials without texture (i.e., materials containing many grains of random orientation within the analyzed area) are rather similar because of averaging the orientation dependence. However, special care must be taken in sputter depth profiling of polycrystalline metals since the sputtering rate is orientation dependent thus causing a degradation of depth resolution with sputtered depth (see Sect. 7.1.4.3).

In quantitative analysis of single crystals, electron diffraction may cause variations in intensity with incidence and emission angles [8.4, 8.5]. For CMA measurements, integration over various orientations through the acceptance cone tends to average out orientation dependencies (Sects. 2.5.1 and 2.5.2). A CHA with large acceptance angle (e.g., Thetaprobe, Sect. 2.5.2) is also helpful. However, diffraction of photoelectrons [8.6] and of Auger electrons [8.5, 8.7] can be used to determine the structure and orientation of the first monolayers [8.8].

If the chemical composition of a sample varies within the analyzed volume, only an average value of the former can be expected. This is particularly important if there are second phases with totally different composition. Therefore, for an unknown sample, only spatially resolved analysis will give the necessary analytical information (laterally resolved using point, line, and map analysis and in-depth resolved using depth profiling). Frequently, additional analysis such as high-resolution TEM or SEM is required. Usually, a thin surface contamination layer of carbon and oxygen and/or a native oxide layer (recognized by the respective peaks) masks the composition of the underlying sample. This fact requires special cleaning techniques (see Sect. 8.3).

8.2.4 *Electrical Conductivity*

Typical insulators like glass and ceramics as well as many oxides, nitrides, and other compounds need special precautions to avoid charging which blurs electron spectra or may impede electron spectroscopy at all. Because of its practical importance, Sect. 8.5 gives a survey of charging and charge compensation in AES and XPS.

8.2.5 *Likelihood of Electron- or Photon-Beam-Induced Damage*

In AES and XPS, interaction of energetic electrons or photons with the sample may often cause nonnegligible changes of the chemical composition and is therefore detrimental to analysis. It is important to estimate the likelihood of sample damage to be aware of the effects that may be expected. Organic materials are usually much more likely to be altered by an impinging electron beam than oxides, metallic compounds, or semiconductors. This is the reason why organic materials most often cannot be analyzed with AES. Although the beam current density (photon flux) is much less in XPS, induced damage is frequently observed here, too [8.9]. Heating by the electron beam can be a severe problem particularly for thin layers on insulators [8.10]. Section 8.6 gives a survey on beam damage and how to minimize its influence on surface analysis.

8.3 Sample Preparation

The specimen size and shape are ultimately limited by the dimensions of the vacuum chamber. In practice, the diameter of the introduction opening gives the size limit. Often sample holders with a recessed opening for the sample is used. The latter is held in place by a diaphragm fixed to the sample holder with a spring (JEOL). In some XPS instruments, the sample holder consists of a larger “table” ($10 \times 10 \text{ cm}^2$, Quantum 2000, PHI, Thetaprobe), on which several samples can be mounted by screws and springs. The location coordinates of each sample (and the small area to be analyzed) can be stored digitally in order to automatically bring one sample after the other to surface analysis within the acceptance area of the analyzer. Shadowing and angular dependence of the electron emission poses difficulties for irregular-shaped and rough samples, and flat samples with smooth surfaces are preferable. A certain roughness can be tolerated for qualitative or semiquantitative analysis but is unfavorable for quantitative work (see Sects. 5.1.4 and 5.2.3).

Sample preparation depends on both the given sample and the aim of the planned study. In this respect, two major aspects can be distinguished: *ex situ* preparation and *in situ* preparation [8.11]. *Ex situ* preparation applies to the study of surfaces of samples processed and stored in atmosphere and those prepared for later in situ experiments and are done before introduction of the sample into the analysis chamber. In situ preparation means treatment of a sample surface under UHV ($< 10^{-7} \text{ Pa}$) or a controlled chemical environment either directly in the analysis chamber or in an attached vessel (see Fig. 8.1). Different approaches are summarized in an excellent book [8.12], and recommendations are given in two ISO standards [8.13, 8.14].

8.3.1 Outside (“Ex Situ”) Preparation

8.3.1.1 “As Received” Samples

If composition of the uppermost layers of the sample in the as received state is asked for, as for example in contamination or corrosion studies, no cleaning procedure should be applied, and the specimen is directly mounted on the sample holder. If deeper layers are of interest, or if the sample is used for more fundamental studies (e.g., segregation, diffusion, adsorption), at least a degreasing procedure is recommended (see below). Samples “from the real world,” for example, to study surface composition changes by contamination or corrosion processes taking place under atmospheric conditions, have to be considered carefully with respect to their compatibility with the UHV instrument chamber. Sample size is limited by the sample holder and its $x - y - z$ movement capacities, the introduction stage flange diameter, and the space in the analysis chamber. Often, the size is limited to typically $20 \times 20 \text{ mm}^2$. The lower size limit is given by the analysis area ($5 \times 10 \text{ mm}^2$ in conventional XPS, and about 1 diameter in AES and small-spot XPS). Compatibility with UHV depends mainly on the volatility, i.e., the vapor pressure of the specific

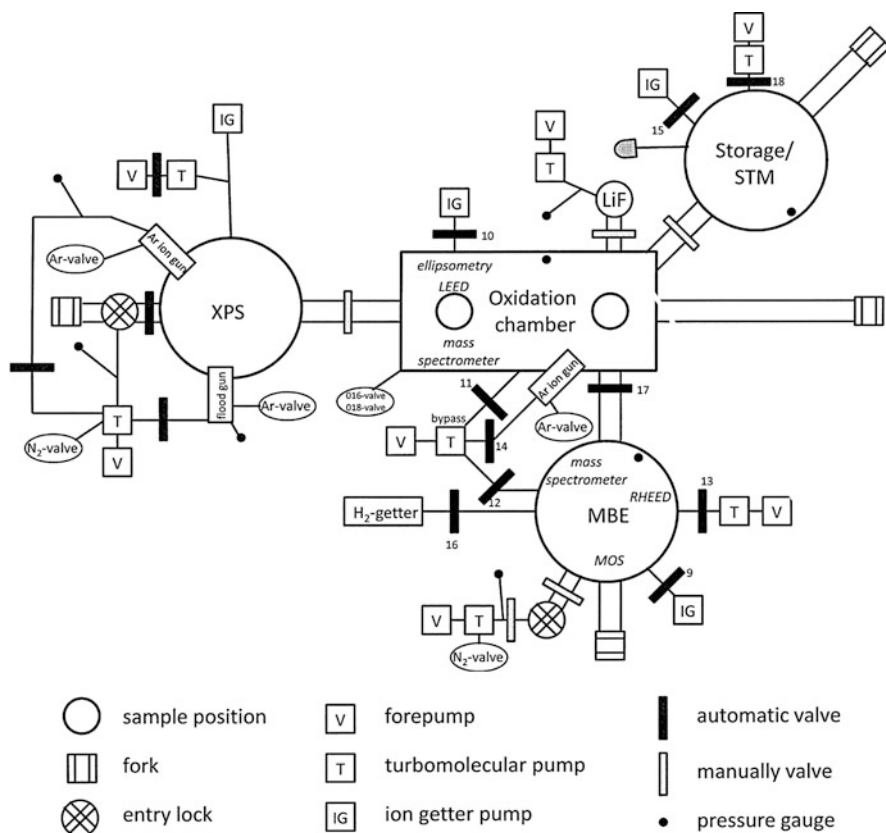


Fig. 8.1 Sketch of a typical modern surface analysis research system, at present (2011), operated by the Surface Analysis group of the Max-Planck Institute for Metals Research in Stuttgart. Attached to an XPS instrument are an oxidation/reaction chamber with ellipsometry and auxiliary AES/LEED system, a molecular beam evaporation (MBE) system for layer growth, and an STM for surface nanotopography (by courtesy of S. Kurz and L.P.H. Jeurgens [8.15])

materials. Biological samples often contain water and therefore are rarely suitable for surface analysis. Oils and greases, even in traces, can be detrimental because, frequently, their vapor pressure is too high for UHV (see Sect. 2.1). Some epoxy resins used in metallography for sample preparation can also be harmful, and some polymers, too. When UHV compatibility is doubtful, the sample should be held for several hours in the introduction stage (entry lock in Fig. 8.1) before transfer in the main chamber. If the pressure rise is unusually high or if the pumping down time too high, the sample should be removed. A residual gas analyzer is useful to find out harmful gaseous species.

Special attention must be paid to preclude any contamination of the sample before insertion into the spectrometer, i.e., mounting the sample directly on a sample holder. This requires use of plastic or lint-free cloth gloves to avoid direct skin contact. Better is the use of carefully degreased tools. Preferably, sample mounting

is done in a dust-free room or in an open bench shroud supplied with a stream of filtered air. The sample is normally fixed by screws or by copper-beryllium clamps. Irregular-shaped samples are often mounted by partly wrapping around a clean aluminum foil. Powders can be handled if they are pressed into a soft indium foil. When samples are prepared under high pressure and reactive atmospheres like in catalysis studies, or in electrolytes, as in corrosion studies, it is important to avoid air exposure between the experimental treatment and analysis. One way to solve this problem is to enclose the sample in a vacuum tight-sealed transfer vessel which can be mounted on an introduction stage (see Fig. 8.1).

8.3.1.2 Samples for Inside (“In Situ”) Experiments

In contrast to the actual surface characterization of “as received” samples, samples for in situ experiments in the analysis chamber, such as studies of adsorption, segregation, oxidation, evaporation layer growth, etc., require special preparation and cleaning before introduction into the UHV system.

8.3.1.3 Cleaning, Angle Lapping, and Ball Cratering

The desired size of a sample is generally prepared by mechanical cutting or spark erosion cutting. Depending on the instrument, the normal size is about 10×10 mm or less, with a thickness between $50 \mu\text{m}$ and some mm. The surface should be as smooth as possible. For metallic samples, this is accomplished by polishing with alumina or diamond paste down to $1 \mu\text{m}$ grit size or less. To avoid contamination of the analysis system by volatile hydrocarbons, the sample has to be carefully degreased. This is usually done by cleaning in an ultrasonic bath, first using acetone, then methanol or ethanol, and lastly distilled water, prior to drying in hot air [8.16]. Special care has to be taken when samples are embedded in organic materials, for example, for polishing, because they are often resistant to any solvent. In this case, mechanical grinding and/or cutting out the inner part of the sample have proved useful. Among the variety of chemical *ex situ* cleaning techniques like etching and electropolishing, oxygen glow discharge cleaning, and ozone/ultraviolet radiation treatment [8.17] were successfully employed to obtain carbon-free silicon dioxide surfaces [8.18].

A convenient method to obtain the in-depth composition of thin films is by line scanning over a cross section of the sample by using high-resolution scanning Auger microscopy (SAM) (see Sect. 7.1.9). To enlarge the resolution limited by the electron-beam diameter (5–10 nm in modern SAM equipment), angle lapping of the sample is often performed. For example, a lapping angle of 5.7° to the horizontal yields an enlargement of the in-depth axis by a factor of 10. Moore et al. [8.19] have attained taper angles of 0.2° corresponding to a magnification factor of 300. A convenient device for angle lapping is crater generation with a rotating steel ball (ball cratering) [8.20], as described in detail in Sect. 7.1.9.

8.3.2 *Inside (“In Situ”) Preparation*

Sample treatment under UHV conditions, for example, for surface chemical reaction studies, is often done in a separate UHV preparation chamber (usually equipped with an ion gun, gas inlets, and evaporation facilities) that is directly connected with a plate valve to the analysis chamber (see Fig. 8.1). This is useful with respect to the limited space in the latter, and in order to avoid contamination of the analyzer or of excitation sources by sample treatment processes.

The meaning of in situ preparation includes any kind of sample treatment in the UHV analysis chamber or in attached chambers from which the sample can be transferred without leaving the UHV environment. For fundamental studies, thin surface films are often prepared by evaporation or sputter deposition in a separate chamber which is linked by sample transport mechanisms and UHV compatible valves to the main analysis chamber. This has the advantage that as-prepared surfaces can be studied without contamination, and chemical, thermal, and other treatments can be performed without possible damage of the analyzer. A typical example of such an arrangement is shown in Fig. 8.1 [8.15]. Attached to the XPS instrument are a reaction chamber (oxidation, heating, etc.) with auxiliary AES/LEED facility and ellipsometry, an MBE chamber for growing layer structures, and a chamber with an STM for nanotopographical studies. In general, ion beam and heat treatments as well as low partial pressure gas treatment are performed directly in the analysis chamber. Observation of dynamic processes, as for example oxidation and segregation kinetics, can only be done directly in the analysis chamber. With respect to the analytical aim, surface analysis, interface analysis, and thin film analysis may be distinguished. Another important item is preparation of reference materials.

8.3.2.1 Analysis of Surfaces

Any surface from the atmosphere is most likely covered with a carbonaceous contamination layer, often above or mixed with an oxide layer of typically a few nanometer thicknesses. Usually, this contamination layer is not the aim of the analysis but the material beneath that layer. Removal of the contamination layer is not only necessary to obtain the bulk concentration but also for further experiments on a well-defined surface. To obtain a clean surface (e.g., for surface segregation or oxidation studies), an appropriate in situ treatment is necessary. For the former purpose, scribing of the surface with a diamond tip is often used in AES [8.12]. Cleaning of the whole surface is necessary for in situ experiments. Methods of the preparation of atomically clean surfaces have been reviewed by many researchers (e.g., [8.21–8.26]). The most frequently used treatments are heating, gas-surface reactions, and ion bombardment. Reactive plasma etching, a combination of the latter two techniques, e.g. by atomic hydrogen source, is often used in semiconductor studies [8.25]. Heating of the sample can be done in a variety

of ways [8.21, 8.26]. Straightforward is resistive heating of metallic materials with the sample spot welded to high-purity electrical leads, for example, platinum or molybdenum. Electron bombardment at the back of the sample using a tungsten filament at negative potential is usually more efficient than thermal radiation alone by the unbiased filament. Direct resistive heating is confined to conductive samples with small cross sections to avoid excessively high currents which heat up the connections. Indirect methods require more time to attain the desired temperature with the danger of contamination by impurities desorbing from the heated parts of the sample holder. These problems may be circumvented by laser irradiation [8.21] or by light emitting heated wires in front of a focusing mirror. For cleaning purposes, heating is recommended up to two-thirds of the melting-point temperature for the elements [8.22]. However, it is restricted to thermally stable materials. Heating may often lead to alterations of the sample by segregation of impurities and diffusion of components from the bulk. Sputter cleaning by ion bombardment is universally applicable and is most frequently used. Modern ion guns provide a focused beam which can be rastered over an area of about $10 \times 10 \text{ mm}^2$. This is normally sufficient to cover the whole sample surface. After a sufficiently high ion dose, the surface contamination/oxide layer is effectively removed. The most efficient cleaning is achieved by applying subsequent sputtering/annealing cycles which can also be used to remove segregants like oxygen, carbon, or sulfur from the bulk [8.16]. A disadvantage of sputter cleaning is chemical and topographical alteration of the surface (see Sect. 7.1.4). Preferential sputtering of one component of an alloy or a compound leads to its depletion in an altered layer at the surface with a thickness in the order of the range of the primary ions. Due to the dependence of the sputtering yield on lattice orientation, surface roughness is generally increased by sputtering, an effect that can be minimized by the use of bombardment with two ion beams from different directions or by sample rotation (see Sect. 7.1.9.2).

Another method of generating clean surfaces is cleavage or in situ fracture. Cleavage is only possible for some materials like alkali halides, silicon, germanium, etc., which can be easily taken apart along certain cleavage planes. Intergranular brittle fracture, often enhanced by grain boundary segregation, can be performed in many metallic materials using commercially available in situ fracture devices. They are generally used to study the composition of grain boundaries [8.27] (see below).

Evaporation, sputter deposition, or molecular beam epitaxy are other in situ techniques for obtaining clean surfaces [8.23].

8.3.2.2 Thin Film and Interface Analysis

Depth profiling by sputtering in combination with surface analysis is a most convenient and versatile method to study the composition of thin films and interfaces (see Sect. 7.1). It can be readily performed after the normal cleaning procedure and insertion of the sample into the analysis chamber, as described above. It is particularly useful for layered structures with interfaces parallel to the surface like oxide films, coatings, evaporation layers, etc. Care must be taken to ensure a flat

crater bottom within the analyzed area, which is important for high depth resolution (see Sect. 7.1.6).

Generating an extended crater edge by ion bombardment can be used for in situ angle lapping to study thin film and interface composition. The easiest way to achieve this is the method of crater edge profiling (see Sect. 7.1.9.3) [8.28]. Line scanning across the crater edge, for example, with scanning electron microscopy (SAM) provides a depth profile of composition. Magnification factors of 10^4 can be obtained by this method [8.28]. Additional methods of creating bevels suitable for SAM are sample movement combined with chemical etching [8.29], or in situ ion etching with a ramp [8.30] or a moving knife edge [8.31].

8.3.2.3 Fracture Surfaces

Internal interfaces like grain boundaries in metallic materials can be accessed by surface analysis if the material is prone to brittle fracture along grain boundaries (see Sect. 4.3.3.8). Interfacial segregation studies [8.27, 8.32, 8.33] have been performed most often by in situ fracture [8.34, 8.35]. A simple fracture device consists of a hammer, i.e., a movable part which can be operated through bellows from outside. It can be moved in front of a block with a U-shaped slit. The free end of a rod-shaped sample with a notch is put in this slit by means of the sample manipulator. The block prevents the latter from the shock force when the sample is broken using the hammer. After fracture, the part of the sample in the holder is moved to the analysis position and analyzed. In general, only this side of the fracture surface can be observed. A more elaborate device for the study of both fracture surfaces is shown in Fig. 8.2 [8.35]. The device has a slide joint to bring the second part in the AES analysis position. It was found that for symmetric boundaries, the fracture path is completely random, and both fracture surfaces show the same amount

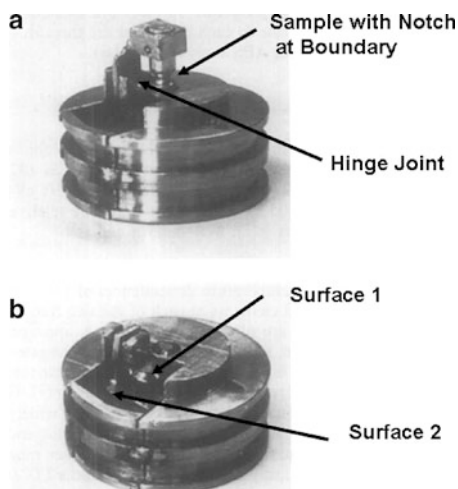


Fig. 8.2 Special sample holder for grain boundary segregation studies on both fracture surfaces in a PHI 600 Multiprobe (Perkin–Elmer). Arrangement (a) before fracture and (b) after fracture of the sample (From P. Lejcek and S. Hofmann [8.35])

of the segregant. Asymmetric boundaries, however, show different compositions according to their surface plane [8.35] (see Fig. 4.39).

8.3.2.4 Preparation of Reference Materials

Qualitative as well as a semiquantitative analysis can be performed using standard spectra and relative sensitivity factors of the elements, of which compilations in handbooks are available (see Sect. 4.3.2). A more exact approach is to determine relative elemental sensitivities using well-defined material under the respective experimental conditions of one's own instrument. (A convenient arrangement of some 50 elements for AES is commercially available, see Sect. 4.2.1 and Ref. [4.26].)

With elements not available in condensed state at room temperature (e.g., nitrogen, oxygen), stable compounds of known composition have to be used. However, when applying sputter cleaning on these materials, the composition of the surface may deviate from the original bulk composition because of preferential sputtering (see Sect. 7.1.4.2). For brittle compounds, cleavage surfaces are another possibility. The scribing technique is thought to give no deviation of the surface composition since no material parameters like tensile strength or selective sputtering of the elements will influence this cleaning technique [8.36, 8.37].

Other methods of standard sample preparation frequently applied include evaporation and adsorption of thin elemental layers in situ [8.38, 8.39] or sputter deposition of alloys and compounds with known composition [8.12].

8.4 Setting Up the Instrument and Measurement

An appropriate setup of the instrument, including calibration and adjustment, is necessary for obtaining well-defined, reliable results. Instrument calibration is based on the operating principles presented in Chap. 2. Focus of this section is on the practical part of calibration, measurement, and prevention of pitfalls.

8.4.1 Calibration of the Energy and Intensity Scales

Reliable measurements for qualitative and quantitative analysis require an accurately calibrated energy scale as well as a calibrated intensity–energy relation. To adjust both scales, measurements with reference standards are necessary. Based on the extensive work of the group of Seah at NPL [8.40–8.44], the respective procedures and data are now ISO standards [8.45–8.48]. Further calibration and adjustment procedures are provided by the instrument manufacturers.

Table 8.2 Reference values for peak positions on the binding energy scale

Peak	Binding energy (eV)		Monochromated AlK α
	AlK α	MgK α	
Au 4f7/2	83.95	83.95	83.96
Ag 3d5/2	368.26	368.26	368.21
Cu L ₃ VV (Auger)	567.93	567.93	—
Cu 2p3/2	932.63	932.63	932.63

From Refs. [8.41, 8.42]

Table 8.3 Reference values for Auger peak positions on the kinetic energy scale for direct and differential spectra referenced to the Fermi level

Differential spectra referenced to the Fermi level		
Peak	Kinetic energy scale in eV	Differential spectra
	Direct spectra	
Cu M _{2,3} VV	62	64
Ag M ₄ N _{4,5} N _{4,5}	356	—
Cu L ₃ VV	919	920
Al KL _{2,3} L _{2,3}	1393	1395
Au M ₅ N _{6,7} N _{6,7}	2016	2026

From Refs. [8.41, 8.42]

The energy scale is based on measurements of sputter-cleaned Au, Cu, and Ag foils. Values for the binding energies referenced to the Fermi level of most intensive XPS peaks of these elements are given in Table 8.2. Values for peak positions on the kinetic energy scale are given in Table 8.3 for medium-resolution AES. The Cu M_{2,3}VV peak is given as the mean energy of the two characteristic peaks at 61.2 and 63.4 eV [8.40, 8.42]. A test with these elements ensures proper behavior of the instrument and a linear energy scale. Adjustments procedures depend on the instrument and are usually provided by the manufacturer. An accuracy of 0.2 eV should be achieved for XPS, while for AES less than 3 eV appears tolerable [8.42]. In practice, a deviation in absolute values is less important than its constancy (i.e., repeatability) (see Sect. 8.4.2).

Linearity of the intensity scale usually is no problem for low count rates (e.g., below 10⁵ counts per second). For high count rates, the dead time of the detector yields too low count rates and therefore a deviation from linearity. Seah et al. [8.41, 8.43] (see Fig. 6.20) and an ISO standard [8.48] describe the methods to check for linearity and to determine the dead time.

When quantitative results are required by comparison with relative elemental sensitivity factors or comparison of peak intensities at different energies, calibration of the intensity scale is necessary. If the analyzed area exceeds the area of excitation, as usually in AES and small spot XPS (see Fig. 5.1), the intensity/energy response function (IERF), $G(E)$, is given by the product of the analyzer transmission function, $T(E)$, and the detector efficiency $D(E)$ [8.43] (see (4.42) in Sect. 4.3.2.1). If the irradiated area is larger, the product of the transmission function and the analyzed area is included in the IERF (i.e., the étendue, see Sect. 4.3.2.1). The IERF is an important characteristic of an instrument and depends on the settings. In the

constant $\Delta E/E$ mode as used in AES, the IERF is proportional to $E \times D(E)$. In the constant ΔE mode, for high kinetic energies, the IERF is proportional to $1/E$, for medium energies it is proportional to $1/E^{0.5}$, and for low energies it is energy independent [8.42]. For XPS instruments, the IERF is often supplied by the manufacturer as a characteristic polynomial correction function. The NPL provides software to generate IERF from measurements with the above used Cu, Au, and Ag foils [8.44].

Another necessary calibration is that of the sputter ion gun, which should be calibrated for three or four settings of emission current and raster to ensure an estimation of the depth scale in sputter depth profiling (see Sect. 7.1.2.1).

8.4.2 Mounting and Alignment of the Sample

In general, the sample is inserted into the analysis chamber via an introduction stage that can be opened to atmosphere (see entry lock, Fig. 8.1). After putting the sample on the tip of a rod and closure, the introduction chamber is evacuated by adsorption and/or turbomolecular pumps to 10^{-2} Pa or less. Then, the UHV gate valve to the main chamber is opened, and the sample is moved by the rod through the gate valve and placed by a forklike device on the sample holder. The rod is withdrawn, and the gate valve is closed.

After a short increase of the pressure when the gate valve is opened (up to 10^{-4} Pa), the pressure will be down to 10^{-7} Pa in less than half an hour (see Sect. 2.1). With nonreactive samples (e.g., noble metals, stainless steel, ceramics), AES investigations can be performed in this pressure range with reasonable accuracy. For more surface active materials (e.g., group IVA, VA, and VIA metals) and careful quantitative analysis, a base pressure in the 10^{-8} Pa (10^{10} Torr) region and below is highly desirable. Depending on the overall state of the vacuum system and the cleanliness of the specimens, this pressure region may be obtained by pumping overnight even without baking. Baking (normally to 150°C) with an external heater shroud, heating bands, and/or with internal heater facilities is highly recommended (see Sect. 2.1.2).

Accurate measurements of electron energies and intensities can only be expected if the sample is correctly located with respect to the electron energy analyzer. The electron optical design of the instrument and the energy of the detected peak determine the sensitivity of the energy shift to sample misalignment, as shown in Sect. 2.5.1 [8.49, 8.50]. The dependence of the AES intensity on sample location measured with a CMA is shown in Fig. 2.14. The CMA is much more sensitive to sample shift than the CHA. For both types of analyzers, procedures for sample alignment are generally supplied by the instrument manufacturer. In any case, care should be taken to ensure that the sample position is kept constant, for example, when the sample is moved for treatment at another station (consider backlash in drive mechanisms). When the sample is tilted, the measured spot at the sample surface should be in a “eucentric” position, i.e., in the tilt axis. If sample rotation

during depth profiling is to be applied, matching between the rotation axis and analyzed spot is extremely important (see Sect. 7.1.9.2). Even if the sample position is fixed, some drift may be possible with time, and heating or cooling cycles need special attention.

Furthermore, observed intensities should not be influenced by inadequately shielded electromagnetic fields or artifact signals (see, for example, Sect. 8.6 on beam effects, Sect. 5.2.1.1 and Fig. 5.47 on distortion by backscattering-induced surrounding area signal, and Sect. 7.1.1 on ion-beam-excited Auger electrons during sputtering). Extreme care should be taken to avoid any stray magnetic field. Even the earth's field can cause difficulties in the low kinetic energy region. If the sample is heated by direct current, the peak heights will be influenced by the magnetic field in a manner difficult to predict. The influence of magnetic fields on AES intensities in case of Joule heating by electric current through a conductive sample in front of a CMA has been determined in Refs. [8.49, 8.50]. In general, high kinetic energy peaks are less sensitive to these effects.

A “worst case” can be encountered if the sample position with respect to the CMA is changed during the course of the experiment, for example, by mechanical shock or thermal expansion (e.g., heating up a thin sample which may lead to bending).

8.4.3 *Measurement Sequence*

The general steps in practical surface analysis measurements are summarized in items 6 and 7 in Table 8.1. The selection of instrument parameters and the type of measurement is mainly determined by the aim of the respective analysis. At first, a survey spectrum with moderate resolution is always necessary to check the overall composition and the state of contamination. Then, a decision has to be made whether sputter cleaning should be performed or any other treatment. Mode of operation, apertures, operating voltages (AES), as well as energy resolution and spatial resolution have to be chosen problem-oriented. Acquisition of spectra (wide or narrow scan), often in conjunction with angle-resolved analysis or sputter depth profiling, has to be optimized. Point analyses or line scans, images, etc., may be required. The required sensitivity should be tested at this stage to estimate the necessary signal-to-noise ratio and, from that, the necessary beam current (AES) and sampling time (AES and XPS) (see Sect. 6.2.7). Optimization criteria for any approach and a respective analytical strategy should be considered (see Table 8.1).

After data evaluation and quantification, a repetition of certain experimental stages with improved instrumental parameters may be necessary to improve the first results (items 8–13 in Table 8.1). Special attention has to be paid on artifacts resulting from interaction of the sample with the excitation beam of photons and/or electrons. These “beam effects” are presented in Sects. 8.5 and 8.6.

8.5 AES and XPS on Insulators

XPS and AES analysis of insulators suffers from two main problems: a difference between the tabulated and measured values of the binding or the kinetic energy of elemental peaks caused by charging and – because the surface potential generally varies across the analyzed area (referred to as differential charging) – a distorted peak shape [8.51–8.56]. In contrast to AES, charging in XPS is always positive because no electrons are supplied by excitation. Therefore, any available electrons will diminish charging, for example, secondary electrons generated in the window in front of the X-ray source in case of nonmonochromatic sources, and the overall shift of spectra is usually small. Monochromatic sources, however, generally need auxiliary flood gun supplying low-energy electrons for charge compensation. For AES, charging is more complex and so are the measures to reduce charging.

For a conductive material, the energy reference of the detected electrons is the Fermi level, because by connection of the sample with the analyzer, the Fermi levels of both are made equal by electron transfer through the electrical connection (see Sect. 3.2.1, Fig. 3.1). For insulators, the conduction band is empty, and such a connection does not exist. Therefore, any charge accumulation will shift the Fermi potential to higher values for negative and to lower values for positive charges.

At semiconductor heterojunctions, charge transfer results in different potentials which can be determined by an according shift of the respective XPS peak [8.57]. In metal/oxide/semiconductor structures, charge transfer and band bending can be studied with bias voltage-dependent shift of XPS peak energy [8.58].

8.5.1 Charging and Charge Compensation in XPS

In XPS, low-energy electrons from a flood gun are generally used to compensate for the positive charge left after electron emission. An excellent description of flood gun action is given by Kelly [8.54]: When a flux of photons strikes the sample, each photoelectron creates a localized positive charge. If the flux of flooding electrons is equal or higher than that of photoelectrons, the former not only compensate the positive charge but the electrons accumulate at the surface until the following ones are repelled, i.e., when the surface potential is equal to the potential of the flood gun, E_{FG} . Then, a stable XPS spectrum is obtained with binding energies shifted from that of an equivalent conductive sample by an amount depending on the flood gun potential and the work function of the sample. In conductive samples, the kinetic energy of the photoelectron leaving the sample is given by $h\nu - E_b - \phi_s$, where $h\nu$ is the X-ray energy, E_b is the binding energy, and ϕ_s and ϕ_A are the work function of sample and analyzer, respectively. Arriving at the detector, the electrons are decelerated by the contact potential, $\phi_A - \phi_s$, and the measured kinetic energy is $h\nu - E_b - \phi_s - (\phi_A - \phi_s) = h\nu - E_b - \phi_A$. Thus, the work function of the

sample cancels, and the analyzer work function is usually taken into account by an according voltage with referencing to the Fermi level of a metallic sample (see Fig. 3.1) [8.53].

In an insulating sample, the emitted electrons cause a positive potential, which subtracts from the kinetic energy and is increasing until electrons from the surroundings limit the potential of the sample. Low-energy flood guns are used to compensate for the electron loss and to stabilize the sample potential. Charge compensation with a flood gun of potential, E_{FG} , the kinetic energy of the electrons leaving the sample is given by $h\nu - E_b - \phi_s + E_{FG}$. Because there are no free electrons (or holes) in the insulator, its (virtual) Fermi level cannot be equilibrated with the Fermi level of the detector. The reference left is the vacuum level, and the energy measured by the detector is given by $h\nu - E_b - \phi_s + E_{FG} - \phi_A$. Even if E_{FG} is known, the binding energy cannot be determined without knowledge of the sample work function. With E_{FG} usually of the order of 5 eV, deviations from Fermi level values are small. For precise measurements, the energy spread of the electrons from the flood gun (<0.5 eV) has to be taken into account [8.53].

8.5.1.1 Calibration of Binding Energies

Since the exact values of the effective energy of the flood gun electrons and the work function are generally unknown, the exact binding energies of spectral peaks in an insulator are not known. However, a measured spectrum can be calibrated with respect to the known energy of a reference peak [8.53, 8.54]:

- (a) An elegant method is determination of the Auger parameter, given by the difference between the Auger energy and the binding energy of the respective peaks of an element. Because both peaks suffer the same charging potential, the difference is charging independent. Thus, the Auger parameter enables chemical identification despite the presence of charging [8.9]. If the Auger electron energy of the chemical state is known, the additional kinetic energy shift of the Auger line is equivalent to the charging potential (see Sect. 3.1.4). Auger parameters for 42 elements are given by Powell [3.86].
- (b) Adventitious carbon is often used for calibration because the carbon peak is found on all samples exposed to the environment. The binding energy of the C1s peak is given as 285.0 ± 0.2 eV, with an accuracy of better than 0.5 eV [8.59].
- (c) Noble metal decorations such as gold or platinum thin layers are often used as an energy reference, for example, the Au 4f_{7/2} line at 84.0 eV [8.60] (Table 8.2).
- (d) Implanted noble gas ions, for example, Ar⁺ ions from a sputter gun can be used to simulate an internal standard [8.60]. The binding energy of the Ar 2p_{3/2} line peak is found to be 242.3 ± 0.2 eV, probably with little variation among different insulators.

- (e) In polymers, an internal standard can be used if the molecular composition is known. Elemental Si or SiO₂ or elements which show little chemical shift, such as Na or F, can serve as internal standard [8.53, 8.54].

8.5.1.2 Differential Charging

Lateral variations of the surface potential, often caused by sample inhomogeneities, can be a source of spectral misinterpretation [8.9]. Different surface potentials may cause different peak energies of the same elemental line or peak broadening similar to chemical shift. Changing the X-ray source operating conditions or the flood gun parameters will result in changing differential-charging-induced peak positions, while the relative position of the chemically shifted peaks remains constant [8.9].

In any case, a flood gun is indispensable in XPS studies of insulators with monochromatic X-ray source. The effectiveness of compensation of differential charging can be best controlled by optimizing the peak width. Using a small sample size or covering the sample periphery with an aluminum foil, or using a metallic mesh covering the surface, or additional flooding with positive ions from an ion gun helps to reduce distorting space charge build up and improves charge compensation.

8.5.2 Charging and Charge Compensation in AES

AES analysis of insulators is a notoriously difficult task. Owing to the injection of a primary electron beam, negative charging of an insulator surface occurs which is much more difficult to compensate than the positive charging encountered in XPS. In the following, some general conclusions and experimental results are summarized, mainly based on the work in Refs. [8.61–8.64] and references therein.

8.5.2.1 Charging and Residual Resistivity

In general, charging is time dependent, and a complicated charge distribution may occur [8.61, 8.62]. For low-electron doses [8.63] and for insulators with a finite residual electrical resistivity, ρ_{el} , a simplified consideration of a steady-state negative charging potential, $-U_C$, is based on the following equation [8.64]:

$$-U_C = \rho_{el} z_s j_p (1 - \delta) \quad (8.1)$$

where z_s is the sample thickness, j_p is the primary beam current density, and $\delta = j_s/j_p$ is the total secondary emission coefficient (including backscattered and Auger electrons in the secondary emission current density j_s). Equation 8.1 enables at first the division in insulators for which we can get rid of charging in any case,

irrespective of the secondary emission coefficient, and in those for which we have to expect problems with charging.

Assuming $\delta = 0$, a typical sample thickness of $z_s = 1$ mm and a negative charging potential $|-U_C| \leq 1$ V to be negligible for AES, a critical maximum resistivity, $\rho_{el,max}$, is defined by (8.1) as

$$\rho_{el,max}(\mu\Omega\text{ cm}) = 10^7/j_p(\text{A cm}^{-2}) \quad (8.2)$$

(unfortunately, the corresponding equation (5) in [8.64] contains a printing error). For any higher resistivity, charging is expected (supposing secondary emission is negligible).

The dimension $\mu\Omega\text{cm}$ was chosen here because the resistivity of pure Cu is $\rho_{el}(\text{Cu}) = 1.6\mu\Omega\text{cm}$, and therefore the numerical values for a material indicate the factor by which its resistivity is higher than that of Cu. Depending on the value of j_p , the analysis condition determines the value of $\rho_{el,max}$ below which charging is negligible. Table 8.4 [8.64] gives a survey of the orders of magnitude encountered in practical surface analysis. It is clear that for high spatial resolution analysis, the maximum tolerable resistivity is much lower than for larger area analysis.

Referring to the most favorable case of large area analysis in Table 8.4 ($\rho_{el,max} = 10^{11}\mu\Omega\text{cm}$), two classes of materials can be distinguished: materials appropriate for AES (“AES conductors”) and materials posing problems for AES (“AES insulators”). Table 8.4 [8.64] presents a survey of typical values of ρ_{el} (in $\mu\Omega\text{cm}$) for some common ceramic materials. It is seen that almost all borides and carbides are “AES conductors,” whereas some nitrides and all (defect free) oxides are “AES insulators,” for which difficulties with charging are expected. Note that high-resolution point analysis (Table 8.5, case a) requires more stringent conductivity criteria, and for this case, even some borides and carbides (SiB_6 , B_4C , SiC) are expected to cause charging (Table 8.5).

8.5.2.2 Charging and Secondary Electron Emission

Of course, the view of the previous paragraph is oversimplified since secondary electron emission is not considered. This fact, as well as the time dependence of the buildup of surface charge, has been treated in detail, for example, by Cazaux [8.61], Melchinger and Hofmann [8.62], and Seah and Spencer [8.63].

Taking into account the secondary emission factor $(1-\delta)$ in (8.1) with $\delta > 0$ means that the charging criteria in Tables 8.4 and 8.5 (for $\delta = 0$) can somewhat be relaxed. For a sufficiently low resistivity ρ_{el} (e.g., metals), δ does not matter at all.

According to (8.1), for a high-resistivity insulator ($\rho_{el} \rightarrow \infty$), the following three cases can be distinguished:

1. $\delta = 1$ no charging
2. $\delta > 1$ positive charging
3. $\delta < 1$ negative charging

Table 8.4 Electrical resistivity ρ_{el} ($\mu\Omega\text{ cm}$) of some typical insulating materials

$\rho_{\text{el}} < 10^{11}\ \mu\Omega\text{ cm}$			$\rho_{\text{el}} > 10^{11}\ \mu\Omega\text{ cm}$	
		$\rho\ (\mu\Omega\text{ cm})$		$\rho\ (\mu\Omega\text{ cm})$
Borides	SiB ₆	10 ⁷	AlB ₁₂	10 ¹²
	TiB ₂	7		
	VB ₂	6		
	CrB ₂	18		
	ZrB ₂	6		
Carbides	TiC	52	C(Diamond)	10 ²⁰
	VC	59		
	ZrC	42		
	NbC	19		
	WC	17		
	B ₄ C	10 ⁶		
	SiC	10 ⁵		
Nitrides	TiN	25	BN	10 ¹⁸
	VN	85	AlN	10 ¹⁵
	CrN	640	Si ₃ N ₄	10 ¹⁸
	ZrN	21		
	NbN	58		
Oxides			BeO	10 ²³
			MgO	10 ¹²
			Al ₂ O ₃	10 ²⁰
			SiO ₂	10 ²²
			ZrO ₂	10 ¹⁶
			ThO ₂	10 ¹⁶

Adapted from Ref. [8.64]
For typical AES area analysis (e.g., 10 nA in 100 × 100 μm^2 , $j_{\text{p}} = 10^{-4}\text{ A cm}^{-2}$), charging is expected in materials with $\rho_{\text{el}} > 10^{11}\ \mu\Omega\text{ cm}$, and no charging is expected for those with $\rho_{\text{el}} < 10^{11}\ \mu\Omega\text{ cm}$. For other AES analysis conditions, compare Table 8.5.

Table 8.5 Maximum tolerable resistivity $\rho_{\text{el,max}}$ with respect to primary electron current density j_{p} and charging for some typical AES analysis conditions

Current and effective area of primary electron current	Electron current density (A/cm^2)	$\rho_{\text{el,max}}\ (\mu\Omega\text{ cm})$
(a) 1 μA in 1 μm^2 10 nA in 0.01 μm^2 (point analysis)	10 ²	10 ⁵
(b) 10 nA in 1 μm^2 (defocused beam)	1	10 ⁷
(c) 1 μA in 100 × 100 μm^2 (area raster, high current)	10 ^{−2}	10 ⁹
(d) 10 nA in 100 × 100 μm^2 (area raster, low current)	10 ^{−4}	10 ¹¹

The ideal case is $\delta = 1$, and the case $\delta > 1$ would lead to positive charging. In AES, however, some of the abundant low-energy secondary electrons will move back to the sample (or are simply not emitted) if the surface potential becomes positive, thus a self-adjustment of the sample potential to ground potential occurs by increasing the total secondary emission. Therefore, the condition $\delta \geq 1$ is sufficient to ensure a vanishing surface charge in AES. For the case $\delta < 1$, a negative charge is built up with time which for high resistivity may result in very high electric potentials up to the limiting case when $-U_C$ is equal to the primary beam voltage. This may cause elastic reflection of the primary electron beam and a mirror-like behavior of the sample surface [8.65].

It should be noted that the simple model of charging presented above does not take into account the in-depth and lateral distributions of the induced charge in the sample, as discussed in detail by Cazaux [8.61] and referred to by Melchinger and Hofmann [8.62]. Internal charges cause high electric fields within the sample and lead to a breakdown by electrical discharges, as demonstrated by LeGressus and coworkers [8.65, 8.66].

8.5.2.3 Consequences of Charging for AES Analysis

Moderate charging which is constant with time and within the analyzed area can be tolerated in AES analysis because the result is mainly a shift of the value of U_C , to higher kinetic energies. Qualitative analysis generally is easy because it is assisted by the shape of the respective Auger peak. Quantitative analysis, however, is often hampered by spatially inhomogeneous charging (e.g., owing to second phases, grains and grain boundaries, defects, etc. and to a fundamental effect at the edge of the primary electron beam [8.61]) which causes broadening of the peak. Furthermore, the width of the energy resolution of the generally used CMA increases since it is proportional to the kinetic energy. Therefore, the usual quantification with peak-to-peak heights in the derivative mode fails, and the direct mode with appropriate background subtraction and peak area determination should be used. Of course, higher charging in the region of thousand and more volts may shift the Auger spectra outside the usual range of the analyzer ($<3,000$ eV). A further effect to be considered in quantitative AES is the influence of increased plasmon losses by “free” electron generation [8.67, 8.68] on the inelastic mean free path of the Auger electrons. In addition, the peak shape may change owing to polarization brought about by excess charges. For example, according to Weissmann and Mueller [8.69], the oxygen O KLL spectrum changes by polarization, i.e., the intensity ratio $I(\text{O KL}_1\text{L}_1)/I(\text{O KL}_{2,3}\text{L}_{2,3})$ decreases with increasing polarization. Radiation damage by electron impact may occur (e.g., generation of color centers (F-centers)), further complicating quantitative AES. In many oxides, electron-stimulated desorption (ESD) leads to a creation of oxygen vacancies and a loss of oxygen in the surface region of oxides (see Sect. 8.6.1). In some cases, instabilities by dynamic, local charging and discharging often lead to “migrating” spectra, making a measurement impossible [8.70]. Even if stable

surface charging is achieved, Auger analysis of some ceramics and glasses suffers from electromigration of mobile ions (e.g., Na^+ in glasses [8.71]).

Owing to the effects mentioned above, it is important to avoid (or at least reduce) charging by suitable experimental methods.

8.5.2.4 Experimental Methods for Charge Compensation in AES

Obviously, reduction of the main parameters in (8.1) is the key to reduce the charging potential in AES. The most important methods are:

Reduction of the Primary Current Density

Lowering the primary electron current density j_p and/or increasing the beam diameter, for example, by defocusing or by rastering the beam (in scanning Auger microscopy (SAM)) is an effective means to reduce charging. A disadvantage of the latter method is the resulting loss in spatial resolution. A lower limit for the current is given by the requested signal-to-noise ratio (see Chap. 5), and the raster width is limited by the acceptance area (in case of a CMA, see Sect. 2.5.1). The minimum, $j_{p,\min}$, is approximately given by case (d) in Table 8.5 (10 nA in $100 \times 100 \mu\text{m}^2$ raster), i.e., $j_{p,\min} \approx 10^{-3} \text{ A cm}^{-2}$.

Reduction of the Sample Thickness

According to (8.1), decreasing the sample thickness z_s means increasing the absorbed current by a shorter path length to the ground. This can be achieved, for example, by fine mesh metallic grids, evaporated grid structures, or a cover of conductive silver paste on the sample surface and by performing Auger analysis in close proximity to these current leads [8.72, 8.73]. A very thin insulating layer, the thickness of which is below the range of high-energy primary electrons, is penetrated by the latter electrons so that a major part of the primary current directly vanishes [8.63]. Because of this effect, thermally generated silicon dioxide layers in microelectronic devices ($z < 100 \text{ nm}$) can be analyzed by high-resolution AES without difficulty, although SiO_2 layers of micrometer thickness and bulk samples show strong charging.

Reduction of the Electrical Resistivity

Lowering the electrical resistivity ρ_{el} is possible by the use of impurities, dopants, and sometimes also by irradiation-induced defects which increase the conductivity. Another method is heating of the sample to enhance intrinsic conductivity [8.74]. However, heating, like ionic conduction, may lead to an enrichment of certain

components of the sample at the surface due to diffusion and segregation, resulting in alteration of the analyzed surface composition.

Increasing the Total Secondary Electron Emission

The most effective way to reduce charging is increasing the total secondary emission coefficient to $\delta \geq 1$. The general dependence of δ on primary electron energy and incidence angle, as schematically shown in Fig. 8.3 [8.63, 8.75, 8.76], offers such a possibility. In general, for relatively low primary beam energies, there exists a region $E_p^I < E_p < E_p^{II}$ for which $\delta > 1$ holds. Increasing the incidence angle with respect to the normal to the sample surface to higher values increases the upper limit, E_p^{II} , which eventually is sufficiently high to enable excitation of low- and medium-energy Auger peaks [8.67]. This fact is confirmed by many practical examples [8.76, 8.77]. An example of the primary electron-beam energy dependence of the negative charging potential is shown in Fig. 8.4 for ZrO_2 -stabilized Al_2O_3 [8.78]. The shape of the curve is almost inverse to that in Fig. 8.3, expected from (8.1),

Fig. 8.3 Schematic diagram of the dependence of the total secondary emission, δ , on the primary beam energy E_{PE} (eV), for different incidence angles (α) with respect to the normal to the sample surface (From S. Ichimura et al. [8.76])

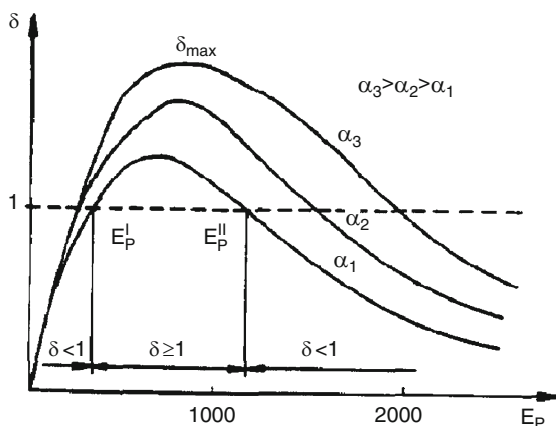


Fig. 8.4 Negative charging potential, U_C , as a function of the primary beam voltage, E_p , determined by the peak energy of the “true” secondary electrons for a ZrO_2 -stabilized, polycrystalline Al_2O_3 sample for $\alpha = 0^\circ$ ($j_p = 1 \times 10^{-4} \text{ A cm}^{-2}$) (Adapted from S. Hofmann [8.78])

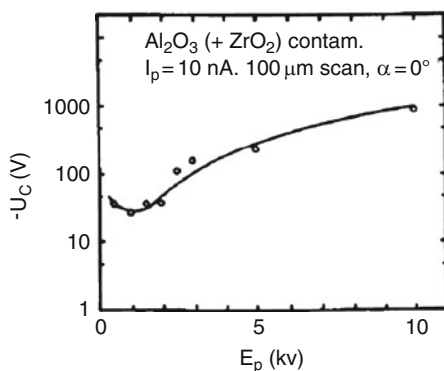
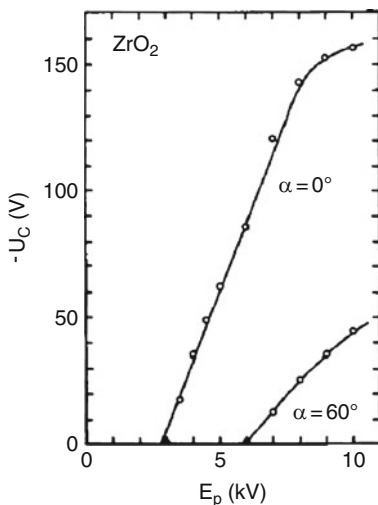


Fig. 8.5 Negative charging potential measured at a sputter-cleaned ZrO_2 surface as a function of the primary beam voltage, E_p ($j_p = 1.6 \times 10^{-3} \text{ A cm}^{-2}$), for the incidence angles $\alpha = 0^\circ$ and 60° (Adapted from S. Hofmann [8.78])



although condition $\delta = 1$ is not attained at the minimum. At fixed E_p , the potential U_C decreases with increasing incidence angle, as shown for ZrO_2 in Fig. 8.5. The upper critical primary electron energy, E_p^{II} , defined in Fig. 8.3, increases from 3 keV at $\alpha = 0^\circ$ to 6 keV at $\alpha = 60^\circ$. This behavior is in accordance with the results of Seah and Spencer [8.63] on other oxides, who established a borderline between low charging (zero to a few eV) and severe charging given by $E_p^{0.6} \cos \alpha = 1.9 \dots 4.0$ (with E_p in keV). The latter number is called the charging index, which varies from 1.9 (bulk SiO_2) to 4.0 (MgO and Al_2O_3). The example of Fig. 8.5 (ZrO_2) is in accordance with a charging index between 1.5 and 2.0. For some materials, an additional irradiation with low-energy electrons may increase secondary emission (or surface conductivity), thereby reducing surface charging [8.76].

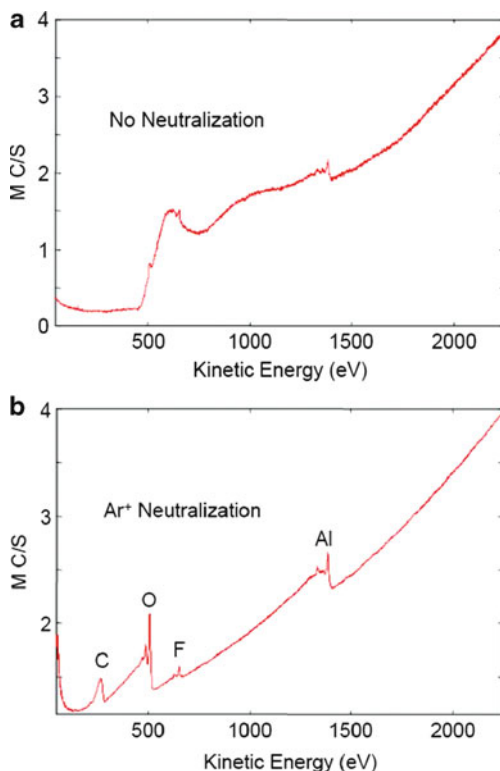
Direct Simultaneous Supply of Positive Ions

Neutralizing a negative surface charge by supply of positively charged ions is an effective experimental means to reduce and compensate negative charging [8.76]. To avoid sputter damage of the surface, the ion energy should be near or below the sputtering threshold (e.g., $< 50 \text{ eV}$ for Ar^+ ions). For optimum effect, the ion beam current value should be close to that of the primary current. An example of successful reduction of charging by low-energy Ar^+ irradiation in AES analysis is demonstrated in Fig. 8.6 [8.79].

Further Methods of Generating Positive Surface Charges

A variety of methods have been used to introduce increased surface conductivity, increased secondary electron emission, and generation of a positive surface charge,

Fig. 8.6 (a) AES spectrum ($N(E)$) of an Al bond pad surrounded by polyimide which causes blurring of the spectrum by charging. (b) Irradiation with 70 eV Ar^+ ions eliminates charging (Reproduced with permission from Phi Application Note 652 [8.79])



whose effects strongly depend on the type of sample [8.76]. All kinds of irradiation (ions, electrons, photons) can be applied to achieve this goal. For example, ultraviolet photon irradiation with energies slightly above the band gap causes an increase in surface conductivity [8.80]. A relatively simple but often successful technique is sputter deposition of a very thin metallic layer in the submonolayer region, making positive use of the redeposition effect which is detrimental in depth profiling [8.81]. If the ion beam or part of it hits a metal sheet placed in the vicinity of (and approximately perpendicular to) the analyzed area, some metal is deposited onto the sample surface. Ichimura et al. [8.76] enabled AES analysis of a sputter-cleaned Si_3N_4 surface by sputter redeposition of Ag which reduced the charging potential from 800 to 100 eV. The amount of metal deposition can also be controlled by AES, and the insulator spectrum can be accordingly corrected for quantitative analysis. The submonolayer Ag deposit exists only in a small area so that the formation of a conductive channel to the sample holder is unlikely. Due to the well-known high-positive secondary ion yield of silver, it is assumed that the secondary emission current is additionally increased by Ag deposition. A supply of low-energy (400 eV) electrons from an additional source was found useful to reduce negative charging induced by the high-energy primary electron beam [8.82], and it appeared

to be stable even after switching off the additional electron beam. Obviously, a positive surface charge can be generated by low-energy electron irradiation.

An explanation of the additional radiation effects is difficult and subject to further research. A reasonable explanation is provided by the double-layer charge model of Cazaux [8.61, 8.62]. Eventually, the charge will decay after a time, depending on the residual resistivity or other detrapping mechanisms, which in general are thermally activated [8.74]. A more detailed description of charge trapping and detrapping mechanisms has been given by LeGressus and coworkers [8.65, 8.66], emphasizing the role of polarons and the dielectric function of the material. Studies of Pireaux and coworkers [8.67, 8.68] demonstrate the capability of high-resolution electron energy loss spectrometry (HREELS) for giving additional information about the charge carrier behavior in insulators, for example, by determination of carrier density, mobility, drift velocity, and “induced resistivity.”

A survey of methods for charge control and charge reduction in AES is reported by Baer [8.98] (see also Table 8.8).

8.6 Electron and Photon-Beam Damage During AES and XPS Analyses

In principle, any analysis technique has the tendency to eventually change the original sample. The crucial question for the analyst is whether these changes are unimportant for the analytical result and/or whether they are too small to be observable within the experimental error. Since for many studies, particularly of metallic samples, the latter aspects are valid, AES and XPS are generally looked upon as nondestructive surface analysis methods (in contrast, e.g., to SIMS). However, a number of examples demonstrate that electron and photon-beam damage processes frequently occur in inorganic and organic compounds. Even in metallic alloys, beam-induced temperature increase may cause diffusion and transformation processes.

Quantitative predictions are hardly possible because of the strong dependence of the effects on the analysis conditions and on the specific sample. Therefore, it is important that basic knowledge of possible phenomena sharpens the critical attitude of the researcher with respect to likely artifacts. Excellent reviews are given in Refs. [8.9, 8.51, 8.82, 8.83].

The main effects of photon and electron-beam irradiation of solid surfaces often are of rather complex nature, but they can roughly be subdivided as follows [8.82, 8.83]:

1. Changes in composition (desorption, adsorption, segregation)
2. Changes in physical structure (defects, bond breaking, crystal structure)
3. Beam heating (interdiffusion, reactions, melting)
4. Charging of insulators (see Sect. 8.5)

Although the effects of X-rays and electrons on solid surfaces are rather similar, the typical fluxes (photons or electrons per time per area) and power densities (Watt/area) are usually orders of magnitude higher in AES as compared to XPS. Therefore, radiation-induced damage is prevalent in AES even for short measurement times, and we will first focus on AES [8.10, 8.77, 8.84].

8.6.1 *AES: Electron Beam Stimulated Changes in Composition and Structure*

Changes in composition during surface analysis are most detrimental. They are mainly caused by electron-stimulated desorption, adsorption, or elemental segregation. Structural changes such as amorphous-crystalline transitions may be induced by beam heating.

8.6.1.1 Electron Stimulated Desorption (ESD)

AES signals are caused by local excitations of atomic and binding electron orbitals due to electron-beam interactions. Such excitations in the surface layer can be additionally brought about by secondary electrons and may result in nonbinding states. If there is no immediate relaxation, the result is electron stimulated desorption (ESD) from the surface. Most often, desorption occurs for the nonmetallic component (O, N, C, B) in insulating compounds [8.70, 8.77, 8.82, 8.85–8.87]. Typical for this effect is a first-order reaction kinetics, given by an exponential decay law with time t [8.77, 8.78, 8.86, 8.87]:

$$X_i(t) = X_i^0 \exp(-k_i t) = X_i^0 \exp\left(-\frac{\sigma_e j_p}{e} t\right), \quad (8.3)$$

where k_i is the reaction rate constant, X_i^0 is the original mole fraction of element “i” in the first surface layer of the respective compound (e.g., O or Al in Al_2O_3), $X_i(t)$ is the fraction existing after irradiation time t with electron current density j_p (Acm^{-2}), e is the elementary charge ($1.6 \times 10^{-19} \text{ C}$), and σ_e (cm^2) is the effective cross section for ESD. The latter is characteristic of the respective compound and depends weakly on the electron energy [8.77]. An example of the validity of (8.3) is shown in Fig. 8.7 for Al_2O_3 , obtained for the Al LVV oxide peak (52 eV) during AES analysis [8.64]. The decrease of the Al peak intensity corresponds to ESD of oxygen. It is important to note that the effect of ESD on the surface monolayer is actually higher than the slope of the line in Fig. 8.7 because in AES, several layers contribute to the signal. For example, the corresponding curve for the Al KLL peak (1,394 eV) would give a lower slope as compared to Fig. 8.7. Because

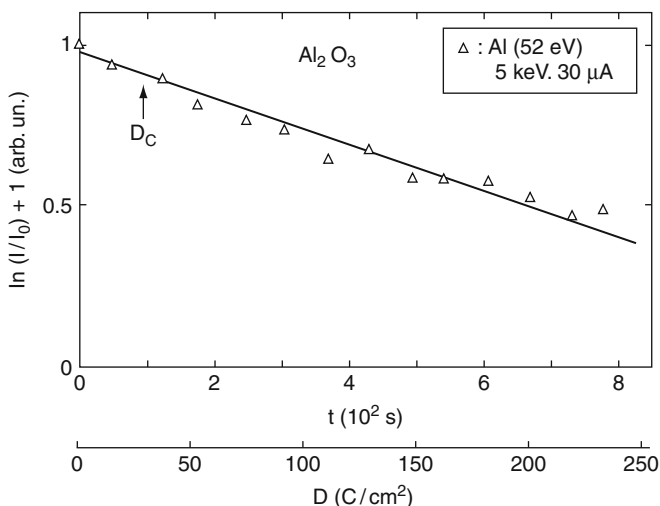


Fig. 8.7 ESD of oxygen observed during AES analysis of an Al_2O_3 sample. The logarithm of the relative intensity, $\ln(I/I_0)$ of the Al (52 eV) Auger peak ($I = I_0$ for $t = 0$), which is a measure of the remaining amount of Al_2O_3 , is plotted against the electron-beam irradiation time t and dose D (From S. Hofmann [8.64])

the attenuation length of the Al LVV peak is about 1 ML, 63% of the intensity in Fig. 8.7 stems from the first monolayer.

In general, borides, nitrides, and carbides are relatively stable against ESD ($\sigma_e < 10^{-24} \text{ cm}^2$), whereas many oxides (SiO_2 , Al_2O_3) are unstable [8.70, 8.77, 8.85, 8.86, 8.87, 8.88].

A measure for the sensitivity to ESD is the electron dose density or fluence $D = j_p t$, for which a measurable change in surface composition is obtained. Following Pantano and Madey [8.77], a maximum allowable critical fluence D_c can be defined for which the decomposition is about 10%, i.e., $X_i/X_i^0 = 0.9$, which gives with (8.3) $D_c (\text{C cm}^{-2}) = e \ln(1.11)/\sigma_e = 1.6 \times 10^{-20}/\sigma_e (\text{cm}^2)$. The critical time for this dose is $t_c = D_c/j_p$. Thus, by lowering the current density (lowering the primary current or increasing the raster size), the useful time for AES measurement can be increased.

The ESD cross section or the critical dose density or critical fluence establishes a quantitative criterion for the limits of lateral resolution and/or detection sensitivity of compounds. For example, for SiO_2 , $\sigma_e = 1.5 \times 10^{-20} \text{ cm}^2$, and for Al_2O_3 , $\sigma_e = 5 \times 10^{-22} \text{ cm}^2$ [8.70, 8.85]. For the latter, this means that $D_c \approx 30 \text{ C cm}^{-2}$ (see Fig. 8.7). Therefore, according to $t_c = D_c/j_p$, point analysis with $I_p = 10 \text{ nA}$ and $0.1 \mu\text{m}$ beam diameter (current density about 10^2 A/cm^2) gives a critical, useful measurement time of only 0.3 s, i.e., impossible for point analysis. However, an area analysis with the same current (10 nA) and a scanned area with raster

Table 8.6 ESD cross sections (σ_e), critical doses (D_c), and critical measurement times (t_c for $j_p = 1 \text{ mA/cm}^2$, i.e., 10 nA in about $30 \times 30 \mu\text{m}^2$), for electron-beam damage in some typical materials

Material	$\sigma_e \text{ (cm}^2\text{)}$	$D_c \text{ (C/cm}^2\text{)}$	t_c	Refs.
Si_3N_4	$<10^{-24}$	$>10^4$ (stable)	$>10^7 \text{ s}$	[8.4, 8.12]
Al_2O_3	1.5×10^{-21}	10	3 h	[8.4]
Al_2O_3	5×10^{-22}	30	8 h	[8.13, 8.14]
SiO_2	1.5×10^{-20}	1	17 min	[8.9, 8.10]
$\text{LiNO}_3, \text{LiSO}_4$	3×10^{-19}	0.05	50 s	[8.4]
KCl	5×10^{-19}	0.03	30 s	[8.4]
C_6H_{12} (film)	5×10^{-17}	0.0003	0.3 s	[8.4]

$10 \times 10 \mu\text{m}^2 (10^{-2} \text{ A/cm}^2)$ gives a useful measurement time of about 3,000 s which is sufficient for quantitative AES analysis [8.64, 8.78].

A careful study of electron irradiation damage by Tanuma et al. [8.88] has shown that for its description, the single exponential function (8.3) has to be replaced by a sum of two of such functions with cross sections σ_{e1} and σ_{e2} , corresponding to the two-step mechanism: $\text{SiO}_2 - \sigma_{e1} \rightarrow \text{SiO} - \sigma_{e2} \rightarrow \text{Si}$. The 5% critical dose density was found to be SiO_2 layer thickness dependent and about 7 C cm^{-2} , i.e., considerably higher than the value after [8.70, 8.85] (see Table 8.6). This fact may be explained by the lower value of σ_{e1} corresponding to the lower dose regime. Table 8.6 gives a survey of ESD cross sections, critical dose densities, and measurement times for a number of compounds. For many hydrocarbons, the high ESD cross section precludes meaningful analysis by AES.

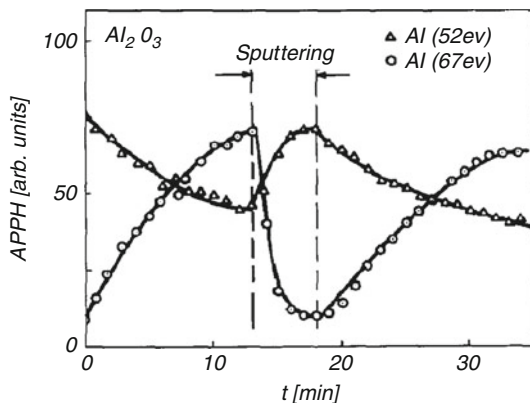
In depth profiling by sputtering, the situation with respect to ESD is generally improved [8.64, 8.78]. This is due to the fact that ESD is at least partially compensated by continuous, homogeneous sputtering (when preferential sputtering can be excluded) which steadily produces fresh surfaces. If continuous sputter erosion is large enough, the effect of ESD can be effectively reduced to almost zero, as shown in the following.

Based on (8.3), the surface composition change with time t of species i , dX_i/dt , is described by [8.64, 8.78]

$$\frac{dX_i}{dt} = -X_i \sigma_e j_p + (X_i^0 - X_i) \sigma_1 j_1 \quad (8.4)$$

The first term is the differentiated form of (8.3), and the second term takes into account the sputter erosion of the instantaneous surface (altered by ESD) by the ion beam density, j_1 , with the cross section for ion sputtering, σ_1 . Assuming that both processes (ESD and sputtering) are confined to the first atomic monolayer, σ_1 is described by the sputtering yield Y (atoms per ion) and the atomic area density

Fig. 8.8 Compensation of ESD on Al_2O_3 by sputtering of the surface with 1 keV Ar^+ ions. Al (52 eV) denotes the oxide and Al (67 eV) denotes the metallic peak of Al, respectively. The time dependence of the oxide peak is described by (8.4) (From S. Hofmann [8.64])



$N_0(A)$ (cm^{-2}), $\sigma_I = Y/N_0(A)$. For a steady-state and a homogeneous sample composition X_i^0 , $dX_i/dt = 0$ and (8.4) gives for the concentration X_i ,

$$X_i = \frac{X_i^0}{1 + \frac{\sigma_e j_p}{\sigma_I j_I}} \quad (8.5)$$

If preferential sputtering occurs, (8.3)–(8.5) have to be modified by an appropriate term (e.g., [8.89]). A test of (8.4) and (8.5) is depicted in Fig. 8.8 for AES on Al_2O_3 . Without sputtering, ESD of oxygen causes decrease of the Al oxide peak. As soon as the ion beam is switched on, this process is reversed, and the original surface is restored because Al_2O_3 shows homogeneous sputtering [8.90]. In the example of Fig. 8.8, the parameters in (8.4) and (8.5) are approximately $j_p = 0.3 \text{ A cm}^{-2}$, $j_I = 1.6 \mu\text{A cm}^{-2}$, $\sigma_e = 5 \times 10^{-22} \text{ cm}^2$, and $\sigma_I = 1 \times 10^{-15} \text{ cm}^2$. With these data, (8.5) gives $X_i/X_i^0 = 0.9$ in accordance with the value obtained after about 5-min sputtering and simultaneous electron-beam irradiation (Fig. 8.8).

Frequently, the result of ESD for contamination layers of hydrocarbons or CO on metallic surfaces is visible in an SED picture. Beam-induced decomposition of hydrocarbons usually results in a deposit of elemental carbon that is an image of the electron-beam impact and can be used in practice to locate the beam and to estimate its diameter. Thus, electron-stimulated desorption (ESD) and adsorption (ESA) can be a problem in case of too high residual gas pressure (see Sect. 2.1).

8.6.1.2 Electron-Beam-Induced Sample Heating

Another detrimental effect of the focused electron beam in AES analysis is Joule heating of the analyzed spot when using point analysis with high electron current density. This effect may lead to a temperature increase of several hundred degrees (particularly in thin films on glass substrates). In turn, diffusion, segregation, and

Table 8.7 Steady-state temperature increase, ΔT , for different bulk materials during typical AES point analysis ($E_p = 10$ keV, $I_p = 10$ nA, $d_e = 0.1$ μ m), estimated after (8.7)

Material	κ ($\text{Wm}^{-1}\text{K}^{-1}$)	ΔT (K)
Cu	390	2
Al	221	3
SiC, AlN	100	6
Si_3N_4	25	25
Al_2O_3	17	40
Glass	0.8	880

even evaporation may occur [8.10, 8.78, 8.84, 8.91]. An analytical expression of the expected temperature rise ΔT in a thin film on a substrate is given by Roell [8.10]:

$$\Delta T = \frac{2P_w}{\pi d_0 \kappa_s [1 + 1.67(\kappa_f/\kappa_s)(h/r_0)]}, \quad (8.6)$$

where P_w (in W) is the input power, d_0 (in m) is the diameter of the electron beam, h is the thickness of the film, and κ_f and κ_s ($\text{Wm}^{-1}\text{K}^{-1}$) are the thermal conductivities of film and substrate, respectively. For bulk samples, (8.6) can be simplified and gives [8.10, 8.84, 8.87]

$$\Delta T = \frac{2P_w}{\pi d_0 \kappa}, \quad (8.7)$$

where κ is the thermal conductivity of the bulk sample and d_0 is the electron-beam diameter. Some typical ΔT values in AES point analysis, calculated with (8.7), are shown in Table 8.7 for different materials. In general, electron-beam heating is relatively limited in metals and some ceramics, owing to their good thermal conductivity. However, it can be very detrimental in glasses and thin films, and for particles connected to the substrate only with a small area [8.87]. For typical AES conditions, Table 8.7 gives the expected temperature increase for different bulk materials after (8.7). A survey of the expected temperature increase with power density (P_w/d_0) for different bulk materials and thin films on glass is shown in Fig. 8.9 [8.78]. Beam heating can be significantly reduced by lowering the electrical power density P_w/d_0 , for example, increasing the effective d_0 by rastering the primary beam. Thus, the temperature increase in a very thin film on glass substrate of 880 K (Table 8.8) for point analysis conditions (10 keV, 1 nA, $d_0 = 10$ nm, $P_w/d_0 = 10^{-3}$ W/ μ m) is reduced to less than 10 K using a beam raster of $1 \times 1 \mu\text{m}^2$ ($P_w/d_0 = 10^{-5}$ W/ μ m) as seen in Fig. 8.9.

Figure 8.10 shows an example of the effect of beam heating on the composition of a thin film double-layer Au/Ag on a glass substrate [8.84]. With an electron-beam diameter of about 150 μ m, condition (a) gives $P_w/d_0 = 1 \times 10^{-4}$ W/ μ m, and $\Delta T = 80$ K after (8.7), whereas condition (b) gives $P_w/d_0 = 1.1 \times 10^{-3}$ W/ μ m, and $\Delta T = 900$ K. These temperature estimations explain why the depth distribution of composition in Fig. 8.10a is completely destroyed by interdiffusion, segregation, and evaporation which occur at the high temperature, as seen in Fig. 8.10b.

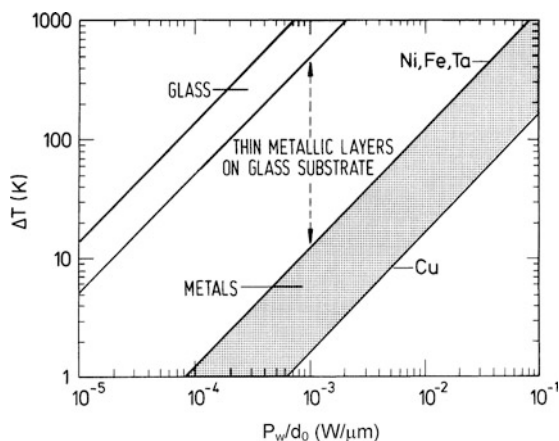


Fig. 8.9 Dependence of the temperature increase ΔT (K) on the electrical power density P_w/d_0 (d_0 = electron-beam diameter) for different bulk materials, calculated after (8.7) and for typical AES analyses. Depending mainly on their thickness, thin metallic layers on glass are between the latter and metals, according to (8.6) (From S. Hofmann [8.78])

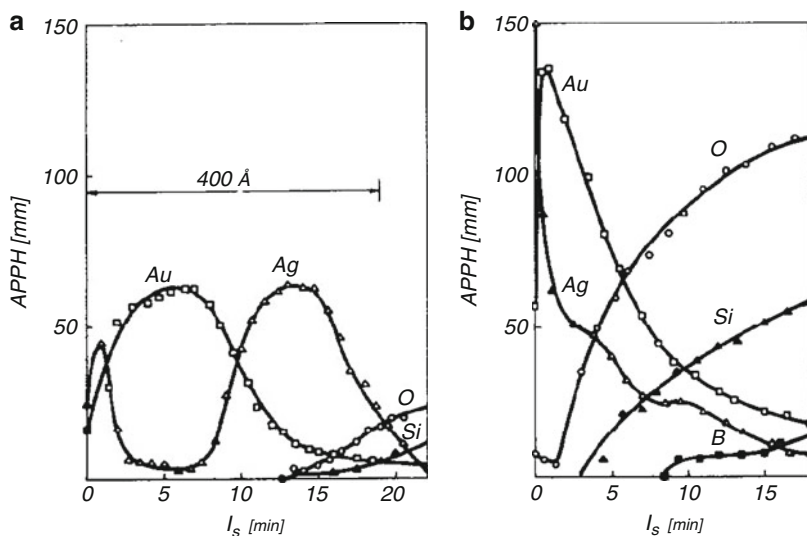


Fig. 8.10 Sputter depth profiles of a gold film of 20 nm thickness deposited on a silver film of another 20 nm thickness, both deposited on a 20-nm-thick silver film, both on a glass substrate. The Auger peak-to-peak heights (APPHs) are plotted against sputtering time t_s , for identical sputtering conditions in (a) and (b). (a) Low-power electron beam, $E_p = 1.5$ keV, $I_p = 10$ μ A, (b) high-power electron beam, $E_p = 5$ keV, $I_p = 35$ μ A (From S. Hofmann and A. Zalar [8.84])

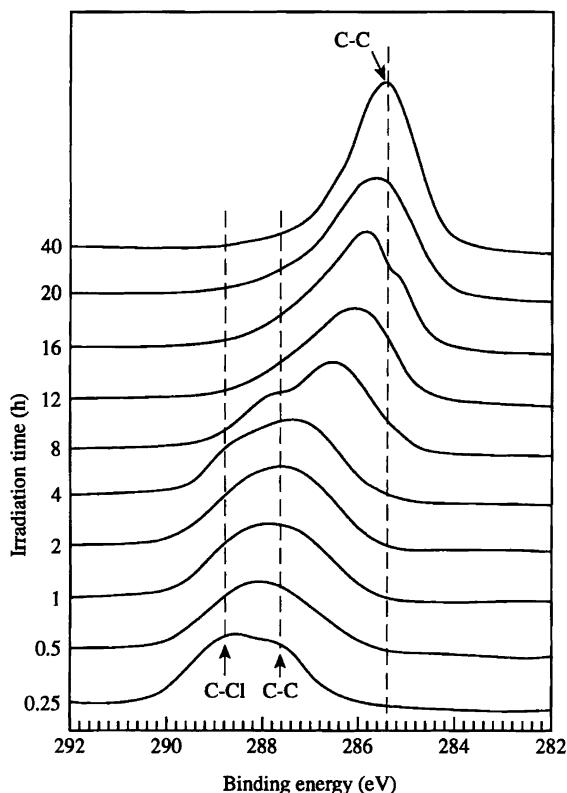


Fig. 8.11 XPS C1s spectra of polyvinyl chloride as a function of X-ray exposure. The C–Cl bond component intensity decreases with irradiation time, and the C–C peak shifts to lower binding energy (Reproduced from J.H. Thomas [8.9]. Copyright Springer Verlag, 1998)

8.6.2 XPS: X-Ray-Induced Changes in Composition

In contrast to popular belief that photon-excited surface analysis techniques are truly nondestructive, surface alterations during XPS are more common than expected. In general, XPS is less effective in changing the chemical state and composition of a sample as compared to AES because photon flux and photoionization cross section are lower than the electron flux and electron ionization cross section. But with focused X-rays in small spot XPS and with synchrotron irradiation sources, the photon flux increases and beam damage effects are observed in XPS as well. As pointed out in detail by Cazaux [8.93], the photon flux in conventional XPS is about $10^{11} \text{ cm}^{-2} \text{ s}^{-1}$, whereas in AES for condition (b) in Table 8.2 ($1 \mu\text{m}$ spatial resolution), the electron flux is about $5 \times 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$. For the same spatial resolution, detection sensitivity and necessary dose (see Chap. 4), and considering

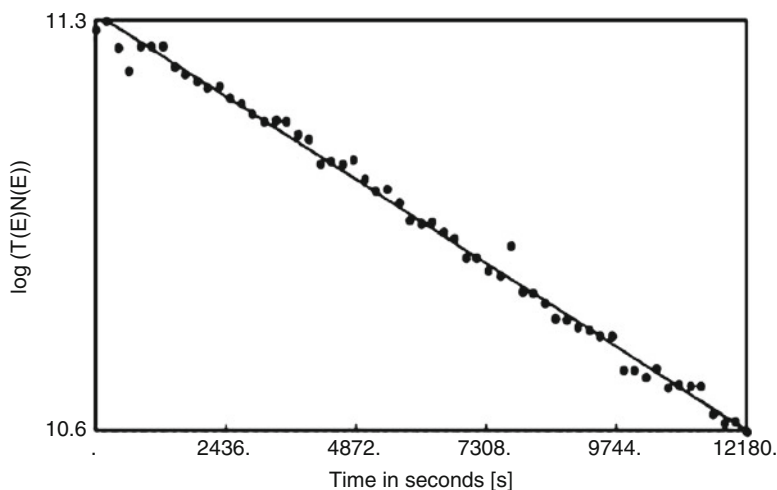


Fig. 8.12 Degradation of PVC by XPS analysis. The Cl 2p peak intensity (in logarithmic scale) is plotted as a function of the analysis time. The constant slope indicates first-order reaction kinetics after (8.3) with the slope giving the rate constant $k_{\text{PVC}} = -2.3 \times 10^{-4} \text{ s}^{-1}$, which is a measure of the X-ray intensity. (Reproduced from K. Yoshihara and A. Tanaka [8.95], with permission of J. Wiley & Sons Ltd.)

that mainly because of the better signal-to-noise factor in XPS the relative sensitivity is about one order of magnitude better, we need at least a factor of 10^6 higher photon flux in XPS for damage comparable to AES. For such a high photon flux, which is only achieved in synchrotron radiation sources, the difference between AES and XPS is strongly reduced. Depending mainly on the material, Cazaux [8.93] estimates the difference in the total cross section for damage between zero and two orders of magnitude lower for XPS.

The basic photon interaction mechanism can be understood as follows [8.9,8.82]: The impinging photons are absorbed by internal photoemission of energetic electrons which may produce excited states, electrons, and even ions. The energetic electrons interact with the surrounding atoms or molecules and produce other excitations. The result is a cascade of further events which may induce chemical changes in the sample surface, such as photon-stimulated desorption (PSD), bond cleavage, or “Coulomb explosion.” In this event, deep core level ionization followed by an Auger cascade process leaves positive ions in a multiple charged state that “explode” from the surface. Bond cleavage may occur if excitation in the valence band decays to a nonbonding state. The damage produced by secondary electrons is rather similar to that expected in AES. Inorganic materials, particularly salts and oxides, are sensitive to photon-induced damage. For example, the Cu^{2+} ion in CuSO_4 is reduced to Cu^+ , and NaClO_4 is reduced to NaCl after prolonged X-ray irradiation [8.82]. Polymers are even less stable. For example, polyvinyl chloride (PVC) degrades by photoionization, resulting in generation of HCl through H and Cl

BOND breaking [8.82]. As shown in Fig. 8.11 [8.9], the C1s peak characteristic for C–Cl bonding decreases with time with first-order kinetics (see (8.3) and Fig. 8.7), while a shift in energy of the C–C bond peak occurs. The latter is caused by the formation of polyene groups $-(\text{HC}=\text{CH})_n-$ [8.9, 8.94]. An interlaboratory study of Yoshihara and Tanaka [8.95] on the degradation of PVC, nitrocellulose, and PTFE by X-rays in XPS revealed that for the latter two, the critical dose (for 5% degradation) is about ten times lower than for PVC. The degradation of the latter is shown in Fig. 8.12. In contrast to PVC, PTFE shows a more complex degradation with higher reaction order. Because of the lower energy density transferred by photons as compared to electron irradiation in AES, beam heating can generally be neglected. However, nonmonochromatized X-ray sources may heat the sample by thermal radiation from the anode, and care has to be taken to ensure sufficient cooling [8.96]. X-ray-induced degradation in insulators is often accompanied by charging, which is presented in Sect. 8.5.1.

Summary and Conclusion

The aim of surface analysis determines the analytical strategy (Sect. 8.1). The type of material, its size, shape, structure and composition, roughness, likelihood of evaporation in UHV, of electron- or photon-induced damage, etc. pose limits to the choice of approaches (Sect. 8.2). Application of sample preparation such as cleaning, *in situ* and *ex situ*, depends on the nature of the sample and the aim of analysis (Sect. 8.3).

More general procedures are the setting up of the instrument for the special task, including calibration of the intensity and energy scale with suitable reference materials (Sect. 8.4). Appropriate setting up includes consideration of the useful signal-to-noise ratio and energy resolution (see, e.g., Chap. 6). Insulator analysis requires special measures (e.g., grazing beam incidence and/or low-energy ion supply in AES, flood gun in XPS) (Sect. 8.5). Especially for nonmetallic samples, electron-beam damage and – for sensitive inorganic compounds and organic material – photon-beam damage may arise. It can be checked by monitoring time-dependent changes of peak shape and intensity (Sect. 8.6) and is reduced by lowering the respective electron or photon fluxes. Careful consideration of the items mentioned in Chap. 8 will ensure a successful surface analysis.

Many practically important issues are the subject of ISO standards worked out by the ISO Technical Committee 201 on surface chemical analysis [8.97]. They are summarized in Table 8.8 [8.98].

Table 8.8 Content List of Published ISO/TC 201 Standards on (1) General Issues, (2) AES, (3) XPS and (4) Sputter Depth Profiling

1. General Issues

Data Format

ISO 14975 *Surface chemical analysis – Information formats* [SIA 2002; **33**: 367].

ISO 14976 *Surface chemical analysis – Data transfer format* [SIA 1999; **27**: 693].

Ion Implantation Areic Dose

ISO 16268 *Surface chemical analysis – Proposed procedure for certifying the retained areic dose in a working reference material produced by ion implantation.*

Preparation and Handling of Specimen

ISO 18117 *Surface chemical analysis – Handling of specimens prior to analysis.*

ISO 18116 *Surface chemical analysis – Guidelines for preparation and mounting of specimens for analysis.*

Vocabulary

ISO 18115 *Surface chemical analysis – Vocabulary – Part 1:General terms and terms used in spectroscopy* [SIA 2001; **31**: 1048].

ISO 18115 *Surface chemical analysis – Vocabulary – Part 2:Terms used in scanning- probe microscopy.*

2. Auger Electron Spectroscopy (AES)

Analysis Area and Lateral Resolution

ISO 18516 *Surface chemical analysis – Auger electron spectroscopy and X-ray photoelectron spectroscopy – Determination of lateral resolution* [SIA 2008; **40**: 966].

ISO 19319 *Surface chemical analysis – Auger electron spectroscopy and X-ray photoelectron spectroscopy – Determination of lateral resolution, analysis area, and sample area viewed by the analyser* [SIA 2004; **36**: 666].

Charge Control and Correction

ISO 29081 *Surface chemical analysis – Auger electron spectroscopy – Reporting of methods used for charge control and charge correction.*

Chemical Information

ISO 18394 *Surface chemical analysis – Auger electron spectroscopy – Derivation of chemical information* [SIA 2007; **39**: 556].

Energy Scale Calibration

ISO 17973 *Surface chemical analysis – Medium-resolution Auger electron spectrometers – Calibration of energy scales* [SIA 2003; **35**: 329].

ISO 17974 *Surface chemical analysis – High-resolution Auger electron spectrometers – Calibration of energy scales for elemental and chemical-state analysis* [SIA 2003; **35**: 327].

(continued)

Table 8.8 (continued)**Instrumental Performance**

ISO 15471 *Surface chemical analysis – Auger electron spectroscopy – Description of selected instrumental performance parameters.*

Peak Intensity and Intensity Scale

ISO 20903 *Surface chemical analysis – Auger electron spectroscopy and X-ray photoelectron spectroscopy – Methods used to determine peak intensities and information required when reporting results* [SIA 2007; **39**: 464].

ISO 21270 *Surface chemical analysis – X-ray photoelectron and Auger electron spectrometers – Linearity of intensity scale* [SIA 2004; **36**: 645].

ISO 24236 *Surface chemical analysis – Auger electron spectroscopy – Repeatability and constancy of intensity scale* [SIA 2007; **39**: 86].

Relative Sensitivity Factors

ISO 18118 *Surface chemical analysis – Auger electron spectroscopy and X-ray photoelectron spectroscopy – Guide to the use of experimentally determined relative sensitivity factors for the quantitative analysis of homogeneous materials* [SIA 2006; **38**: 178].

3. X-ray Photoelectron Spectroscopy (XPS)**Analysis Area and Lateral Resolution**

ISO 18516 *Surface chemical analysis – Auger electron spectroscopy and X-ray photoelectron spectroscopy – Determination of lateral resolution.*

ISO 19319 *Surface chemical analysis – Auger electron spectroscopy and X-ray photoelectron spectroscopy – Determination of lateral resolution, analysis area, and sample area viewed by the analyser* [SIA 2004; **36**: 666].

Analysis Guidelines

ISO 10810 *Surface chemical analysis – X-ray photoelectronspectroscopy – Guidelines for analysis.*

Charge Control and Correction

ISO 19318 *Surface chemical analysis – X-ray photoelectron spectroscopy – Reporting of methods used for charge control and charge correction* [SIA 2004; **37**: 524].

Energy Scale Calibration

ISO 15472 *Surface chemical analysis – X-ray photoelectron spectroscopy – Calibration of energy scales* [SIA 2001; **31**: 721].

Instrumental Performance

ISO 15470 *Surface chemical analysis – X-ray photoelectron spectroscopy – Description of selected instrumental performance parameters* [SIA 2008; **40**: 966].

(continued)

Table 8.8 (continued)**Peak Intensities, Intensity Scale and Background**

ISO 18392 *Surface chemical analysis – X-ray photoelectron spectroscopy – Procedures for determining backgrounds* [SIA 2006; **38**: 1173].

ISO 20903 *Surface chemical analysis – Auger electron spectroscopy and X-ray photoelectron spectroscopy – Methods used to determine peak intensities and information required when reporting results* [SIA 2007; **39**: 464].

ISO 21270 *Surface chemical analysis – X-ray photoelectron and Auger electron spectrometers – Linearity of intensity scale*.

ISO 24237 *Surface chemical analysis – X-ray photoelectron spectroscopy – Repeatability and constancy of intensity scale* [SIA 2007; **39**: 370].

Relative Sensitivity Factors

ISO 18118 *Surface chemical analysis – Auger electron spectroscopy and X-ray photoelectron spectroscopy – Guide to the use of experimentally determined relative sensitivity factors for the quantitative analysis of homogeneous materials*.

4. Sputter Depth Profiling (SDP)

ISO 14606 *Surface chemical analysis – Sputter depth profiling – Optimization using layered systems as reference materials* [SIA 2002; **33**: 365].

ISO 15969 *Surface chemical analysis - Depth profiling – Measurement of sputtered depth* [SIA 2002; **33**: 453].

ISO 22335 *Surface chemical analysis – Depth profiling – Measurement of sputtering rate: mesh-replica method using a mechanical stylus profilometer and X-ray photoelectron spectroscopy – Determination of lateral resolution*.

Adapted from Baer [8.98], with Summary references in brackets

Note: ISO standards may be purchased from national standards bodies, directly from the ISO Central Secretariat, Case Postale 56, CH-1211 Geneva 20, Switzerland, or through the internet at <http://www.iso.ch>. More information about ISO/TC 201 on Surface Chemical Analysis may be obtained from this internet site or from Dr. Hidehiko Nonaka [hide.nonaka@aist.go.jp], Secretariat of ISO/TC 201, Japanese Standards Association, Toraya Bldg 7F, 4-9-22 Akasaka, Minato-ku, Tokyo 107-0052, Japan

References

- 8.1. C.J. Powell, M.P. Seah, J. Vac. Sci. Technol. **A8**, 735 (1990)
- 8.2. I. Kartio, K. Laajaleto, E. Suoninen, S. Karthe, R. Szargan, Surf. Interface Anal. **18**, 807 (1992)
- 8.3. G. Iucci, L. Rossi, N. Rosato, I. Savini, G. Duranti, G. Polzonetti, J. Mater. Sci. Mater. Med. **17**, 779 (2006)
- 8.4. C. Fadley, Prog. Surf. Sci. **16**, 275 (1984)
- 8.5. H.E. Bishop, Surf. Interface Anal. **15**, 27 (1990)
- 8.6. M. Zharnikov, M. Neuber, M. Grunze, Surf. Rev. Lett. **5**, 501 (1998)
- 8.7. R. Fasel, P. Aebi, L. Schlapbach, J. Osterwalder, Phys. Rev. B **52**, R2313 (1995)
- 8.8. D.P. Woodruff, A.M. Bradshaw, Rep. Prog. Phys. **57**, 1029 (1994)
- 8.9. J.H. Thomas III, Photon Beam Damage and Charging at Solid Surfaces, in *Beam Effects, Surface Topography and Depth Profiling in Surface Analysis*, ed. by A.W. Czanderna, C.J. Powell, T.E. Madey (Plenum Press, New York, 1998), pp. 1–37

- 8.10. K. Röhl, *Appl. Surf. Sci.* **5**, 388 (1980)
- 8.11. S. Scanning Microsc **1**, 989 (1987)
- 8.12. A.W. Czanderna, C.J. Powell, T.E. Madey (eds.), *Specimen Handling, Preparation, and Treatments in Surface Characterization* (Kluwer Academic/Plenum Publishers, New York, 1998)
- 8.13. ISO 18116, *Surface Chemical Analysis – Guidelines for Preparation and Mounting of Specimens for Analysis* (ISO, Geneva, 2005)
- 8.14. ISO 18117, *Surface Chemical Analysis – Handling of Specimens Prior to Analysis* (ISO, Geneva, 2009)
- 8.15. S. Kurz, Diploma thesis, Stuttgart University, Stuttgart, 2010
- 8.16. S. Hofmann, R. Frech, *Anal. Chem.* **57**, 716 (1985)
- 8.17. J.R. Vig, UV/Ozone Cleaning of Surfaces: A Review, in *Surface Contamination*, ed. by K.L. Mittal (Plenum Press, New York, 1979), pp. 235–254
- 8.18. J.H. Thomas III, S. Hofmann, *J. Vac. Sci. Technol. A* **3**, 1921 (1985)
- 8.19. R.L. Moore, L. Salvat, G. Sundberg, V. Greenhut, *J. Vac. Sci. Technol. A* **3**, 2426 (1985)
- 8.20. J.M. Walls, D.D. Han, D.E. Sykes, *Surf. Interface Anal.* **1**, 204 (1979)
- 8.21. J. Verhoeven, Techniques to Obtain Atomically Clean Surfaces, in *Surface Contamination*, ed. by K.L. Mittal (Plenum Press, New York, 1979), pp. 499–512
- 8.22. R.G. Musket, W. McLean, C.A. Colminares, D.M. Makowiecki, W.J. Siekhaus, *Appl. Surf. Sci.* **10**, 143 (1982)
- 8.23. J.C. Rivière, Instrumentation, in *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, 2nd edn., ed. by D. Briggs, M.P. Seah (Wiley, Chichester, 1990), pp. 19–83
- 8.24. H.E. Farnsworth, *J. Vac. Sci. Technol.* **20**, 275 (1982)
- 8.25. J.L. Vossen, J.H. Thomas III, J.S. Maa, O.R. Mesker, G.O. Fowler, *J. Vac. Sci. Technol. A* **1**, 1452 (1983)
- 8.26. J.C. Fuggle, XPS in Ultra High Vacuum Conditions, in *Handbook of X-ray and Ultraviolet Photoelectron Spectroscopy*, ed. by D. Briggs (Heyden, London, 1977), pp. 273–312
- 8.27. P. Lejček, *Grain Boundary Segregation in Metals* (Springer, Berlin, 2010)
- 8.28. A. Zalar, S. Hofmann, *Surf. Interface Anal.* **2**, 183 (1980)
- 8.29. J.F. Bresse, *Scann. Electron Microsc.* **IV**, 1465 (1985)
- 8.30. W.H. Gries, *Surf. Interface Anal.* **7**, 29 (1985)
- 8.31. M. Procop, A. Klein, I. Rechenberg, D. Krueger, *Surf. Interface Anal.* **25**, 458 (1997)
- 8.32. P. Lejček, S. Hofmann, *Crit. Rev. Solid State Mater. Sci.* **33**, 133 (2008)
- 8.33. S. Hofmann, P. Lejček, *Int. J. Mater. Res.* **100**, 1167 (2009)
- 8.34. P. Lejček, *Anal. Chim. Acta* **297**, 165 (1994)
- 8.35. P. Lejček, S. Hofmann, *Surf. Sci.* **307–309**, 798 (1994)
- 8.36. P. Braun, W. Färber, *Surface Sci.* **47**, 57 (1975)
- 8.37. J. Liday, S. Hofmann, R. Harman, *Vacuum* **43**, 331 (1992)
- 8.38. E. Bauer, H. Poppa, F. Bonczek, *J. Appl. Phys.* **45**, 5164 (1974)
- 8.39. M.P. Seah, *Surface Sci.* **40**, 595 (1973)
- 8.40. M.P. Seah, Appendix 1, in *Practical Surface Analysis*, vol. 1, 2nd edn., ed. by D. Briggs, M.P. Seah (Wiley, Chichester, 1990), pp. 531–540
- 8.41. P.J. Cumpson, M.P. Seah, S.J. Spencer, *Surf. Interface Anal.* **24**, 687 (1996)
- 8.42. M.P. Seah, Instrument Calibration for AES and XPS, in *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, ed. by D. Briggs, J.T. Grant (IM Publications, Chichester, 2003), pp. 167–189
- 8.43. M.P. Seah, I.S. Gilmore, S.J. Spencer, *J. Electron Spectrosc. Relat. Phenom.* **104**, 73 (1999)
- 8.44. *NPL Systems for the Intensity Calibration of Auger and X-ray Photoelectron Spectrometers, A1 and X1* (NPL, Teddington). www.npl.co.uk/npl/cmmmt/sis/index.html
- 8.45. ISO 15472, *Surface Chemical Analysis-X-ray Photoelectron Spectrometers – Calibration of Energy Scales* (ISO, Geneva, 2001)
- 8.46. ISO 17973, *Surface Chemical Analysis-Medium Resolution Auger Electron Spectrometers – Calibration of Energy Scales for Elemental Analysis* (ISO, Geneva, 2002)

- 8.47. ISO 17974, *Surface Chemical Analysis – High Resolution Auger Electron Spectrometers – Calibration of Energy Scales for Elemental and Chemical State Analysis* (ISO, Geneva, 2002)
- 8.48. ISO 21270, *Surface Chemical Analysis – X-ray Photoelectron and Auger Electron Spectrometers – Linearity of Intensity Scale* (ISO, Geneva, 2003)
- 8.49. S. Hofmann, Auger Electron Spectroscopy, in *Wilson & Wilson's Comprehensive Analytical Chemistry*, vol. IX, ed. by G. Svehla (Elsevier, Amsterdam, 1979), pp. 89–172
- 8.50. S. Hofmann, G. Blank, H. Schultz, Z. Metall. **67**, 189 (1976)
- 8.51. A.W. Czanderna, C.J. Powell, T.E. Madey (eds.), *Beam Effects, Surface Topography and Depth Profiling in Surface Analysis* (Plenum Press, New York, 1998)
- 8.52. M.P. Seah, Quantification in AES and XPS, in *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, ed. by D. Briggs, J.T. Grant (IM Publications, Chichester, 2003), pp. 345–375
- 8.53. M.P. Seah, Charge Referencing Techniques for Insulators, Appendix 2, in *Practical Surface Analysis*, vol. 1, 2nd edn., ed. by D. Briggs, M.P. Seah (Wiley, Chichester, 1990), pp. 541–554
- 8.54. M.A. Kelly, Analyzing Insulators with XPS and AES, in *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy* (IM Publications, Chichester, 2003), pp. 191–210
- 8.55. J. Cazaux, J. Electron Spectrosc. Relat. Phenom. **105**, 155 (1999)
- 8.56. J. Cazaux, J. Electron Spectrosc. Relat. Phenom. **113** (2000) 15
- 8.57. J.R. Waldrop, E.a. Kraut, S.P. Kowalczyk, R.W. Grant, Surf. Sci. **132**, 513 (1983)
- 8.58. M. Yoshitake, K. Ohmori, T. Chikyow, Surf. Interface Anal. **42**, 70 (2010)
- 8.59. P. Swift, Surf. Interface Anal. **4**, 47 (1982)
- 8.60. W.E.S. Unger, T. Gross, O. Boese, A. Lippitz, T. Fritz, U. Gelius, Surf. Interface Anal. **29**, 535 (2000)
- 8.61. J. Cazaux, J. Appl. Phys., **59**, 1418 (1986)
- 8.62. A. Melchinger, S. Hofmann, J. Appl. Phys. **78**, 6224 (1995)
- 8.63. M.P. Seah, S.J. Spencer, J. Electron Spectrosc. Relat. Phenom. **109**, 291 (2000)
- 8.64. S. Hofmann, J. Electron Spectrosc. **59**, 15 (1992)
- 8.65. C. LeGressus, F. Valin, M. Heuriot, M. Gautier, J.P. Durand, T.S. Sudarshan, R.G. Bomakanti, G. Blaise, J. Appl. Phys. **69**, 6325 (1991)
- 8.66. G. Blaise, C. LeGressus, J. Appl. Phys. **69**, 6339 (1991)
- 8.67. M. Liehr, P.A. Thiry, J.J. Pireaux, R. Caudano, J. Vac. Sci. Technol. **A 2**, 1079 (1984)
- 8.68. P.A. Thiry, M. Liehr, J.J. Pireaux, R. Caudano, J. Electron Spectrosc. Relat. Phenom. **39**, 69 (1986)
- 8.69. R. Weissmann, K. Miller, Surf. Sci. Rep. **1**, 261 (1981)
- 8.70. C. LeGressus, D. Massignon, R. Sopizet, Surf. Sci. **68**, 338 (1977)
- 8.71. F. Ohuchi, M. Ogino, P.H. Holloway, C.-G. Pantano, Surf. Interface Anal. **2**, 85 (1980)
- 8.72. A. Zalar, Mikrochim. Acta **12**, 435 (1980)
- 8.73. A.H. Clark, T.L. Michalka, J. Mally, J. Vac. Sci. Technol. **20**, 254 (1982)
- 8.74. W. Goepel, D. Schmeisser, Sens. Actuat. **25**, 325 (1987)
- 8.75. K.Y. Young, R.W. Hoffmann, Surf. Interface Anal. **10**, 121 (1987)
- 8.76. S. Ichimura, H.E. Bauer, J. Seiler, S. Hofmann, Surf. Interface Anal. **14**, 250 (1989)
- 8.77. C.-G. Pantano, T.E. Madey, Appl. Surf. Sci. **7**, 115 (1981)
- 8.78. S. Hofmann, Mater. Wiss. u. Werkstofftechn. **21**, 93 (1990)
- 8.79. *Physical Electronics Application Note 652* (2002)
- 8.80. D.W. Vance, J. Appl. Phys. **42**, 5430 (1971)
- 8.81. A. Zalar, S. Hofmann, Surf. Interface Anal. **12**, 83 (1988)
- 8.82. C.-G. Pantano, A.S. D'Souza, A.M. Then, Electron Beam Damage at Solid Surfaces, in *Beam Effects, Surface Topography and Depth Profiling in Surface Analysis*, ed. by A.W. Czanderna, C.J. Powell, T.E. Madey (Plenum Press, New York, 1998), pp. 39–96
- 8.83. D.R. Baer, D.J. Gaspar, M.H. Englhard, A.S. Lea, Beam Effects During AES and XPS Analysis, in *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, ed. by D. Briggs, J.T. Grant (IM Publications, Chichester, 2003), pp. 211–233

- 8.84. S. Hofmann, A. Zalar, Thin Solid Films **56**, 337 (1979)
- 8.85. H.E. Bauer, H. Seiler, Electron Microsc. **3**, 214 (1980)
- 8.86. G.B. Hoflund, Scann. Electron Microsc. **IV**, 1391 (1985)
- 8.87. S. Hofmann, Mikrochim. Acta **Part I**, 321 (1987)
- 8.88. S. Tanuma, T. Kimura, K. Nishida, S. Hashimoto, M. Inoue, T. Ogiwara, M. Suzuki, K. Miura, Appl. Surf. Sci. **241**, 122 (2005)
- 8.89. S. Hofmann, J.M. Sanz, Surf. Interface Anal. **6**, 75 (1984)
- 8.90. S. Hofmann, J.M. Sanz, Fres. Z. Anal. Chem. **314**, 215 (1983)
- 8.91. H.J. Dudek, Z. Angew. Phys. **31**, (1971) 331
- 8.92. B.G. Baker, B.A. Sexton, Surf. Sci. **52**, 353 (1975)
- 8.93. J. Cazaux, Appl. Surf. Sci. **20**, 457 (1985)
- 8.94. H.P. Chang, J.H. Thomas III, J. Electron Spectrosc. Relat. Phenom. **26**, 203 (1982)
- 8.95. K. Yoshihara, A. Tanaka, Surf. Interface Anal. **33**, 252 (2002)
- 8.96. J.C. Klein, C.P. Li, D.M. Hercules, J.F. Black, Appl. Spectrosc. **38**, 729 (1984)
- 8.97. S.J. Harris, Documentary Standards in Surface Analysis: The Way of the Future?, in *Handbook of Surface and Interface Analysis*, ed. by J.C. Rivière, S. Myrha, (Marcel Dekker, New York 1998), Appendix 5, pp. 907–927
- 8.98. D. Baer: Surf. Interface Anal. **43**, 1444 (2011)

Chapter 9

Typical Applications of AES and XPS

A survey of the analysis of surfaces, interfaces, and thin films in typical fields of materials science is shown in Table 1.1 (Chap. 1). In practice, the analytical task and strategy (Sect. 8.1) decide about sample preparation and handling (Sect. 8.3) [8.1, 8.11, 8.12, 9.1, 9.2]. Sample preparation can be performed either outside the UHV environment of the analysis system (*ex situ* preparation, Sect. 8.3.1) or inside the UHV system (in situ, Sect. 8.3.2). Summarized under these two categories, a survey of the main phenomena that are studied with surface analysis methods is given in Table 9.1. *Ex situ* preparation is usually performed in the laboratory atmosphere (e.g., with samples from outside sources) or in carefully controlled experimental environments (heat treatment and quenching, corrosion studies, etc.). In situ preparation is performed either directly in the analysis chamber or in attached preparation chambers (see Fig. 8.1).

To illustrate different types of applications, a few typical examples are summarized, most of them from the laboratory of the author.

9.1 *Ex Situ* Sample Preparation

Materials from outside sources are generally contaminated and have to be carefully cleaned, for example, by an ultrasonic cleaning bath (see Sect. 8.3.1). Samples prepared in the laboratory by cutting, abrasion, angle lapping, or ball cratering, may require similar treatment before introduction in the analysis chamber. Nevertheless, there always remains a thin contamination layer and, on metals and semiconductors, a native oxide layer of usually less than 3-nm thickness [9.3, 9.4]. As shown in Sects. 4.3.3.9 and 4.3.3.4, XPS and AES have the capability to analyze this layer and the material beneath (with limited accuracy). The contamination layer can be ignored when deeper layers or buried interfaces are of interest, which are most often accessed by sputter depth profiling (Sect. 7.1). A few typical application examples are given in the following.

Table 9.1 Survey of some of the main topics studied with AES and XPS, categorized in *ex situ* and in situ preparation

	<i>Ex situ</i> preparation	In situ preparation
Surfaces	Contamination	Layer deposition Initial oxidation Ion beam interaction Surface segregation and diffusion
Thin films and interfaces	Coatings and layered structures HT oxidation and corrosion Interfacial reactions and diffusion Interfacial segregation Implantation layers	Grain boundary segregation

9.1.1 Coatings and Layered Structures

The in-depth composition of (magnetron sputtered) hard coatings and that of the coating/substrate composition as related to sputtering parameters and residual gas atmosphere is frequently studied by AES and XPS [9.5–9.10] combined with sputter depth profiling [9.9, 9.10, 9.11] (see Sect. 7.1).

Quantitative AES from TiN coating analysis suffers from peak overlap of the N ($KL_{2,3}L_{2,3}$) and Ti ($L_{2,3}M_{2,3}M_{2,3}$) lines at 383–389 eV in the derivative mode [9.9] (see Sect. 4.1.2). From the various methods used by different researchers to overcome this difficulty, a very simple method of using the nonoverlapping Ti ($L_{2,3}M_{2,3}M_{4,5}$) at 418 eV as a reference to subtract the Ti contribution from the 383 eV peak and get the N contribution [9.9]. This approximate quantification is considerably improved when using factor analysis (FA) [9.12], principal component analysis (PCA), and linear least-squares fitting (LSS) methods [7.131, 9.13] (see Sects. 4.1.4 and 9.3).

In contrast to AES, XPS analysis of titanium nitride coatings can be performed straightforward since the Ti $2p_{1/2,3/2}$ doublet in TiN with the $2p_{3/2}$ peak at about 455 eV is in a different region than the N1s peak (395 eV) and separated from that in pure Ti by about 3.5 eV and by about 2 eV from the oxide-bonded [9.9, 9.14, 9.15]. However, an exact quantitative XPS analysis has to take into account the particularly strong loss peaks in TiN and TiAlN [9.14, 9.15] which were previously ignored [9.9]. As shown by Strydom and Hofmann in Fig. 9.1a [9.14, 9.16], electron energy loss spectroscopy (EELS) in the reflection mode (REELS) performed with an AES instrument (PerkinElmer SAM 600) at about the same primary energy (500 eV) as the XPS kinetic energy quantitatively discloses the loss peaks. These loss peaks have to be subtracted from the measured XPS spectrum for reliable quantitative analysis. The measured REELS loss peaks and their interpretations are summarized in Table 9.2 [9.16]. With these loss peaks, an improved spectral synthesis was performed by Bertóti et al. [9.15, 9.132] who additionally considered Ti oxides in

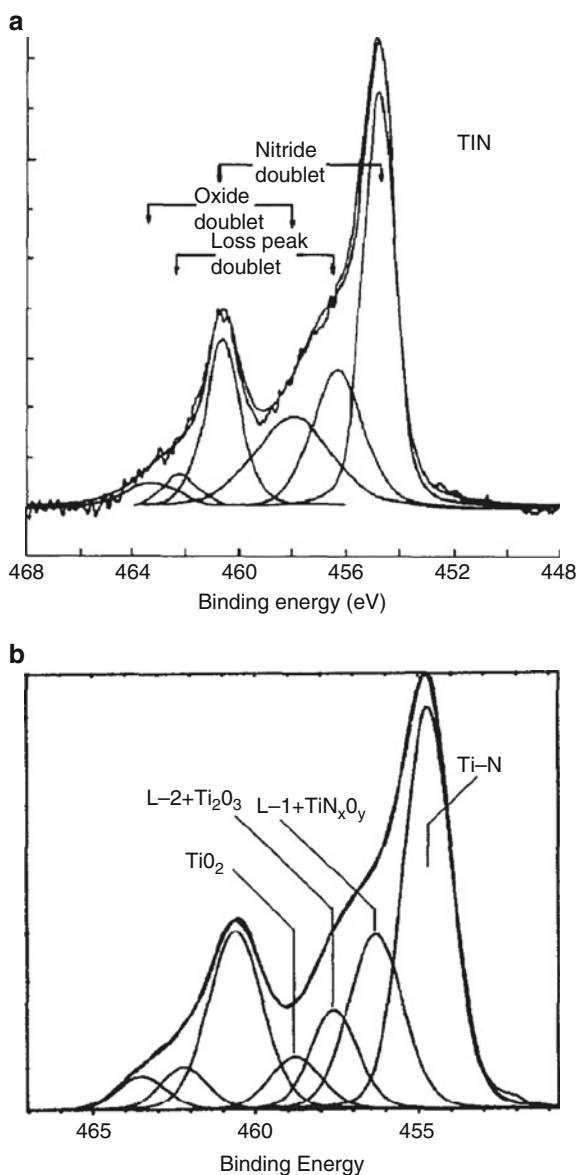


Fig. 9.1 XPS spectrum of the Ti $2p_{1/2,3/2}$ core level of plasma-nitrided TiN with oxygen. (a) Spectrum with main loss peaks determined by REELS [9.14]. (b) Spectrum represented by two loss doublets including oxynitride and oxide XPS peaks of lower valence states, $L-1+TiN_xO_y$ and $L-2+Ti_2O_3$ ((a) – from I. leR. Strydom and S. Hofmann [9.14], (b) – reproduced from I. Bertóti et al. [9.15], with permission of Elsevier B.V.)

Table 9.2 Energy losses and relative intensities obtained by reflection electron energy loss spectroscopy (REELS) on TiN and (Ti,Al)N

Material	Energy loss (eV)	Relative intensity (elastic peak = 1)	Loss peak designation
TiN	1.6	0.41	$t_{1g} \rightarrow t_{2g}$ (Ti3d-derived) intraband transition
	3.1	0.11	$2t_{2g} \rightarrow 3e_g$ transition
	6.2	0.17	N2p $\rightarrow$ Ti3d
	12.8	0.07	N2p $\rightarrow$ Ti4s
	22.6		TiN volume plasmon
	≈ 37		Ti3p $\rightarrow$ Ti3d
	≈ 48		Ti3p resonance
	≈ 61		Ti3s $\rightarrow$ Ti3d
(Ti,Al)N	1.55	0.20	Ti3d-derived intraband transitions
	3.0	0.15	Ti3d-derived intraband transitions
	6.3	0.17	N2p $\rightarrow$ Ti3d
	12.7	0.10	N2p $\rightarrow$ Ti4s
	22.0		(Ti,Al)N volume plasmon
	≈ 36		Ti3p $\rightarrow$ Ti3d
	≈ 48		Ti3p resonance
	≈ 62		Ti3s $\rightarrow$ Ti3d

From Ref. [9.16]

lower valence states (Ti_2O_3) and oxynitrides (TiN_xO_y) as seen in Fig. 9.1b, with the respective loss peaks L-1 and L-2 indicated in the figure.

XPS measurements of the valence band electron densities of hard coatings reveal the degree of metal–ligand bonding which can be correlated with the stoichiometry and mechanical properties of the coatings. Figure 9.2 shows valence band spectra (Mg $K\alpha$ X-rays) of TiN and TiAlN coatings obtained by magnetron sputter deposition with different N_2 pressures [9.16]. The higher nitrogen content decreases the electron density of the Ti3d band and shifts the Ti3p peak to higher binding energy. In (Ti,Al)N, the Ni2p band at about 4 eV binding energy is broadened substantially, because the broad 3p band of Al convolutes the Ni2p band.

The compositional in-depth distribution of thin films and coatings can be directly disclosed by depth profiling (see, e.g., Figs. 7.22 and 7.38). An example of a (Ti,Pd)N coating deposited with a slowly rotating substrate (5.5 rpm) in front of 3 sources, 2 for Ti and 1 for Pd, respectively, is shown in Fig. 9.3 [9.17]. Whereas the nitrogen content varies inversely with the nonreactive Pd, the Ti content is almost constant with depth. Besides the double frequency of the Ti source exposure, the higher reactivity and lower atomic mass enhance the broadening of its distribution.

9.1.2 Corrosion and High-Temperature Oxidation

Increasing the oxidation resistance of hard coatings by addition of a third component was studied extensively with AES and XPS. An example is shown in Fig. 9.4a [9.18] by the AES depth profile of a (Ti,Al)N layer after annealing for 5 h at

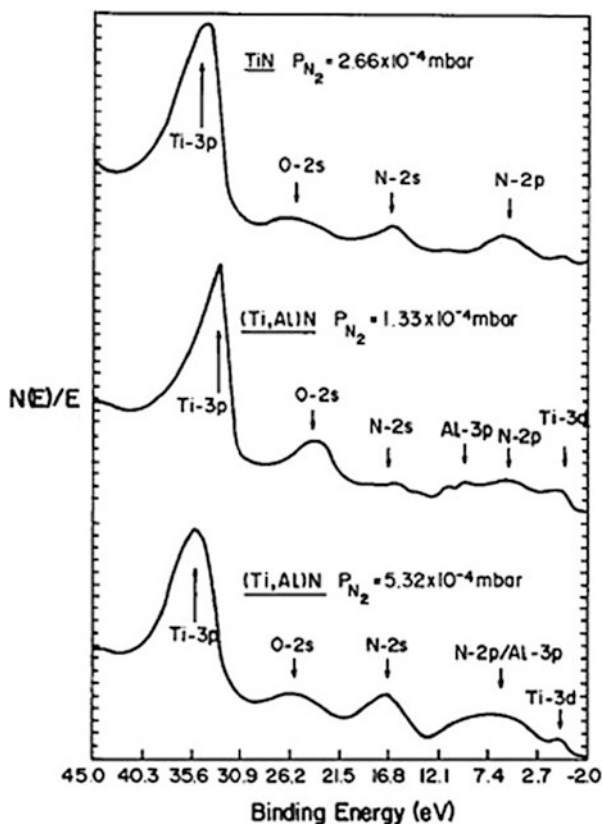


Fig. 9.2 Valence band XPS spectra of TiN and (Ti,Al)N coatings, magnetron sputtered with different N_2 partial pressures p_{N_2} given in the *inset* (From I. leR. Strydom and S. Hofmann [9.16])

650°C in air [9.18–9.20]. The APPHs were recorded for titanium (Ti2: 418 eV), aluminum (Al1: 45–72 eV, Al2: 1380–1402 eV, Al3: 66 eV), oxygen (O: 510 eV), carbon (C: 272 eV), and for the signal at 383 eV (N1) which contains an overlap of both the N 381 eV and the Ti 383 eV. Three regions can be qualitatively distinguished in the composition-sputtering time profile of Fig. 9.4a: surface oxide (0–9 min), interfacial mixed oxide/nitride (oxynitride) (9–18 min), and original nitride (>18 min). Comparison of peak energies and shapes of AES spectra in the oxide shows that oxynitride and nitride regions show only a slight shift for the Ti2 (418 eV) peak but a marked effect on the Al peaks. The high-energy Al2 peak ($KL_{2,3}L_{2,3}$) shifts from 1386 eV in the oxide to 1392 eV in the nitride. The respective shift of the low-energy ($L_{2,3}VV$) peak from 55 to 65 eV is evident from Fig. 9.4b. This enables distinction between Al in the oxide state (Al1–Al3) and in the nitride state (Al3), and thus to determine oxygen in Al oxide as depicted in Fig. 9.4c (upper picture), with the remaining oxygen bound to Ti in the interface. The N1

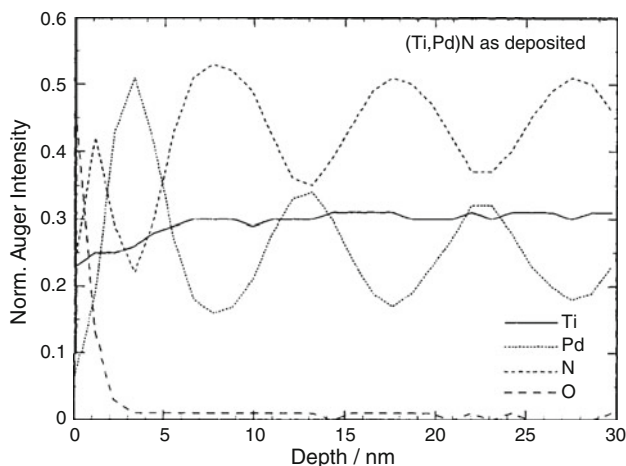


Fig. 9.3 AES depth profile of a magnetron sputtered (Ti,Pd)N coating with low frequency substrate rotation (From H.A. Jehn et al. [9.17])

contains both Ti and N contributions, and the latter can be corrected for the Ti 383-eV peak, roughly by subtracting 70% of the Ti2 (418 eV) peak [9.9]. This yields the “true” nitrogen intensity as shown in Fig. 9.4c (dashed line for N in upper picture). Assuming a constant amount of Ti bonded to N, we can estimate this amount from its proportionality to the true N curve (dashed line for Ti in Fig. 9.4c). This leaves oxygen not bonded to Al and Ti not bonded to nitrogen in the interlayer between the (Ti,Al)N and Al₂O₃, as shown in Fig. 9.4c, lower picture. In addition, a second N 1s peak was observed in XPS which is shifted by 4 eV from the nitride peak to higher binding energies. It can be ascribed to N in a metal–N–O bond which is an additional indication of an oxynitride layer. Taking the Ta₂O₅ equivalent sputtering rate ($\approx 5.5 \text{ nm min}^{-1}$), the outer oxide layer of almost complete Al oxide is about 50 nm thick. Compared to this scale, the difference in the attenuation lengths of O (510 eV) and Al (56 eV) is less than 1 nm and can be ignored (compare Figs. 7.1 and 7.2). Annealing of (Ti,Al)N coatings in air between 500°C and 800°C shows a gradual buildup of an oxide layer, which grows according to a diffusion law with an effective activation energy of 200 kJ mol^{-1} [9.19]. Al is depleted in the outer part of the (Ti,Al)N layer and enriched in the top oxide layer owing to selective oxidation of Al. The high mobility of Al in the nitride and the fact that the top oxide layer consists almost completely of Al₂O₃ are in agreement with the higher binding energy of Al in the oxide and its lower binding energy in the nitride as compared to Ti. The AES depth profiles and the differentiations between the chemical binding states of Al allow a clear distinction of a titanium oxynitride layer between the bulk (Ti,Al)N and the top Al₂O₃ layer. Figure 9.4c only gives a semiquantitative picture since some preferential sputtering of Al in (Ti,Al)N [9.18] was ignored, and, as discussed in [9.20], an additional correction for the Ti oxide bond to the 383 eV peak causes some underestimation of Ti oxide content. Application of target factor

Fig. 9.4 Surface layer of a (Ti,Al)N coating after 1 h annealing in air at 650°C. **(a)** AES sputter depth profile of the peaks O (510 eV), N1 (383 eV), Ti2 (420eV), Al1 and Al3 (see **(b)**), and Al2 (1386–1392), sputtering rate (Ta₂O₅) is $\approx 16 \text{ nm min}^{-1}$; **(b)** low-energy valence band Auger peaks (derivative mode) of Al ($L_{2,3}$ VV) in oxide (Al1 in **(a)**) and nitride (Al3 in **(a)**). Surface layer of a (Ti,Al)N coating after 1 h annealing in air at 650°C. **(c)** Chemical bonding in the AES depth profile of **(a)**: Evaluation of the O (510 eV) intensity profile according to aluminum oxide and the N content in ($N1 = N + Ti$) using the Ti2 (418 eV) peak for Ti content, which leaves oxygen and oxygen-bound titanium in the interlayer (Ti–oxynitride) (From S. Hofmann and H. A. Jehn [9.18])

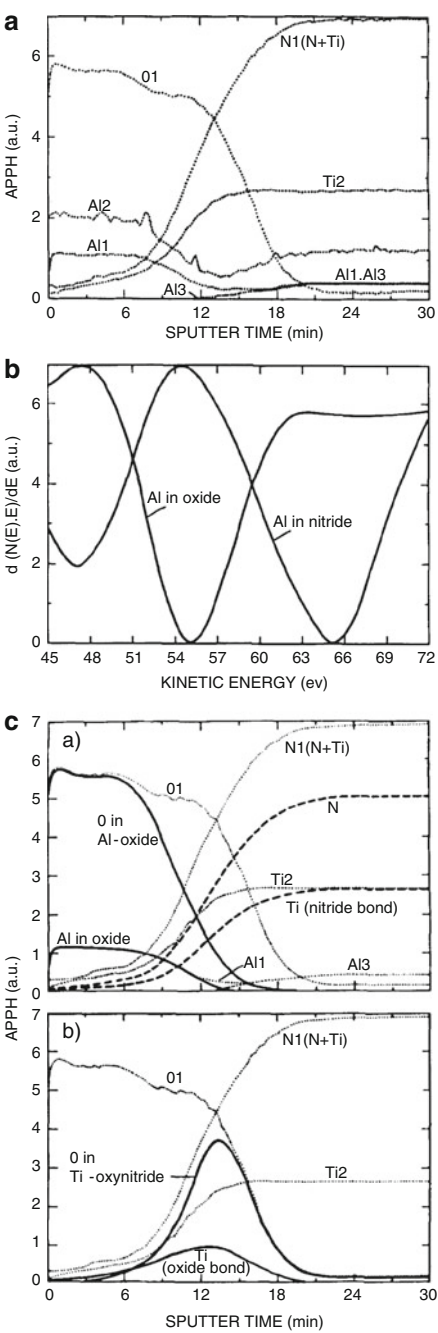
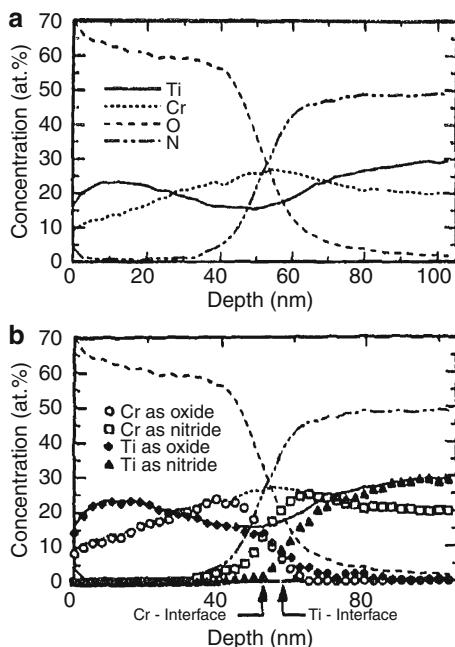


Fig. 9.5 AES sputter depth profile of $(\text{Ti}_{0.6}\text{Cr}_{0.4})\text{N}$, oxidized at 700°C for 1 h. (a) Approximate concentrations were calculated using the sensitivity factors given in Ref. [4.21]; (b) Result of factor analysis applied to the Ti and Cr spectra used for the depth profile in (a). Arrows show the location of the oxide/nitride interface of Ti and Cr, respectively (From Y. Otani and S. Hofmann [9.21])



analysis (software not yet available at that time) will be the better method here, as shown below.

The addition of different amounts of Cr to TiN results in a rather complex oxidation behavior [9.21]. An example is shown in Fig. 9.5a where the AES sputter depth profile of $(\text{Ti}_{0.6}\text{Cr}_{0.4})\text{N}$ after oxidation in air for 1 h at 700°C is shown. Target factor analysis was successfully applied to differentiate between the contributions of Cr and Ti in oxide- and nitride-bonding states in a quantitative manner as depicted in Fig. 9.5b. Obviously, the location of the oxide/nitride interface of Ti is deeper than that of Cr (see arrows in Fig. 9.5b). This can be interpreted by inward oxygen diffusion through the mixed Ti–Cr oxide layer that promotes the oxidation of TiN. Systematic and quantitative studies of the oxidation behavior of $(\text{Ti}_{(1-x)}\text{Cr}_x)\text{N}$ coatings with different mole fractions x of Cr_x between 350°C and 800°C . The mutually restrictive influence of Ti oxide on the diffusion of Cr and of Cr oxide on the diffusion of O results in a minimum of the oxidation rate for coatings with the composition $(\text{Ti}_{0.6}\text{Cr}_{0.4})\text{N}$, which at 400°C is about 20 times lower than that of TiN and 5 times lower than that of CrN [9.20].

Studies of thin surface layers formed by corrosion and passivation have been and still are one of the major applications of XPS and AES [9.22–9.27]. Depth profiling of passive layers on Fe–Cr-based alloys by angle-resolved XPS and sputter depth profiling with XPS and AES [9.23–9.25] have led to a better understanding of the

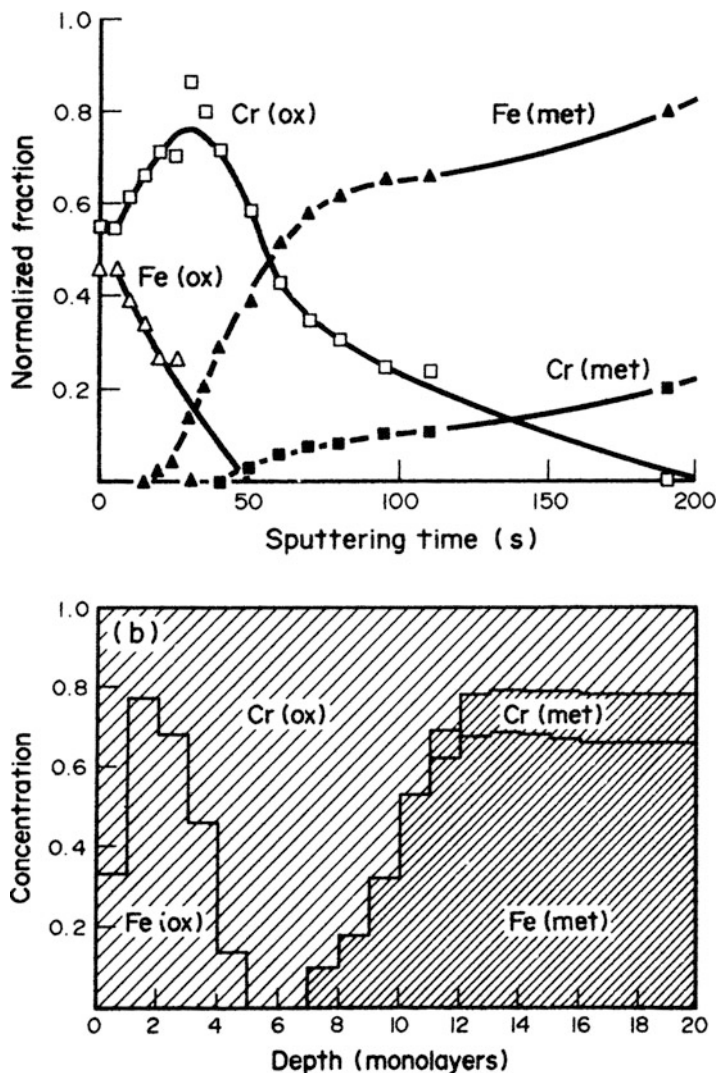


Fig. 9.6 Chemical composition of a passive layer on Fe-18 at% Cr (24 h in 0.5N H₂SO₄ at 1 V SHE). (a) Normalized fractions of the metallic (met) and oxide (ox) standard components of Fe and Cr in the measured MVV Auger spectra (20–70 eV), obtained from the corresponding AES sputter depth profile by target factor analysis; (b) concentrations of the elements in metallic and oxidic states after fitting all fractions of the respective components to $I(z)/I^0$ in (7.26), Sect. 7.1.7 (represented by the *full curves* in (a)) (Adapted from J. Steffen and S. Hofmann [9.25])

mechanism of passive layer formation [9.26]. An example of an AES sputter depth profile of the passive layer formed on an Fe-18 at % Cr alloy (24 h in 0.5 N H₂SO₄ at 1 V SHE) is shown in Fig. 9.6 [9.25]. Figure 9.6 shows the result of factor analysis applied to the AES raw data, which still suggest a mixed oxide of Cr and Fe in

the passive layer. Application of the SLS model using (7.16) in Sect. 7.1.7 shows that the mixed oxide is confined to the very first surface layer above a layer of pure chromium oxide. This result was confirmed by Mischler et al. [9.24], who only corrected for the electron escape depth effect via (7.7) in Sect. 7.1.2 (ideal layer removal). XPS is frequently used to characterize fine features of passivation of stainless steels [9.27].

9.1.3 *Interfacial Reactions and Diffusion*

Reactions at internal interfaces can be studied by sputter depth profiling or via interfacial fracture (see grain boundary segregation, Sect. 9.1.4). Diffusion across interfaces and formation of new phases at interfaces are disclosed in great detail [9.20]. An example of carbide formation at a C/Ti interface was already shown in Sect. 7.1.2.3 (Fig. 7.5). Silicide formation and interdiffusion in various Si/Me/Si sandwich layers with Me = Al, Ni, Co, Cr, Zr, and W were studied by Zalar et al. [9.28] with AES depth profiling after linear programmed temperature increase up to 150–1000°C. The change of the interface width with temperature, determined from the profiles after various final temperatures was used to quantitatively determine the interdiffusion coefficient of these systems [9.28]. In Si/Al/Si sandwich layers, more precisely amorphous Si/polycrystalline Al/amorphous Si, a special phenomenon was observed, namely, layer exchange between Al and Si as shown in Fig. 9.7 [9.29]. This was the starting point of a number of papers by Wang and coworkers [9.30–9.33] who found Al-induced crystallization of amorphous Si and subsequent aluminum-induced layer exchange, monitored by AES depth profiles as seen in Fig. 9.8 [9.32]. Finally, a consistent, quantitative thermodynamic interpretation of both phenomena was presented [9.33].

One of the most successful applications of the MRI model in obtaining interdiffusion data at interfaces by quantitative depth profiling was shown in Sect. 7.1.8 (Fig. 7.34, [9.33]) for Si/Ge nanolayers. Diffusion lengths of about 1 nm were found to be large enough to determine diffusion coefficients.

9.1.4 *Interfacial Segregation*

Quantitative AES and, to a minor extend, XPS, applied to surfaces generated by intercrystalline fracture are the most frequently used means to study the thermodynamics of grain boundary segregation [9.34–9.54]. Special experimental means were developed (see Fig. 8.2, Sect. 8.3.2) to make both surfaces of an intercrystalline fracture accessible to surface analysis (see Sect. 4.3.3, Figs. 4.38, 4.39) or to obtain at the same time free surface and grain boundary composition [9.34–9.46]. An example of the latter approach is shown in Fig. 9.9 [9.44, 9.45]. Oriented bicrystals of Ni with 1.2 at % In, where the surface of one single crystal surface before joining was specially prepared by generating a pattern of cavities of about 100- μ m diameter

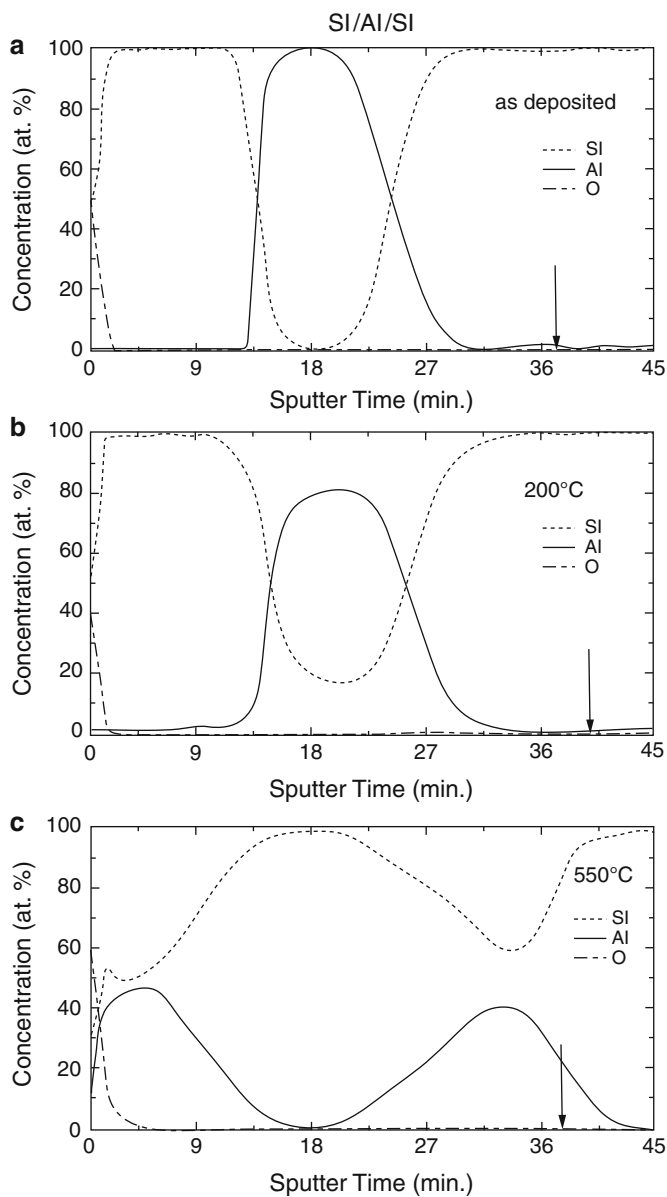


Fig. 9.7 AES sputter depth profiles of a-Si/Al/a-Si (60/50/60 nm) on Si(111): (a) as deposited by magnetron sputtering; (b, c) after linear programmed heating from room temperature up to 200°C and 550°C, respectively. Depth profiling with 3 keV Ar^+ ions at 56° incidence angle. Arrows denote the layer structure/substrate interface (Reproduced from A. Zalar et al. [9.29])

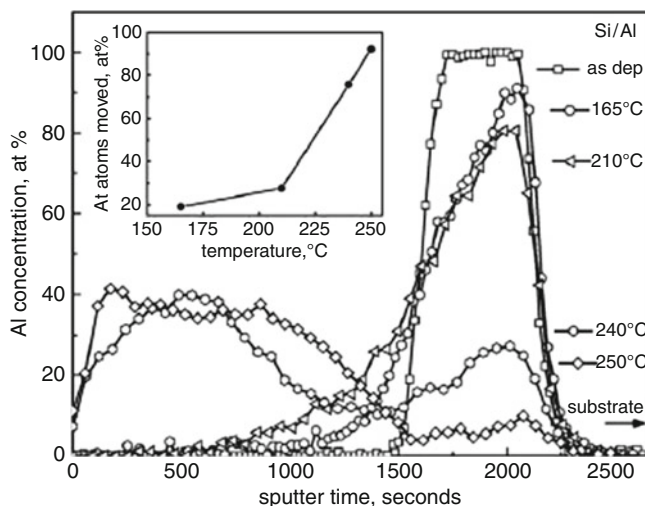


Fig. 9.8 AES sputter depth profiles of a bilayer of Si/Al (150/50 nm) on SiO₂/Si (50/510 nm) as deposited and after annealing at 250°C at increasing times indicated in the figure (Reproduced from D. He et al. [9.32], with permission of Elsevier B.V.)

were annealed at temperatures between 820 and 1311 K and subject to fracture in an AES chamber after quenching. Figure 9.9a shows the fracture surface (secondary electron (SE) picture in the SE mode of a Phi 600 SAM instrument) with grain boundary (GB) and free surface (FS) areas. Typical AES spectra of both parts are presented in Fig. 9.9b. Whereas both parts contain different amounts of In, only the free surface contains S. An AES line scan of In, S, and Ni across the surface depicted in Fig. 9.9c illustrates the difference. The temperature dependence of the amounts of In and S in both locations, normalized to Ni intensity, is shown in Fig. 9.9d. Quantitative evaluation with the expressions for quantification of segregation layers given in Sects. 4.3.3 (relation (4.123)) and 4.4.3 revealed the segregation enthalpies and interactive cosegregation between In and S at the free surface but not at the grain boundaries.

The strong influence of some ppm of Bi on the decrease of grain boundary cohesion of Cu was the starting point of a number of AES studies [9.47, 9.48, 9.49]. Quantitative evaluation (see Sects. 4.3.3 and 4.4.3) disclosed that the “hump” in the temperature of dependence of grain boundary enrichment in Fig. 9.10 corresponds to a sudden change from two to one monolayer of Bi (at about 700°C). Correct evaluation of AES raw data is a prerequisite for this result (see critical remarks in [9.36]). Figure 9.10 shows a typical result from the detailed study of Chang et al. [9.49] which led to new interpretations of the Fowler interaction terms [9.34, 9.35] by a so-called prewetting model and finally to a new generalized Langmuir–McLean concept based on an “interfacial coherent energy” term [9.50].

The dependence of grain boundary enrichment on solute solubility found by Seah and Hondros [9.51] is strongly influenced by grain boundary orientation [9.34, 9.40,

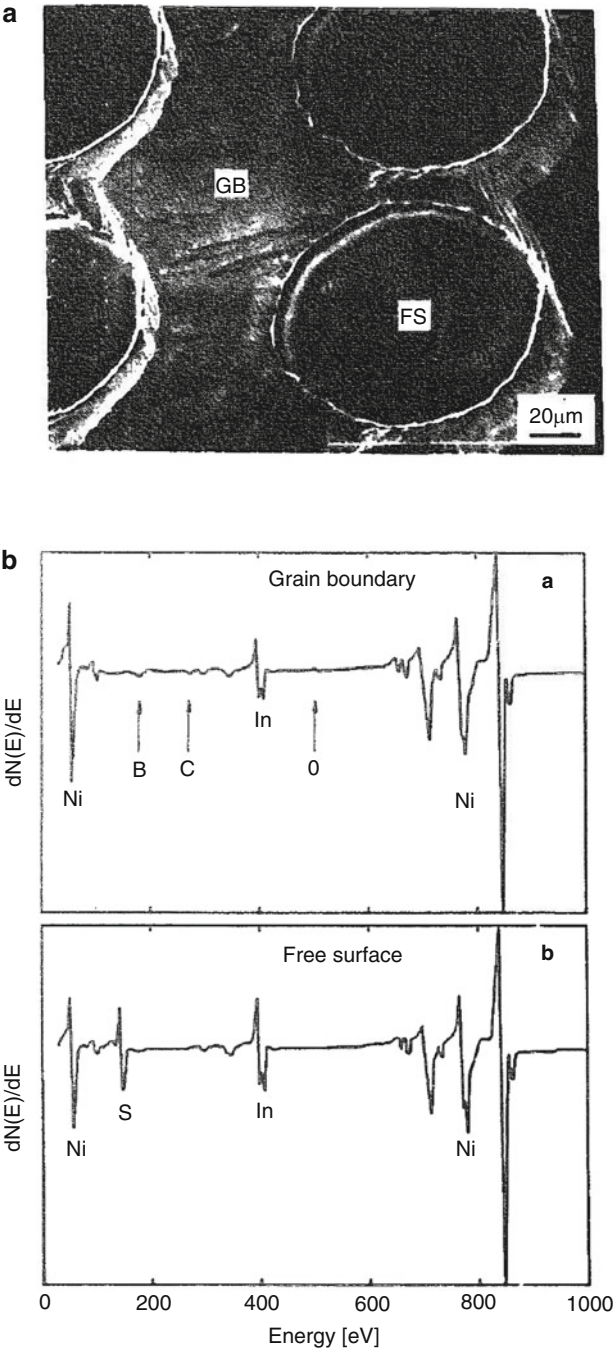


Fig. 9.9 (continued)

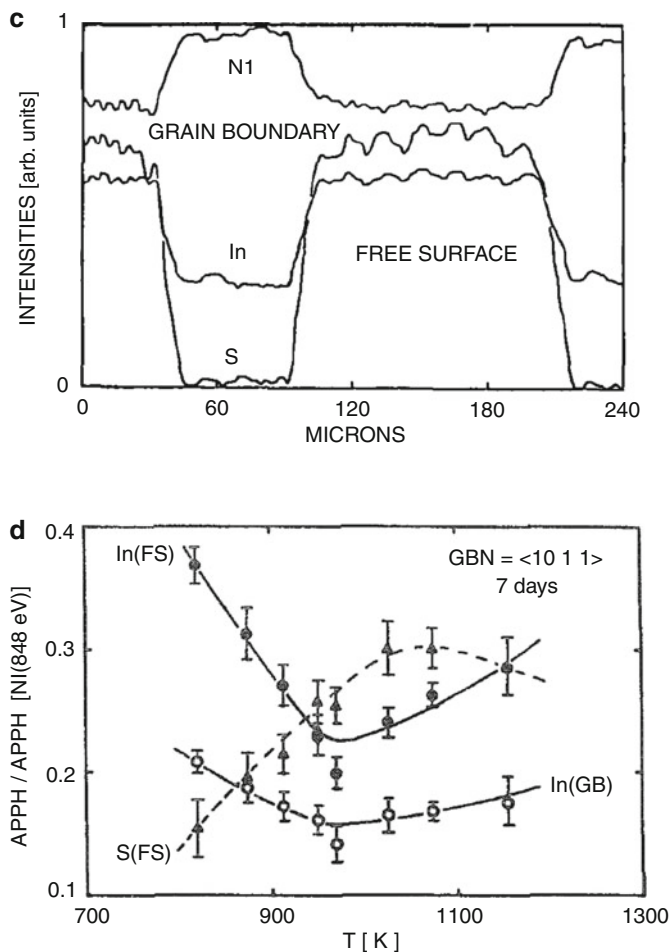


Fig. 9.9 (continued) Interfacial segregation in Ni–In–S system. (a) Typical fracture surface of a bicrystal showing grain boundaries (GB) and free surfaces (FS) of identical orientation; (b) AES spectra obtained from the grain boundary (a) and the free surface (b) of a bicrystal with grain boundary orientation (511). Aged for 1 day at 1119 K. Interfacial segregation in Ni–In–S system. (c) AES line scan (depicted in (a) as a fine *bright horizontal line*). The intensities (differences of peak and background count rates in the integral mode) of all observed elements are rather uniform at the grain boundary as well as the free surface. Small variations are due to geometrical features of the analyzed surfaces. (d) Temperature dependence of the APPH ratio of In(404 eV) and S(152 eV) to Ni(848 eV) at the grain boundary (GB) and at the free surface (FS) of the as-quenched specimen with grain boundary orientation $\langle 10 \ 1 \ 1 \rangle$ aged for 7 days (From T. Muschik et al. [9.44,9.45])

9.41]. This fact caused Watanabe et al. [9.52] to propose a three-dimensional so-called grain boundary segregation diagram with the enrichment factor as a function of both solid solubility and grain boundary orientation. The comprehensive work of Lejček and Hofmann [9.35] on anisotropy of grain boundary segregation free

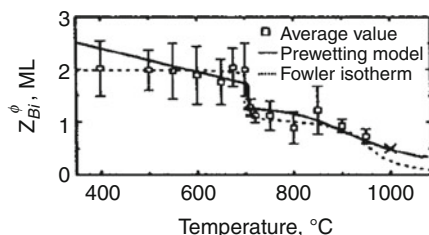


Fig. 9.10 Annealing temperature dependence of grain boundary segregation of 25 at. ppm Bi in Cu. The *open circles* are quantified values of the amount of Bi (in monolayers) measured after in situ fracture in a SAM 600 Auger spectrometer ($\times$ denotes nonbrittle fracture). Two types of theoretical predictions, prewetting model and Fowler isotherm, are indicated with *full* and *dashed lines* (From L.-S. Chang et al. [9.49])

enthalpy of Si, C, and P in α -iron studied by quantitative AES at fracture surfaces of oriented bicrystals resulted in the first experimental grain boundary segregation diagram depicted in Fig. 9.11 [9.53], where the enrichment factor is replaced by the more appropriate grain boundary segregation enthalpy. After more refined measurements including vicinal surfaces and other tilt boundaries [9.34, 9.54], important consequences emerged: The enthalpy–entropy compensation effect for grain boundary segregation as well as a model of predicting grain boundary segregation parameters [9.34, 9.35]. Finally, the concept of selecting a texture with reduced segregation by the so-called *grain boundary engineering* [9.55–9.57] was proposed.

Accurate measurements of the composition of surfaces require negligible surface contamination or its careful control [9.58]. This is particularly harmful if the segregant is a constituent of the residual gas atmosphere, such as carbon or oxygen [9.59]. A useful approach to distinguish between fracture surface amount of C and O is to follow the time dependence of the respective Auger intensities and those of the underlying metallic elements and extrapolation of the dependencies to zero time [9.59]. Nevertheless, carbon contamination is presumably the reason of discrepancies of carbon segregation parameters found by different researchers [9.34].

9.1.5 Implantation Layers

Ion implantation in solids is frequently used for doping in semiconductors and fabrication of shallow junctions and for generating new compounds of conducting layers, insulators, or high bandgap semiconductors [9.60, 9.61]. Whereas low-energy ion implantation can be performed in situ with the auxiliary ion gun (see below), high-energy ion implantation in the range of > 10 nm requires special accelerators and therefore *ex situ* preparation. Characterization of the products as received

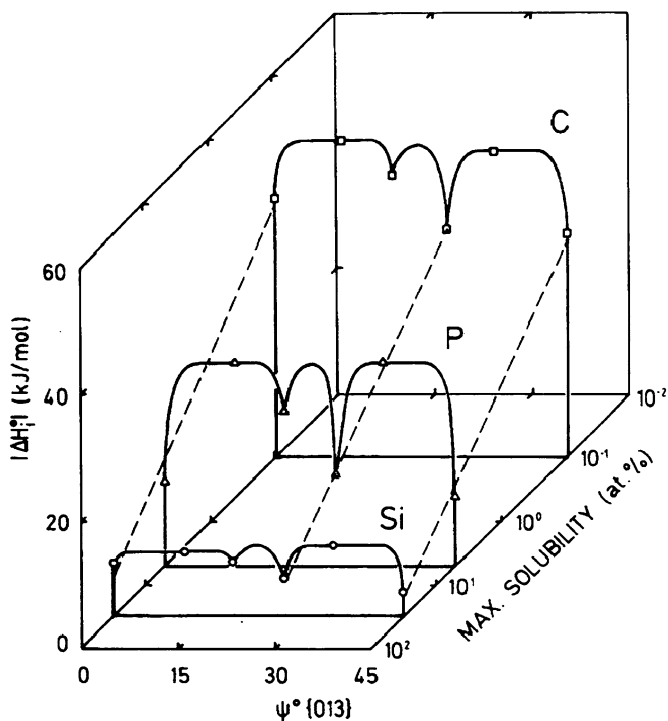


Fig. 9.11 Grain boundary segregation diagram for the $36.9^\circ[100]$ tilt grain boundaries in α -iron. The segregation enthalpy, ΔH_i^0 , for Si, P, and C is plotted as a function of the solid solubility limit X_i^* (improved $T \ln X_i^*$ [9.34, 9.54]) and the boundary orientation characterized by the deviation angle ψ° from the $\{013\}$ symmetrical orientation in $36.9^\circ[100]$ tilt bicrystals (From S. Hofmann and P. Lejček [9.53])

and after annealing is preferably done with sputter depth profiling in combination with XPS or AES. Both are used to disclose chemical bonding states. However, newly generated phases in semiconductor material with covalent bonds are difficult to distinguish by chemical shift as compared to metals [9.61–9.64]. Here, factor analysis applied to Auger spectra is able to disclose the in-depth distribution of new phases, as shown, for example, by Morant et al. [9.61] who identified SiBCN and SiBN compounds in that way after N^+ , C^+ , and BF_2^+ implantation in Si with energies of 25, 21, and 77 keV, respectively.

A promising approach to characterize heterogeneous materials or phase mixtures on the nm scale using plasmon loss information of low- and high-energy Auger spectra (e.g., LVV and KLL of Si) was demonstrated by Steffen and Hofmann [9.63, 9.64]. Figure 9.12a shows the depth profile of the chemical states of Si after a high-dose Si^+ irradiation of a carbon-implanted sample [9.64]. The fractions of the elemental and the carbide states of silicon, Si(Si) and Si(SiC), respectively, as a function of depth are obtained by linear least-squares fitting of the respective

standard spectra (principal components) shown in Fig. 9.12b. The amount of elemental Si is proportional to the APPH of the Si LVV spectrum. Plasma oscillations describe the state of matter and represent a significant phase property of the characteristic excitation volume. Plasmon energies for different modifications of Si and C are summarized in Table 9.3. They contain information about the electron density and in addition about the shape and size of the excited volume. Hence, phases and their size distribution in nanometer dimensions can be identified by plasmon energy measurements. The schematic picture in Fig. 9.12c elucidates the identification of the approximate minimum or maximum size of the particles by plasmon loss measurements near the respective AES peak, since the loss range detected is of the order of the IMFP [9.64].

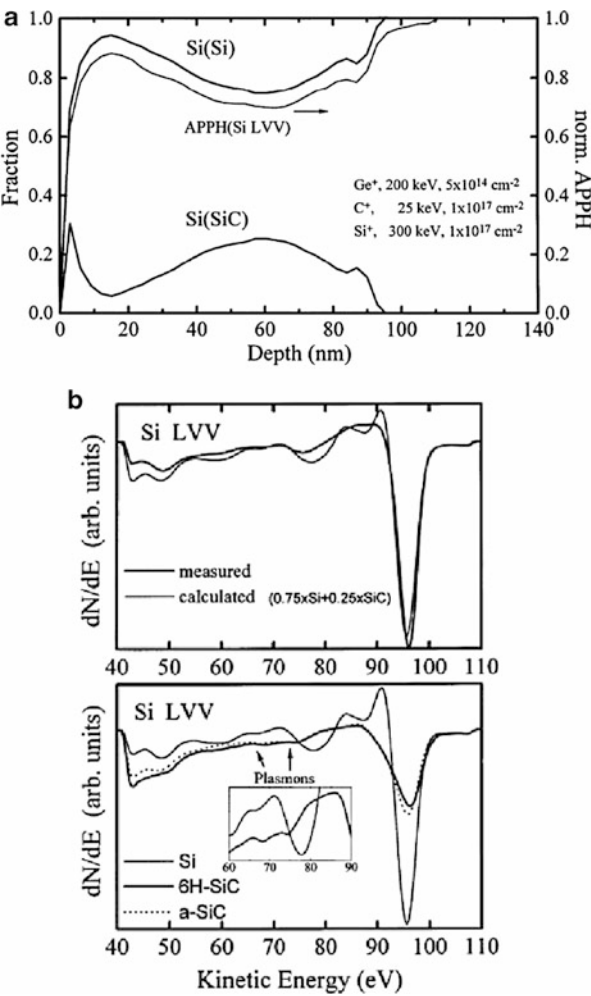


Fig. 9.12 (continued)

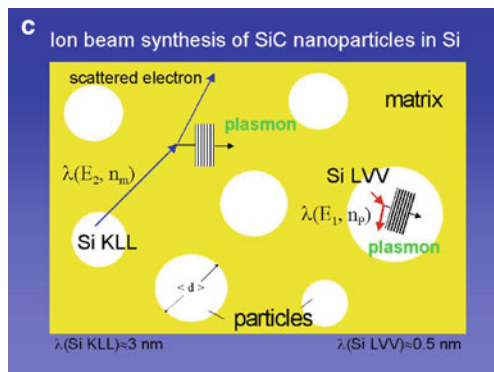


Fig. 9.12 (continued) Depth profile of the chemical states of Si after a high-dose Si^+ irradiation of the carbon-implanted sample. (Low-dose Ge^+ implantation was applied previously for amorphization.) (a) The fractions of the elemental and the carbide states of silicon, $\text{Si}(\text{Si})$ and $\text{Si}(\text{SiC})$, respectively, as a function of depth are obtained by least-squares fitting of the respective standard spectra shown (b). The amount of elemental Si is proportional to the APPH of the Si LVV spectrum. (c) Scheme of the inhomogeneous C^+ -implanted Si matrix with electron density n_m and SiC nanoscale particles with electron density n_p . The IMFP of Si KLL electrons with $E_2 = 1616 \text{ eV}$ is about $\lambda(E_2, \text{nm}) \approx 3 \text{ nm}$, larger than the average particle diameter $\langle d \rangle$. Therefore, plasmon excitation within SiC particles is not very likely compared to such events within the silicon–carbon matrix. In contrast, about 63% of Si LVV electrons with $E_1 = 90 \text{ eV}$ suffer inelastic scattering after a distance of only $\lambda(E_1, \text{nm}) \approx 0.5 \text{ nm}$ and cause plasmon excitations in both matrix and particles corresponding to n_m and n_p (From H.J. Steffen [9.64], with permission of J. Wiley & Sons Ltd.)

Table 9.3 Experimental and theoretical plasmon energies for different phases of silicon and carbon

	E_{exp} (eV)	E_{theor} (eV)
Si (cryst.)	16.7	16.6
Si (amorphous)	16.3	
SiO_2 (α -quartz)	23.6	24.2
SiC (α, β)	22.1	22.9
C (graphite)	7; 27	13; 22
C (diamond)	33.3	31
C (amorphous)	25	24

After Ref. [9.65]

9.1.6 Further Methods and Materials

For methods and materials for which the author has no genuine experience, the reader is referred to other work. For example, a very good survey on XPS on organic materials in adhesion is given by Watts [9.66]. Tribology [9.67] and catalysis [9.68] are frequently studied with XPS and AES. Besides the traditional materials such

as metals, semiconductors, ceramics [9.69, 9.70] and polymers, biomaterials [9.71, 9.72] are more and more subject to surface analysis, despite obvious limitations by beam effects (see Sect. 8.6)

9.2 *In Situ* Sample Preparation

Studies of clean, well-defined surfaces require preparation *in situ*, i.e., in the analysis chamber with the advantage of direct observation of the kinetics of change. Alternatively, an attached vessel is used from which transfer to the analysis chamber under UHV conditions is possible (see Sect. 8.3.2 and Fig. 8.1). Most often, chemical changes on the surface by adsorbed material, reactions with gases, and segregation from the bulk are the aim. Therefore, some examples are given in Sects. 4.3.3 and 4.4.3. A few typical examples are added here.

9.2.1 *Surface Layer Formation by Deposition*

Layer growth mechanisms during evaporation are frequently studied by AES and XPS and can be quantitatively disclosed according to expressions presented in Sect. 4.3.3.7 (see Fig. 4.36). Reactions with the substrate resulting in chemical changes of the substrate/film interface can also be studied *in situ*. An example is shown in Fig. 9.13, revealing the initial stages of the interface formation between ultrathin Ti layers and α -Al₂O₃ (0001) substrates studied at room temperature by *in situ* AES [9.73]. Applying a low-density primary beam (3 keV, $\leq 0.010 \text{ Acm}^{-2}$) and recording spectra every 5 min, it was assured that any measurable electron-beam effect is precluded (tested for 45 min on clean Al₂O₃) (see Sect. 8.6.1). In Fig. 9.13a, the development of the low-energy Auger spectra with (nominal) Ti film thickness (derived from quartz microbalance evaporation monitor) shows appearance of the metallic Al L_{2,3} VV peak in addition to the cross-transition oxide peak Al(L_{2,3})O(L_{2,3})O(L_{2,3}). This is attributed to the reduction of the sapphire (0001) surface by titanium. In comparison with the measured standard spectra of Ti, Ti₂O₃, and TiO₂ (and with TiO from [9.74]), the development of the ratios of the APPHs of (Ti LMV)/(Ti LMM), typical for these bonding states, with thickness is shown in Fig. 9.13b. The start with TiO-like bonding in the beginning shifts toward pure metallic Ti with increasing thickness. This fact and further quantitative analysis shows that the oxide of Ti is confined to the interface.

In an AES study of the Sc-O/W(100) system, Nakanishi et al. [9.75] have demonstrated the necessity of backscattering correction for thin layer quantification (see Sect. 4.4.3) when evaporating Sc on W (with $[1 + r_{\text{W,E(Sc)}}]/[1 + r_{\text{Sc,E(Sc)}}] = 1.31$). They also show how to model surface concentration changes induced by phase transition in combination with oxidation, surface segregation, and diffusion.

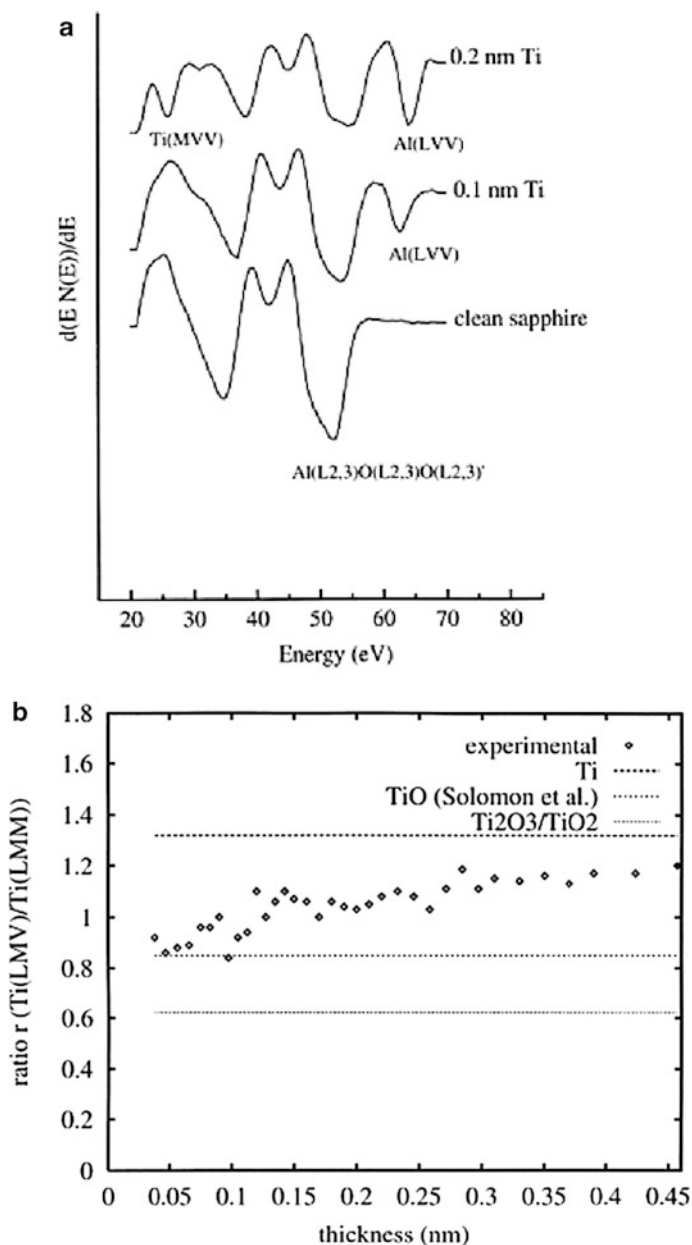


Fig. 9.13 Derivative low-energy Auger spectra of the clean (0001) sapphire surface and after deposition of 0.1 and 0.2 nm Ti. (a) The appearance of metallic Al LVV transition is clearly visible, indicating transfer of O to Ti. (b) Variation of the (Ti LMV)/(Ti LMM) ratio (APPH) (open symbols) compared to the ratios for Ti, Ti₂O₃, and TiO₂ from (a) and TiO from Ref. [9.74] (dotted lines) (From S. Bernath et al. [9.73])

9.2.2 *Early Stages of Oxidation*

9.2.2.1 Oxidation of Pure Metals

Since the pioneering work of Holloway and Hudson [9.76] (cited more than 420 times) on the reaction kinetics of oxygen with Ni(100) surfaces studied with AES, the early stages of oxidation of elements and alloys were studied frequently with AES [9.76–9.86], electron energy loss spectroscopy (EELS) [9.86–9.88] and XPS [9.77, 9.78, 9.83, 9.89–9.92], as well as with AES and XPS combined [9.77, 9.78, 9.92]. In general, the latter work reveals similar or complementary results, thus disproving the argument that AES is less useful for surface reaction studies than XPS. As discussed in Sect. 8.6.1, high electron-beam intensity in AES has to be avoided. However, special caution applies for XPS too with respect to effective electron generation (see Sect. 8.6.2). Most authors agree with the finding that the initial oxidation process on metal surfaces as a function of oxygen dose (usually given in Langmuir (L) units, $1 \text{ L} = 1 \times 10^{-6} \text{ Torr s} = 1.33 \times 10^{-4} \text{ Pa s}$) can be divided in three distinct stages [9.76, 9.80–9.93]: (i) dissociative chemisorption [9.93] of oxygen on the surface (typically 0...5 L), (ii) formation of nuclei of oxide which grow until coalescence to a uniform layer (typically 5–50 L), and (iii) further growth of the oxide film in thickness, usually following a logarithmic law as predicted by the Mott–Cabrera theory and subsequent improvements [9.94–9.96], up to a limiting thickness of the order of 1–2 nm. A typical example of the initial oxidation of Ni is presented in Fig. 9.14 [9.81], where the oxygen AES signal intensity is plotted as a function of the oxygen dose. Using factor analysis (see Sects. 4.1.4 and 9.3), the oxygen signal was decomposed in two principal components: chemisorbed oxygen (slightly shifted to lower binding energy) and oxygen in oxide bond. The three stages described above can be clearly distinguished. These findings were confirmed for Cr by Palacio and Mathieu [9.83], who extended the application of factor analysis to the metal peak. Low-energy LVV peaks in AES are particularly useful for the study of submonolayer and monolayer processes [9.80, 9.81]. In contrast, XPS peaks with higher energy and therefore larger attenuation lengths are better suited for the study of interface layers through overlayers [9.77]. An early example of the initial stages of the interaction of Ta with oxygen disclosed by XPS is shown in Fig. 9.15a [9.77]. Using peak decomposition according to the doublet binding energies for the different oxide states presented in Table 9.4, the development of the surface oxide layer formation is disclosed (see also Fig. 3.5 for Ta $4f_{7/2,5/2}$ peak decomposition to different oxide states applied to ion bombardment reduced Ta_2O_5). The metallic Ta peak (Ta^0) represents the expected decay with the growth of the oxide layer, whereas at higher dose ($>10 \text{ L}$), growth of the full Ta_2O_5 pentoxide layer (Ta^{5+}) follows that of the oxygen O1s signal. Most interesting is the behavior of the suboxides. At low dose, mainly TaO is generated (Ta^{2+}) and some TaO_2 (Ta^{4+}). After about 5–10 L, these suboxides form a stable, time-independent interface layer which is clearly recognized by the steady decrease of the Ta^{2+} intensity beginning at about 5 L and that of the Ta^{4+} from

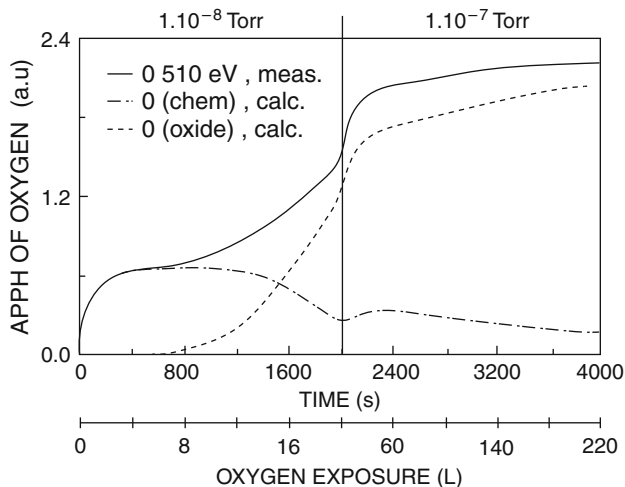


Fig. 9.14 Measured O(KL_{2,3} L_{2,3}, 510 eV) Auger peak-to-peak height (APPH) as a function of oxygen exposure and time for polycrystalline Ni. The fractions of chemisorbed and oxide oxygen, O(chem) and O(oxide), were calculated from the decomposition of the oxygen signal in these two principal components by factor analysis. Note the pressure change from 1×10^{-8} to 1×10^{-7} Torr at 2000 s (20 L) (From J. Steffen and S. Hofmann [9.81])

Table 9.4 Binding energies, E_b , of Ta in different oxide states (see also Chap. 3, Fig. 3.5)

	Ta	TaO	TaO ₂	Ta ₂ O ₅
E_b (eV) 4f _{7/2}	21.8 ± 0.2	23.8 ± 0.4	25.7 ± 0.4	26.8 ± 0.4
E_b (eV) 4f _{5/2}	23.6 ± 0.2	25.6 ± 0.4	27.5 ± 0.4	28.6 ± 0.4

From Ref. [9.77]

about 10 L onward. The Ta²⁺ signal decays more pronounced than the Ta⁴⁺ signal, despite similar energy. This fact indicates that TaO is adjacent to the metal and TaO₂ above TaO. Presumably, TaO represents subsurface oxygen dissolved in the metal [9.77]. Thus, the layer structure depicted in Sect. 4.3.3, Fig. 4.40b, is developing for oxygen dose >10 L, with expressions (4.127a–c) describing quantitatively the relations between layer and interface layer thickness and intensities (see Fig. 4.46 in Sect. 4.3.3.10). The linear dependencies for logarithmic scale of pt (for $pt > 10$ L) are explained by a logarithmic growth law with oxygen exposure described by the relative oxide layer thickness $d/(\lambda \cos \theta) = 0.29 + 0.03 \ln(1 + pt)$ [9.77]. The latter equation has to be inserted in expressions (4.127a–c) (depicted in Fig. 4.46) to yield the lines in Fig. 9.15a. The same expression is shown in Fig. 9.15b as the lower straight line, fitted to the full circles referring to $d/(\lambda \cos \theta)$ from (4.127c) and the points for Ta⁰ in Fig. 9.15a, for which $I^0(pt = 0)$ is known. Similar results were obtained for Nb, with shifted relative thickness values because of different λ values [9.77]. The relative thickness of the metal/oxide interface layer can be determined with (4.127b) based on the data in Fig. 9.15a. It is seen that at 10 L, the surface layer consists basically of the suboxide TaO₂, with a thickness of about 0.6 nm (with $\lambda \cos \theta = 1.9$ nm) [9.77]. This is the interfacial layer which stays practically

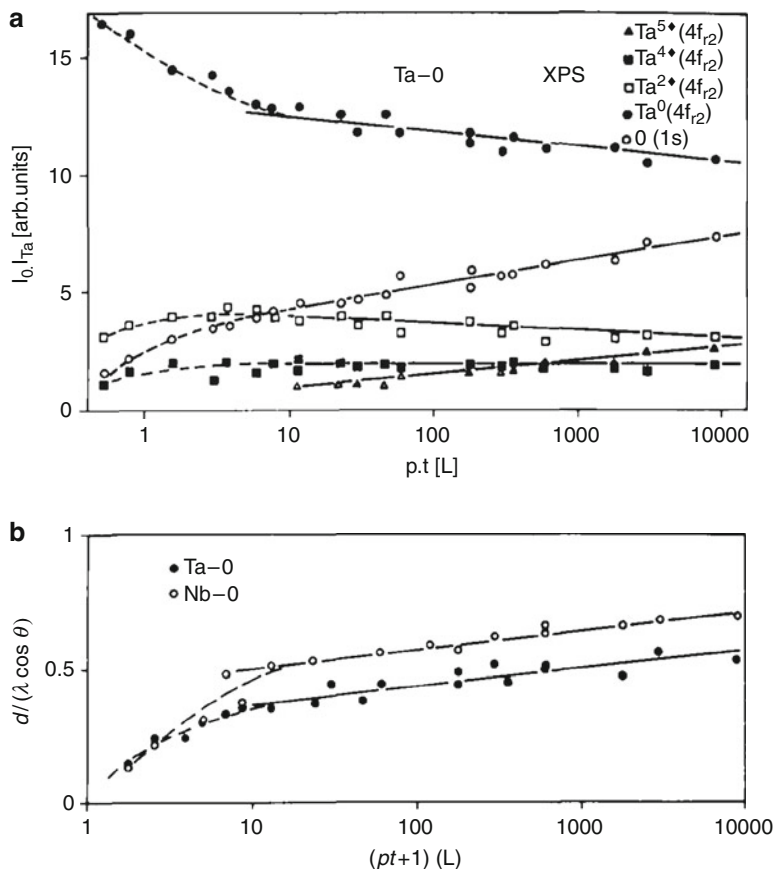


Fig. 9.15 (a) XPS intensities (peak areas) of the Ta $4f_{7/2}$ peak for the various oxidation states of Ta (see *inset*) and for O1s as a function of the oxygen dose. (b) Growth of the relative oxide layer thickness $d/(\lambda \cos \theta)$ as a function of oxygen exposure $(pt + 1)$ (L) on logarithmic scale. The *lower line* for the system Ta–O is fitted to the *full circles* referring to $d/(\lambda \cos \theta)$ taken from (4.127c) with the points for Ta^0 in (a), for which $I^0(pt = 0)$ is known. (The *upper line* is for the system Nb–O similarly studied) (Adapted from J.M. Sanz and S. Hofmann [9.77])

constant with further pentoxide formation above. Similar results were obtained for other transition metals. Zirconium has been frequently studied [9.85, 9.89, 9.90]. Although the $Zr3d$ peak in the detailed study of Morant et al. [9.89] could be formally decomposed in four different oxidation states, the only directly confirmed phase was the stable ZrO_2 , which was already formed below 5 L. The presence of lower valence states confirmed by substoichiometric oxygen content remains close to the metal/oxide interface, and at exposures >100 L, the saturation region is attained and an 1.6 nm thick oxide layer with an average composition of $ZrO_{1.6}$ is formed [9.89, 9.90].

Any AES instrument can be used to obtain additional information by electron energy loss spectroscopy (EELS or ELS) in the reflection mode (therefore often

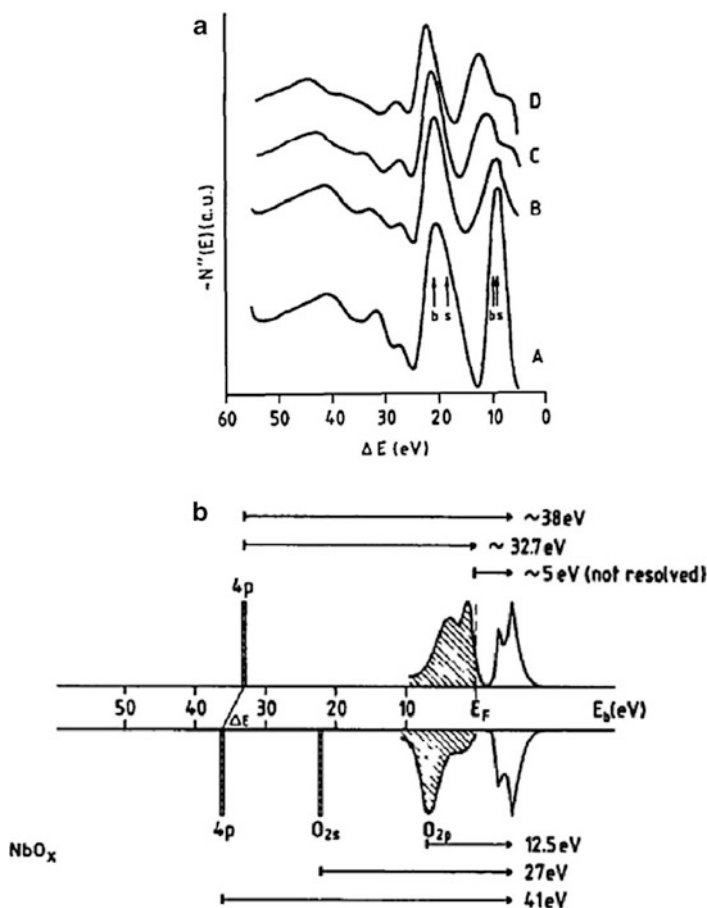


Fig. 9.16 (a) Electron energy loss spectra ($-N''(E)$) for Nb as a function of oxygen exposure ($A = 0$ L, $B = 0.8$ L, $C = 4$ L, $D = 23$ L). Arrows in (A) indicate the values for surface (s) and bulk (b) plasmons. (b) Tentative assignments of observed ELS peaks for metallic Nb (upper half) and Nb oxide (lower half) corresponding to curves (A) and (D) in (a) (From J.M. Sanz and S. Hofmann [9.85])

called REELS) (see, e.g., Fig. 9.1). EELS has been shown to give useful information about the electronic properties of the surface and is particularly sensitive to differences in chemical states because electron excitations depend on the filled and empty states near the Fermi level [9.96, 9.97]. Therefore, EELS is frequently used as a complementary technique to conventional AES and XPS in oxidation studies [9.86–9.88, 9.96, 9.97]. In addition to angle-resolved emission, selecting different primary energies enables depth-dependent information (see Sect. 7.2.2). An example from oxidation of Nb is shown in Fig. 9.16. In Fig. 9.16a, the loss spectra are depicted for different oxygen exposures of a clean, polycrystalline Nb surface (after twofold differentiation to increase “visibility” of peaks) [9.85].

Exposure values are $A = 0$, $B = 0.8$ L, $C = 4$ L, and $D = 23$ L. The two strong peaks observed for the pure metal (A) at about 10 and 20 eV correspond to an overlap of bulk and surface plasmon losses (arrows b and s). As schematically indicated in Fig. 9.16b, the peaks at about 32 and 40 eV are attributed to the transitions from the Nb 4p core level to empty states near and above the Fermi level (32.7 and 38 eV, respectively). With increasing oxygen exposure, the peak at about 20 eV decreases and gets sharper, whereas the region at about 10 eV is completely altered. As a consequence of oxygen at the surface, the surface plasmon vanishes and the corresponding contribution at about 20 eV disappears. Only the bulk plasmon loss from the metallic substrate remains with a peak at around 21 eV. The appearance of the loss peak at 12.5 eV after > 4 L oxygen exposure is attributed to excitation from the emerging O 2p band to empty states above the Fermi level, and likewise those from the O 2s and Nb 4p (shifted) with energies 27 and 41 eV, respectively. Similar results were obtained in [9.85] for Ta oxidation.

9.2.2.2 Oxidation of Alloys

Compared to oxidation of pure metals, oxidation of alloys is complicated by several components which compete with surface segregation and diffusion processes as well as with different thermodynamic free enthalpies of oxide formation [9.98]. Even in low-temperature initial oxidation stages, formation enthalpies play a dominant role [9.80, 9.82, 9.90–9.99]. AES valence band transitions are particularly useful for two reasons: They are very sensitive to chemical changes and their low kinetic energy (in general below 100 eV) ensures highly surface specific information. Because spectral changes caused by chemical effects, although usually more pronounced as compared to XPS, are more complicated to interpret (see Sects. 3.2.3, 3.2.4), the “fingerprint” method of factor analysis (FA) (see Sect. 9.3) is frequently used. An example is shown in Fig. 9.17a for FA applied to the initial oxidation at room temperature of the alloy Fe-19 at% Cr-9 at% Ni at 2.8 L of oxygen exposure [9.98]. A least-square fit of standard Auger MVV spectra between 20 and 70 eV (obtained as principal components) to the measured spectra results in the indicated quantities of the components. Three components of each metal were distinguished: metallic (Me-met), oxide (Me-ox), and chemisorption bonding Me–O(chem). The latter was extracted by factor analysis in an earlier study [9.82]. Factor analysis enabled the detailed information shown in Fig. 9.17b, disclosing the sequential oxidation of Cr, Fe, and Ni with increasing oxygen exposure. Preferential oxygen chemisorption on Cr and oxidation of Cr is accompanied by oxygen-induced segregation and is followed by Fe oxidation on top of the previously formed Cr oxide.

Nickel oxidation is drastically reduced in this Fe-rich alloy and below detection limit in the shown exposure range. After exposure to 900 L of oxygen, oxidation results in a layered structure as confirmed by AES sputter depth profiles which were resolved into oxide and pure metal components as seen in Fig. 9.17c. Together with the small electron escape depth of only about two atomic layers, this procedure

gives well-resolved depth distributions within the total oxide thickness of about 11 monolayers [9.99].

9.2.3 Altered Layers by Ion Bombardment

Angle-resolved XPS (AR-XPS) is frequently used to study oxide layers [9.80, 9.89–9.92] and other surface reaction layers, for example, generated by evaporation [9.100], by ion-induced implantation [9.101], or compositionally changed surface layers during sputtering (e.g., Sect. 7.2.1, Fig. 7.30 (AR-AES)) [7.189]. An early example of AR-XPS applied to the study of the composition of the altered layer during sputter depth profiling of several oxide layers (Ta_2O_5 , Nb_2O_5 , TiO_2 , ZrO_2 , HfO_2 , Al_2O_3) is reported in Refs. [9.102–9.104]. For Ta_2O_5 , the change of the bonding states of the $\text{Ta}4f_{7/2,5/2}$ XPS peak during the three stages, initial state, steady state, and metal, is indicated in Sect. 7.1.4, Fig. 7.12, where the intensities

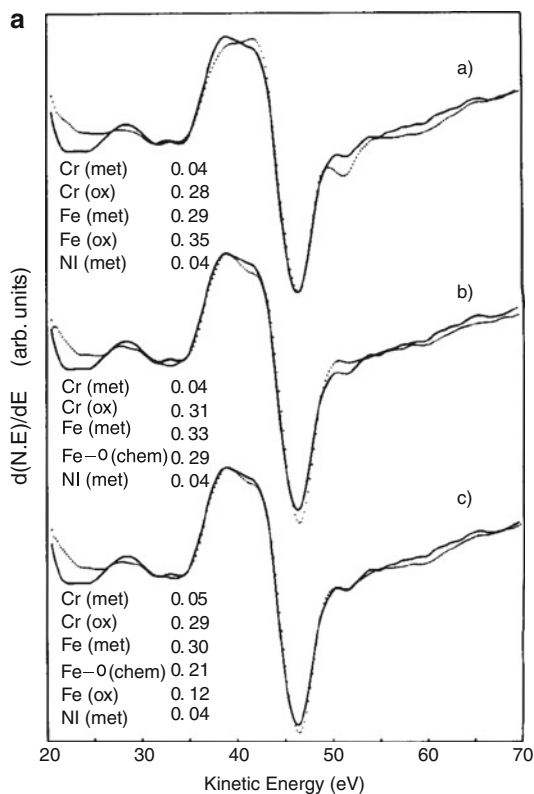


Fig. 9.17 (continued)

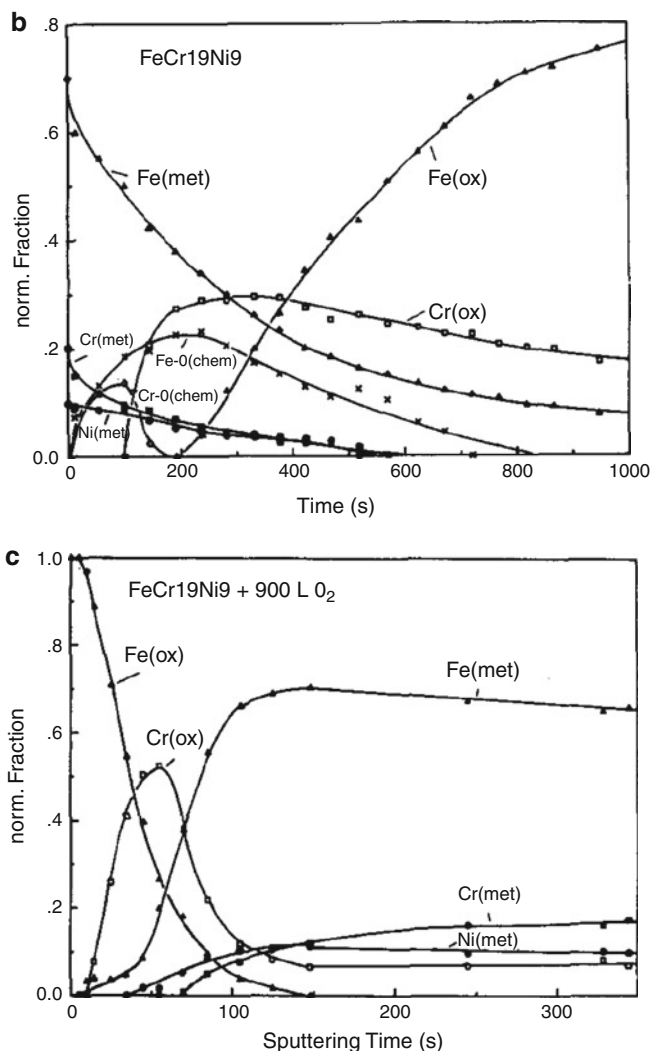


Fig. 9.17 (continued) (a) Results of least-squares fittings of the measured MVV Auger spectrum of FeCr19Ni9 after exposure to 2.8 L of oxygen (*solid line*). The calculated spectra (*dotted lines*) are the superposition of the standard spectra from Ref. [9.99] with the respective compositions indicated in the figure. Only the application of both the components Fe-O(chem) and Fe(ox) gives the optimum fit in curve (c). (b) normalized fractions of the metallic, oxide, and intermediate (chemisorption) states of the alloy elements during oxygen exposure of FeCr19Ni9 at a pressure of 1.3×10^{-6} Pa as a function of time (100 s $\approx$ 1 L of O exposure). These fractions are obtained by least-squares fitting of the respective standard spectra as shown in (a). The different components are shown with the following symbols: Ni(met) (*full circles*), Fe(met) (*full triangles*), Fe-O(chem) (*crosses*), Fe(ox) (*open triangles*), Cr(met) (*full squares*), Cr-O(chem) (*open diamonds*), and Cr(ox) (*open squares*); (c) depth profile of the chemical composition of FeCr19Ni9 after exposure to 900 L of O. The normalized fraction of the metallic and oxide states of the alloy elements is plotted as a function of the sputtering time. The corresponding sputtering rate for NiO is about 0.03 nms^{-1} [80] (From H.J. Steffen and S. Hofmann [9.99])

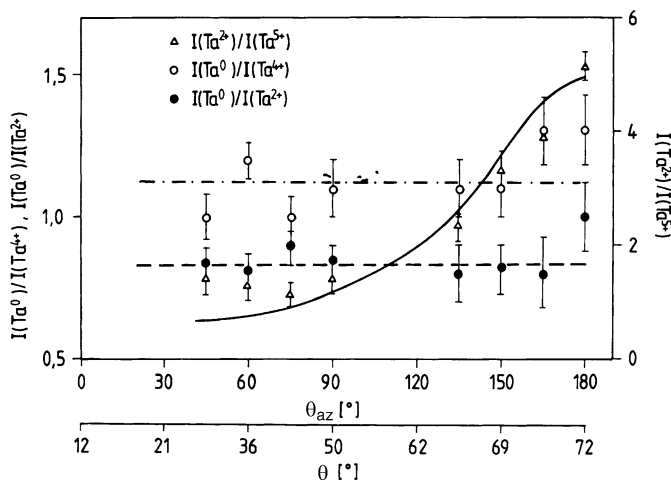


Fig. 9.18 AR-XPS results of the altered layer of sputtered Ta_2O_5 : Intensity ratios of the decomposed Ta4f spectra $\text{Ta}^0/\text{Ta}^{4+}$, $\text{Ta}^0/\text{Ta}^{2+}$, and $\text{Ta}^{2+}/\text{Ta}^{5+}$ are shown as a function of the emission angle θ . Note the nonlinear scale of θ , whereas that of the azimuth angle θ_{azi} is linear (see Sect. 5.1.2, Figs. 5.4 and 5.6). After (5.3) the relation here is: $\cos \theta = 0.64 + 0.34 \cos \theta_{\text{azi}}$. (From S. Hofmann and J.M. Sanz [9.104])

of the different valence states of Ta are also shown. For 3 kV Ar^+ ions, in the steady state regime, the deconvoluted Ta 4f peak is shown in Fig. 3.3, Sect. 3.2.3. AR-XPS results of the intensity ratios derived from a series of XPS spectra acquired at different emission angles (performed with a double pass CMA, see Sects. 2.5.1 and 5.1.2, Figs. 5.4, 5.5) are shown in Fig. 9.18 for the ratios $I(\text{Ta}^0/\text{Ta}^{4+})$, $I(\text{Ta}^0/\text{Ta}^{2+})$, and $I(\text{Ta}^{2+}/\text{Ta}^{5+})$. The nearly independence of the lower valence peak ratios on the emission angle corresponds to a relatively homogeneous distribution of Ta^0 , Ta^{2+} , and Ta^{4+} . In contrast, the pronounced emission angle dependence of $I(\text{Ta}^{2+}/\text{Ta}^{5+})$ is characteristic of a thin layer containing Ta^{2+} above the bulk, undistorted oxide given by Ta^{5+} with a mole fraction of $X(\text{Ta}^{5+}) = 0.29$, and (7.58) (Sect. 7.2.1) applies with the respective variables,

$$\frac{I(\text{Ta}^{2+})}{I(\text{Ta}^{5+})} = \frac{X(\text{Ta}^{2+})}{X(\text{Ta}^{5+})} \left[\exp \frac{d(\text{Ta}^{2+})}{\lambda_{\text{Ta,ox}} \cos \theta} - 1 \right]. \quad (9.1)$$

As shown in Sects. 4.3.3 and 7.2.1, (9.1) can be solved for the two unknown values of the mole fraction $X(\text{Ta}^{2+})$ and the relative altered layer thickness $d/\lambda_{\text{Ta,ox}}$ by iterative fit, for example, by comparing intensity ratios at different emission angles θ . The optimum fit in Fig. 9.18 corresponds to $X(\text{Ta}^{2+}) = 0.35$ and $d/\lambda_{\text{Ta,ox}} = 0.64$. With $\lambda_{\text{Ta,ox}} = 2.9$ nm, this gives about 2 nm for the thickness of the altered layer. The overall composition of the altered layer is about 50% Ta and O (TaO), corresponding to a loss of oxygen of about 20 at% by preferential sputtering. A recent study of Baer et al. [9.105] on oxide sputtering shows similar values for oxygen depletion but a marked increase of the overall intensity ratio $I(\text{O})/I(\text{Ta})$

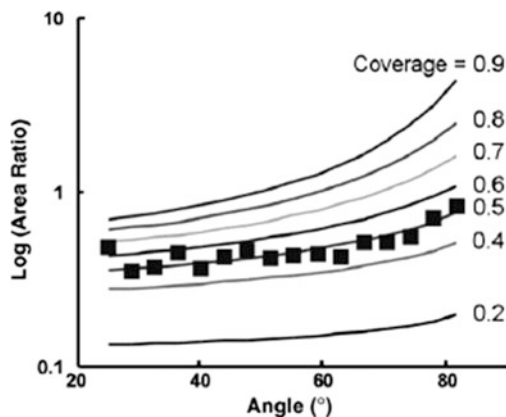


Fig. 9.19 Dependence of the experimentally determined area ratio of the peak intensities of $I(\text{Al } 2p)/I(\text{Si } 2p)(\text{oxidized})$ (on logarithmic scale) on the emission angle. The layer structure consists of Al_2O_3 islands (coverage < 1) on a 0.8-nm-thick SiO_2 layer on an Si wafer (similar to Fig. 7.47b), i.e., the predicted curves with coverage as a parameter are given by the ratio corresponding to the ratio of expressions (7.68)–(7.71) in Sect. 7.2.1. Optimum fit is obtained for a fractional coverage of 0.5 (Reproduced from P. Mack et al. [9.106], with permission of Elsevier B.V.)

with increasing Ar^+ ion incidence angle. However, such an effect is expected since with increasing incidence angle, the ion range decreases, and therefore the altered layer thickness decreases too.

9.2.4 Deposited Layer Structure

Thin layers deposited in UHV are frequently studied in situ by AR-XPS [9.106–9.109]. In general, fractional layers occur and the results are quantified by expressions (7.68)–(7.71) in Sect. 7.2.1, as demonstrated in Fig. 7.47. In a study of fractional coverage of high k dielectric materials on SiO_2 surfaces, Mack et al. [9.106] used expressions of this type to get the fractional coverage of an Al_2O_3 layer on SiO_2 after five cycles of atomic layer deposition (ALD) as an optimum fit of the intensity ratio $I(\text{Al } 2p)/I(\text{Si } 2p)(\text{oxidized})$ to the measured AR-XPS values depicted in Fig. 9.19.

9.2.5 Surface Segregation

Since the early days of surface analysis, equilibrium and kinetics of surface segregation have been one of the main in situ applications of AES [9.110–9.120] and – to a lesser degree – of XPS [9.121–9.123]. Low-energy AES is very surface sensitive for the first layer where Langmuir–McLean-type segregation takes place, for example,

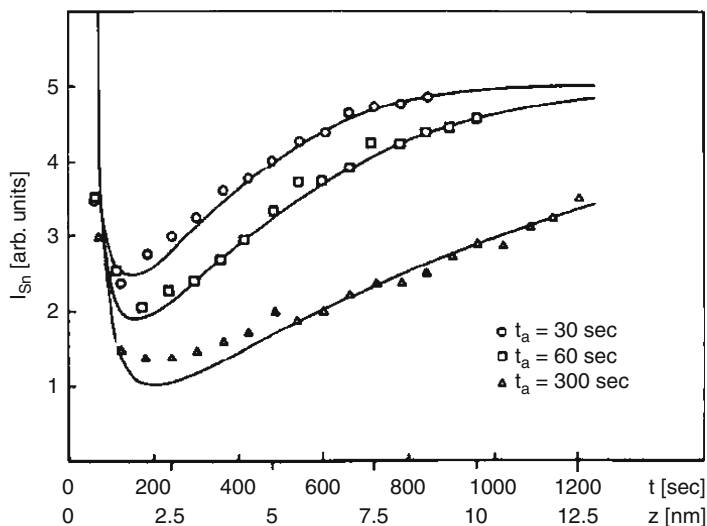


Fig. 9.20 Segregation kinetics of Sn on a Cu(111) surface: Sputter depth profiles of the APPH of Sn MNN (430 eV) (I_{Sn}) plotted against sputtering time t (triangle, square and circle) after quenching at three different annealing times (t_a for $T = 673$ K) shown in the inset. Solid lines are a fits to the respective profiles obtained by application of the SLS model (see Sect. 7.1.7) to the calculated in-depth distribution according to the depth scale z (nm) (From S. Hofmann and J. Erlewein [9.112])

in the systems Sn in Cu [9.110–9.112] or S in Cu [9.40, 9.114–9.118]. Measuring the intensity of the solute at different temperatures and evaluation with the Langmuir–McLean equation directly yields segregation enthalpy and entropy. For some systems and surfaces, this equation has to be extended by an atomic interaction term (Fowler term) (e.g., Ag at Cu(111)) [9.119]. Based on measurements of time-dependent increase of the APPH of the solute at different temperatures, the bulk diffusion constant of Sn in Cu was determined from segregation kinetics in 1976 by Hofmann and Erlewein [9.110]. A detailed model of the concentration profile in the surface and subsurface layers enabled the test of the model and of the restriction of segregation to the first monolayer by quantification of experimentally determined sputter depth profiles as shown in Fig. 9.20 [9.112]. Using ion surface scattering which detects the first monolayer, Swartzfager et al. [9.123] confirmed these profiles for Cu segregation on a Ni–Cu alloy.

Diffusion of sulfur in Cu was determined and used for trace analysis of S in Cu in the ppm range [9.115]. Combination with sputtering at elevated temperatures served to determine the bulk diffusion constant of oxygen in niobium [9.113]. Du Plessis and Viljoen [9.116] developed an elegant method of determination of both segregation enthalpy and diffusion constant in one experimental run by monitoring the Auger signal intensity during linear temperature increase [9.116, 9.119, 9.124]. Of special interest in practical systems is competitive segregation of different elements. An illustration is given in Fig. 9.21 for P and S at Cu (110) [9.117, 9.118].

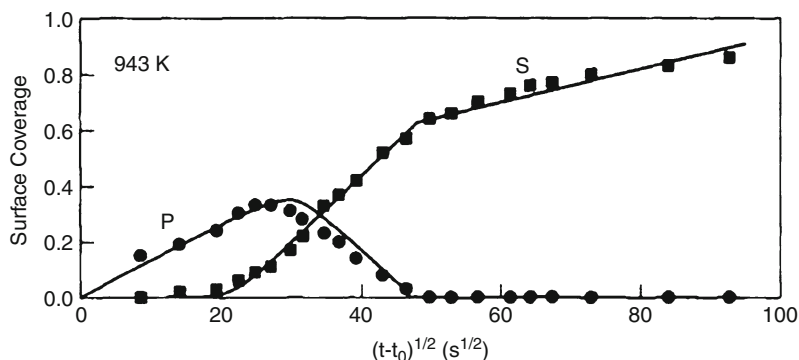


Fig. 9.21 Competitive segregation kinetics of P (circles) and S (squares) on a Cu(110) surface measured by Frech [9.114], fitted to predictions of a model developed in Refs. [9.117,9.118] (From M. Militzer and S. Hofmann [9.117])

While P is faster at the surface, it is replaced by sulfur because of repulsive interaction and higher segregation enthalpy of the latter. A structural transition in the surface layer from $c(2 \times 2)$ to $p(1 \times 1)$ occurs, which (in combination with the back diffusion of P) results in a vanishing diffusion flux from fast diffusion paths such as dislocations and an according slowing down of S coverage increase toward the final stage of the segregation process [9.118].

9.3 Treatment of AES and XPS Data by Factor Analysis

One of the most powerful mathematical tools for pattern recognition in large data sets is factor analysis (FA) [9.12, 9.82, 9.83, 9.99, 9.125–9.128]. The multivariate statistical method of factor analysis is a standard procedure of data handling and interpretation in analytical chemistry [9.127] which was introduced to data evaluation in AES by the pioneering work of Gaarenstroom [9.128]. Factor analysis is used to determine the number and the quantity of characteristic features contained in an array of spectra. Therefore, its main applications in AES and XPS are extraction of chemical bonding features in oxidation, sputter depth profiling, and chemical mapping of metals, semiconductors, alloys, and compounds [9.125]. The technique is briefly outlined in the following, using the notation of the standard work of Malinowski and Howery [9.127]. Several articles are recommended for introduction to FA [9.82, 9.125, 9.126], and an ISO standard is also available [9.129].

The aim of factor analysis consists of the determination of the relevant factors (components) and their respective fractions (concentrations) which can be linearly combined to represent a whole sequence of measured spectra as a function of an outer parameter (e.g., oxidation or sputtering time). The sequence of z spectra, each with N channels, which are contained as column vectors in matrix $[D]$ with the

dimension (N, z) can be decomposed by factor analysis in a product of two matrices $[D] = [R] \times [C]$.

The number of relevant factors (components) is obtained by the so-called principal component analysis (PCA) [9.127]. Mathematical routines enable the determination of the minimum number of “eigenvectors” to reproduce the measured spectra above the noise limit by the so-called indicator function (IND) [9.126, 9.127]. As a final result, the mathematical FA routine applied to a series of spectra gives (a) the number of principal components and (b) synthesis of each measured spectrum by linear superposition of the appropriate fraction of each component in the spectra.

Factor analysis is particularly useful in AES with derivative spectra where different components are not easy to recognize. Thus, hitherto unknown components such as chemisorbed Ni, Fe, and Cr during oxidation studies [9.82, 9.83] (see Fig. 9.17) were disclosed. Because background noise can be treated as one component, its subtraction improves sputter depth profiling results [9.130] in quantitative AES, the use of the whole spectral information in FA (typically some hundred spectral points instead of the two points in usual Auger peak-to-peak height (APPH) analysis) not only reduces the error by chemical bonding influence but also improves the signal-to-noise figure and therefore the sensitivity [9.129, 9.130]. Further application examples can be found in [9.125] and in a special issue of *Surface and Interface Analysis*, “On multivariate analysis in surface science” [9.131].

References

- 9.1. J.C. Rivière, S. Myrha, *Handbook of Surface and Interface Analysis* (Marcel Dekker, New York, 1998)
- 9.2. M. Grasserbauer, H.J. Dudek, M.F. Ebel, *Angewandte Oberflächenanalyse mit SIMS, AES und XPS* (Springer, Berlin-Heidelberg, 1987)
- 9.3. S. Suzuki, High Temp. Mater. Process. **17**, 1 (1998)
- 9.4. J. Iijima, J.-W. Lim, S.-H. Hong, S. Suzuki, K. Mimura, A. Isshiki, Appl. Surf. Sci. **253**, 2825 (2006)
- 9.5. S. Hofmann, Thin Solid Films **191**, 335 (1990)
- 9.6. H.A. Jehn, U. Kopacz, S. Hofmann, J. Vac. Sci. Technol. **A3**, 2406 (1985)
- 9.7. S. Hofmann, H.A. Jehn, Surf. Coat. Technol. **41**, 167 (1990)
- 9.8. H.A. Jehn, J.-H. Kim, S. Hofmann, Surf. Coat. Technol. **36**, 715 (1988)
- 9.9. S. Hofmann, J. Vac. Sci. Technol. A **4**, 2789 (1986)
- 9.10. P.Y. Jouan, M.C. Peignon, C. Cardinaud, G. Lemperiere, Appl. Surf. Sci. **68**, 595 (1993)
- 9.11. S. Hofmann, Rep. Prog. Phys. **61**, 827 (1998)
- 9.12. D.G. Watson, W.F. Stickley, A.C. Diebold, Thin Solid Films **193/194**, 305 (1990)
- 9.13. *Physical Electronics Application Note* 812 (2005).
- 9.14. I.leR. Strydom, S. Hofmann, J. Electron Spectrosc. Relat. Phenom. **56**, 85 (1991)
- 9.15. I. Bertóti, M. Mohai, J.L. Sullivan, S.O. Saied, Appl. Surf. Sci. **84**, 357 (1995)
- 9.16. I.leR. Strydom, S. Hofmann, Vacuum **41**, 1619 (1990)
- 9.17. H.A. Jehn, E. Huber, S. Hofmann, Surf. Interface Anal. **22**, 156 (1994)
- 9.18. S. Hofmann, H.A. Jehn, Surf. Interface Anal. **12**, 329 (1988)
- 9.19. H.A. Jehn, S. Hofmann, W.-D. Muenz, Thin Solid Films **153**, 45 (1987)

- 9.20. S. Hofmann, *Thin Solid Films* **193/194**, 648 (1990)
- 9.21. Y. Otani, S. Hofmann, *Thin Solid Films* **287**, 188 (1996)
- 9.22. J.E. Castle, J. Adhesion **84**, 368 (2008)
- 9.23. P. Bruesch, K. Mueller, A. Atrens, H. Neff, *Appl. Phys. A* **38**, 1 (1985)
- 9.24. H. Mischler, H.J. Mathieu, D. Landolt, *Surf. Interface Anal.* **11**, 182 (1988)
- 9.25. J. Steffen, S. Hofmann, *Fres. Z. Anal. Chem.* **333**, 408 (1989)
- 9.26. R. Kirchheim, B. Heine, H. Fischmeister, S. Hofmann, H. Knotte, U. Stolz, *Corrosion Sci.* **29**, 899 (1989)
- 9.27. W. Fredriksson, K. Edstrom, C.-O. Olsson, *Corrosion Sci.* **52**, 2505 (2010)
- 9.28. A. Zalar, S. Hofmann, P. Panjan, *Vacuum* **48**, 625 (1997)
- 9.29. A. Zalar, S. Hofmann, F. Pimentel, P. Panjan, *Thin Solid Films* **253**, 293 (1994)
- 9.30. A. Zalar, J.Y. Wang, Y.H. Zhao, E.J. Mittemeijer, P. Panjan, *Vacuum* **71**, 11 (2003)
- 9.31. J.Y. Wang, D. He, Y.H. Zhao, E.J. Mittemeijer, *Appl. Phys. Lett.* **88**, 061910 (2006)
- 9.32. D. He, J.Y. Wang, E.J. Mittemeijer, *Appl. Surf. Sci.* **252**, 5470 (2006)
- 9.33. J.Y. Wang, Z.M. Wang, L.P.H. Jeurgens, E.J. Mittemeijer, *J. Nanosci. Nanotechnol.* **9**, 3364 (2009)
- 9.34. P. Lejček, *Grain Boundary Segregation in Metals* (Springer, Berlin-Heidelberg, 2010)
- 9.35. P. Lejček, S. Hofmann, *Crit. Rev. Solid State Mater. Sci.* **33**, 133 (2008)
- 9.36. S. Hofmann, P. Lejček, *Int. J. Mater. Res.* **100**, 1167 (2009)
- 9.37. P. Lejček, *Anal. Chim. Acta* **297**, 165 (1994)
- 9.38. P. Lejček, S. Hofmann, *Surf. Sci.* **307-309**, 798 (1994)
- 9.39. A. Joshi, D.F. Stein, *J. Inst. Metals* **99**, 178 (1971)
- 9.40. M.P. Seah, *J. Phys. F Metal Phys.* **10**, 1043 (1980)
- 9.41. S. Szuki, K. Abiko, H. Kimura, *Scr. Metall.* **15**, 1139 (1981)
- 9.42. S. Hofmann, *Vacuum* **40**, 9 (1990)
- 9.43. S. Hofmann, Segregation at Grain Boundaries, in *Surface Segregation Phenomena*, ed. by P.A. Dowben, A. Miller (CRC Press, Boca Raton, 1990), pp. 107–134
- 9.44. T. Muschik, S. Hofmann, W. Gust, *Scr. Metall.* **22**, 349 (1988)
- 9.45. T. Muschik, S. Hofmann, W. Gust, B. Predel, *Appl. Surf. Sci.* **37**, 349 (1989)
- 9.46. T. Muschik, W. Gust, S. Hofmann, B. Predel, *Acta Metall.* **37**, 2917 (1989)
- 9.47. A. Fraczekiewicz, M. Biscondi, *J. Phys.* **46**, C4–497 (1985)
- 9.48. M. Menyhard, B. Blum, C.J. McMahon, *Acta Metall.* **37**, 549 (1989)
- 9.49. L.-S. Chang, E. Rabkin, B. Straumal, P. Lejček, S. Hofmann, W. Gust, *Scr. Mater.* **37**, 729 (1997)
- 9.50. L.-S. Chang, C.-H. Yeh, B.B. Straumal, *Rev. Adv. Mater. Sci.* **21**, 1 (2009)
- 9.51. M.P. Seah, E.D. Hondros, *Scr. Metall.* **7**, 735 (1973)
- 9.52. T. Watanabe, S. Kitamura, S. Karashima, *Acta Metall.* **28**, 455 (1980)
- 9.53. S. Hofmann, P. Lejček, *Scr. Metall. Mater.* **25**, 2259 (1991)
- 9.54. P. Lejček, S. Hofmann, *Interface Sci.* **1**, 161 (1993)
- 9.55. T. Watanabe, *Res. Mech.* **11**, 47 (1984)
- 9.56. S. Kobayashi, S. Tsurekawa, T. Watanabe, G. Palumbo, *Scr. Mater.* **62**, 294 (2010)
- 9.57. P. Lejček, S. Hofmann, V. Paidar, *Acta Mater.* **51**, 3951 (2003)
- 9.58. M.S. Dhlamini, H.C. Swart, J.J. Terblans, C.J. Terreblanche, *Surf. Interface Anal.* **38**, 339 (2005)
- 9.59. U. Otterbein, S. Hofmann, *Surf. Interface Anal.* **24**, 263 (1996)
- 9.60. T. Itoh (ed.), *Ion Beam Assisted Film Growth* (Elsevier, Amsterdam, 1989)
- 9.61. C. Morant, P. Prieto, M.J. Hernandez, M. Cervera, E. Elizalde, J.M. Sanz, *Surf. Interface Anal.* **36**, 849 (2004)
- 9.62. G.G. Fuentes, E. Elizalde, J.M. Sanz, *Surf. Interface Anal.* **34**, 257 (2002)
- 9.63. H.J. Steffen, S. Hofmann, *J. Surf. Anal.* **3**, 464 (1997)
- 9.64. H.J. Steffen, *Surf. Interface Anal.* **26**, 825 (1998)
- 9.65. R.F. Egerton, *Electron Energy-Loss Spectroscopy in the Electron Microscope*, 3rd edn. (Springer, Berlin, 2011)

- 9.66. J.F. Watts, Adhesion Science and Technology, in *Handbook of Surface and Interface Analysis*, ed. by J.C. Rivière, S. Myrha (Marcel Dekker, New York, 1998), pp. 781–834
- 9.67. P.K. Chu, L.H. Li, *Mater. Chem. Phys.* **96**, 253 (2006)
- 9.68. T. Mathew, N.R. Shiju, K. Sreekumar, B.S. Rao, C.S. Gopinath, *J. Catal.* **210**, 405 (2002)
- 9.69. G.S.A.M. Theunissen, A.J.A. Winnbust, A.J. Burggraaf, *J. Mater. Sci.* **27**, 5057 (1992)
- 9.70. L. Srisombat, O. Khamman, R. Yimnirun, S. Ananta, T.R. Lee, *Key Eng. Mater.* **421–422**, 415 (2010)
- 9.71. L. Sabbatini, P.G. Zamboni, *J. Electron Spectrosc. Relat. Phenom.* **81**, 285 (1996)
- 9.72. C. O’Connell, R. Sherlock, M.D. Ball, B. Aszalos-Kiss, U. Prendergast, T.J. Glynn, *Appl. Surf. Sci.* **255**, 4405 (2009)
- 9.73. S. Bernath, T. Wagner, S. Hofmann, M. Ruehle, *Surf. Sci.* **400**, 335 (1998)
- 9.74. J.S. Solomon, W.L. Baun, *Surf. Sci.* **51**, 228 (1975)
- 9.75. Y. Nakanishi, T. Nagatomi, Y. Takai, *Surf. Sci.* **602**, 3696 (2008)
- 9.76. P.H. Holloway, J.B. Hudson, *Surf. Sci.* **43**, 123 (1974)
- 9.77. J.M. Sanz, S. Hofmann, *J. Less Common Met.* **92**, 317 (1983)
- 9.78. J. Steffen, S. Hofmann, *Fres. Z. Anal. Chem.* **329**, 250 (1987)
- 9.79. J.M. Sanz, C. Palacio, Y. Casas, J.M. Martínez-Duart, *Surf. Interface Anal.* **10**, 177 (1987)
- 9.80. J. Steffen, S. Hofmann, *Surf. Interface Anal.* **11**, 617 (1988)
- 9.81. J. Steffen, S. Hofmann, *Surf. Sci.* **202**, L 607 (1988)
- 9.82. S. Hofmann, J. Steffen, *Surf. Interface Anal.* **14**, 59 (1989)
- 9.83. C. Palacio, H.J. Mathieu, *Surf. Interface Anal.* **16**, 178 (1990)
- 9.84. J.-G. Yang, X.-L. Wang, Ch.-L. Jiang, H. Xiao, L. Lu, *Surf. Interface Anal.* **38**, 498 (2006)
- 9.85. J.M. Sanz, S. Hofmann, *J. Electron Spectrosc. Relat. Phenom.* **34**, 149 (1984)
- 9.86. K. Nishita, K. Saiki, A. Koma, *Appl. Surf. Sci.* **169**, 180 (2001)
- 9.87. L. Lu, B. Bai, J.S. Zou, *Rare Met. Mater. Eng.* **33**, 839 (2004)
- 9.88. C. Morant, L. Galan, J. M. Sanz, *Surf. Interface Anal.* **16**, 304 (1990)
- 9.89. A. Lyapin, L.P.H. Jeurgens, P.C.J. Graat, E.J. Mittemeijer, *Surf. Interface Anal.* **36**, 989 (2004)
- 9.90. V. Maurice, G. Despert, S. Zanna, P. Josso, M.-P. Bacos, P. Marcus, *Acta Mater.* **55**, 3315 (2007)
- 9.91. E. Panda, L.P.H. Jeurgens, E. Mittemeijer, *J. Appl. Phys.* **106**, 114913 (2009)
- 9.92. T. Do, S.J. Splinter, C. Chen, N.S. McIntyre, *Surf. Sci.* **387**, 192 (1997)
- 9.93. E. Fromm, *Kinetics of Metal–Gas Interactions at Low Temperatures* (Springer, Berlin-Heidelberg, 1998)
- 9.94. N. Cabrera, N.F. Mott, *Rep. Prog. Phys.* **12**, 163 (1948)
- 9.95. F.P. Fehlner, *J. Electrochem. Soc.* **131**, 1645 (1984)
- 9.96. G.B. Hoflund, G.R. Corallo, *Phys. Rev. B* **46**, 7110 (1992)
- 9.97. G.B. Hoflund, H.A.E. Hagelin, J.F. Weaver, G.N. Salaita, *Appl. Surf. Sci.* **205**, 102 (2003)
- 9.98. Z. Tokei, H. Viehhaus, H.J. Grabke, *Appl. Surf. Sci.* **165**, 23 (2000)
- 9.99. H.J. Steffen, S. Hofmann, *Surf. Interface Anal.* **19**, 157 (1992)
- 9.100. S. Oswald, F. Oswald, *Anal. Bioanal. Chem.* **396**, 2805 (2010)
- 9.101. C. Palacio, A. Arranz, *Surf. Interface Anal.* **40**, 676 (2008)
- 9.102. S. Hofmann, J.M. Sanz, *J. Trace Microprobe Techn.* **1**, 213 (1982–1983)
- 9.103. S. Hofmann, J.M. Sanz, *Fres. Z. Anal. Chem.* **314**, 215 (1983)
- 9.104. S. Hofmann, J.M. Sanz, *Mikrochim. Acta Suppl.* **10**, 135 (1983)
- 9.105. D.R. Baer, M.H. Engelhard, A.S. Lea, P. Nachimuthu, T.C. Droubay, J. Kim, B. Lee, C. Mathews, R.L. Opila, L.V. Saraf, W.F. Stickle, R.M. Wallace, B.S. Wright, *J. Vac. Sci. Technol. A* **28**, 1060 (2010)
- 9.106. P. Mack, R.G. White, J. Wolstenholme, T. Conard, *Appl. Surf. Sci.* **252**, 8270 (2006)
- 9.107. S. Oswald, *Surf. Interface Anal.* **42**, 1289 (2010)
- 9.108. O. Renault, L.G. Gosset, D. Rouchon, A. Ermoliev, *J. Vac. Sci. Technol. A* **20**, 1867 (2002)
- 9.109. R.L. Opila, *J. Eng. Prog. Surf. Sci.* **69**, 125 (2002)
- 9.110. S. Hofmann, J. Erlewein, *Scr. Metall.* **10**, 857 (1976)
- 9.111. J. Erlewein, S. Hofmann, *Surf. Sci.* **68**, 71 (1977)

- 9.112. S. Hofmann, J. Erlewein, *Surf. Sci.* **77**, 591 (1978)
- 9.113. S. Hofmann, *Mater. Sci. Eng.* **42**, 55 (1980)
- 9.114. R. Frech, Ph.D. thesis, University of Stuttgart, Stuttgart, 1983
- 9.115. S. Hofmann, R. Frech, *Anal. Chem.* **57**, 716 (1985)
- 9.116. J. duPlessis, E.C. Viljoen, *Appl. Surf. Sci.* **59**, 71 (1992)
- 9.117. M. Militzer, S. Hofmann, *Scr. Metall. Mater.* **31**, 1501 (1994)
- 9.118. M. Militzer, S. Hofmann, *J. Vac. Sci. Technol. A* **13**, 1493 (1995)
- 9.119. J.Y. Wang, J. duPlessis, J.J. Terblans, G.N. vanWyk, *Surf. Sci.* **423**, 12 (1999)
- 9.120. B. Egert, G. Panzner, *Surf. Sci.* **118**, 345 (1982)
- 9.121. G. Hetzendorf, P. Varga, *Nucl. Instr. Meth. Phys. Res. B* **18**, 501 (1987)
- 9.122. N. Tabet, J. Electron Spectrosc. Relat. Phenom. **114**, 415 (2001)
- 9.123. D.G. Swartzfager, S.B. Ziemecki, M.J. Kelly, *J. Vac. Sci. Technol.* **19**, 185 (1981)
- 9.124. I. Jaeger, *Surf. Sci.* **366**, 166–176 (1996)
- 9.125. W.F. Stickley, The Use of Chemometrics in AES and XPS Data Treatment, in *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, ed. by D. Briggs, J.T. Grant (IM Publications, Chichester, 2003), pp. 377–396
- 9.126. A. Arranz, C. Palacio, *Surf. Interface Anal.* **22**, 93 (1994)
- 9.127. E.R. Malinowski, D.G. Howery, *Factor Analysis in Chemistry*, 3rd edn. (Wiley, New York, 2002)
- 9.128. S.W. Gaarenstroom, *J. Vac. Sci. Technol.* **16**, 600 (1979)
- 9.129. ISO/TR 18394:2006, *Surface Chemical Analysis – Auger Electron Spectroscopy – Derivation of Chemical Information* (Int. Org. for Standardization, Geneva, 2006)
- 9.130. *Perkin-Elmer Application Note 9201*, 2/92 (1992)
- 9.131. I. Gilmore, M. Wagner, P. Trevorow, *Surf. Interface Anal.* **41**, 634 (2009)
- 9.132. I. Bertóti, *Catalysis Today* **181**, 95 (2012)

Chapter 10

Surface Analysis Techniques Related to AES and XPS

10.1 Overview of Surface Analysis Methods

Any analysis technique will provide a given characteristic property of a surface, such as atomic composition, chemical states, structural composition, topography, or electronic states. The considerable refinement of measurement techniques in the past three decades, all these characteristics of surfaces and interfaces can be analyzed using an abundant variety of methods. All of the methods used for surface studies (together with method variants probably more than 50) cannot be comprehensively treated here. Only the typical characteristics of the four principal methods for surface chemical analysis [10.1] XPS, AES, SIMS, and ISS are compared here. For more information, the reader is referred to numerous books and review articles on this broad topic [10.1–10.13].

Methods to be used for the analysis of surfaces must be selective in response to the surface region relative to the bulk, ranging from one to several monolayers (typically 0.3–3 nm). Surfaces are most commonly explored using techniques based on the interaction of photons, electrons, or ions with the surface or using an electric or electromagnetic field force. These excitations generate a response involving the production of photons, electrons, and ions or the alteration of a force that is used for analysis. Thus, the often shown matrix of exciting and analyzed species in Table 10.1 can be generated [10.11, 10.12] (to the authors knowledge first shown by Benninghoven in 1973 [10.14]). The choice of one or more of the techniques compiled in Table 10.1 depends on the nature of information required of the surface and near surface layers. The fundamental questions are about:

- (a) Morphology and structure of the surface
- (b) Elemental composition of the surface
- (c) Chemical bonds and/or the electronic and molecular structure of the surface
- (d) In-depth composition (thickness) of the surface layer

Table 10.1 provides us an overview of the main techniques (given by their usual acronyms) available for the characterization of surfaces. These techniques

Table 10.1 Surface analysis techniques categorized after species utilized for excitation and analysis

Excitation by	Emission and Detection of			
	Photons	Electrons	Ions (neutrals)	Force
Photons	Ellipsometry	XPS (ESCA)	PSD (PD)	
	IRS (FTIR)	UPS		
	SERS	PEEM		
	SEXAFS	APECS		
	TRXF			
Electrons	IPES	AES (SAM)	ESD (ESDIAD)	
	CLS (EPMA)	REELS		
		SEM		
		SEELFS (EBSD)		
		LEELS		
		(HREELS)		
		APS		
		LEED		
		RHEED		
		PAES		
Ions	GDOES	IAES	SIMS	
		INS	SNMS	
		SHeIM	ISS (LEIS)	
			RBS (HEIS)	
E-field, force, or heat		FEM, STM	FIM (AP-FIM) PTD	AFM

For acronyms and further explanations, see following sections.

are briefly described in the following, categorized on the basis of the nature of the exciting and detected species.

10.2 Photon-Beam Excitation

10.2.1 Detection of Photons

10.2.1.1 Ellipsometry

In ellipsometry, a change in polarization (amplitude and phase) is detected for light reflected from a surface. The measured change depends on optical properties and thickness of individual materials. Therefore, the technique is frequently used to determine film thickness and optical constants. It can also be applied to characterize other material properties such as composition, crystallinity, and roughness, which show up in a change of optical parameters. [10.15, 10.16]. For known optical constants, fractions of a monolayer can be accurately determined [10.17].

10.2.1.2 *Infrared Spectroscopy (IRS) or Fourier Transform Infrared Spectroscopy (FTIR)*

This is a technique to study vibrations of adsorbates on a surface, which are detected by infrared reflection–absorption spectroscopy (IRAS or RAIRS) [10.18].

10.2.1.3 *Surface-Enhanced Raman Scattering (SERS)*

Another vibrational spectroscopy is the detection of Raman scattering by frequency shifts of incident laser light. The frequency shift corresponds to vibrational transitions within the adsorbed molecule. Particularly at rough surfaces, the signal intensity can be increased by several orders of magnitude, known as SERS [10.19, 10.20]. The information obtained from SERS is complementary to both IRS and low-energy, high-resolution electron loss spectroscopy (LEELS or HREELS) in the meV range.

10.2.1.4 *Surface-Extended X-ray Absorption Fine Structure (SEXAFS or S-EXAFS)*

This is the surface sensitive modification of EXAFS. The fine structure of the near the absorption edge of X-rays is generated by interference effects of backscattering of atoms close to the emitting atoms, and therefore it is a probe of local coordination and interatomic distances [10.21, 10.22] and is frequently used with synchrotron radiation [10.23].

10.2.1.5 *Total Reflection X-ray Fluorescence analysis (TRXF)*

As in TRXPS (see Sect. 5.1.3), the incidence angle of the X-ray beam is at the total reflection angle or slightly below. This ensures a high excitation density in the outermost surface layer, the elemental composition of which is determined by X-ray fluorescence spectrometry. With synchrotron radiation, sensitivities of ppm of a monolayer are achieved [10.82].

10.2.2 *Detection of Electrons*

10.2.2.1 *X-ray-Induced Photoelectron Spectroscopy (XPS) and Ultraviolet-Induced Photoelectron Spectroscopy (UPS)*

Today, the most popular surface analysis method is XPS (or ESCA, electron spectroscopy for chemical analysis). Its concepts, advantages, and disadvantages are

explained in Chaps. 1–9 of this book. Furthermore, special techniques using XPS in conjunction with synchrotron radiation (SR-XPS) (Sect. 2.2.3), scanning XPS microscopy (Sect. 2.2.4), imaging XPS (Sect. 2.5.4), and photoelectron diffraction (XPD) (Sect. 3.2.8) were briefly discussed. Special applications using grazing incidence, for example, in total reflection XPS (TRXPS) [10.24] are pointed out in Sect. 5.1.3.

A technique directly related to XPS is ultraviolet photoelectron spectroscopy (UPS) [10.25], which is performed with the same electron analyzer. Compared to conventional XPS, UPS has a narrow line width and a low excitation energy (usually He I radiation of 21.2 eV). This restricts application to low energy levels but ensures a highly surface-specific valence band spectroscopy.

10.2.2.2 Photoemission Electron Microscopy (PEEM)

Similar to XPS and UPS, PEEM utilizes the photoelectric effect to generate photoelectrons by radiation with UV light, X-rays, or synchrotron beam. Usually, these electrons are accelerated into an electron optical column which provides an image of the surface at the exit, given by local variations of electron emission. Addition of energy filtering is used in the technique of photoelectron spectromicroscopy (PESM) [10.3] and can increase lateral resolution to less than 10 nm (see Fig. 2.18).

10.2.2.3 Auger-Photoelectron Coincidence Spectroscopy (APECS)

Time resolved coincidence measurement of an Auger- and a photoelectron emission after ionization of a specified electron level with two different analyzers results in APECS spectra, which are mainly used for fundamental research of understanding quantum mechanical processes in complex spectra [10.79].

10.2.3 Detection of Ions and Neutral Particles

10.2.3.1 Photon-Stimulated Desorption (PSD or PD)

Excitation of a molecule by photons may result in an antibonding state which leads to desorption from the surface. The desorbed particles (ions or neutrals) can be detected in a mass spectrometer (neutrals after postionization, see SNMS) [10.26, 10.27]. PSD is preferably performed with bright light sources like synchrotrons (see Sect. 2.2.3). It is the main source of photon-beam damage in XPS (see Sect. 8.6.2).

10.3 Electron-Beam Excitation

10.3.1 *Detection of Photons*

10.3.1.1 *Inverse Photoemission Spectroscopy (IPES)*

The incident electron beam of low-energy electron ($< 20\text{eV}$, ensuring surface specificity) couples with the unoccupied states above the Fermi level. Some of the transitions to lower unoccupied states are radiative, and the photon counts as a function of the primary electron energy generate the IPES spectrum. Thus, IPES probes the electron levels above the Fermi level, comparable to EELS and complimentary to XPS [10.28, 10.29].

10.3.1.2 *Cathodoluminescence Spectroscopy (CLS)*

More precisely called cathode-ray (=electron)-induced luminescence spectroscopy probes the luminescence properties of insulators or semiconductors that are irradiated with an electron beam. This causes excitation of electrons from the valence band into the conduction band. If direct radiative transitions are possible, recombination occurs by visible light emission for many semiconductors, and by spectroscopy, the band gap and interband levels can be explored. The technique is generally combined with microscopic methods such as SEM or TEM, and like these, it is not intrinsically surface specific (except when combined with low-energy SEM, see Sect. 10.3.2). It is often used for failure analysis in semiconductors [10.30, 10.31].

10.3.2 *Detection of Electrons*

10.3.2.1 *Auger-Electron Spectroscopy (AES), Reflection Electron Energy Loss Spectroscopy (REELS), and Scanning Electron Microscopy (SEM)*

Being one of the main two topics of the book, AES is extensively treated in Chaps. 1–9 (the high-resolution instrumental technique is frequently called scanning Auger microscopy, SAM). Electron energy loss spectroscopy (ELS or EELS) can be directly performed in any Auger spectrometer as reflection electron energy loss spectroscopy (REELS). REELS contains plasmon losses and losses by excitation into unoccupied electron states (see example in Sect. 9.2.2, Fig. 9.16) thus exploring the valence band. REELS data are used as physically correct background subtraction for XPS spectra (see Sect. 4.4.1.1 [10.32]) and for determination of the inelastic mean free path (IMFP) (see Sect. 7.1.8). For the latter, the cross section of the elastic

peak backscattering is applied in the so-called elastic peak electron spectroscopy (EPES) [10.33]. Because of the dependence of the backscattering cross section on the atomic number, EPES can be used for analytical purposes, for example, in depth profiling with AES (see example in Sect. 7.1.8, some typical applications) or for chemical mapping. The high intensity of the elastic peak permits working with a considerably lower primary current than in AES which results in increased lateral resolution and reduced beam damage (see Sect. 8.6.1). Usually, any AES instrument contains a simple secondary electron detector to perform SEM with the resolution basically given by the primary beam diameter. Because all backscattered and low-energy emitted electrons are detected, the primary current can be 2–3 orders of magnitude lower than for AES, and the resolution is increased accordingly. SEM in AES is extremely helpful to explore the surface morphology. However, high-voltage SEM is not surface specific in the monolayer regime. This is the case with low-voltage SEM (as in the Gemini instrument, see Sect. 2.3) where a spatial resolution of 1.5 nm can be achieved at 1.5 keV primary energy [2.18, 2.19].

10.3.2.2 *Surface Electron Energy Loss Fine Structure (SEELFS)*

This is a special method to obtain structural information with AES equipment. It is the electron-exited analogue to SEXAFS (see Sect. 10.2.1). With a primary beam above threshold energy, the fine structure of the losses is carefully separated from the background, and its Fourier transform results in a spectrum of intensity versus the inverse atomic distance, where the first maximum denotes the distance of the first neighbor [10.34, 10.35, 10.36].

10.3.2.3 *Electron Backscatter Diffraction (EBSD)*

This is a crystallographic method for characterization of crystal structures by channeling of backscattered electrons (Kikuchi lines). Although not surface specific, it can easily be combined with AES-SAM and gives orientation distributions of polycrystalline material [10.37].

10.3.2.4 *Low-Energy Electron Loss Spectroscopy (LEELS), Often Called High-Resolution Electron Loss Spectroscopy (HREELS)*

This is used to determine vibrations of adsorbates on the surface analog to SERS (see Sect. 10.2.1) by determination of energy losses at typically some 100 eV energy. Therefore, an electron beam with high resolution of typically several meV is required which is obtained by a monochromator (actually a second electron energy analyzer) [10.38, 10.39].

10.3.2.5 *Appearance Potential Spectroscopy (APS)*

In contrast to AES with fixed primary energy, in APS, the primary beam energy is sweeping through an energy interval (usually 50–2000 eV), and the onset of the emission of photons or Auger electrons is detected as soon as the beam energy matches the threshold energy for ionization of the respective electron energy level [10.40]. Since the energy (and IMFP) is given by the exciting beam, no spectrometer for the emission is necessary. If the onset of Auger-electron emission is observed, the method is called AE-APS (Auger electron-APS), and for photon emission SX-APS (soft X-ray APS). When a sudden drop of elastically backscattered electron flux is monitored, the method is called DAPS (disappearance potential spectroscopy). Similar to the extended electron loss fine structure (EELFS), these techniques contain information about the local structure and can be used to determine, for example, the next nearest neighbor distance [10.41].

10.3.2.6 *Low-Energy Electron Diffraction (LEED)*

This is probably the most traditional technique to study the crystalline structure of the top surface layer [10.42–10.45]. Since low-energy electrons of about 150 eV energy have a wavelength of about 0.1 nm, backscattering of an electron beam of this energy impinging on a crystalline surface produces an angular diffraction pattern which can be observed on a luminescent screen. The LEED pattern represents the reciprocal space from which the real surface layer structure can be constructed. Dependence of LEED spot intensity on energy ($I(V)$ curves) and diffuse background can be used to reveal more details about local structure in adsorbate clusters [10.44]. LEED with a four grid system for analyzing the secondary electron emission (retarding field analyzer) can be used to acquire Auger spectra, and one of the first commercial AES instruments was of this type (see Sect. 1.1).

10.3.2.7 *Reflection High-Energy Electron Diffraction (RHEED)*

This is another electron diffraction technique which uses an energy beam of typically 5–100 keV. This means, in contrast to LEED, an electron attenuation length of about 3–30 nm [10.44, 10.46]. Therefore, RHEED can only be made surface specific if used in glancing incidence. This makes RHEED sensitive to surface roughness on an atomic scale, which fosters its main use of monitoring layer-by-layer growth (Frank-van der Merwe (FV) growth, see Sect. 4.3.3).

10.3.2.8 *Positron-Annihilation-Induced Auger Electron Spectroscopy (PAES)*

With electron vacancies created by low energy positron annihilation ($<10\text{eV}$), background free Auger peaks are generated for atoms in the outermost surface layer. The technique can be used e.g. for observing growth of ultra-thin films on metal and semiconductor substrates [10.80].

10.3.3 *Detection of Ions and Neutrals*

10.3.3.1 *Electron-Stimulated Desorption (ESD)*

The technique of ESD is closely related to photon-stimulated desorption (PSD). Like there, the basic mechanism is excitation of an adsorbed molecule into an antibonding state may lead to its desorption [10.9]. ESD can be directly observed during AES, for example, by monitoring the desorbed species (see Sect. 8.6.1). For analysis of the desorbed species, a mass spectrometer for detecting ions and neutrals is required. The directionality of adsorbate bonds can be studied by observation of the angular distributions of desorbed ions with a technique called *electron-stimulated desorption in ion angular distributions (ESDIAD)* [10.47, 10.48].

10.4 Ion-Beam Excitation

10.4.1 *Detection of Photons*

10.4.1.1 *Glow Discharge Optical Emission Spectroscopy (GDOES)*

This technique is based on glow discharge plasma (most often radio frequency excitation) which erodes the surface by ion impact as in SIMS. The sputtered species are excited and emit optical lines by which elemental analysis is enabled [10.49, 10.50]. Owing to high ionic current densities, the sputtering rate is rather high, thin surface films can be analyzed in seconds, and a wide range until $100\text{ }\mu\text{m}$ can be covered. Although GDOES is rather a thin film than a surface analysis technique, and is not operating under ultra high vacuum conditions, it can be used for ex situ analysis of the first few atomic layers with high-depth resolution [10.50, 10.51]. As disclosed by MRI modeling (see Sect. 7.1.8), the atomic mixing length is close to the theoretical limit of about 0.3 nm because of the low-energy primary ions, and with the information depth and roughness of the same order of magnitude, the resulting depth resolution for the first atomic layers is about 1 nm [10.51]. For larger depth, the increasing unevenness of the crater and the crater wall effect cause a strong degradation of depth resolution with depth.

10.4.2 Detection of Electrons

10.4.2.1 Ion-Excited Auger Electron Spectroscopy (IAES)

IAES is a technique of limited importance since only three common elements, Mg, Al, and Si, have a cross section large enough that IAES can be measured under normal conditions [10.52]. IAES spectra are different from usual electron or X-ray-excited Auger spectra and can serve for cluster structure and chemical environment of atoms. In AES depth profiling, during sputtering of the above materials, IAES is a detrimental effect which distorts the electron-induced Auger spectra [10.53].

A rather special technique is ion neutralization spectroscopy (*INS*). Surface excitation with low-energy He^+ or He^{++} ions (5–10 eV) results in neutralization of the ions, and the energy gain produces valence band Auger spectra which contain information about the density of states [10.6].

10.4.2.2 Scanning Helium Ion Microscopy (SHeIM)

SHeIM is a new technique based on a scanning He ion beam. Because of the short de Broglie wavelength of the He ions, the secondary electron emission pictures offer high, sub-nanometer resolution and strong contrast of topographic, material, crystallographic and electrocal properties of the sample [10.84].

10.4.3 Detection of Ions and Neutrals

10.4.3.1 Secondary Ion Mass Spectrometry (SIMS)

When a surface is bombarded by energetic ions (or atoms), secondary particles are emitted which are constituents of the sample surface: neutrals, positive, and negative ions, partly in different clusters and multiply charged. The emitted ions are separated by a mass spectrometer in terms of the ratio mass/electric charge (m/e). All elements including hydrogen can be detected. A unique feature is the capability to detect isotopes [10.54]. In addition to mass analysis, energy-resolved SIMS spectra can be used for detailed analysis [10.55].

Really surface sensitive is the so-called static SIMS (*SSIMS*) method, introduced by Benninghoven [10.56]. This is a practically nondestructive method because the primary ion density is so low that only a small fraction of the first monolayer (typically 1%) is used up for analysis. In contrast, dynamic SIMS (*DSIMS*) is used for depth profiling with a much faster sputtering rate [10.57]. Since, practically independent of the primary ion energy, 90% of the sputtered particles originate in the first monolayer (ML) [10.58] (see also Fig. 14 in Ref. [10.11]), the information depth and therefore the intrinsic depth resolution of SIMS is about 1ML (see Sect. 7.1.8).

Quantification of SIMS in unknown samples with different main constituents is complicated mainly by the large scatter of relative sensitivity factors given by the ionization probability which varies by about five orders of magnitude between the elements. Matrix effects are lowered, and the positive ion yield is increased by using oxygen primary ions or cesium ions for negative ions. Of increasing importance is the technique of time-of-flight SIMS (ToF-SIMS) with the advantage of high transmission (up to 50% of the emitted ions), independent of mass range and with a very high mass number that is particularly important to detect ionized fragments of high-mass organic molecules as often encountered in studies of biological matter. In ToF-SIMS [10.59, 10.60], a pulsed high potential (typically 10 ns pulses at $E = 10 \text{ keV}$) is used to accelerate the secondary ions (mass m and velocity v) to the same kinetic energy, $(m/(2v^2)) = eE$ (with e being the electrical elementary charge). After the secondary ions fly through a field free drift tube, they arrive at the detector at a time depending inversely on their velocity that is in turn proportional to the square root of the mass. ToF-SIMS has been developed to a highly efficient technique for imaging SIMS with submicron resolution and for depth profiling with high elemental sensitivity. Because SIMS is basically free of background, the sensitivity is outstanding and often in the ppb range.

Only a small fraction of the sputtered particles is ionized, and the majority is neutrals. The detection of these neutrals would mean increased detection sensitivity and much less variation in the relative sensitivity factors. This goal is approached by ionization of the sputtered matter and called postionization, which is automatically achieved by plasma excitation in glow discharge mass spectrometry (GDMS) (similar to the easier GDOES). In UHV, the technique is called SNMS (sputtered neutrals mass spectrometry) [10.61, 10.62], and postionization can be also performed by laser radiation [10.62] or an electron beam.

New developments and present state of SIMS and SNMS are found in the SIMS conference proceedings published every two years [10.63].

10.4.3.2 Ion Scattering Spectroscopy (ISS) and Rutherford Backscattering (RBS)

Measurement of the energy loss of backscattered primary ions is the principle of both techniques. The main difference is in the ion energy, which is typically 0.5–5 keV for ISS and 100 keV–3 MeV for RBS. Whereas the latter (also called HEIS for high-energy ion scattering) basically is a thin film depth profiling method (with high-resolution analyzers and/or medium energy ion scattering (MEIS) made surface specific [10.81]), ISS, or – more precisely – low-energy ion scattering (LEIS) is perhaps the ultimate surface-specific method [10.64–10.67]. The relative energy loss of ions elastically scattered at the surface depends on the difference between the primary ion mass and the target atom mass and on the scattering angle according to physical momentum and energy transfer laws for two bodies, making qualitative interpretation of LEIS spectra rather simple and straightforward. Quantification of LEIS is more complicated because of reneutralization at the

surface, which confines analysis to the first monolayer. Using shadowing cone concepts, a structural analysis of the surface is possible [10.66]. Isotope detection is obtained for lower atomic mass but difficult for higher mass because of decreasing resolution. Chemical state determination is impossible. LEIS can easily included in AES or XPS instruments since ion guns and energy analyzer are available. In principle, energy analysis can be performed just by reversing the potential of the analyzer electrodes to energy select the positive ions (usually He^+ or Ne^+) [10.67].

10.5 Excitation by Electric Field or Heat

10.5.1 *Detection of Photons*

10.5.1.1 *Thermoluminescence (TL)*

The emission of light during continuous heating up of a sample which contains trapped electrons is a traditional method to obtain information about interband levels and can be used for analysis. Not being intrinsically surface specific, the dependence of the emitted light frequency on structural details of nanomaterials may foster its future use in that field [10.68].

10.5.2 *Detection of Electrons*

10.5.2.1 *Field Electron Microscopy (FEM) and Scanning Tunneling Microscopy (STM)*

In FEM, a specially prepared emitter tip with a radius of typically 100 nm is employed in combination with a voltage of a few keV to extract electrons which are collected at a screen. Spots can be obtained with an intensity basically related to the local work function, and with a spatial resolution of about 2 nm. In time-resolved mode, the highly surface-specific technique is capable of detection of surface oscillations of adsorbates [10.69]. It is mainly used in fundamental studies and has fewer applications because of only indirect specific to elements.

Invented by Binnig and Rohrer in 1982 [10.70], STM is now widespread in use to characterize the real structure of surfaces with atomic resolution [10.69–10.72]. The STM image at constant tunneling current represents a map of constant density of states at the first monolayer. Consequently, for covalent bond as for Si, atomic resolution is easy to obtain as compared to metals with milder variations over the surface. By variation of the tunneling voltage, the density of states function can be obtained with more detail by the technique of scanning tunneling spectroscopy (STS) with more element or bonding specific characterization capability [10.71, 10.72]. STM instruments can often be used as AFM instruments too (see Sect. 10.5.4.1).

10.5.3 Detection of Ions and Neutral Particles

10.5.3.1 Field Ion Microscopy (FIM) and Atom Probe (FIM-AP)

Like with FEM, a fine tip of typically 100 nm radius is required for proper operation. With a positive voltage of 5–30 keV applied to the tip, a low-pressure image gas (He) is ionized, and the ions are accelerated along the radial field lines until they hit a phosphor screen in a few millimeters distance to form an image of the surface. This is the nondestructive imaging mode (FIM). By increasing the voltage to a value high enough to overcome the surface bond ($> 108 \text{ V/cm}$), field evaporation occurs. Applying a pulsed high-voltage, a time-of-flight mass spectrometer can analyze the mass of each desorbed atom separately (FIM-AP) [10.73, 10.74]. Subsequent field evaporation of atomic layers generates a three-dimensional elemental analysis with near atomic resolution [10.74]. Thus, FIM-AP is the ultimate nanostructure analysis technique [10.73], but its general usage is mainly restricted by the special sample shape.

10.5.3.2 Thermal Desorption or Temperature Programmed Desorption (TPD)

Adsorbed species on a surface can be desorbed by heating the sample and observing the pressure increase. The concept is simple, but evaluation of results is difficult. The latter contain information about the nature of adsorbed species, their interaction, and desorption energies [10.75, 10.76]. Combination with a quadrupole mass spectrometer serves to analyze adsorbed species. The technique is restricted to relatively weakly bound adsorbate layers.

10.5.4 Detection of Forces

10.5.4.1 Atomic Force Microscopy (AFM)

The most important offspring of STM is AFM, which, together with many other variants, constitutes the family of scanning probe microscopy (SPM) [10.69]. In contrast to STM, AFM (sometimes called scanning force microscopy, SFM) probes interatomic forces as described, for example, by the Lennard-Jones potential. Its first derivative is the force which in the contact mode is repulsive and is usually measured by laser reflection of a bending cantilever [10.69, 10.77]. The advantage of AFM is that it can be used on insulators and on biological material [10.78], and in gaseous or liquid environment. Scanning probe microscopy reveals a detailed three-dimensional morphology of the surface, with atomic resolution in many cases. In general, no chemical analysis is provided.

10.6 Comparison of the Principal Surface Chemical Analysis Techniques

10.6.1 Main Features of AES, XPS, SIMS and ISS

The most important features of the four basic techniques for surface *chemical* analysis, XPS, AES, SIMS, and ISS, are summarized and compared in Table 10.2 [10.7, 10.11, 10.12]. In Fig. 10.1, a diagram of depth resolution versus lateral resolution is presented. Common to all surface analysis techniques is a depth resolution between one and a few atomic monolayers. With exception of the atomic resolution techniques AP-FIM, AFM (STM), and Transmission Electron Microscopy (TEM), the lateral resolution of the four principal techniques is steadily developing into the direction of the former. The main advantage of XPS, AES, SIMS, and ISS is that they are capable of directly determining the chemical composition of unknown surfaces. Further capabilities and limitations of these techniques are:

10.6.1.1 XPS

Capabilities: Easy interpretation of spectra with chemical information by simple peak shift. Good peak-to-background ratio ensures reliable quantification using peak area after background subtraction. Relative elemental sensitivities of main peaks are within one order of magnitude (as in AES). Usually less beam damage than AES is encountered.

Limitations: Restricted sensitivity (0.1 at %), limited lateral resolution (less than AES, see Table 10.2 and Fig. 10.1), frequently kinetic electron energy higher than in AES, resulting in higher attenuation lengths.

Table 10.2 Comparison of the main features of the four principal surface analysis techniques XPS, AES, SIMS, and ISS

	XPS	AES	SIMS	ISS
Excitation	Photons	Electrons	Ions	Ions
Detection	Electrons	Electrons	Ions	Ions
Analysis	Energy	Energy	Mass (m/e)	Energy
Information depth (ML)	3–20	2–30	1–2	1
Lateral resolution	150 nm–15 μm	3–30 nm	20 nm–1 μm	1 mm
Typical detection limit (at%)	0.1	0.1	10^{-6}	0.1
Detection capability				
Elements	$Z > 1$	$Z > 2$	All	$Z > 1$
Isotopes	No	No	Yes	Yes
Chemical bonding	Yes	Yes	Yes (molecules)	No

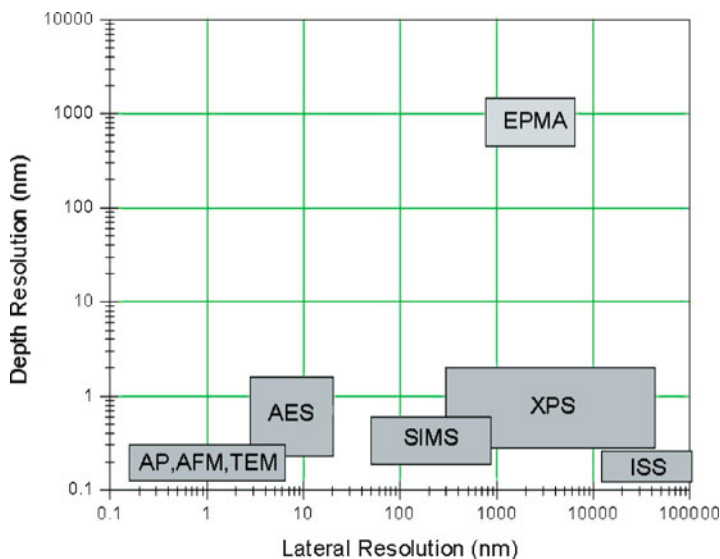


Fig. 10.1 Typical values of depth resolution and present lateral resolution of surface analysis techniques. While atom probe (AP = AP-FIM), AFM (STM), and TEM (STEM) possess atomic resolution, the principal surface analysis techniques are typically nanometer depth resolution techniques (with ISS an exception), and EPMA (electron microprobe analysis) basically is a bulk technique. Non-UHV-TEM is restricted to ex situ surface layer analysis after FIB cross section preparation

10.6.1.2 AES

Capabilities: The main feature is its high spatial resolution and versatility of the electron beam, enabling scanning electron image of the analyzed area, point, line, and chemical maps. AES is optimal for high-resolution depth profiles. Chemical effects are often larger than in XPS and accessible by factor analysis. Fine features of electronic structure are revealed by easy to perform REELS and EPES techniques.

Limitations: Quantitative AES is more difficult to perform as compared to XPS, because peak area determination is restricted by more complicated spectra, electron backscattering and a large electron background. Chemical effects are pronounced but difficult to interpret. Charging of insulators is often difficult to overcome.

10.6.1.3 SIMS

Capabilities: High sensitivity in the ppb range, detection of isotopes of all elements including hydrogen, and high dynamic range (up to 10^8) are the main features. High intrinsic depth resolution of 1–2 ML enables high-resolution depth profiles. High spatial resolution and scanning electron image of analyzed area are possible. There

is no chemical bonding detection, but identification of the molecular structure is possible by typical fragment analysis.

Limitations: SIMS is a destructive analysis method, with wide range of elemental sensitivity factors (up to five orders of magnitude), enhancing large matrix effects with difficulties in quantification of nondilute systems.

10.6.1.4 ISS

Capabilities: Unique analysis of the outermost atomic layer, with additional information about its structure by shadowing experiments, can be performed. ISS principally is a nondestructive technique.

Limitations: ISS is extremely sensitive to surface contamination and difficult to quantify. Slight sputtering effects lead to gradual change of the surface with time. ISS is more useful for fundamental studies than in applications.

10.6.2 Combination of Techniques

Surface analysis can be optimized by using the strength of each method in a combined approach. Thus, the combination of XPS and AES has proved very useful, for example, for determination of plasmon losses by AES for use in background subtraction in complicated XPS spectra (see Fig. 9.1). XPS and AES are often used in combination with ISS to disclose the composition of the first surface layer from layers below as, for example, generated by preferential sputtering of a component in depth profiling (see Fig. 7.13). Combining an ultraviolet source with XPS, UPS can be performed to reveal the valence band electronic structure with high energy resolution. SIMS and AES are complementary with respect to depth profiling, because principally SIMS is not sensitive to preferential sputtering in contrast to AES (see Sect. 7.1.4.2). Depth profiling with both techniques under similar conditions enables detection of nonlinearity in cluster formation of SIMS spectra and helps to understand the transient state in depth profiling. While quantification of the main constituents is easier for AES, SIMS reveals the minor concentration constituents. A comprehensive comparison of various techniques for the elemental distribution in a thin film sample of Cu(In, Ga)Se₂ with participation of 20 laboratories is given in Ref. [10.83].

References

- 10.1. J.C. Vickerman, I.S. Gilmore (eds.), *Surface Analysis – The Principal Techniques*, 2nd edn. (Wiley, Chichester, 2009)
- 10.2. S. Hofmann, Surface and Interface Analysis, in *Kirk-Othmer Encyclopedia of Chemical Technology*, 5th edn. (Wiley, Chichester, 2007), pp. 71–117

- 10.3. J.C. Rivi re, S. Myrha (eds.), *Handbook of Surface and Interface Analysis* (Marcel Dekker, New York, 1998)
- 10.4. R.W. Cahn, E. Lifshin (eds.) *Concise Encyclopedia of Materials Characterization* (Pergamon Press, Oxford, 1993)
- 10.5. D.J. Connor, B.A. Sexton, R.S.C. Smart (eds.), *Surface Analysis Methods in Materials Science* (Springer, Berlin, 1992)
- 10.6. J.C. Rivi re, *Surface Analytical Techniques* (Oxford University Press, New York, 1990)
- 10.7. J.M. Walls (ed.), *Methods of Surface Analysis: Techniques and Applications* (Cambridge University Press, Cambridge, 1989)
- 10.8. L.C. Feldman, J.W. Mayer, *Fundamentals of Surface and Thin Film Analysis* (Elsevier, Amsterdam, 1986)
- 10.9. D.P. Woodruff, T.A. Delchar, *Modern Techniques of Surface Science* (Cambridge University Press, Cambridge, 1986)
- 10.10. A.W. Czanderna (ed.), *Methods of Surface Analysis* (Elsevier, Amsterdam, 1975)
- 10.11. S. Hofmann, Surf. Interface Anal. **9**, 3 (1986)
- 10.12. S. Hofmann, Talanta **26**, 665 (1979)
- 10.13. A. Benninghoven, Thin Solid Films **39**, 3 (1976)
- 10.14. A. Benninghoven, Appl. Phys. **1**, 1 (1973)
- 10.15. M. Schubert, Infrared Ellipsometry on Semiconductor Layer Structures: Phonons, Plasmons, and Polaritons, (Springer, Berlin, 2004)
- 10.16. H.G. Tompkins, *A User's Guide to Ellipsometry* (Dover Publications, Mineola, 2006)
- 10.17. E. Panda, L.P.H. Jeurgens, E.J. Mittemeijer, J. Appl. Phys. **106**, 114913 (2009)
- 10.18. N. Ikemiya, T. Suzuki, M. Ito, Surf. Sci. **466**, 119 (2000)
- 10.19. J.A. Creighton, Surf. Sci. **124**, 209 (1983)
- 10.20. S.A. Meyer, E.C. Le Ru, P.G. Etchegoin, Anal. Chem. **83**, 2337 (2011)
- 10.21. C. Likwan, N.C. Sturchio, M.J. Bedzyk, Phys. Rev. B **61**, 4877 (2000)
- 10.22. M.E. Pemble, P. Gardener, Vibrational Spectroscopy from Surfaces, in *Surface Analysis – The Principal Techniques*, 2nd edn., ed. by J.C. Vickerman, I.S. Gilmore (Wiley, Chichester, 2009), pp. 333–390
- 10.23. P. Keil, D. Luetzenkirchen-Hecht, J. Synchr. Rad. **16**, 443 (2009)
- 10.24. A. von Bohlen, Spectrochim. Acta B **64**, 821 (2009)
- 10.25. W.J. Chun, A. Ishikawa, H. Fujisawa, T. Takata, J.N. Kondo, M. Hara, M. Kawai, Y. Matsumoto, K. Domen, J. Phys. Chem. B **107**, 1798 (2003)
- 10.26. T. E. Madey, Science **234**, 316 (1986)
- 10.27. T. Sekiguchi, H. Ikeura-Sekiguchi, Y. Baba, Appl. Surf. Sci. **254**, 7812 (2008)
- 10.28. S. Derossi, F. Ciccacci, Surf. Sci. **307**, 496 (1994)
- 10.29. M. Shimomura, Y. Sano, N. Sanada, L.L. Cao, Y. Fukuda, Appl. Surf. Sci. **244**, 153 (2005)
- 10.30. B.G. Yacobi, D.B. Holt, *Cathodoluminescence Microscopy of Inorganic Solids* (Plenum Press, New York, 1990)
- 10.31. P.R. Edwards, R.W. Martin, Semicond. Sci. Technol. **26**, 064005 (2011)
- 10.32. M.P. Seah, I.S. Gilmore, S.J. Spencer, J. Electron Spectrosc. Relat. Phenom. **120**, 93 (2001)
- 10.33. W.S.M. Werner, C. Tomastik, T. Cabela, G. Richter, H. Stoeri, J. Electron Spectrosc. Relat. Phenom. **113**, 127 (2001)
- 10.34. S. Bartuschat, J. Urban Philos. Mag. **A 76**, 783 (1997)
- 10.35. C. Goyhenex, C.R. Henry, J. Electron Spectrosc. Relat. Phenom. **61**, 65 (1992)
- 10.36. M. De Crescenzi, J. Vac. Sci. Technol. A **5**, 869 (1987)
- 10.37. F.J. Humphreys, J. Mater. Sci. **36**, 3833 (2001)
- 10.38. J. Bevol, J. D. Verhoeven, M. Noack, Surf. Sci. **134**, 499 (1983)
- 10.39. M.A. Henderson, Surf. Sci. **355**, 151 (1996)
- 10.40. Y. Fukuda, Anal. Sci. **26**, 187 (2010)
- 10.41. M.L. den Boer, T.L. Einstein, W.T. Elam, R.L. Park, L.D. Roelofs, G.E. Laramore, J. Vac. Sci. Technol. **17**, 59 (1980)
- 10.42. J.B. Pendry, *Low Energy Electron Diffraction* (Academic Press, New York, 1974)
- 10.43. J.E. Demuth, T.N. Rhodin, Surf. Sci. **45**, 249 (1974)

- 10.44. C.A. Lucas, Surface Structure Determination by Interference Techniques, in *Surface Analysis – The Principal Techniques*, 2nd edn., ed. by J.C. Vickerman, I.S. Gilmore (Wiley, Chichester, 2009), pp. 391–478
- 10.45. S.M. Sutin, N.S. Sokolov, J. Roy, J. Zegenhagen, *Surf. Sci.* **605**, 153 (2011)
- 10.46. K. Mascaronek, P. Blumentrit, J. Beran, T. Skaacutela, I. Pinodotacuscron, J. Libra, V. Matolinodotacuten, *Surf. Interface Anal.* **42**, 540 (2010)
- 10.47. P. Netzer, T.E. Madey, *Surf. Sci.* **110**, 251 (1981)
- 10.48. K. Irokawa, R. Tanaka, H. Miki, *Surf. Sci.* **602**, 3438 (2008)
- 10.49. R. Payling, T. Nelis, *Glow Discharge Optical Emission Spectroscopy: A Practical Guide* (The Royal Society of Chemistry, Cambridge, 2003)
- 10.50. K. Shimizu, R. Payling, H. Habazaki, P. Skeldon, G.E. Thompson, *J. Anal. Atom. Spectrom.* **19**, 692 (2004)
- 10.51. S. Hofmann, J.Y. Wang, *J. Surf. Anal.* **13**, 142 (2006)
- 10.52. J.T. Grant, Ion Excited Auger Electron Spectroscopy, in *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, ed. by D. Briggs, J.T. Grant (IM Publications, Chichester, 2003), pp. 763–744
- 10.53. A. Zalar, S. Hofmann, F. Pimentel, P. Panjan, *Surf. Interface Anal.* **21**, 560 (1994)
- 10.54. A. Benninghoven, F.G. Rüdenauer, H.W. Werner, *Secondary Ion Mass Spectrometry* (Wiley, New York, 1987)
- 10.55. L. Desgranges, B. Pasquet, I. Roure, *Appl. Surf. Sci.* **257**, 6208 (2011)
- 10.56. A. Benninghoven, *Surf. Sci.* **35**, 427 (1973)
- 10.57. D. McPhail, M. Dowsett, Dynamic SIMS, in *Surface Analysis – The Principal Techniques*, 2nd edn., ed. by J.C. Vickerman, I.S. Gilmore (Wiley, Chichester, 2009), pp. 207–268
- 10.58. W. Eckstein, J. Biersack, *Nucl. Instrum. Meth.* **82**, 550 (1984)
- 10.59. A. Benninghoven, *Angew. Chem.* **33**, 1023 (1994)
- 10.60. J.C. Vickerman, D. Briggs (eds.) *ToF-SIMS: Surface Analysis by Mass Spectrometry* (IM Publications, Chichester, 2003)
- 10.61. H. Oechsner, E. Stumpe, *Appl. Phys.* **14**, 43 (1977)
- 10.62. N. Kubota, S. Hayashi, *Appl. Surf. Sci.* **255**, 1516 (2008)
- 10.63. J. Gardella, P. Clark, *Surf. Interface Anal.* **43**, 1 (2011)
- 10.64. E. Taglauer, Low-Energy Ion Scattering and Rutherford Backscattering, in *Surface Analysis – The Principal Techniques*, 2nd edn., ed. by J.C. Vickerman, I.S. Gilmore (Wiley, Chichester, 2009), pp. 267–331
- 10.65. H.H. Brongersma, M. Draxler, M. de Ridder, P. Bauer, *Surf. Sci. Rep.* **62**, 63 (2007)
- 10.66. M. Walker, M.G. Brown, M. Draxler, M.G. Dowsett, C.F. McConville, T.C.Q. Noakes, P. Bailey, *Phys. Rev. B* **83**, 085424 (2011)
- 10.67. G.B. Hoflund, Spectroscopic Techniques: XPS, AES, and ISS, in *Handbook of Surface and Interface Analysis*, ed. by J.C. Riviere, S. Myrha (Marcel Dekker, New York, 1998), pp. 57–158
- 10.68. Z. Knezevic, M. Ranogajec-Komor, S. Miljanic, J.I. Lee, L.L. Kim, S. Music, *Rad. Measure.* **46**, 329 (2011)
- 10.69. S. Myrha, Introduction to Scanned Probe Microscopy, in *Handbook of Surface and Interface Analysis*, ed. by J.C. Riviere, S. Myrha (Marcel Dekker, New York, 1998), pp. 395–446
- 10.70. G. Binnig, H. Rohrer, *Helv. Phys. Acta* **55**, 726 (1982)
- 10.71. W.T. Pong, C. Durkan, *J. Phys. D Appl. Phys.* **38**, R329 (2005)
- 10.72. M. Nakaya, M. Aono, T. Nakayama, *Carbon* **49**, 1829 (2011)
- 10.73. T.T. Tsong, *Surf. Interface Anal.* **39**, 111 (2007)
- 10.74. K. Hono, *Prog. Mater. Sci.* **47**, 621 (2002)
- 10.75. T.E. Madey, J. T. Yates, *J. Vac. Sci. Technol.* **8**, 39 (1971)
- 10.76. T. Izumi, G. Itoh, *Mater. Trans.* **52**, 130 (2011)
- 10.77. P.K. Hansma, V.B. Elings, O. Marty, C.E. Bracker, *Surf. Sci.* **242**, 209 (1988)
- 10.78. L. Sun, D.X. Zhao, Y. Zhang, F.G. Xu, Z.A. Li, *Appl. Surf. Sci.* **257**, 6560 (2011)

- 10.79. S.M. Thurgate, Electron Coincidence Measurements, in *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, ed. by D. Briggs, J.T. Grant (IM Publ., Chichester, 2003), pp. 787–796
- 10.80. T. Ohdaira, R. Suzuki, Positron-Annihilation-Induced Auger Electron Spectroscopy, in *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, ed. by D. Briggs, J.T. Grant (IM Publ., Chichester, 2003), pp. 775–786
- 10.81. H.D. Carstanjen, Nucl. Instr. Methods B136-138, 1183 (1998)
- 10.82. C. Strelt, P. Wobrauschek, F. Meirer, G. Pepponi, J. Anal. At. Spectrom. **23**, 792 (2008)
- 10.83. D. Abou-Ras, R. Caballero, C.-H. Fischer, C.A. Kaufmann, I. Lauermann, R. Mainz, H. Mönig, A. Schöpke, C. Stephan, C. Streeck, S. Schorr, A. Eicke, M. Dbeli, B. Gade, J. Hinrichs, T. Nunney, H. Dijkstra, V. Hoffmann, D. Klemm, V. Efimova, A. Bergmaier, G. Dollinger, T. Wirth, W. Unger, A.A. Rockett, A. Perez-Rodriguez, J. Alvarez-Garcia, V. Izquierdo-Roca, T. Schmid, P.-P. Choi, M. Mller, F. Bertram, J. Christen, H. Khatri, R.W. Collins, S. Marsillac, I. Kötschau, Microscopy a. Microanal. **17**, 728 (2011)
- 10.84. R. Hill, F.H.M. Faridur Rahman, Nucl. Instr. Meth. Phys. Res., **A 645**, 96 (2011)

Index

- Absorbed current, 26
- Acceptance angle, 29, 35, 180, 236
- Acceptance area, 29, 33
- Acceptance cone (CMA), 36, 210, 238, 251
- Accuracy
 - definition, 259
 - MRI applications, 363
 - quantification by RSFs, 86
- Accuracy and precision
 - in profile reconstruction, 363
 - in pulse counting, 259–260
- ADAM. *See* Angular distribution Auger microscopy
- Adatoms, 155
- Adsorbate
 - structure, 59, 60
 - in thin film growth, 155–159
- Adsorption, 13
- Adventitious carbon, 49, 425
- ADXPS, angle dependent XPS. *See* Angle resolved XPS
- AED. *See* Auger electron diffraction
- AES. *See* Auger electron spectroscopy
- AFM. *See* Atomic force microscopy
- Ag. *See* Silver
- Al. *See* Aluminium
- ALD. *See* Atomic layer deposition
- Alignment procedures, 422. *See also* Experimental setup
 - depth profiling, 300
- Alloy
 - oxidation (*see* Oxidation of alloys)
 - sputtering, 327, 328
- Altered layer
 - by ion bombardment, 304, 325, 476
 - by sputter cleaning, 418
 - thickness and composition, 393–396
- Aluminium (Al)
 - AlB₁₂ (electrical resistivity), 428
 - Al K_α (*see* X-ray source)
 - Al L_{2,3}VV shift by oxidation, 455
 - AlN
 - electrical conductivity, 428
 - thermal conductivity, 439
 - Al₂O₃ (*see* Al oxide)
 - Al peak
 - AES, 72, 457
 - Al2p, oxide, 53, 56, 132–134
 - Al (thermal conductivity), 439
 - Al 2p line scan, 39
 - anode, 18
 - attenuation length comparison for 1500 eV, 96
 - Auger energy
 - Al KL_{2,3}L_{2,3}, 421, 455
 - Al L_{2,3}VV, 72, 364, 455, 457
 - backscattering factor (KLL), 178
 - depth profile in GaAs/AlAs, 341, 363–365
 - AR-AES, 361, 395
 - atomic mixing length, 395
 - ESD of Al₂O₃, 435, 436
 - foil, 18
 - oxide, Al₂O₃
 - α–Al₂O₃ (0001), 469
 - AR-XPS, 397, 398
 - charging, 431
 - ESD, 435–438
 - islands on SiO₂, 479
 - layer thickness, 397, 398, 400
 - preferential sputtering, 324
 - quantification, 131–135
 - thermal conductivity, 439
 - oxide peak
 - AES, 72, 457

- Al ($L_{2,3}$)O($L_{2,3}$)O($L_{2,3}$) cross transition, 469
- amorphous to crystalline transition, 50
- XPS, Al2p, 53
- peak asymmetry, 54–56
- peaks
 - AES, LVV, 72, 457
 - XPS Al 2p, 53
- plasmon, intrinsic (Al, Al_2O_3), 53, 138–141
- sapphire, 469
- selective oxidation, 456
- Si/Al/Si, 460
- sputtering yield, 301
- thermal conductivity, 439
- Amorphous materials, 58, 105, 412
 - by ion bombardment, 337
- Analog data acquisition systems, 293–295
- Analysis chamber, 16, 417
- Analysis of the remaining surface, 298
- Analysis of the sputtered matter, 298
- Analytical strategy, 409–411
- Analyzed area. *See* Electron energy analyzer
- Analyzer. *See* Electron energy analyzer
- Angle dependence of
 - asymmetry factor, 106–109
 - backscattering effect, 176–179
 - CHA, 229–234
 - CMA, 239–240
 - elastic scattering effect, 99–102
 - intensity (*see* Emission and incidence angle dependence)
 - surface excitation parameter (SEP), 92–95
- Angle lapping, 416
- Angle resolved AES (AR-AES), 382–398
 - of atomic mixing in GaAs/AlAs, 361
 - with CHA, 239, 241–250, 361, 383, 395
 - flat and rough surface with CMA, 250–255
 - for nondestructive depth profiling, 382–402
- Angle resolved XPS (AR-XPS), 382–398
 - of Al_2O_3 islands on SiO_2 , 479
 - of altered layer on Ta_2O_5 , 476, 478
 - of contamination layer on Nb_2O_5 , 388–390
 - flat and rough surface, 214–226
 - for nondestructive depth profiling, 382–402, 476, 478, 479
- Angular distribution Auger microscopy (ADAM), 73
- Angular relations in AES and XPS, 100, 103, 205–256
- Anisotropy of photoemission. *See* Asymmetry factor in XPS
- Anisotropy of segregation. *See* Segregation
- Anode
 - Al, Mg (*see* X-ray source)
- APECS. *See* Auger-photoelectron coincidence spectroscopy
- Aperture angle, 24, 30, 31, 35, 111. *See also* Electron energy analyzer
- AP-FIM. *See* Atom-probe field ion microscopy
- Apparent depth profile, 326
- Apparent layer thickness, 219–226
- Appearance potential spectroscopy (APS), 493
- APPH. *See* Auger-peak-to-peak-height
- APPH depth profile, 310, 311
- Applications of AES and XPS, 451–482
- APS. *See* Appearance potential spectroscopy
- Ar. *See* Argon
- AR-AES. *See* Angle resolved AES
- Argon (Ar)
 - Ar^+ ions, 28
 - Ar_n^+ clusters, 28
 - Ar $2p_{3/2}$ peak in sputter depth profiling, 425
 - gas in chamber, 14
 - gas in ion gun, 27
 - neutrals in beam, 27, 28
 - sputtering yields, 301
- Arrhenius plot of diffusion, 368
- Arsenic (As)
 - AsAl/GaAs (*see* Gallium)
 - sputtering yield, 301
- Artifacts, 434
- AR-XPS. *See* Angle resolved XPS
- As. *See* Arsenic
- Asymmetry factor in XPS, 106–109
 - Atomic
 - concentration, 77, 85
 - density, 104, 113
 - electron levels, notation, 43
 - force microscopy (AFM), 498
 - layer deposition (ALD), 479
 - mixing, 338, 349, 351–352, 395
 - definition, 323
 - monolayer (*see* Monolayer)
 - percent and mole fraction, 84, 85
 - sensitivity factor, 114
- Atom-probe field ion microscopy (AP-FIM), 498
- Attenuation length (AL), 88, 95–99, 173. *See also* Effective attenuation length (EAL)
 - definition, 97
- Au. *See* Gold
- Auger
 - parameter
 - charging, 425
 - definition, 49–51

- peak-to-peak-height (APPH), 66, 77, 81–83, 86, 283
- photoelectron coincidence spectroscopy (APECS), 212, 490
- spectra (*see also* Spectra, AES)
 - shift, 70, 429
- spectrometer, 4, 11, 12
- transition, 63–66
 - probability, 172, 174
- yield, 174
- Auger electron
 - backscattering (*see also* Backscattering)
 - channeling and diffraction, 72–74
 - quantitative aspects of, 74
 - diffraction, 72–73
 - emission, 63–64
 - energy, 63–65, 67, 421
 - intensity, 172, 174, 180
- Auger electron diffraction (AED), 73
- Auger electron spectroscopy (AES), 1, 491, 500
 - analytical strategy of, 409–411
 - capabilities and limitations, 500
 - chemical bonding, 68–71
 - depth profile and sputtered depth, 302
 - direct and derivative spectra, 66–68
 - history, 1
 - instruments
 - comparison of, 6, 276
 - line scan, 25, 251, 252, 462
 - outline, 7
 - principle of, 63–64
 - qualitative analysis, 63–74
 - lineshape, 66
 - plasmon losses, 66, 68
 - spectra and elemental identification, 64–68
 - quantitative analysis (data evaluation), 172–200
 - attenuation length (*see* Effective attenuation length)
 - Auger peak-to-peak-height (APPH), 66, 77, 81–83, 86, 283
 - backscattering effect, 174–179, 252
 - homogeneous material analysis, 179–189
 - intensity, 77–79, 84–86, 172, 179, 227–255
 - CMA tilt, 250
 - relative sensitivity factors (RSFs), 84–87
 - thin surface layers, contamination, 189–200
- Auger, Pierre, 3
- Average
 - macroscopic surface, 215
 - matrix correction factor, 123–126, 184
 - matrix relative sensitivity factor (AM-RSF), 126, 184
 - practical EAL (effective attenuation length), 95, 96, 97, 103
- Axial movement of CMA, 32
- B. *See* Boron
- Background
 - count rate, 79
 - counts, 77, 78
 - for depth profile correction, 359
 - in GI-AES, 235
 - intensity, 77, 261
 - shape (peak shape analysis), 400–402
 - in signal-to-noise considerations, 259–295
 - subtraction
 - in AES, 79–81
 - in XPS, 79–81
 - in TR-XPS, 213
- Background-to-peak extension, 82
- Backscattering
 - contribution to AES, 71–72, 229–234
 - correction, 232, 233, 359
 - correction factor (BCF), 174–179
 - correction in AES depth profiling, 359
 - decay length (*see* Mean effective backscattering decay length (MEBDL))
 - effect in AES depth profiling, 357–360
 - effect on Auger line scan, 252
 - factor (BF), 174–179
 - in AES on surface layers, 189–200
 - beam incidence angle dependence, 229–234
 - correction in AES depth profiling, 357–360
 - effective, 359
 - in elemental RSF (E-RSF), 180–181
 - Ichimura–Shimizu equations for BF, 176
 - in matrix correction factors, 182–187
 - ratio, 191, 359
 - induced Auger electrons, 25, 71
 - intensity, 229
 - quantitative aspects of, 74
- Baking, bake-out and out-gassing of UHV system, 15–18, 422
- Ball cratering, 381–382
- Band bending, 424
- Bandgap energy, 90

- B_4C . *See* Boron carbide (B_4C)
 BCF. *See* Backscattering correction factor
 Be. *See* Beryllium
 Beam current, 24
 Beam diameter, 24
 Beam effects
 electron beam, 329, 426–434, 438–440
 ion beam, 323–330
 photon beam, 329, 423–424, 441–443
 Begrenzungs-Effekt. *See* Surface excitation parameter
 BeO. *See* Beryllium oxide (BeO)
 Beryllium (Be)
 BeO, Beryllium oxide
 electrical resistivity, 428
 preferential sputtering, 324
 Bevel profiling, 378
 BF. *See* Backscattering factor
 Bi. *See* Bismuth
 Bicrystal fracture surface, 160, 462–464
 Bicrystals of Ni, 460
 Bilayer, 165
 B-implanted Si (CRM), 344
 Binary
 matrix relative sensitivity factor (BM-RSF)
 in AES, 185–188
 in XPS, 127–130
 relative matrix correction factor
 in AES, 182–188
 in XPS, 115–130
 system, 115, 181
 segregation, 145–154, 159
 Binding energy, 43–50, 421, 471, 472. *See also* Photoelectron energy
 Bismuth (Bi)
 EAL comparison for 1500 eV, 96
 grain boundary segregation in Cu, 465
 IMFP, 91
 sputtering yield, 301
 BM-RSF. *See* Binary matrix relative sensitivity factor
 BN. *See* Boron nitride
 Bonding states
 in AES, 68–71
 in XPS, 48–49
 Borides, 428
 Boron (B)
 B_4C , Boron carbide (electrical resistivity), 428
 BN, Boron nitride (electrical resistivity), 428
 Bremsstrahlung, 18, 19
 Brightness, 22, 23, 24
 Brittle fracture, 159, 160
 Bulk diffusion constant, 480
 Bulk plasmon, 46, 52, 66, 475. *See also* Plasmon loss
 C. *See* Carbon
 Calibration
 of the depth scale in sputter profiling, 307–308
 of the energy scale, 420–422, 425–426
 Auger energies, 421
 binding energies, 421, 425–426
 ISO standard, 444, 445
 of the intensity scale, 421, 422
 ISO-standard, 445, 446
 of the sputter ion gun, 300, 303, 422
 Carbon (C)
 adventitious, 49, 425
 for energy calibration, 425
 backscattering factor, 178, 186
 carbide
 AES spectrum, 71, 313
 carbonaceous contamination layer, 417
 C_{60}^+ cluster ions, 28
 C-Fe system quantification
 AES, 187–189
 XPS, 127–129
 CH_4 , 14, 15
 C_6H_{12} (ESD cross section), 437
 CO, CO_2 , 14–15
 contamination, 18
 CO on Ni (001), electron scattering, 59, 60
 dioxide (CO_2), in residual gas, 14–15
 EAL
 comparison at 1500 eV, 96
 for quantification
 AES, 186
 XPS, 120
 hydrocarbons, 18
 IMFP, 91
 layer of C on Fe, 198
 layer of C on Ti, 358
 methane (CH_4), 14, 15
 monoxide (CO) in residual gas, 13–15
 spectrum (C KVV), 71, 313
 sputtering yield, 301
 CAT. *See* Constant analyzer transmission
 Cathodoluminescence spectroscopy (CLS), 491
 CeO_2 (sputtering yield), 301
 Cerium (Ce)
 CeO_2 sputtering yield, 301
 Certainty. *See* Confidence criterion

- Certified reference materials (CRMs)
for sputter depth profiling (SDP), 343
- CH₄, 14, 15
- CHA. *See* Concentric hemispheres analyzer
- Chandrasekar function, 99
- Channeling
and diffraction of electrons
AES, 72–73
XPS, 59–60
of ions in sputtering, 336
- Channeltron
multichannel detection, 36, 37, 286
- Characteristic energy
in AES, 43, 63
in XPS, 7, 43, 44
- Charging and Auger parameter, 49, 425
- Charging and charge compensation, 49,
424–434
Cazaux double layer charge model, 434
charge transfer, 424
charging potential, 425, 426, 430–433
in depth profiling, 329
differential charging, 426
electrical resistivity, 430–431
inhomogeneous charging, 429
positive ions, 432
positive surface charge, 432–434
primary current density, 430
sample thickness, 430
secondary electron emission, 427–429,
431–432
- Chemical bonding
in AES, 68–71
and background subtraction, 71
influence on peak shape, 71, 312, 457
in ion bombardment, 476, 478
in ion implantation, 465–468
in oxidation, 454–459, 469–477
and peak area, 71, 79, 82
in plasmon energies, 466
and quantitative analysis, 71, 82, 310
and standard spectra, 71
in XPS, 43–45
- Chemical composition, 72, 311, 413. *See also*
Quantitative analysis
in sputter depth profiling, 310–313,
355–359, 468
- Chemical shift, 48–49
- Chemisorption of oxygen, 471, 475
- Chemometric methods
factor analysis (FA), 83, 481
linear least squares fit (LSS), 84, 310
- Chromium (Cr)
backscattering factor, 186
CrB₂ (electrical resistivity), 428
Cr/CrO_x multilayer
certified reference material (CRM)
for sputter depth profiling, 343
Cr-Fe system for quantification
with AES, 187–189
with XPS, 129–130
CrN (electrical resistivity), 428
Cr/Ni multilayer (*see* Ni/Cr multilayer)
Cr₂O₃, chromium oxide
passive layer, 460
preferential sputtering, 324
sputtering yield, 301
Ti-Cr oxide, 458
EAL for quantification
AES, 186
XPS, 120
sputtering yield, 301
(Ti, Cr)N coating oxidation, 458
- Clean surface, 417, 418
- Cleavage, 418
- CLS. *See* Cathodoluminescence spectroscopy
- Cluster primary ions, 28
- CMA. *See* Cylindrical mirror analyzer
- CO, 14, 15, 59, 60
- Co. *See* Cobalt
- CO₂, 14, 15
- Coatings and layered structures, 452–454
- Coatings, composition of magnetron sputtered,
452
- Cobalt (Co)
Co₃O₄, preferential sputtering, 324
sputtering yield, 301
- Cold cathode ion guns, 26
- Combination of techniques, 501
- Comparison
of CMA and CHA, 36
of the EAL of selected elements at 1500eV,
96
of non-destructive and destructive depth
profiling methods, 402
of the principal surface analysis techniques,
499–501
of the signal-to-noise ratio of pulse
counting and analog detection, 295
- Competitive segregation of P and S on Cu
(110), 480, 481
- Component depth profiles, 310–313, 477
- Component spectra. *See* Principal components
- Component spectra in sputter depth profiling
of graphite and carbide at C/Ti interface,
311, 313
of NiCrFe oxide layer, 310, 311
of Ti, TiN and TiO₂, 311, 312

- Compositional depth profiling. *See* Depth profiling
- Composition and thickness of thin layers, 384
- Composition dependence
 composition independent matrix correction factor
 AES, 184–187
 XPS, 123–126
 of EAL, 87–90
 of matrix correction factor
 AES, 183–187
 XPS, 118–121
- Compound formation and decomposition in
 sputter depth profiling, 305, 325, 476, 478
- Concentric electron gun, 31
- Concentric hemispherical analyzer (CHA),
 33–36
- Cone formation during sputtering, 333
- Confidence criterion, 260, 264 (*See also*
 Uncertainty)
- Constant
 analyzer transmission (CAT), 35
 retard ratio (CRR), 32, 35, 36, 46
 sputtering rate, 299, 303
- Contamination
 of a hard disk, 235
 from residual gas, 13, 14, 300, 320
 sample preparation, cleaning, 416, 451
- Contamination layer, 161–168, 213
 on Nb₂O₅ (AR-XPS), 388–390
 in quantitative AES, 199–200
 in quantitative AR-XPS, 397
 in quantitative XPS, 161–168, 397
 on SiO₂, 162–165
- Continuous mode in sputter depth profiling,
 299
- Conversion of sputtering time to sputtered
 depth, 303–305
- Convolution integral, 349
- Copper (Cu), 228, 462, 480
 Cu (001) Auger-electron hologram, 62
 Cu LMM, 270, 284
 backscattering (angle dependence), 232
 intensity, angle dependence
 with CHA, 229
 with CMA, 240
 intensity, detection limit, 278–280
 Cu L₃M_{4,5}M_{4,5} (=Cu L₃VV or Cu LMM)
 Auger peak, 261
 Cu LMM Auger spectra, 228
 Cu L_α radiation, 18
 Cu L₃VV energy, 421
 Cu M_{2,3}VV energy, 421
 CuO, Cu₂O XPS spectra, 54
 Cu 2p_{3/2}, 402
 binding energy, 421
 Cu-Pt alloy, 328
 CuSO₄, photon stimulated desorption
 (PSD), 442
 EAL comparison for 1500 eV, 96
 IMFP, 92
 segregation kinetics in Cu
 of P and S, 480
 of Sn (depth profile), 480
 sputtering yield, 301
 thermal conductivity, 439
 trace analysis of S in Cu, 480
- Core electron binding energy, 48
- Correction factor (term)
 for backscattering, 174–179
 depth profiling, 357–360
 thin surface layers, 189–200
 for elastic scattering, 101
 for matrix influence (*see* Matrix correction
 factor)
 for SEP, 92–95
- Corrosion and passivation, 458–459
- Corrugated surfaces, 244
- Cosegregation of In and S on Ni, 462–464
- Cosine dependence on emission angle, 103,
 207–209
- Coster–Kronig transitions, 173
- Coulomb explosion
 in photon stimulated desorption (PSD), 442
- Coverage of surface
 incomplete, 396
 fractional
 AES, 195–198
 AR-XPS, 396–398, 478, 479
 XPS, 144–154
- Cr. *See* Chromium
- Crater depth measurement, 303
- Crater edge profiling, 378–380
- Critical angle
 of CMA tilt, 236, 237
 of shadowing by surface roughness, 214,
 215
 for total reflection, 213
- Critical dose density (fluence) for ESD, 436,
 437
- CRMs. *See* Certified reference materials
- Cross section
 of electron induced ionization
 Gryzinski, Casnati, 173
 of ESD, 437
 of photoionization
 Scofield, 52, 105, 106
- CRR. *See* Constant retard ratio

- Crystalline structure effect
 in electron channeling and diffraction. (*see* Channeling)
 in sputter depth profiling (SDP), 331, 334–338
- CS2 formula, 95
- Cu. *See* Copper
- Current density, 25
- Curve fitting. *See* Peak fitting
- CuSO₄
 photon stimulated desorption (PSD), 442
- Cylindrical mirror analyzer (CMA), 30–33
- Damage by electron and photon-beam, 434–443. *See also* Beam effects
- Data analysis. *See* Intensity determination
- Database
 for AES energies (Handbooks), 64
 for backscattering correction factors (BCF), 179
 for IMFP and EAL values. (*see* NIST database)
 for photoelectron energies (Handbooks), 45
- DCSM model. *See* Diffusion-corrected simultaneous multilayer growth model
- Decomposition of compounds
 by ESD in AES, 435–438
 during ion sputtering, 325
 by photoionization, 441–443
 by XPS of polymers, 442
- Decomposition of peaks, 47
- Deconvolution
 in depth profiling, 338 (*see also* MRI model)
 in spectral interpretation (*see* Peak decomposition; Peak fitting)
- Delta layer response function, 346
- Delta layer, 346. *See also* Depth resolution function
- Density correction, 114. *See also* Matrix correction factor
- DEPES. *See* Directionally resolved elastic peak electron spectroscopy
- Deposited layer structure, 479
- Deposition of thin films, 155
- Depth analysis. *See* Depth profiling
- Depth profile
 Al₂O₃ layer on SiO₂ (AR-XPS), 479
 and beam heating, 439
 with changing λ , 356–357
 chemical composition, 311
 contamination layer (AR-XPS), 388
 crater edge profiling, 378–380
 C/Ti (backscattering), 358
 ESD artifact, 434
 FeCrNi oxide layer, 475
 Fe–Cr passive layer, 459
 GaAs/AlAs nanolayers, 363–365
 Ge/Si layer structure, 367, 368
 modeling and reconstruction, 344–348
 multilayer
 certified reference material (CRM), 343
 depth resolution definition, 314–315
 with different layer thickness, 318
 GaAs/AlAs, 347, 351
 Ni/C, backscattering effect, 359
 Ni/Cr
 certified reference material (CRM), 343
 depth resolution determination, 318
 depth scale determination, 308
 different surface roughness, 332
 elevated temperature, 327
 ion incidence angle dependence, 335–337
 redeposition, 321, 322
 roughness, 332
 sample rotation, 372, 373, 375–377
 sputtering rate determination, 307–308
 sputtering with nitrogen ions, 304
 Ta/Si, preferential sputtering, 335, 354, 356, 379
 Si/Al layers, 460
 Si–SiC layer, 466
 Ta₂O₅ (AR-XPS of altered layer), 476
 Ta₂O₅/Ta
 CRM, 325, 343
 TiAlN coating (oxidized), 455–457
 TiCrN coating (oxidized), 458
 Ti,Pd,N coating, 454, 456
- Depth profiling
 of alloys, 305
 by angle lapping and ball cratering, 381–382
 by angle-resolved AR-XPS and AR-AES, 382–398
 and chemical bonding, 310–313, 466
 destructive (*see* Sputter depth profiling)
 ion gun for depth profiling, 26–28
 by ion sputtering (*see* Sputter depth profiling)
 non-destructive, 382–402
 optimum conditions for, 339–344
 by peak shape analysis, 400–402
 quantitative compositional, 297–402

- on rough surfaces, 321, 331–333
- with and without sample rotation, 333, 335
- by variation of the excitation energy, 398–400
- Depth resolution (DR)
 - altered layer, 323 (*see also* Mixing length)
 - definition and measurement, 314–318
 - depth dependent, 318, 330, 338–339
 - depth independent, 338, 347
 - depth resolution concepts, 316
 - derived from layer structures, 315–318
 - high, 339, 340, 342
 - ion incidence angle dependence, 335–337
 - limiting factors, 319–338
 - of multilayer structures, 315–318
 - optimum, 339–344
 - and sample rotation, 333, 335, 372–378
 - of a single layer, 316
 - and sputtering induced roughness, 334
 - superposition of different contributions, 338
 - surface roughness dependence, 331
- Depth resolution function (DRF), 344–347
 - asymmetric, 314, 318, 350
 - of atomic mixing, 347, 349–352
 - for delta layers, 315
 - empirical approach, 346
 - Gaussian DRF, 314
 - logistic function DRF, 346
 - of the MRI model, 349–351
 - and noise limitations, 345
 - non-Gaussian, 314
 - partial resolution functions, 349
 - of the SLS model, 347–348
- Depth scale. *See also* Sputtering rate
 - in depth profiling, 305–310
 - determination from AES depth profiles, 307–308
 - and sputtered depth, 302–310
 - and sputtering yield, 301, 303
- Derivative spectra (AES), 66, 78, 81–83
 - signal-to-noise, 283–285
- Desorption
 - from chamber walls, 16
 - electron stimulated desorption (ESD), 435–438
 - photon stimulated desorption (PSD), 442, 490
- Destructive depth profiling. *See* Sputter depth profiling
- Detection limit, 259, 260, 263–265, 279–281
- Detection of
 - electrons, 488, 490–495, 497
 - forces, 488, 498
 - ions and neutrals, 488, 490, 494–498
 - photons, 488–489, 491, 494, 497
- Detector efficiency, 111, 275, 276
- Differential
 - charging, 424
 - pumping of the ion gun, 27, 298
 - spectra (AES), 81–83, 283
 - sputtering (*see* Preferential sputtering)
- Diffusion
 - coefficient and interfacial reactions, 460
 - interdiffusion of Ge in Si, 367
 - permeation and outgassing, 16, 17
 - radiation enhanced, 327
 - of S in Cu, 480, 481
 - of Sn in Cu, 480
- Diffusion-corrected simultaneous multilayer growth model (DCSM), 156–157
- Diffusion-correction coefficient in thin film deposition, 157
- Dilute alloy approximation, 118
- Direct and derivative spectra, 66–68
- Directionally resolved elastic peak electron spectroscopy (DEPES), 72, 73
- Discontinuous mode in sputter depth profiling, 299
- Doniach–Sunjic line shape, 55–57
- Double layer quantification
 - AR-XPS, 386, 391–393
 - XPS, 166–168
- Double pass cylindrical mirror analyzer (DP-CMA), 33, 207, 209, 211, 212, 388
- Doublet peak structure, 47, 48, 79
- DP-CMA. *See* Double pass cylindrical mirror analyzer
- DRF. *See* Depth resolution function
- Drum device in DP-CMA, 211
- DSIMS. *See* Dynamic SIMS
- Duoplasmatron ion sources, 27
- Dynamic SIMS (DSIMS), 493
- EBSD. *See* Electron backscatter diffraction
- EDDF. *See* Emission depth distribution function
- EELS. *See* Electron energy loss spectroscopy
- Effective
 - asymmetry parameter, 107–109
 - attenuation length (EAL), 87–104, 173
 - depth, 171, 172
 - mean electron escape depth, 357
- Elastic peak electron spectroscopy (EPES), 72
 - in depth profiling, 368–370
- Elastic peak in AES, 33, 68

- Elastic scattering correction factor (Q)
 - definition, 99–101, 103
 - emission angle dependence, 99–102
 - in quantification, 95, 96
 - AES, 184, 186, 187
 - XPS, 108, 109, 117, 126, 132
- Elastomeres, 17
- Electrical
 - conductivity, 413
 - power density in AES, 439
 - resistivity of insulating materials, 426–431
- Electromigration, 430
- Electron
 - analyzer (*see* Electron energy analyzer)
 - attenuation length (*see* Effective attenuation length (EAL))
 - backscatter diffraction (EBSD), 492
 - backscattering correction factor (BCF), 174–179 (*see also* Backscattering)
 - backscattering effect and background, 71–72, 74
 - backscattering factor (BF), 174–179 (*see also* Backscattering)
 - beam
 - current, 24, 25
 - diameter, 24
 - energy, 26
 - excitation (AES) (*see* Electron ionization cross section)
 - excitation methods in surface analysis, 491–494
 - halo of backscattering induced Auger electrons, 25
 - induced charging, 426–434
 - induced heating, 438–440
 - stimulated changes in composition and structure, 435–443
 - diffraction, 412 (*see also* Channeling and diffraction of electrons)
 - emission angle
 - AES and XPS, 62, 205–256 (*see also* Emission and incidence angle dependence)
 - energies, 63
 - energy analyzer, 29–39
 - analyzer resolution, peak width and S/N ratio, 270–274
 - concentric hemispheres analyzer (CHA), 33–36
 - acceptance angle, 29, 35, 36
 - aperture angle, 35
 - constant or fixed retard ratio (CRR or FRR), 32, 35, 46
 - energy resolution, 29, 35, 36
 - geometrical transmission, 29, 31, 35
 - input lens, 35
 - luminosity (étendue), 29, 36
 - multichannel detection, 36–37, 286–288
 - position sensitive detector, 35
 - transmission, constant/fixed (CAT or FAT), 35
 - concentric spherical sector analyzer (CSSA) (*see* Concentric hemispherical analyzer)
 - cylindrical mirror analyzer (CMA)
 - analyzer transmission, 31
 - aperture angle, 30, 31
 - axial movement of sample, 32
 - CMA compared to CHA, 36
 - concentric cylinders, 31
 - constant retard ratio (CRR), 32
 - double pass CMA (DP-CMA), 29, 33, 34
 - energy resolution, 29, 32, 36
 - focal point, 33
 - luminosity (étendue), 29, 33, 36
 - resolution and transmission, 29, 31, 33, 35
 - transmission and acceptance area, 33
 - efficiency, 111, 180
 - retarding field analyzer (RFA), 29
 - and roughness, 251
 - spherical mirror analyzer (SMA), 29, 37, 38, 61
 - Staib analyzer, 29
 - energy-loss
 - spectra, 474
 - spectroscopy (EELS), 452, 471, 473 (*see also* Reflection electron energy loss spectroscopy (REELS))
 - escape depth, 103
 - correction at interfaces, 306
 - mean electron escape depth (MED), definition, 102–104
 - in sputter depth profiling, 305–310, 347–349, 356, 357
 - gun, 23–26, (*see also* Electron beam)
 - aperture angle, 24
 - brightness, 23, 24
 - cold cathode, 26
 - current absorbed, 26
 - current density, 24
 - electron impact ionization, 27
 - field emission, 23, 24
 - filaments, 23
 - flicker noise, 23

- LaB₆ cathode, 24
- lateral resolution, 39
- line scan, 25, 462, 464
- resolution test, Au-on-C sample, 25
- scanning Auger microscopy (SAM), 23
- Schottky field emitter, 23
- spatial resolution, 24, 25
- thermionic emission, 23
- W thermal field emitter, 24
- W(Zr), 24
- impact ionization (*see* Electron gun)
- ionization cross section, 65, 173–174
- levels (*see* Atomic electron levels)
- and photon beam damage, 434–443
 - effect in depth profiling, 329–330
- scattering, 59, 266 (*see also* Backscattering, and Channeling and diffraction of electrons)
 - elastic scattering, 88, 95, 96, 99
 - inelastic scattering, 81, 89, 95
- spectroscopy for chemical analysis (ESCA), 2, 6
- stimulated adsorption (ESA), 438
- stimulated desorption (ESD), 329, 435–438, 494
 - compensation by sputtering, 438
 - cross sections, 437
 - ion angular distributions (ESDIAD), 494
 - of oxygen, 435–438
- Electronic properties of the surface, 474
- Electro-polishing, 416
- Electrotransport, 329
- Elemental
 - identification, 45–48, 64–68
 - reference sample, 303
 - relative sensitivity factor (E-RSF), 84, 117, 130, 180–181
 - definitions, 131
 - standard intensities, 84, 85
- Ellipsometry, 488
- ELS. *See* (Electron) energy loss spectroscopy
- Emission and incidence angle dependence of
 - intensity, 105, 111, 205–255
- AES
 - with CHA
 - flat surface, 180, 210, 211, 227–235
 - rough surface, 239, 241–250
 - with CMA
 - flat surface, 180, 235–239
 - rough surface, 250–255
- XPS
 - with CHA
 - flat surface, 105, 209–212
 - rough surface, 214–226
 - with DP-CMA and Thetaprobe
 - flat surface, 131–135, 209–212
- Emission angle effects
 - diffraction
 - AES, 72–73
 - XPS, 58–62
 - mean escape depth, 102–104
- Emission depth distribution function (EDDF), 87, 96
- Emission function decay length, 97
- Energy
 - analyzer. (*see* Electron energy analyzer)
 - calibration, 420–422
 - dependence
 - of Auger intensity, 172
 - of backscattering, 174–179
 - of IMFP, EAL and SEP, 92–99
 - filtered image, 39
 - intervals per channel, 79
 - loss spectroscopy (EELS), 471
 - of reference peak, 425–426
 - resolution (*see* Electron energy analyzer)
 - shift
 - AES peak, 68–71, 429
 - XPS peak, 48–49
- Enthalpy–entropy compensation effect, 465
- EPES. *See* Elastic peak electron spectroscopy
- EPES depth profile, 368
- Error, systematic and random, 259
- E-RSFs. *See* Elemental relative sensitivity factors
- ESA. *See* Electron stimulated adsorption
- ESCA. *See* Electron spectroscopy for chemical analysis
- Escape depth. *See* Electron escape depth
- Escape depth correction at interfaces, 305–310
- ESD. *See* Electron stimulated desorption
- ESDIAD. *See* Electron stimulated desorption in ion angular distributions
- Étendue, 29, 33, 111
- Eucentric sample position, 422
- Evaporation, 32, 443. *See also* Thin film deposition
 - layer, 143
 - of Mo on W, 192
- Exchange interaction, 54
- Excitation angle, 205. *See also* Emission and incidence angle dependence of intensity
- Excitation depth distribution function (EXDDF), 87
- Excitation in surface analysis methods by electric field or heat, 497–498

- electron beam, 491–494
- ion beam, 494–497
- photon beam, 488–490
- EXHV. *See* Extreme high vacuum
- Experimental setup for SDP, 298–302
- Expert systems, 39
- Exponent of IMFP energy dependence, 89–91, 99
- Ex situ cleaning, 414
- Ex situ preparation, 417. *See also* Sample preparation
- Extreme high vacuum (EXHV), 12
- Extrinsic plasmon, 52
-
- F. *See* Fluorine
- Factor analysis (FA), 83–84, 310, 452, 471, 472, 475, 481–482
- Faraday cup, 26, 303
- FAT. *See* Fixed analyzer transmission
- Fe. *See* Iron
- Fermi level (energy), 44, 63, 421, 424, 425
- FIB. *See* Focused ion beam (sectioning)
- Field electron microscopy (FEM), 497
- Field emission electron gun, 24
- Field ion microscopy-atom probe (FIM-AP), 498
- Figure-of-merit and detection limit, 276, 279–281
- Film thickness determination, 96
- Fingerprint method, 475. *See also* Factor analysis
- Fixed analyzer transmission (FAT), 35
- Fixed retard ratio (FRR), 35
- Flanges, 17
- Flat sample surface, 214, 217, 225, 246, 255
- Flicker noise, 23
- Flood gun, 424
- Fluorescence yield. *See* Auger transition probability
- Fluorine (F)
 - F 1s XPS standard peak intensity, 86
- Focal point, 33
- Focused ion beam (sectioning) (FIB), 381
- Focused X-ray beam, 23, 206
- Fourier transform infra-red spectroscopy (FTIR), 489
- Fractional surface coverage, 143–144, 195–198, 396–398, 479. *See also* Surface segregation layer
- Fraction of components in factor analysis (FA), 475–477, 482
- Fracture device, 419
- Fracture surfaces in grain boundary segregation, 159–161, 419
- Franck-van der Merwe (FM) growth mode, 155–157
- FRR. *See* Fixed retard ratio
- FTIR. *See* Fourier transform infrared spectroscopy
- Full coverage, single element layer, 136–138
- Full width at half maximum of intensity (FWHM), 29, 314
- Future development of AES and XPS, 8–9
- Fu–Wagner model of layer deposition, 157
-
- Ga. *See* Gallium
- Gallium (Ga)
 - Ga₂O₃, preferential sputtering, 324
 - monolayer of AlAs in GaAs, 363–365
 - multilayer of GaAs/AlAs, 343, 347, 351
 - sputtering yield, 301
- Gallon equations, 136, 155
- Gas release, 17
- Gate valve, 422
- Gaussian
 - analyzer resolution, 270, 272
 - broadening by diffusion, 366
 - depth resolution function, 314, 338, 349–350
 - distribution (statistics), 259, 260, 347
 - ion beam intensity distribution, 378
 - line shape, 48
- Gaussian/Lorentzian superposition in line shape, 55–58
- GDMS. *See* Glow discharge mass spectrometry
- GDOES. *See* Glow discharge optical emission spectroscopy
- Ge. *See* Germanium
- Geometrical
 - analyzer transmission, 31
 - relations, 103, 236 (*see also* Angular relations in AES and XPS)
- Germanium (Ge)
 - diffusion in Si, 367–368
 - Ge LMM depth profile, 369, 370
 - Ge/Si layer, 367, 370
 - sputtering yield, 301
- Ghost profile, 321, 322
- Ghost spectra, 18
- GI-AES. *See* Grazing incidence AES
- GIXRD (Grazing incidence X-ray diffraction), 350
- Glass, (thermal conductivity), 439
- Glow discharge
 - mass spectrometry (GDMS), 496

- optical emission spectroscopy (GDOES), 494, 496
- Gold (Au)
 - Au/Ag on glass substrate, 439
 - Au 4f_{7/2} binding energy, 421
 - Au M₅N_{6,7}N_{6,7} kinetic energy, 421
 - gold-on-graphite resolution test, 25
 - matrix, 401
 - sputtering yield, 301
 - thin film on TiO₂/Kapton, 358–359
- Grain boundary
 - engineering, 465
 - fracture surfaces, 159–161
 - orientation, 160, 462
 - segregation, 160, 460, 462–466
 - anisotropy, 464
 - at asymmetrical boundaries, 160, 161
 - of Bi in Cu, 465
 - diagram, of C, P, Si in α -Fe, 465–466
 - of In in Ni, 460, 462–464
- Grain size, 334
- Graphite and carbide
 - AES spectra, 71, 313
 - in the C/Ti interface, 311, 313
- Grazing incidence AES (GI-AES), 234–235, 268
- Growth of oxide layer, 53, 168, 471–476
- H. *See* Hydrogen
- Hafnium (Hf)
 - HfO₂
 - preferential sputtering, 324
 - sputtering yield, 301
 - sputtering yield, 301
- Halo of backscattering induced Auger electrons, 25
- Handbooks and databases, 64, 66
- Hard disk contamination, 235
- He. *See* Helium
- HEIS. *See* High energy ion scattering
- Helium (He)
 - gas, 18
 - ion microscopy (*see* Scanning Helium ion microscopy)
- Hemi-spherical analyzer (HSA). *See* Concentric hemispherical analyzer (CHA)
- Hf. *See* Hafnium
- High energy ion scattering (HEIS), 496
- High resolution electron energy loss spectroscopy (HREELS), 492
- High spatial resolution
 - AES, 24, 25
 - XPS, 20, 22, 37, 39
- High vacuum. *See* Vacuum
- Historical background of AES and XPS, 1–5
- H₂O. *See* Water
- Holography with photo-and Auger-electrons, 61
- Homogeneous material analysis
 - AES, 179–189
 - surface layer
 - AES, 189–200
 - XPS, 135–171
 - XPS, 109–135
- Hydrogen (H), 14, 15
 - hydrocarbons, 416, 438
 - hydroxide, 389
- IAES. *See* Ion excited Auger electron spectroscopy
- Ichimura–Shimizu equations, 175
- ID. *See* Information depth
- Ideal sputter depth profile, 306
- IERF. *See* Intensity/energy response function
- Imaging XPS, 37–39
- IMFP. *See* Inelastic mean free path
- Implantation layers, 465–468
- Implanted Ar⁺ ions, 46, 425
- Impurities in primary ion beam, 320
- In. *See* Indium
- Incidence angle, 206, 208, 227, 229–235, 240, 266–270, 431
- Inclination angles of roughness microplanes, 331–332
- In-depth distribution of composition, 110, 297. *See also* Depth profile
- Indium (In)
 - foil in sample preparation, 412, 416
 - In-Sn oxide (ITO) sputtering yield, 301
 - segregation in Ni, 460, 462–464
 - sputtering yield, 301
- Inelastic mean free path (IMFP), 87–104. *See also* Effective attenuation length (EAL)
- Inelastic scattering. *See* Effective attenuation length (EAL)
- Information depth (ID), 5
 - definition, 104
 - ISO standard Nr. 18115, 443
 - in MRI model, 104, 321, 349, 352, 362
- Infrared spectroscopy (IRS), 489
- Inhomogeneous charging, 429
- Inhomogeneous structure and composition, 412–413
- Initial oxidation
 - of FeCr19Ni9, 475–479
 - of Nb, 474–475

- of Ni, 471–472
- of Ta, 169, 471–473
- of Zr, 473
- Inner-shell rearrangement, 173
- Input lens, 35
- INS. *See* Ion neutralization spectroscopy
- In situ
 - fracture, 419
 - preparation, 414, 416–420, 469–481
- Instabilities in charging, 429
- Instantaneous sputtering rate, 302, 304
- Instrumental factors limiting depth resolution, 319–323
- Instrument for surface analysis, 11
 - AES, 12
 - XPS, 12
- Insulating materials, 428
- Intensity
 - measurements, 77–84
 - in quantification, 84–87
 - AES, 172, 178–180
 - XPS, 105, 109–111
- Intensity/composition/depth scale relation, 305–310
- Intensity/energy response function (IERF), 114, 276, 421–422
- Intensity of Cu LMM peak (914 eV), 228, 229
- Intensity–sputtering time profile, 326
- Intercrystalline fracture, 460
- Interdiffusion, 367, 439, 460
- Interface
 - C/Ti, 460
 - electron escape depth correction at, 306
 - layer in Ta oxidation, 471, 472
 - layer thickness, 150, 168–172
 - profile, 314, 318
 - width, 338, 460
- Interfacial
 - brittle fracture, 160
 - reactions and diffusion, 460
 - segregation, 147 (*see also* Grain boundary segregation)
- Intergranular brittle fracture, 159
- Internal standard, 85, 146, 159, 363, 425, 426
- Intrinsic plasmon, 52–53, 138–141
- Introduction
 - to AES and XPS, 5–9
 - chamber, 18
 - stage, 422
- Inverse maximum slope, 314. *See also* Depth resolution (DR), definition
- Inverse photoemission spectroscopy (IPES), 491
- Ion
 - beam, 26, 299, 340
 - alignment, 298, 300
 - diameter, 319–320
 - static and rastered, 299, 319–320
 - beam-sample interactions, 298, 323–330 (*see also* Sputtering)
 - channeling, 336
 - current density, 303, 320
 - energy in SDP, 323, 363, 364
 - excitation of Auger electron emission, 299, 495
 - excited Auger electron spectroscopy (IAES), 495
 - gun, 26–28, 298–300, 319–320
 - implantation, 323, 465
 - incidence angle, 298, 330, 333, 335–337, 372–374
 - induced decomposition, 305, 325, 326
 - neutralization spectroscopy (INS), 495
 - pump, 15
 - scattering spectroscopy (ISS), 496–497, 499
 - sputtering, 298, 301, 325 (*see also* Sputtering)
- Ionic conduction, 430
- Ionization cross section. *See* Cross section
- Ionization energy, 173
- IPES. *See* Inverse photoemission spectroscopy, 491
- Iron (Fe)
 - backscattering factor, 186
 - C layer on Fe
 - AES, 198
 - XPS, 161
- EAL
 - comparison for 1500 eV, 96
 - for quantification
 - AES, 186
 - XPS, 120, 127
- Fe–C quantification
 - AES, 187–189
 - XPS, 120, 127–129
- FeCrNi alloy oxidation, 475–476
- FeCr passive layer, 459, 460
- Fe–Cr quantification
 - AES, 187–189
 - XPS, 120, 127–129
- Fe₂O₃
 - preferential sputtering, 324
 - sputtering yield, 301
- Fe₃O₄
 - preferential sputtering, 324
 - sputtering yield, 301

- Fe(Si, P, C) grain boundary segregation, 464–465
- IMFP, 91
- sputtering yield, 301
- Irradiated area, 206
- IRS. *See* Infrared spectroscopy
- Island
 - formation and coverage, 143, 396, 398, 402
 - growth (Volmer–Weber (VW) mode), 155, 158, 159
 - thickness, 158
- ISO standards for surface analysis with AES and XPS, 443–446
- Isotropic emission, 103
- ISS. *See* Ion, scattering spectroscopy (ISS)

- $j - j$ -coupling, 43

- Kapton, 359
- Kaufmann ion source, 26
- KCl, potassium chloride, 437
- Kinetic electron energy, 44, 63, 421
- KL_{2,3}L_{2,3} Auger transition of Al, 421, 455
- K _{β} X-ray line, 19
- K _{α 1,2} X-ray line width, 19

- LaB₆ cathode, 24
- Lambda parameter. *See* Effective attenuation length
- Lambert–Beer law, 88
- Langmuir–McLean type segregation, 147, 148, 479, 480
- Laplace transformation, 382
- Large area analysis, 427
- Lateral (spatial) resolution
 - AES, 23, 24, 499, 500
 - XPS, 38, 39, 499
- Layer
 - composition, 150, 384, 455, 459
 - deposition and growth, 153, 155–159
 - plus island growth (Stranski–Krastanov (SK) mode), 155
 - structure analysis, 384–393
 - thickness determination, 53, 61, 137–138, 142, 150, 191, 384, 391, 393, 399, 401
- Layer-by-layer growth (Franck–van der Merwe (FM) mode), 155
- Layer-by-layer quantification
 - in AES, 189
 - in XPS, 135
- Layered structure, 199
- Layer-on-layer problem, 167
- Layer/substrate intensity ratio, 253–255
- Lead (Pb), sputtering yield, 301
- Leak detection, 18
- Least-squares fitting (LLS), 466
- LEELS. *See* Low energy electron loss spectroscopy
- LEIS. *See* Low energy ion scattering
- Li. *See* Lithium
- Lifetime broadening. *See* XPS line shape
- Limiting depth in AR-XPS, 383
- Linear
 - background subtraction (XPS), 80
 - energy scale, 421
 - least squares (LLS) fitting, 84, 310–313, 466
- Line fitting and peak width, 56
- Line scan, 22, 25, 39, 462, 464
- Line shape, 54–58. *See also* XPS line shape
- Lithium
 - in AES, 64
 - LiNO₃, LiSO₄, 437
- LLS fitting. *See* Linear, least squares (LLS) fitting
- Local EAL, 97
- Local sputtering rate, 334
- Lock-in amplifier, 82
- Logarithmic growth law, 471, 472
- Logistic function, 346
- Lorentzian peak shape. *See* XPS line shapes
- Loss peaks, TiN and TiAlN, 452. *See also* Satellite peaks
- Low energy
 - electron diffraction (LEED), 493
 - electron loss spectroscopy (LEELS), 492
 - ion scattering (LEIS), 496
- Lower limit of the sputtering rate, 307
- Luminosity (étendue), 29, 33, 111
- L_{2,3}VV shift, 455

- Magic angle
 - of emission on rough sample surfaces, 223
 - in XPS, 102, 107, 113, 205
- Magnesium (Mg), 45
 - or Al anodes, 18
 - Mg K _{α} radiation, 18
 - MgO
 - electrical resistivity, 428
 - preferential sputtering, 324
 - XPD, 59
- Mg 2p, 208
- Mg 2s, 46

- spectra, 45, 46, 52
- sputtering yield, 301
- Magnetic field influence, 423
- Manganese (Mn)
 - MnO₂, preferential sputtering, 324
- Mass spectra of residual gas, 14
- Matrix
 - correction factor, 6, 115–130, 182–187
 - AES, 183–187
 - XPS, 115–130
 - density factor, 117
 - effects, 1, 86, 115, 181
 - relative sensitivity factor (M-RSF), 86, 87, 115–117, 128–130, 133, 134, 182, 184, 187
- Matrix composition dependence of sensitivity, 88, 119–121
- Matrix-less (binary matrix) sensitivity factor (BM-RSF), 126, 184–188
- Maximum tolerable resistivity, 427, 428
- mbar, millibar (pressure unit), 11
- Mean atomic distance, 89
- Mean effective backscattering decay length (MEBDL), 192, 357–359
- Mean escape depth (MED), definition, 102–104
- Mean free path
 - of electrons (*see* Inelastic mean free path)
 - of molecules, 11
- Medium ion energy scattering (MEIS), 496
- Metal-ligand bonding, 454
- Metal oxidation, 471–475
- Metal oxide, 48, 471–475
- Metal/oxide interface layer, 472, 473
- Mg. *See* Magnesium
- MgO. *See* Magnesium
- Micro-planes on rough surfaces, 214–215, 332
- Microroughening by sputtering statistics, 330
- Minimum rotation speed, 376
- Mixing length, 349, 361
- Mixing-roughness-information depth (MRI) model, 348–371
- Mn. *See* Manganese
- Mo. *See* Molybdenum
- Modeling of depth profiles, 344–348
- Modulation voltage, 82
- Molecular collisions, 11
- Mole fraction, 84, 85, 116
- Mole fraction ratio, 289
- Molybdenum (Mo)
 - layer on W, 192, 194
 - MoO₃, preferential sputtering, 324
 - sputtering yield, 301
 - W/Mo backscattering ratio, 192–194
- Monochromatic X-rays, 19–20, 45, 206
- Monochromatic X-ray source, 19–20
- Monolayer
 - deposition, 155, 158, 194
 - depth resolution, 315
 - formation time, 13
 - fractions, 147
 - segregation, 148, 150, 195
 - thickness, 89
- Mott–Cabrera theory, 471
- MRI model. 348–371. *See also* Mixing-roughness-information depth model
- Multichannel data acquisition (detection), 36, 37, 286–288
- Multidirectional ion bombardment, 334
- Multielement system, 115
- Multilayer depth profile. *See* Depth profile, multilayer
- Multiple point depth profiling, 371
- Multiplet splitting, 53–54, 83
- Multivariate analysis, 481. *See also* Factor analysis
- NanoESCA, 22, 38, 39
- Nanolayer
 - backscattering correction, 191–196
 - depth profile, 363, 365
- Nano-particles of SiC in Si, 467, 468
- Nano-topography
 - island growth, 155, 158
 - sputtering induced, 330
- Nb. *See* Niobium
- Negative charge. *See* Charging and charge compensation
- Neutrals in ion beam, 28, 320
- Nickel (Ni)
 - CO on Ni (001), electron scattering, 59–60
 - Ni/C multilayer, backscattering effect, 359–360
 - NiCrFe alloy oxidation, 310, 311
 - Ni/Cr multilayer (*see* Depth profile, multilayer)
 - Ni(In,S) segregation, 463, 464
 - sputtering yield, 301
- Niobium (Nb)
 - NbC (electrical resistivity), 428
 - NbN (electrical resistivity), 428
 - Nb₂O₅
 - contamination layer on, 388–390
 - preferential sputtering, 324
 - oxidation, 473–475

- sputtering yield, 301
- surface segregation of O, 148, 196
- NIST database
 - backscattering correction factor (BCF), 179
 - effective attenuation length (EAL), 88, 96, 112
- Nitrides, electrical conductivity of, 427, 428
- n*-octanethiol, 225, 226
- Noise
 - and background, 294
 - limitations in deconvolution, 345
 - and uncertainty, 259–260
- Nomenclature of electron levels. *See* Notation
- Non-centric sample tilt, 208
- Non-destructive depth profiling, 213, 382–402
- Non-Gaussian depth resolution function, 350
- Non-linear
 - intensity/concentration relation, 355–362
 - sputtering time/depth relation, 354–355
- Non-monochromatic X-ray source, 52, 207
- Notation of electron levels, 44
- Number of sweeps, 262, 291
- Oil-free vacuum, 18
- O, O₂. *See* Oxygen
- Optimized depth profiling conditions, 339–344
- Optimizing
 - certainty, detection limit, signal-to-noise ratio, 259–295
 - the measured signal intensity, 205–256
 - the P/B ratio, 263–293
- Optimum
 - rotation speed, 375
 - S/N ratio, 270–274
 - strategy for data acquisition, 292
- Orange peel type roughness, 224–225
- Orientation dependence of the sputtering yield, 336, 337
- Original (intrinsic) surface roughness, 331–333, 338
- Oswald–Werner equation, 93
- Outgassing, 16, 17
- Outgassing rate, 412
- Outline of electron spectroscopy (XPS and AES), 5–8
- Outside (“ex-situ”) preparation, 414–416
- Overlapping peak decomposition, 56, 83
- Overlayer
 - intensity, 136, 190
 - and backscattering, 190–200
 - and surface roughness
 - AES
 - with CHA, 246–250
 - with CMA, 253–255
 - XPS, 214–226
 - thickness
 - flat surface, 136–138, 384–398
 - rough surface, 253–255
- Overmodulation, 83
- Overpotential, 173
- Overvoltage in AES, 173, 176
- Oxidation
 - of alloys, 475–477
 - of (Al,Ti)N, 454–457
 - of coatings, 452–454
 - of metals, 471–475
 - of Nb, 474
 - rate, 458
 - of Ta, 478
 - of (Ti,Cr)N, 458
- Oxide
 - layer thickness, 53, 138–145, 169–172, 401, 476
 - reduction by ion bombardment, 325, 333–334, 476–479
 - valence states, 136, 454, 472, 473
- Oxide/nitride interface, 458
- Oxygen (O)
 - chemisorption, 471, 475, 477
 - exposure (dose), 473–475, 477
 - O₂, 51
 - O 2p band, 475
 - surface segregation on niobium, 148
- Oxygen/silicon mole fraction, 165
- Oxynitride, 454–457
- P. *See* Phosphorus
- PAES, Positron-annihilation-induced Auger electron spectroscopy, 494
- Palladium (Pd)
 - sputtering yield, 301
 - (Ti,Pd)N coating, 454, 456
- Pa (Pascal), pressure unit, 11–13
- Parallel data acquisition, 131. *See also* Multichannel data acquisition
- Parameters
 - affecting P/B and S/N ratios, 266–293
 - of the MRI model, 349–353
- Partial
 - pressure, 14, 18
 - resolution functions, 349
 - surface coverage (*see* Fractional surface coverage)
- Pascal (Pa), 11–13
- Pass energy, 35, 112
- Passive layer, 458, 459

- Payling matrix correction factor, 121–123
 AES, 187
 XPS, 121–123
- Pb (lead), sputtering yield, 301
- P/B ratio. *See* Peak-to-background ratio
- PD. *See* Photon, stimulated desorption
- Pd. *See* Palladium
- Peak
 area, 71, 82
 decomposition, 47, 48
 energy shift, 48–49
 fitting, 48, 56, 58, 452, 453
 intensity (count rate), 87, 275, 276, 278
 overlap and factor analysis (APPH of TiN), 312, 452
 shape
 analysis (PSA), 400–402
 change, 71, 72, 313, 429, 474
 in photoemission, 54–58
 synthesis, 83 (*see also* Peak fitting)
 width, 56
 and analyzer resolution, 271
 and differential charging, 426
- Peak-to-background (P/B) ratio. *See also* S/N ratio
 and analyzer resolution, 270–274
 definitions, 263–265
 values for
 CHA, 229, 231, 234
 CMA, 240
 different instruments, 276
- Peak-to-peak height. *See* Auger peak-to-peak height (APPH)
- PEEM. *See* Photoelectron emission microscopy
- Permeation, 16
- Phosphorus (P)
 grain boundary segregation in Fe (Si,P,C), 464–466
 surface segregation in Cu, 480, 481
- Photoelectron, 43
 diffraction (XPD), 59–60
 holography, 61
 spectra, 45–48
 emission microscopy (PEEM), 38, 490
 energy, 44, 48–50
- Photoionization
 cross sections, 105
 in PSD, 442
- Photon
 beam
 excitation methods, 488–490
 damage, 442–443
 in depth profiling, 339, 342
 energy dependent depth profiling, 400
 flux, 442
 stimulated desorption (PSD or PD), 442, 488, 490
- Plasma etching, 417
- Plasmon
 bulk (volume), 47, 53, 475
 correction factor, 140
 energies, 68
 of Al, 53
 of Mg, 46
 of Si and C, 467, 468
 excitation, 468
 extrinsic, 53
 intrinsic, 52–53, 66, 140–143
 loss peaks, 52, 66, 467, 475
 structure in XPS peak, 45
 surface, 47, 53, 66, 475
- Platinum (Pt), 425
 Pt-Cu alloy, 328
 Pt MN_{6.7}N_{6.7}, backscattering factor, 178, 179
 sputtering yield, 301
- Point analysis, 427
- Poisson distribution, 347
- Poisson statistics, 260
- Polarizability, 50
- Polarization, 429
- Polarization energy shift, 50
- Polishing, 416
- Polycrystalline metallic materials, 330, 334, 412
- Polymers, 426
- Polyvinyl chloride (PVC), 442–443
- Position sensitive detector, 35, 38
- Positive charge, 424
- Positive ions, 432
- Positron-annihilation-induced Auger electron spectroscopy (PAES), 494
- Practical EAL, 97. *See also* Effective attenuation length (EAL)
- Precision. *See* Accuracy and precision
- Preferential sputtering
 of alloys, 327, 328
 in the MRI model, 354–356
 of oxides, 324–326
 principle, 323–325
- Preparation of samples, 414–420
- Pressure in analysis chamber, 16, 27
- Primary electron beam, 68, 72
 current, 277–280
 current density, 24, 430
 energy, 26, 66
- Primary ion (beam) energy, 28, 337
- Principal Auger electron peaks, 67

- Principal component analysis (PCA), 452, 467, 471, 482
- Principal methods of surface analysis, 487
- Principle of
- AES, 63–64
 - XPS, 43–45
- Profile reconstruction, 345, 348
- PSA. *See* Peak shape analysis
- PSD. *See* Photon stimulated desorption
- Pt. *See* Platinum
- Publications per year with AES and XPS, 3
- Pulse counting
- and analog detection compared, 295
 - and S/N ratio, 259, 260
- Pumping speed, 15
- Pumping time, 15
- Quadrupole mass analyzer, 18
- Qualitative analysis, 43–74
- using AES, 63–74
 - using XPS, 43–62
- Quantitative analysis (data evaluation), 77–201
- key parameters (IMFP, EAL) for, 87–104
 - using AES, 172–200
 - using XPS, 104–172
- Quantitative aspects
- of APPH, 66
 - of backscattering, channeling and diffraction, 74
- Quantitative (compositional) depth profiling, 297–402
- Quantum numbers of electron states, 43
- Quartz crystal, 19
- QUASES software. *See* Tougaard peak shape analysis
- Radiation damage. *See* Beam effects
- Radiation enhanced diffusion and segregation, 327–329
- Random errors, 259, 260
- Rastering (scanning, x-y deflection)
- of electron beam, 23
 - of ion beam, 26, 28
- Ratio of intensities, layer thickness, 219–226
- Rayleigh criterion of resolution, 363
- Reaction chamber, 417
- Reaction kinetics, 471
- Reactions with substrate, 469
- Reactive gases, 13
- Reconstruction of depth profiles, 345–348
- Re-deposition and re-sputtering, 321, 322, 331
- Reduction of
- negative charging, 431–433
 - oxides by sputtering, 324–326
- REELS. *See* Reflection electron energy loss spectroscopy
- Reference peak positions (energies), 425
- Reference samples (Standards). *See also* Certified reference materials
- for depth resolution, 300, 315, 343–344
 - for sputtering rate, 303
 - for standard energies and intensities, 48, 64–68, 466–467
- Reflection electron energy loss spectroscopy (REELS), 81, 93, 452, 491
- Reflection high energy electron diffraction (RHEED), 493
- Relative binary matrix correction factor
- in AES, 184–187
 - in XPS, 127
- Relative intensity, 45, 64
- Relative layer thickness, 137, 138, 142–145, 190, 387–392
- definition, 137–138
- Relative matrix correction factor
- in AES, 183–187
 - in XPS, 115–127
- Relative sensitivity factor
- for average matrix (AM-RFS)
 - AES, 187
 - XPS, 123–126
 - for binary matrix (BM-RSF)
 - in AES, 184–185
 - in XPS, 126–127
 - for element (E-RSF), 84–87
 - in AES, 180–181, 279, 289
 - in XPS, 112–115
 - for matrix (M-RSF)
 - in AES, 187
 - in XPS, 112–115, 129, 130
- Relative uncertainty, 260, 262
- Relaxation energy, 50
- Re-neutralized Ar⁺ ions, 28
- Residual gas, 13–14, 17
- Residual gas composition, 14, 18
- Resolution
- of depth (*see* Depth resolution (DR))
 - of energy (*see* Electron energy analyzer)
 - test (lateral), 25, 39
 - and transmission, 31
- Re-sputtering, 331
- Retarding field analyzer (RFA), 29
- Retarding lens. *See* Electron energy analyzer (CHA)

- RHEED. *See* Reflection high energy electron diffraction
- Root-mean-square (rms)
 amplitude of roughness, 332
 noise of the background, 294
 roughness, 214
- Rotating sample during sputter depth profiling, 334
- Rotational depth profiling, 372–278
- Rotation axis adjustment, 300, 423
- Rotation speed, 373
- Roughing pump (forepump), 15
- Roughness
 angle, 219, 250
 effect on intensity in AES, 239–255
 effect on intensity in XPS, 214–226
 model of surface roughness, 214–215
 parameter in MRI model, 349, 353, 355, 362
 in sputter depth profiling, 334
- Roughness (geometry) parameters, 214, 215, 225
- Rough (sample) surface, 216, 217, 250, 321, 374
- Rowland sphere, 19
- Ruthenium XPS spectrum, 79
- Rutherford backscattering (RBS), 496–497
- S. *See* Sulphur
- SAM. *See* Scanning Auger microscopy
- Sample
 alignment, 422
 ambience in depth profiling, 340
 characteristics in depth profiling, 319
 degreasing, 416
 holder, 11
 holder for two fracture surfaces, 419
 inhomogeneities, 426
 for inside (“in situ”) preparation, 417–420
 misalignment, 422
 mounting, 422–423
 with overlayer, 218–226, 246–250, 253–255
 position, 209, 423
 potential, 425
 preparation, 414–420
 properties, 411–413
 rotation during sputter depth profiling, 4, 298, 333, 335, 372–378
 rotation facility, 300
 stage, 18
 thickness, 430
 tilt, 35, 237, 240
 using AES
 with CHA, 227–235
 with CMA, 235–240
 using XPS with CHA, 208–209
 without overlayer, 216–217, 239, 241–247, 250–252
- Sandwich layer, 315
- Sapphire, 469
- Satellite peaks in XPS, 45, 52–54
 in spectra, 45, 46, 53, 54
 from X-ray source, 20, 52
- Savitzky–Golay differentiation, 83
- Scanning
 Auger microscopy (SAM), 4, 23
 electron microscopy (SEM), 491
 Helium ion microscopy (SHeIM), 495
 probe microscopy (SPM), 498
 tunneling microscopy (STM), 497
 tunneling spectroscopy (STS), 497
 XPS microscopy, 20
- Schottky field emitters, 23
- Scofield cross section, 52, 105, 106, 113, 116, 141
- Scribing technique, 420
- SDP. *See* Sputter depth profiling
- Seah and Dench relation (IMFP), 89
- Secondary
 electron emission, 427–429, 431–432
 electrons, 424
 emission coefficient, 426
 emission factor, 427
 ion mass spectrometry (SIMS), 495, 501
- SEELFS. *See* Surface electron energy loss fine structure
- Segregant coverage, 143–154, 195–198
- Segregation. *See also* Grain boundary and/or surface segregation
 in alloys, 395
 kinetics
 of Sn in Cu (depth profile), 480
 of S and P in Cu, 480, 481
 layer thickness, 143–154, 195–198
- Selected area depth profiling, 321, 322, 371
- SEM. *See* Scanning electron microscopy
- Semiconductors, 49, 465
- Selective oxidation of Al, 456
- Sensitivity and detection limit, 259, 265, 268, 279–281
- Sensitivity factors. *See* Relative sensitivity factor
- SEP. *See* Surface excitation parameter
- SEP correction factor, 93–94
- Sequential layer sputtering (SLS) model, 347
- Sequential oxidation, 475

- SERS. *See* Surface enhanced Raman scattering
- SEXAFS. *See* Surface extended X-ray
absorption fine structure
- Shadowing by rough sample surface
of emission and excitation, 216, 217,
241–246
of ion beam, 332, 333
and sample rotation, 372, 374
- Shake-off satellites, 54
- Shake-up satellites, 53, 54
- “Shave off” depth profiling, 381
- SHeIM. *See* Scanning Helium ion microscopy
- Shimizu equations for backscattering. *See*
Ichimura–Shimizu equations
- Shirley background, 80
- Si. *See* Silicon
- Signal-to-noise ratio (S/N ratio), 234,
268, 275
definitions, 260–263
in multichannel detection, 286–288
and smoothing, 285–286
uncertainty and detection limit, 259–295
- Silicon (Si)
compounds Wagner plot, 50
EAL comparison at 1500 eV, 96
Si/Al/Si, 460
SiB₆ (electrical resistivity), 428
SiC
electrical resistivity, 428
nanoscale particles, 468
thermal conductivity, 439
Si, C and P in grain boundary segregation,
465, 466
- Si/Ge
diffusion, 366–368
layer structure, 367, 369, 370
- Si IMFP, 95
- Si KLL peak
angle dependence, 232
backscattering, 232
intensity (CHA), 233, 234
- Si LVV peak, 269
- Si₃N₄
ESD cross section, 437
thermal conductivity, 439
- single layer CRM, 344
- SiO₂
with contamination layer, 162–165
electrical resistivity, 428
ESD cross section, 437
preferential sputtering, 324
sputtering yield, 301
- Si 2s (CS2, EAL, IMFP), 95
- Si (S/N ratio), 268, 269
- Si/Ta (*see* Ta/Si multilayer)
- sputtering yield, 301
- wafer surface contamination, 235
- Silver (Ag)
AES intensity standard for E-RSFs, 86
Ag 3d_{5/2}, SEP correction, 94
Ag M₄N_{4.5}N_{4.5} Auger energy, 421
Au/Ag layer on glass substrate, 439, 440
backscattering factor (MNN), 178
sputtering yield, 301
- SIMS. *See also* Secondary ion mass
spectrometry
- Simultaneous
AES and ISS, 329, 501
multilayer (SM) growth mode, 155–157
diffusion corrected (DCSM), 156, 157
- Single
crystal, 60–62
layer depth profile, 315–316
layer on substrate, 387–389
scattering albedo, 99, 103
- SiO₂. *See* Silicon
- SLS model, 460
- SLS roughness term, 347
- SMA. *See* Spherical mirror analyzer
- Small spot XPS, 20–22, 206, 299, 342
- Smoothing, 83, 285
- Smooth sample surface. *See* Flat sample
surface
- Sn. *See* Tin
- SNMS. *See* Sputtered neutrals mass
spectrometry, 498
- S/N ratio. *See* Signal-to-noise ratio
- Solid solubility, 464
- Spatial aperture angle, 111
- Spatially resolved XPS, 23. *See also* Imaging
XPS
- Spatial resolution, 20, 22
- Specimen. *See* Sample
- Spectra. *See* Derivative spectra (AES)
- Spectra (in figures)
AES
Al L_{2,3}VV, 72, 457, 470
C KV (graphite, carbide), 71, 313
Cu, L₃M_{4.5}M_{4.5}, 78, 228, 261, 284, 287,
288
Cu, survey, 69
Fe–Cr–Ni MVV (oxidation), 477
GI-AES, surface contamination, 235
Ni(In,S) survey, 464
Si LVV, 468
Ti (TiN, TiO₂), 312
- EELS
Nb oxidation, 474

- EPES
 - Cu (111) (DEPES), 73
- mass (residual gas), 14
- XPS
 - Ag (valence band), 47
 - Al 2p, 53
 - C 1s, 441
 - Cu 2p (CuO, Cu₂O), 54, 421
 - Mg (survey and Mg 2s), 46
 - O 1s, 390
 - Ru 3d, 79
 - Ta 4f, 48
 - Ti 2p (Ti-N-O), 453, 455
 - TR-XPS, surface contamination, 213
- Spectral synthesis, 84
- Spectrometer. *See* Electron energy analyzer
- Spectrometer constant, 35
- Spectrometer function, 111, 112, 130, 276, 279. *See also* Intensity/energy response function (IERF)
- Spectroscopic notation, 43
- Spherical mirror analyzer (SMA), 29, 61
- Spin-orbit coupling, 47
- Spin
 - doublet peaks, 47, 48, 58, 79
 - resolved structural analysis, 60
- SPM. *See* Scanning probe microscopy
- Sputter
 - crater depth, 303
 - depth profile, 298, 302, 323 (*see also* Depth profile)
 - depth profiling (SDP), 4, 298–382 (*see also* Depth profiling)
 - of compounds, 305, 325
 - of Ta₂O₅, 325, 326
 - ion gun calibration, 422
- Sputtered
 - depth, 302–310
 - neutrals mass spectrometry (SNMS), 496
 - spot, 28
- Sputtering, 298, 299, 325. *See also* Ion sputtering
 - continuous and discontinuous, 299–300
 - induced nanotopography, 330
 - rate
 - definition, 303, 307
 - from escape depth shift, 307–308
 - ratio, 301, 303, 304, 354, 355
 - statistics, 347
 - time/depth conversion, 302–305
 - yield, 301, 303, 304, 336
 - table for elements and oxides, 301
- Sputtering-induced changes of chemical bonding, 311, 325
- SRIM. *See* Stopping and range of ions in matter
- Standard
 - deviation, 259, 314
 - element peak intensity, 84–86
 - reference material, 86 (*see also* Certified reference materials)
 - spectra, 48, 467
 - table of ISO standards for surface analysis, 443–446
- Static ion beam of Gaussian intensity distribution, 319, 378
- Static SIMS (SSIMS), 495
- Stationary sample during sputter depth profiling, 333, 373
- Statistical variations (noise), 259
- Sticking coefficient, 13
- STM. *See* Scanning tunneling microscopy
- Stopping and range of ions in matter (SRIM), 345, 350, 361, 362
- Straight line assumption (SLA), 103
- Stranski–Krašanow (SK) growth mode, 155
- Structure analysis, 58–62, 73, 413
- STS. *See* Scanning tunneling spectroscopy
- Suboxide interlayer thickness, 169
- Suboxides, 325, 471
- Substrate/film interface, 469
- Substrate intensity, 218, 219
- Subsurface layers, 480
- Sulphur (S), 63
 - Auger energies, 65
 - cosegregation with In, 462
 - surface segregation on Cu, 480, 481
- Surface analysis
 - instruments (scheme), 11
 - techniques (survey), 487–501
 - chemical analysis, ISO standards, 445, 488
 - conductivity, 433
 - contamination (*see* Contamination)
 - corrugation (*see* Roughness)
 - coverage (complete and incomplete), 396
 - diffusion, 155
 - electron energy loss fine structure (SEELFS), 492
 - enhanced Raman scattering (SERS), 489
 - enrichment and depletion, 144–153
 - excitation parameter (SEP), 92–95
 - extended X-ray absorption fine structure (SEXAFS or S-EXAFS), 489
 - layer, 145
 - layer formation by deposition, 155–159, 469
 - plasmon, 46, 47, 92, 140, 475

- potential, 424–429
- roughness, 214–226, 251, 275, 349
- segregation, 143–154
 - layer of carbon on iron, 153, 154, 198
 - of In in Ni(In)460, 462–464
 - of O in Nb, 196
 - of S in Cu, 480, 481
 - of S in Ni(In), 462–464
 - of Sn in Cu, 327, 480
- topography and structure, 214, 251, 382
- Survey spectrum, 49, 423
- Synchrotron
 - radiation, 214, 399
 - X-ray source, 22–23
- Systematic error, 259

- Ta. *See* Tantalum
- Take-off angle. *See* Emission angle
- Tantalum (Ta)
 - EAL comparison at 1500 eV, 96
 - IMFP, 91
 - oxidation, 471, 473
 - sputtering yield, 301
 - Ta 4f_{7/2,5/2}, in different oxide states, 48, 471, 472, 476, 478
 - Ta interaction with oxygen, 471–472
 - Ta M₅N_{6,7}N_{6,7} (backscattering factor), 177
 - TaO, TaO₂, 471, 472
 - Ta₂O₅
 - sputtered depth equivalent, 303
 - formation, 471, 473
 - ion bombardment, 476, 478
 - preferential sputtering, 324–326
 - sputtering yield, 301
 - Ta₂O₅/Ta multilayer (CRM), 343
 - Ta₂O₅/Ta reference layer sample for sputter depth profiling, 300, 303, 320, 325, 326, 344
 - Ta/Si multilayer, 335, 354–356, 379–380
- Temperature increase, 329 (*see also* Electron beam heating)
- Terminology. *See* Vocabulary
- Thermal conductivities, 439
- Thermal desorption (TD)/temperature
 - programmed desorption (TPD), 498
- Thermionic emission, 23
- Thermoluminescence (TL), 497
- Thetaprobe instrument, 131–135, 207, 209
- Thickness of
 - adsorbate layers, 157–159
 - the altered layer (mixing length), 325, 355–356, 476, 478–479
 - contamination layers, 161–168
 - evaporation layers, 143–144
 - interface layers, 168–172
 - layers by AR-XPS, 382–398, 476–479
 - layers on rough surfaces, 222–226
 - oxide layers, 136–138
 - segregation layers, 143–144, 159–161, 327–329
- Thickogram, 143
- Thin film (layer)
 - analysis
 - by AR-XPS, 382–398
 - by sputter depth profiling, 302–313
 - deposition and growth, 155–159
 - double layer structure, 166–168
 - interface analysis, 168–172
 - three layers, 384, 385
- Thin-film diffusion, 366–368
- Thin surface contamination layers, 161–168, 199
- ThO₂, thorium oxide (electrical resistivity), 428
- Three stages
 - in initial oxidation, 471
 - in Ta₂O₅ depth profiling, 325, 326, 476
- Ti. *See* Titanium
- Tilt angle, 210
- Time-of-flight SIMS (ToF-SIMS), 496
- Tin (Sn)
 - in Cu, 480
 - SnO₂, preferential sputtering, 324
- Titanium (Ti)
 - layer deposition on sapphire, 469
 - sputtering yield, 301
 - suboxides, 469, 470
 - (TiAl)N coating
 - oxidation, 456, 457
 - valence band spectra, 455
 - TiB₂(electrical resistivity), 428
 - TiC(electrical resistivity), 428
 - (Ti,Cr)N coating oxidation, 458
 - TiN coating
 - electrical resistivity, 428
 - Ti 2p_{1/2,3/2} spectra, 452–454
 - valence band spectra, 455
 - TiO₂
 - Cu layer deposition, 158
 - sputtering yield, 301
 - Ti₂O₃, TiO₂ and TiO, 469, 470
 - (Ti,Pd)N coating, 454, 456
- TL. *See* Thermoluminescence
- Topographical features, 251
- Topography development during sputtering, 333
- Torr (pressure unit), 11

- Total
 - depth resolution, 338
 - error, 259
 - geometrical transmission, 29
 - reflection XPS (TR-XPS), 213–214
 - relative uncertainty, 289
 - secondary electron spectrum, 68
- Tougaard background subtraction, 80–81
- Tougaard peak shape analysis, 400–402
- TPD. *See* Thermal desorption
- TPP-2M equation, 90–91
- Transgranular fracture, 146, 159
- Transition metal oxidation, 168
- Transmission. *See also* Electron energy analyzer; Intensity/energy response function (IERF)
 - and acceptance area, 29
 - and detector efficiency, 112
 - geometrical, 29, 31, 35
- Transport mean free path, 100
- Transport of ions in matter (TRIM), 345, 355
- Tungsten (W)
 - sputtering yield, 301
 - thermal field emitter, 23–24
 - WC (electrical resistivity), 428
 - W(Zr), 24
- Turbomolecular pump, 16, 18
- Twin anode, 18
- Two-dimensional analysis, 215
- Two layer model, 391–393
- Two layers on substrate, 385, 386
- Two-point depth profiling, 341, 342
- Typical applications of AES and XPS, 451–482
- Typical research topics for surface analysis, 2, 5
- Ultimate limit of depth resolution, 323
- Ultra-high vacuum (UHV), 15–18. *See also* Vacuum system
 - chamber, 14
 - components, 17
 - preparation chamber, 415, 417
- Ultraviolet induced photoelectron spectroscopy (UPS), 489–490
- Ultraviolet photon irradiation, 433
- Uncertainty, 235, 259, 260
 - definition, 260
 - in layer thickness, 388
 - S/N ratio and detection limit, 260, 262–263
 - in strategy for data acquisition, 289–293
 - and total number of sweeps, 291
- Universal curve for IMFP, 89, 90
- UPS. *See* Ultraviolet induced photoelectron spectroscopy
- V. *See* Vanadium
- Vacuum, 11–18. *See also* Ultra-high vacuum (UHV)
 - characteristics, 12
 - system, 11–18, 422
- Valence band
 - electron densities, 454
 - XPS spectra, 45, 52, 455
- electrons, 90
- states
 - of Ta, 48, 325, 326
 - of Ti, 453, 454
- Vanadium (V)
 - VB₂ (electrical resistivity), 428
 - VC (electrical resistivity), 428
 - VN (electrical resistivity), 428
 - V₂O₅ preferential sputtering, 324
- Vocabulary of surface chemical analysis, 175. *See also* ISO standards
- Voigt function. *See* Gaussian-Lorentzian peak shape
- Volatile species, 17
- Volmer-Weber (VW) growth mode, 155, 158, 159
- Voltage/frequency converter, 293
- Volume plasmon. *See* Bulk plasmon
- W. *See* Tungsten (W)
- Wagner plot, 50. *See also* Auger parameter
- Water, 14
- Weak relative matrix correction factor, 123, 125, 126
- Work function, 425
- XAES. *See* X-ray induced AES
- XPD. *See* X-ray induced photoelectron diffraction
- XPS. *See* X-ray (induced) photoelectron spectroscopy
- XPS, AES, SIMS and ISS comparison, 499
- XPS-PSA (XPS-peak shape analysis), 400–402
- X-ray
 - beam, focused, 206
 - fluorescence yield, 174
 - induced
 - AES (XAES), 45
 - changes in composition, 441–443

- photoelectron diffraction, 59–60
- line width, 18–20
- monochromator, 20–22
- notation, 43
- satellites, 19
- source, 18–23
- X-ray (induced) photoelectron spectroscopy (XPS), 489–490
 - and AES typical applications, 451–482
 - capabilities and limitations, 499
 - equipment, 18
 - geometry, 58, 100, 102
 - historical background, 1–3
 - imaging, 21, 38, 39
 - instrument, 6, 11
 - line
 - scan, 39
 - shape, 54–58
 - width (FWHM), 54–58
 - number of publications per year, 3
 - outline of, 5–8
 - qualitative analysis, 43–62
 - quantitative analysis, 104–172
 - scanning microscopy, 20
- $x-y$ rastering. *See* Rastering
- Yield
 - Auger electron, 174
 - fluorescence, 174
 - sputtering, 301, 303, 304 (*see also* Sputtering yield)
- Zinc (Zn)
 - ZnO
 - preferential sputtering, 324
 - sputtering yield, 301
- Zn. *See* Zinc
- Zr. *See* Zirconium
- Zirconium (Zr)
 - ZrB₂, (electrical resistivity), 428
 - ZrC, (electrical resistivity), 428
 - ZrN, (electrical resistivity), 428
 - ZrO₂
 - charging, 431, 432
 - electrical resistivity, 428
 - preferential sputtering, 324