

Do Tran Cat
Annemarie Pucci
Klaus Wandelt
Editors

SPRINGER PROCEEDINGS IN PHYSICS 127

Physics and Engineering of New Materials



Springer

SPRINGER PROCEEDINGS IN PHYSICS

- | | |
|---|---|
| <p>113 Theoretical and Numerical Unsaturated Soil Mechanics
Editor: T. Schanz</p> <p>114 Advances in Medical Engineering
Editor: T.M. Buzug</p> <p>115 X-Ray Lasers 2006
Proceedings
of the 10th International Conference,
August 20–25, 2006, Berlin, Germany
Editors: P.V. Nickles, K.A. Janulewicz</p> <p>116 Lasers in the Conservation of Artworks
LACONA VI Proceedings,
Vienna, Austria, Sept. 21–25, 2005
Editors: J. Nimmrichter, W. Kautek,
M. Schreiner</p> <p>117 Advances in Turbulence XI
Proceedings of the 11th EUROMECH
European Turbulence Conference,
June 25–28, 2007, Porto, Portugal
Editors: J.M.L.M. Palma and A. Silva Lopes</p> <p>118 The Standard Model and Beyond
Proceedings of the 2nd International
Summer School in High Energy Physics,
Mgla, 25–30 September 2006
Editors: M. Serin, T. Aliev, N.K. Pak</p> <p>119 Narrow Gap Semiconductors 2007
Proceedings
of the 13th International Conference,
8–12 July, 2007, Guildford, UK
Editors: B. Murdin, S. Clowes</p> <p>120 Microscopy
of Semiconducting Materials 2007
Proceedings of the 15th Conference,
2–5 April 2007, Cambridge, UK
Editors: A.G. Cullis, P.A. Midgley</p> | <p>121 Time Domain Methods
in Electrodynamics
A Tribute to Wolfgang J. R. Hoefer
Editors: P. Russer, U. Siart</p> <p>122 Advances in Nanoscale Magnetism
Proceedings of the International
Conference on Nanoscale Magnetism
ICNM-2007, June 25–29, Istanbul, Turkey
Editors: B. Aktas, F. Mikailov</p> <p>123 Computer Simulation Studies
in Condensed-Matter Physics XIX
Editors: D.P. Landau, S.P. Lewis,
and H.-B. Schüttler</p> <p>124 EKC2008 Proceedings
of the EU-Korea Conference
on Science and Technology
Editor: S.-D. Yoo</p> <p>125 Computer Simulation Studies
in Condensed-Matter Physics XX
Editors: D.P. Landau, S.P. Lewis,
and H.-B. Schüttler</p> <p>126 Vibration Problems ICOVP 2007
Editors: E. Inan, D. Sengupta,
M.M. Banerjee, B. Mukhopadhyay,
and H. Demiray</p> <p>127 Physics and Engineering
of New Materials
Editors: D.T. Cat, A. Pucci,
and K. Wandelt</p> |
|---|---|

Do Tran Cat
Annemarie Pucci
Klaus Wandelt

Editors

Physics and Engineering of New Materials

With 267 Figures

 Springer

Professor Dr. Do Tran Cat

Hanoi University of Technology, Institute of Engineering Physics
Dai Co Viet Road 01, Hai Ba Trung District, Hanoi, Vietnam
E-mail: stacoproft@hn.vnn.vn

Professor Dr. Annemarie Pucci

Universität Heidelberg, Fakultät Physik und Astronomie, Kirchhoff-Institut für Physik
Im Neuenheimer Feld 227, 69120 Heidelberg, Germany
E-mail: a.pucci@urz.uni-heidelberg.de

Professor Dr. H.C. Klaus Wandelt

Universität Bonn, Institut für Physikalische und Theoretische Chemie
Wegelerstr. 12, 53115 Bonn, Germany
E-mail: k.wandelt@uni-bonn.de

Springer Proceedings in Physics

ISSN 0930-8989

ISBN 978-3-540-88200-8

e-ISBN 978-3-540-88201-5

Library of Congress Control Number: 2008936471

© Springer-Verlag Berlin Heidelberg 2009

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilm or in any other way, and storage in data banks. Duplication of this publication or parts thereof is permitted only under the provisions of the German Copyright Law of September 9, 1965, in its current version, and permission for use must always be obtained from Springer-Verlag. Violations are liable to prosecution under the German Copyright Law.

The use of general descriptive names, registered names, trademarks, 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.

Production: SPI Publisher Services
Cover concept: eStudio Calamar Steinen
Cover design: SPI Publisher Services

SPIN: 12167500 57/3180/SPI
Printed on acid-free paper

9 8 7 6 5 4 3 2 1

springer.com

Preface

This book presents the majority of the contributions to the Tenth German-Vietnamese Seminar on Physics and Engineering (GVS10) that took place in the Gustav-Stresemann-Institut (GSI) in Bonn from June 6 to June 9, 2007. In the focus of these studies are the preparation and basic properties of new material systems, related investigation methods, and practical applications. Accordingly the sections in this book are entitled *electrons: transport and confinement, low-dimensional systems, magnetism, oxidic materials, organic films, new materials, and methods*.

The series of German-Vietnamese seminars was initiated and sponsored by the Gottlieb Daimler- and Karl Benz -Foundation since 1998 and took place alternately in both countries. These bilateral meetings brought together top-notch senior and junior Vietnamese scientists with German Scientists and stimulated many contacts and co-operations. Under the general title “Physics and Engineering” the programs covered, in the form of keynote-lectures, oral presentations and posters, experimental and theoretical cutting-edge material-physics oriented topics. The majority of the contributions was dealing with modern topics of material science, particularly nanoscience, which is a research field of high importance also in Vietnam. Modern material science allows a quick transfer of research results to technical applications, which is very useful for fast developing countries like Vietnam. On the other hand, the seminars took profit from the strong cross-fertilization of the different disciplines of physics.

This book is dedicated to the tenth anniversary of the seminars and nicely shows the scientific progress in Vietnam and the competitive level reached. Because of that and since also leading scientists present their actual studies we hope that the readers will enjoy studying this book.

The editors, i.e. the organizers of the seminar series Annemarie Pucci (Heidelberg) and Do Tran Cat (Hanoi) and the local organizer of GVS10, Klaus Wandelt (Bonn), would like to express their thanks to all contributors to this book. Financial support of the 10th anniversary seminar by the Gottlieb Daimler- and Karl Benz -Foundation and, in addition, by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. Many thanks go also to Conrad Becker and Anneliese Kirschfink (Bonn) for their great help in the organization of the meeting and in the preparation of this book.

July 2008

K. Wandelt (Bonn)

A. Pucci (Heidelberg)

Do Tran Cat (Hanoi)

Table of Contents

Preface.....	v
Hierarchical Diffusive Properties of Electrons in Quasiperiodic Chains.....	1
<i>Michael Schreiber</i>	
Effect of Single-Side Modulation Doping on Low-Temperature Transport Properties in Square Infinite Quantum Wells.....	11
<i>Nguyen Huyen Tung, Doan Nhat Quang and Do Thi Hien</i>	
Nonlinear Optical Conductivity in Doped Semiconductor Superlattices Due to LO Phonon Scattering.....	23
<i>Luong Van Tung, Tran Cong Phong and Nguyen Thi Le Thuy</i>	
The Effects of the Polarization Charges on the Quantum Lifetime of the Two-Dimensional Electron Gas in a Uniformly-Doped Heterostructure	31
<i>Nguyen Viet Minh</i>	
Possible T_C Superconducting Enhancement in Q2D Materials by Incommensurate Structural Phase Transition.....	41
<i>Do Tran Cat and Ong Phuong Khuong</i>	
Compressed Electron Distribution in the Nanostructure	51
<i>Nguyen Van Tri</i>	
Time and Space Resolved Studies on Metallic Nanoparticles	61
<i>D. Bayer, J. Lange, C. Wiemann, M. Rohmer, M. Bauer and M. Aeschlimann</i>	
Ultra-small One-Dimensional Metallic Nanostructures.....	69
<i>H. Pfnür</i>	
Synthesis and Optical Properties of Colloidal CdS/CdSe/CdS Quantum Wells	79
<i>Le Ba Hai, Nguyen Xuan Nghia, Pham Thu Nga, Vu Duc Chinh, Pham Thuy Linh and Nguyen Thi Thu Trang</i>	

Preparation and Optical Properties of One Dimensional Nano Hydroxides and Oxides.....	87
<i>Lam Thi Kieu Giang, Nguyen Vu, Dinh Xuan Loc, Man Hoai Nam, Gyu- Chul Yi, Tran Kim Anh and Le Quoc Minh</i>	
Hydrothermal Synthesis and Photocatalytic Properties of TiO₂ Nanotubes.....	95
<i>D.D. Vuong, D.T.N. Tram, P.Q. Pho and N.D. Chien</i>	
UHV studies on CO and methanol adsorption and decomposition on pristine and oxidized alumina-supported Co nanoparticles.....	103
<i>T. Nowitzki, V. Zielasek and M. Bäumer</i>	
Surface confined electrochemical compound formation: Incipient sulfidation of Au(111)	113
<i>C. Schlaup, D. Friebe, P. Broekmann, K. Wandelt</i>	
Giant Spin-Polarization and Magnetic Anisotropy of Nanostructures at Surfaces.....	123
<i>H. Brune</i>	
The Role of Spin-Polarized Tunneling on Transport Properties of (1-x) La_{0.7}Ca_{0.3}MnO₃ + xAl₂O₃ Nanocomposites (x = 0 ÷ 5wt%).....	133
<i>Pham Thanh Phong, Nguyen Van Khiem, Nguyen Xuan Phuc and Le Van Hong</i>	
Advanced Metallic Magnetic Materials Prepared by Electro-Chemical Deposition, Vapor Deposition and Rapid Quenching.....	141
<i>Nguyen Hoang Nghi, Mai Thanh Tung, Hoang Nhat Hieu, Nguyen Van Dung, Nguyen Huu Tinh, Le Cao Cuong and Trinh Thi Thanh Nga</i>	
Magnetic Interaction Between Polycrystalline Ultrathin Antiferromagnetic and Ferromagnetic Films	151
<i>Roland Mattheis and Klaus Steenbeck</i>	
The (100) → (111) Transition in Epitaxial Manganese Oxide Nanolayers...	163
<i>F. Allegretti, M. Leitner, G. Parteder, B. Xu, A. Fleming, M.G. Ramsey, S. Surnev, and F.P. Netzer</i>	

Growth and Structure of Zinc Oxide Nanostructured Layer Obtained by Spray Pyrolysis.....	171
<i>Son Vo Thach, Michel Jouan, Sang Nguyen Xuan, Thoan Nguyen Hoang and Hung Pham Phi</i>	
Influence of Different Post-treatments on the Physical Properties of Sprayed Zinc Oxide Thin Films	177
<i>Thoan Nguyen Hoang, Son Vo Thach, Michel Jouan, Sang Nguyen Xuan and Hung Pham Phi</i>	
The Effect of SiO₂ Addition in Hydrophilic Property of TiO₂ Films.....	185
<i>Tran Thi Duc, Nguyen Thi Mai Huong, Vu Thi Bich, Nguyen Dinh Dung, Nguyen Trong Tinh, and Tran Xuan Hoai</i>	
Investigation of the Transformation of a Modified Iron Oxide Structure During Redox Reaction	193
<i>Luu Thi Lan Anh, Nguyen Ngoc Trung, Van Dinh Son Tho</i>	
Structural Modification of Near-Surface Region of Strontium Titanate Single Crystal Under the Influence of a Static Electric Field Enhanced by X-ray Irradiation.....	201
<i>Alexandr A. Levin and Dirk C. Meyer</i>	
Thermoelectric Properties of Heavily Doped Polycrystalline SrTiO₃	209
<i>Nguyen Trong Tinh and Toshihide Tsuji</i>	
Optimization Study of TiO₂ Film Deposited by IAD Process.....	219
<i>Pham Hong Tuan</i>	
Polymorphs in GeO₂ Liquid.....	225
<i>P.K. Hung, N.T. Nhan, L.T. Vinh ,T.T.B. Phuong</i>	
Formation of Chiral Aggregates of Tetralactam Macrocycles on the Au(111) Surface	235
<i>Iordan Kossev, Thorsten Felder, Christoph A. Schalley, Fritz Vögtle, Mortiz Sokolowski</i>	
Surface Resonant Raman Spectroscopy at Indium-Nanowire-Terminated Si(111).....	247
<i>N. Esser, K. Fleischer, S. Chandola, J. McGilp</i>	

The Properties of Nano-Hexaferrite Sr-La Prepared by Citrate-Gel Method	257
<i>Dang Le Minh, Le Thanh Cong, Luu Tuan Tai, Nguyen Hanh</i>	
Glucose Sensor Based on Multi-wall Carbon Nanotubes Doped Polypyrrole.....	263
<i>T.T.N. Lien, L.H. Bac, T.D. Lam, and P. Q. Pho</i>	
Structural and Spectral Properties of Curcumin and Metal- Curcumin Complex Derived from Turmeric (Curcuma longa).....	271
<i>Vu Thi Bich, Nguyen Thi Thuy, Nguyen Thanh Binh, Nguyen Thi Mai Huong, Pham Nguyen Dong Yen, and Tran Thanh Luong</i>	
In-situ Chemically Polymerized PANi-SWNTs Composites: Characterizations and Gas Sensing Feature	279
<i>Duong Ngoc Huyen</i>	
Design, Simulation and Experimental Characteristics of Hydrogel-based Piezoresistive pH Sensors	287
<i>Thong Quang Trinh, Jorge Sorber, and Gerald Gerlach</i>	
Optimization of the Thermostable Nanogel Systems for High Temperature Reservoir Application	295
<i>Nguyen Phuong Tung, Nguyen T.Phuong Phong, Nguyen Hoang Duy and Nguyen T. Quynh Anh</i>	
Discovery of Nanotubes in Ancient Damascus Steel.....	305
<i>Marianne Reibold, Peter Paufler, Aleksandr A.Levin, Werner Kochmann, Nora Pätzke, and Dirk C.Meyer</i>	
Materials Research with Energetic Heavy Ions at GSI.....	311
<i>Reinhard Neumann</i>	
Nanoantennas for Surface Enhanced Infrared Spectroscopy	321
<i>F. Neubrech, M. Klevenz, F. Meng, and A. Pucci</i>	
Ultrafast Switching of Coherent Electronic Excitation: Great Promise for Reaction Control on the Femtosecond Time Scale	327
<i>Matthias Wollenhaupt, Tim Bayer, Andrea Klumpp, Cristian Sarpe-Tudoran and Thomas Baumert</i>	

InGaAsP/InP Semiconductor Optical Amplifiers and their Some Nonlinear Effects.....	337
<i>Vu Doan Mien, Vu Thi Nghiem, Tong Quang Cong and Pham Van Truong</i>	
Simulation and Lock-In Phase Analysis in Photoreflectance Modulation Spectroscopy of GaAs and Photoreflectance Investigations of The Heterojunction Structure $\text{Al}_x\text{Ga}_{1-x}\text{As}(\text{N}^+)/\text{GaAs}(\text{P}^-)/\text{GaAs}(\text{P}^+)$	345
<i>Nguyen Thi Ngoc Ha, Truong Kim Hieu, Le Hong Vu, Huynh Sa Hoang, Pham Thanh Tam, Vuong Trung Kien</i>	
Principally Basic Effects of Laser on the Bulk Semiconductor Bands	355
<i>N.Vinh Quang</i>	
Controlling the Bragg Wavelength Spectral Profile Expansion of FBG Sensors by Nano-Particle Coated Layers	363
<i>Pham Van Hoi, Pham Thanh Binh, Ha Xuan Vinh, Tran Thi Cham</i>	
Controlled Cantilever-Tips Adapted from the Scanning Probe Microscopies as Active Working Elements in Smart Systems.....	371
<i>Michael Hietschold, Falk Müller, Anne-Dorothea Müller, and Thomas Gessner</i>	
Design and Fabrication of a Miniaturized Three-Degree-of-Freedom Piezoresistive Acceleration Sensor Based on MEMS Technology Using Deep Reactive Ion Etching	377
<i>Vu Ngoc Hung, Nguyen Van Minh, Le Van Minh, Nguyen Huu Hung, Chu Manh Hoang, Dzung Viet Dao, Ranjith Amarasinghe, Bui Thanh Tung, and Susumu Sugiyama</i>	
Contributors.....	385

Hierarchical Diffusive Properties of Electrons in Quasiperiodic Chains

Michael Schreiber

Technische Universität Chemnitz, 09107 Chemnitz, Germany
E-mail: schreiber@tu-chemnitz.de

Abstract. Electronic states have been calculated for a simple model Hamiltonian describing a quasiperiodic chain constructed according to the silver-mean sequence. The diffusive properties are described by the return probability and the evolution of the width of the wave packet over very long time scales. For small hopping probability, a hierarchical structure can be observed. Introducing an impurity site on the chain allows us to control the wave-packet dynamics.

1. Introduction

Quasicrystalline structures are characterized by the presence of long-range order but no translational symmetry [1]. These solids can be viewed as intermediate structures between crystalline and amorphous materials [2]. Unusual electronic properties result [3]. Although quasicrystals are usually composed of elements which in their pure form are good conductors, they show very low electric conductivity which decreases with decreasing temperature and also with the structural perfection of the quasicrystal [4-6]. This unusual behavior can be explained by the formation of localized states, by the reduction of the density of states at the Fermi energy, and/or unusual diffusive properties due to the quasicrystalline structure [4-6].

In order to find out more about the characteristic behavior of electronic states in quasicrystals, it is useful to analyse the behavior of non-interacting electrons moving in a quasiperiodic system. Here we present a numerical investigation of the electronic structure and the diffusive properties for a particular one-dimensional model system, namely the quasiperiodic silver-mean sequence. Mathematically rigorous results have been obtained for a large class of comparable one-dimensional discrete aperiodic Schrödinger operators which can be constructed from substitution sequences [7]. The so-called trace maps constitute another interesting method to investigate the transport properties of one-dimensional quasiperiodic systems by means of transfer matrices [8].

Due to the quasiperiodic order the electronic states cannot be expected to be extended Bloch states as in conventional periodic crystals, where the conduction electrons can move freely through the perfect periodic system. There electronic transport is possible, the system is metallic, unless the Fermi energy falls into a band gap. Weak disorder does not change this behavior qualitatively in three-dimensional crystals. In one dimension, however, already weak disorder leads to exponential localization of the electronic states, which makes the system insulating.

Strong disorder always leads to localization and therefore insulating behavior. The origin of these localization effects is the interference of the electronic wave functions scattered at the disordered potential [9].

Classical waves have been shown to propagate in quasiperiodic structures [10]. In quasicrystals the long-range order means that the same structural units appear over and over again, although this does not lead to translational symmetry. The question now is, whether this has a delocalizing effect and how this might counterbalance the non-periodic behavior which can be interpreted as a certain kind of disorder so that one would expect localization. The answer is that in simple model Hamiltonians usually the electronic states are neither extended nor exponentially localized, but they are so-called critical states [3]. The spatial distribution of their wave-function probability is multifractal and exhibits self-similarity [11,12]. This behavior is reminiscent of the critical states at the metal-insulator transition in the Anderson model of localization, which are neither extended nor localized but self-similar and multifractal [9]. It can be shown in a mathematically rigorous way for many one-dimensional quasiperiodic systems that the corresponding energy spectra are purely singular continuous [7,13] which means that they do not contain a continuous part corresponding to extended states, nor do they comprise a point part, reflecting localized eigenstates. As a consequence, the density of states is also a fractal, like a Cantor set, and the integrated density of states is a devil's staircase [3,14].

The model Hamiltonian that we have investigated [14] belongs to such a class of one-dimensional discrete aperiodic Schrödinger operators.

2. Model Hamiltonian and Energy Spectra

The silver-mean sequence is defined by the inflation rule $\{S \rightarrow L; L \rightarrow LSL\}$ operating on the letters L and S which will be interpreted as large and small hopping elements between the sites of the one-dimensional quasiperiodic structure. Starting with the letter S the inflation rule is iterated m times yielding the word $LSLLL SLLSLLSLLLSL.LSLLL SL.LSLLL SLLSLLSLLLSL = LSL = \mathbf{L}$ after the first five iterations. The dots in this sequence indicate another construction principle: this fifth approximant $\mathbf{L}$ can also be obtained by combining the fourth approximant L and the third approximant S according to LSL . Consequently the length of the word in each iteration is given by twice the length of the word in the previous iteration plus the length of the word of the preprevious iteration. Therefore, the number of letters increases inflationary, and the next seven iterations lead to words with $N = 99, 239, 577, 1393, 3363, 8119, 19601$ letters for $m = 6, \dots, 12$, respectively. The ratio of the lengths of two successive approximants approaches the so-called silver mean $\boxtimes_s = 1 + \sqrt{2}$ for large m . In the continuous fraction notation this irrational number is given by $\boxtimes_s = [2, 2, 2, \dots]$.

The matrix elements of the tight-binding Hamiltonian, which we employ [15] to describe the electronic states, are given by $H_{ij} \boxtimes_{i,j \pm t}$, where i and j label the sites of the chain. As indicated by the Kronecker symbol only nearest neighbor hopping integrals t are taken into account. Their values are determined by the

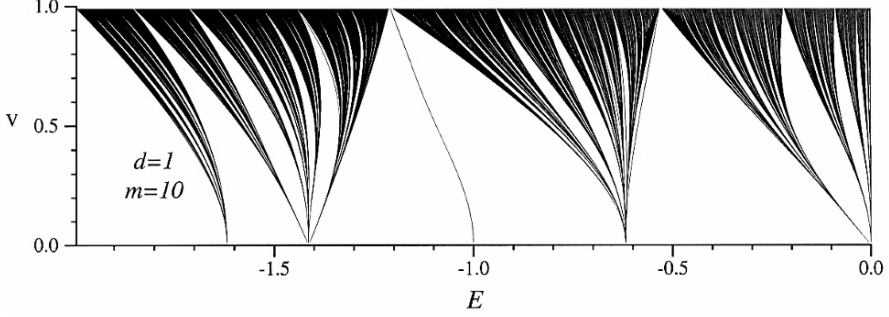


Fig. 1. Dependence of the eigenenergies on the hopping parameter ν for the 10th approximant of the silver-mean quasiperiodic chain with 3364 sites. Only eigenvalues $E < 0$ are shown because of the symmetry of the spectrum about the center of the band. The single line starting at $E = -1$ for $\nu = 0$ reflects two states which are a consequence of the open boundary conditions which we have used [15]

quasiperiodic sequence and we choose $t_L = 1$ and $t_S = \nu$ with $0 < \nu < 1$. These off-diagonal matrix elements comprise the kinetic energy in the tight-binding Hamiltonian and thus reflect the itineracy of the electrons. The diagonal elements of the Hamiltonian matrix, which correspond to the potential energy, are set to zero which means that there is no energetic disorder present in the simulation.

The diagonalization of the Hamiltonian matrix yields the eigenenergies, and their dependence on the hopping parameter ν is displayed in figure 1. It is a characteristic feature of these spectra that gaps of various sizes exists. The gap-labeling theorem allows for an enumeration of all possible gaps [13,16]. In the limit of vanishing ν the silver-mean bond sequence disintegrates into clusters of two different sizes, namely of three and four sites with LL and LLL bonds respectively, separated by S bonds with vanishing hopping probabilities. In this limit we get seven eigenenergies, namely $E_{LLL} = \pm(\sqrt{5} \pm 1)/2$ and $E_{LL} = \pm\sqrt{2}$, 0. In the other limit $\nu \rightarrow 1$ the fully periodic system is recovered with a continuous energy band between $E_{\min} = -2$ and $E_{\max} = +2$.

In figure 2 the density of states is shown for three different values of the parameter ν . As mentioned in the introduction it is well known that the spectrum of such systems is singular continuous and a Cantor set of zero Lebesgue measure [7]. The integrated density of states, which just counts the number of eigenvalues up to a given energy E is also shown in figure 2 and the prominent plateaus correspond of course to the gaps in the spectrum. Just as gaps of various sizes appear, there exist plateaus of all sizes and such step functions have been given the name devil's staircase.

3. Quantum Diffusion and Transport

To investigate the transport properties of the electrons on the quasiperiodic chain we utilize the eigenfunctions $\vec{\psi}_k = (\psi_{0k}, \dots, \psi_{jk}, \dots, \psi_{Nk})^T$ of the states with eigenenergy

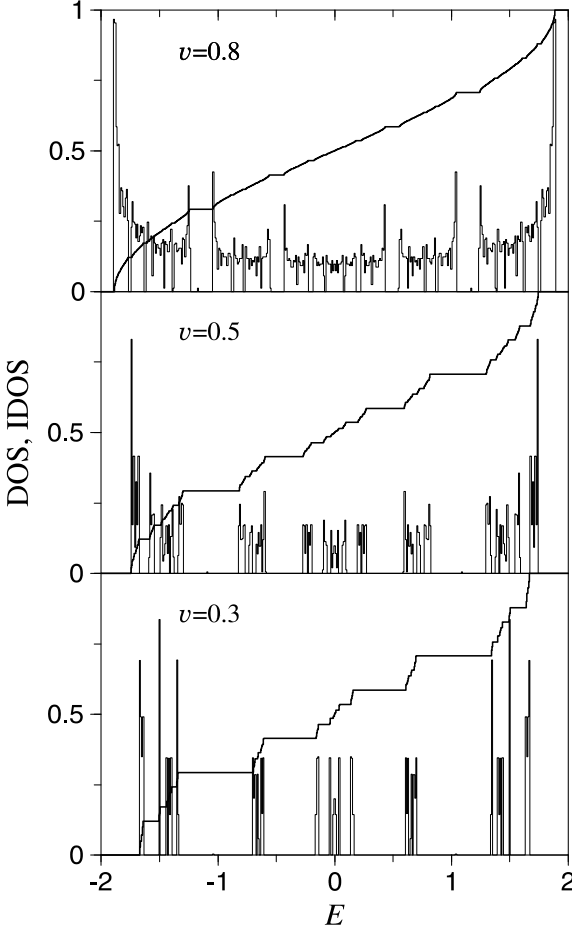


Fig. 2. Density of states (arbitrary scale) and integrated density of states of the 12th approximant of the silver-mean quasiperiodic chain with 19602 sites for $\nu = 0.8$, 0.5, and 0.3 (from top to bottom) [14]

E_k at site j which are obtained from the diagonalization and construct initially localized wave packets by a suitable linear combination of these wave functions:

$$\vec{\Psi} = \sum_k a_k \vec{\psi}_k = (\Psi_0, \dots, \Psi_j, \dots, \Psi_N)^T$$

The time evolution of the wave packets is then given by the time evolution of the contributing wave functions, namely $\vec{\psi}_k = \vec{\psi}_k e^{-iE_k t}$. In particular, we start with a wave packet that is initially localized on one site i_0 only: $\Psi_j(t=0) = \delta_{j,i_0}$. The spreading of such a wave packet can be characterized by the temporal autocorrelation function and the mean-square displacement [17].

The temporal autocorrelation function

$$C(t) = \frac{1}{t} \int_0^t |\Psi_{i_0}(t')|^2 dt'$$

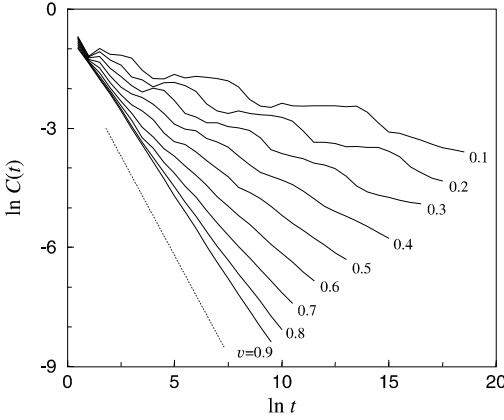


Fig. 3. Autocorrelation function $C(t)$ of the 12th approximant of the silver-mean quasiperiodic chain with 19602 sites for different values of the hopping parameter ν [14]

describes the return probability of the wave packet to the initial site. A characteristic feature of quasiperiodic systems is that the asymptotic behavior of $C(t)$ for large times is given by a power law

$$C(t) \sim t^{-\delta}.$$

In figure 3 the results of our investigation [3,14] of the silver-mean quasiperiodic chain are displayed for various values of the parameter ν . The doubly logarithmic plot clearly shows that the power law is fulfilled with exponents δ decreasing from $\delta \approx 1$ for large ν to $\delta \approx 0.13$ for $\nu = 0.1$. An interesting feature of these plots is the appearance of steps in the autocorrelation function for small values of the parameter ν . This means that the return probability remains relatively constant for long periods of time and then drops substantially to a lower value. On the doubly logarithmic scales of the plots these constant values appear to be approximately equidistant. This reflects the hierarchical structure of the quasiperiodic sequence, which in turn follows from the construction procedure, namely the inflation.

Another commonly studied quantity for characterization of the electron dynamics is the mean-square displacement $d(t)$ of the wave packet, defined as

$$d^2(t) = \sum_j |j - i_0|^2 |\Psi_j(t)|^2,$$

which directly reflects the spatial spreading of the wave packet. This quantity is also expected to asymptotically follow a power law

$$d(t) \sim t^\beta$$

for large times t . Our results [3,14] are displayed in figure 4 and confirm this expectation. The exponent β is close to unity for large ν ($\beta \approx 0.95$ at $\nu = 0.9$) and decreases with decreasing ν nearly linearly to $\beta = 0.3$ at $\nu = 0.1$. For $\nu = 0.1$ again distinct steps can be observed which mean that for long periods in time the wave packet does not spread much further, but then a substantial increase of the

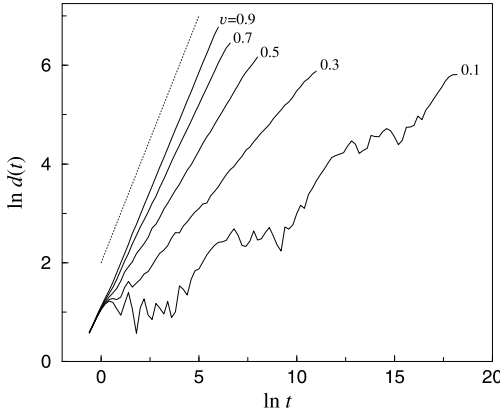


Fig. 4. Mean-square displacement $d(t)$ of the 9th approximant of the silver-mean quasiperiodic chain with 1394 sites for different values of the hopping parameter ν [14]

width occurs. This behavior again reflects the hierarchical construction of the quasiperiodic chain.

For a closer inspection of these steps we have simulated the chain for much longer times at three small values of the hopping parameter [18]. The results are shown in figure 5 where the steps are very prominent. The overall behavior can be fitted by a power law yielding, e.g., $\mathcal{E} \approx 0.2$ for $\nu = 0.025$. But this is an average over two distinctly different behaviors, namely a strong expansion that can be described by a power law with $\mathcal{E} \approx 0.79$ and a constrained behavior where the mean square displacement fluctuates strongly but remains bounded from above by more or less a constant value. The insets in figure 5 demonstrate that these fluctuations are self-similar, they grow exponentially in time and in spatial extent. Here the hierarchical structure is shown most impressively. A direct visual inspection of the temporal evolution of the wave packet reveals that the

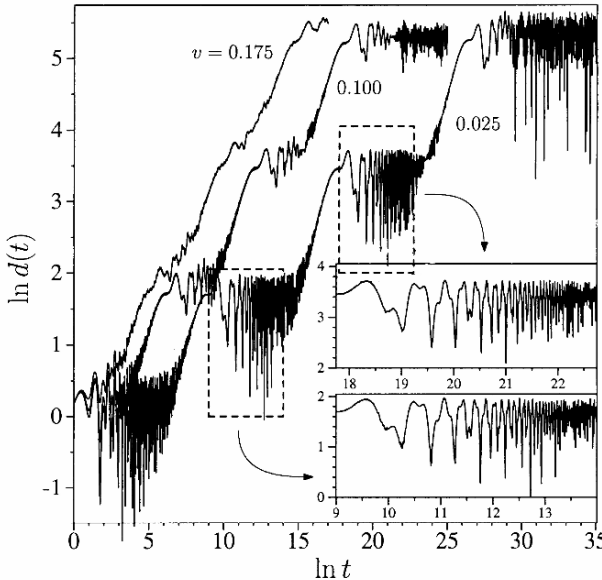


Fig. 5. Same as figure 4, but for longer times and three small values of the parameter ν . In the insets a magnification of the regions which are indicated by dashed boxes in the main plot is displayed [18]

fluctuations are due to breathing modes. Most of the time only a small part of the wave packet leaks out of the confinement region and then sometimes there happens a somewhat sudden expansion to the next level of the hierarchy. It is interesting to note that this fast spreading occurs according to a power law with nearly the same exponent for the three different values of the hopping parameter in figure 4. This is an indication that the fast expansion is not governed by the small hopping parameter, but rather it is a kind of resonance between different hierarchical levels of the clusters. A similar step-like behavior with $\omega = 1$ was proposed [19] for a qualitative model of the spreading of wave packets in a semiclassical approximation for a hierarchical splitting of the spectrum in two bands of constant widths. As shown in figures 1 and 2, in the present investigation the band widths are not constant which might be the reason for the deviation of the exponent.

4. Effect of an Impurity

Finally, we have studied the influence that an impurity might have on the spreading of the wave function [18]. For this purpose, we have added a diagonal matrix element $H_{ii} = u$ at a single site. For large u this will just be an impenetrable barrier. For small values of u , we find an interesting dependence of the wave-packet dynamics on the position of the impurity. This is demonstrated in figures 6 and 7, where one can follow the evolution of the same wave packet starting from the same initial site and interacting with an impurity located at two different sites, in particular two different local environments. The site where the wave packet starts belongs to a cluster of type LLL. In the first case, the impurity is located in a cluster of the other type LL and in this case the evolution is only slightly different from that without any impurity at all. The snapshots in figure 6 show the spreading

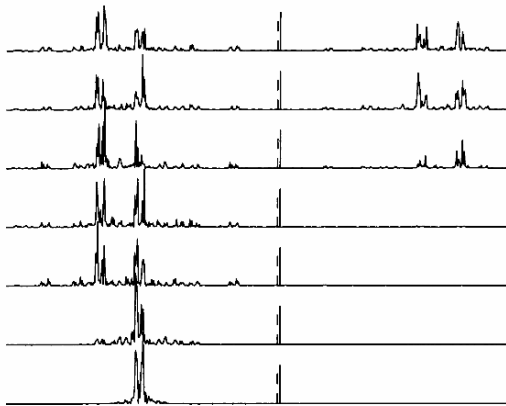


Fig. 6. Snapshots of the evolution of a wave packet on the 8th approximant of the silver-mean quasiperiodic chain with 578 sites for $\nu = 0.1$ in the presence of an impurity with $u = 0.1$ which is located on a cluster with two L bonds at a position which is indicated in each panel by the vertical line. The wave packet is initially localized at a single site. The vertical dashed lines mark the position of the impurity in figure 7. The panels show $|\Psi_j(t)|$ for $t = e^{24}, e^{21}, e^{18}, e^{15}, e^{12}, e^9$, and e^6 (from top to bottom) [18]



Fig. 7. Same as figure 6 but for an impurity which is located on a cluster with three L bonds at the position marked in each panel by a vertical line. The vertical dashed lines indicate the position of the impurity in figure 6 [18]

and they also demonstrate again the hierarchical or step-wise expansion, because for a long time, actually three orders of magnitude in time, the appearance of the wave packet remains nearly the same, before it appears doubled. Then it remains nearly the same again for approximately another three the same orders of magnitude in time, before it appears again doubled.

When the impurity is located on a cluster of the same type as the initial site of the wave packet like in figure 7 then it acts effectively as a barrier and instead of transmission now a strong reflection can be observed. Only a negligible part of the probability leaks through the barrier and appears in those spatial regions in which there were strong wave function contributions in the other case at longer times. It is interesting to note that the reflected parts of the wave functions build up a significant amplitude much earlier than the “normally” transmitted parts in the first case. This can be seen at $t = e^{15}$ where the reflections in figure 7 are already prominent, while there is no corresponding structure in figure 6.

5. Summary and Outlook

We have investigated the electronic spectra and the wave-packet dynamics of electronic states on a quasiperiodic chain. The structure of the chain was determined by the silver-mean sequence of the hopping integrals. Comparable simulations (not shown here) with constant hopping elements and diagonal Hamiltonian matrix elements chosen according to a quasiperiodic sequence have given similar results. The spectrum is singular continuous with gaps of various sizes in agreement with the gap labeling theorem. The autocorrelation function and the return probability show anomalous diffusion. For small hopping parameters small steps occur in both functions reflecting the hierarchical structure of the quasiperiodic chain. Introducing an impurity into the system allows us to control the wave-packet dynamics. Thus it might be feasible by externally influencing the strength of such an impurity to switch between the transmitting and the reflecting behavior and in this way it might be possible to control the

localization of the wave packet on a subsystem and thus to confine or not to confine the wave packet.

Acknowledgements

I acknowledge the work of V.Z. Cerovski, who performed some of the computations. I thank U. Grimm for further calculations and for many stimulating discussions.

References

1. D. Shechtman, I. Blech, D. Gratias, and J.W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984).
2. T. Ishimasa, H.U. Nissen, and Y. Fukano, Phys. Rev. Lett. **55**, 511 (1985).
3. U. Grimm and M. Schreiber, in *Quasicrystals – Structure and Physical Properties*, edited by H.-R. Trebin (Wiley-VCH, Berlin 2003), p. 210-235; arXiv: cond-mat/0212140.
4. J.B. Suck, M. Schreiber, and P. Häussler (editors), *Quasicrystals – An Introduction to Structure, Physical Properties and Applications*, Springer Series in Material Science **55**, (Springer, Berlin, Heidelberg, 2002).
5. H.-R. Trebin (editor), *Quasicrystals – Structure and Physical Properties* (Wiley- VCH, Berlin, 2003).
6. M. Baake and R.V. Moody (editors), *Directions in Mathematical Quasicrystals* (American Mathematical Society, Providence, RI, 2000).
7. D. Damanik, in [6], p. 277-305; arXiv: math-ph/9912005.
8. X. Wang, U. Grimm, and M. Schreiber, Phys. Rev. B **62**, 14 020 (2000).
9. M. Schreiber and H. Grussbach, Phys. Rev. Lett. **67**, 607 (1991).
10. M. Torres, J.P. Adrados, J.L. Aragón, P. Cobo, and S. Tehuacanero, Phys. Rev. Lett. **90**, 114501 (2003).
11. T. Tokihiro, T. Fujiwara, and M. Arai, Phys. Rev. B **38**, 5981 (1988).
12. P. Repetowicz, U. Grimm, and M. Schreiber, Phys. Rev. B **58**, 13 482 (1998).
13. M. Kohmoto, B. Sutherland, and C. Tang, Phys. Rev. B **35**, 1020 (1987).
14. H.Q. Yuan, U. Grimm, P. Repetowicz, and M. Schreiber, Phys. Rev. B **62**, 15 569 (2000).
15. V. Cerovski, M. Schreiber, and U. Grimm, Phys. Rev. B **72**, 054203 (2005).
16. J. Bellissard, A. Bovier, and J.M. Ghez, Rev. Math. Phys. **4**, 1 (1992).
17. R. Ketzmerick, K. Kruse, S. Kraut, and T. Geisel, Phys. Rev. Lett. **79**, 1959 (1997).
18. V. Cerovski, M. Schreiber, and U. Grimm, “Multiscaling, ergodicity and localization in quasiperiodic chains”, arXiv: cond-mat/0412618.
19. M. Wilkinson and E.J. Austin, Phys. Rev. B **50**, 1420 (1994).

Effect of Single-Side Modulation Doping on Low-Temperature Transport Properties in Square Infinite Quantum Wells

Nguyen Huyen Tung¹, Doan Nhat Quang² and Do Thi Hien²

¹ Institute of Engineering Physics, HUT, 1 Dai Co Viet Road, Hanoi, Vietnam

² Centre for Theoretical Physics, VAST, 10 Dao Tan Str., Hanoi, Vietnam

Abstract. A variational approach is given for the effect from single-side modulation doping on low-temperature transport properties of the charge carriers confined in a square infinite quantum well (QW). We obtained analytic expressions which describe the doping effects on the carrier distribution in the well, their roughness-induced scattering in the in-plane and screening by them. The calculation of the transport lifetimes is performed for holes in a SiGe/Ge/SiGe square QW, and the result is found in quantitative agreement with recently measured dependence on experimental conditions such as channel width and carrier density.

1. Introduction

Modulation doped strained Ge and SiGe-based quantum wells (QWs) have received enormous attention in recent years due to their importance in device applications. In order to upgrade the hole mobility of the above-quoted QWs, one needs to identify the key scattering mechanisms limiting the transport properties of their two-dimensional hole gas (2DHG), and reduce their detrimental effects. It is well known [1,2] that the best way for this purpose is to study the dependence of 2DHG mobility on experimental conditions such as sample temperature, carrier density, and channel width.

It is worth to mention that although the above dependencies were explored by a number of authors, they still remain as challenging problems. Firstly, there are several reports [3–5] on the channel width dependence of the 2DHG mobility measured in a strained Ge channel in $\text{Si}_{1-x}\text{Ge}_x/\text{Ge}/\text{Si}_{1-x}\text{Ge}_x$ QWs. This exhibits a pronounced peak, which is in sharp contrast to the monotonic increase predicted by the normally adopted theories [6], but, to date no theoretical analysis available. Secondly, the key scattering mechanisms for these QWs are a subject under debate. The previous interpretations of some experimental findings are quite different even due to one and the same research group [4,8]. Indeed, from the 2DHG mobility dependence on temperature ($\leq 100\text{K}$) and on channel width some authors [3,4,8] assumed surface roughness scattering to be the key mechanism. However, from the carrier density dependence of the mobility and the transport to quantum lifetime ratio, the others [8] assumed ionized impurity scattering to be dominant. Thirdly, in their calculations the roughness-related misfit deformation potential scattering has been ignored, which was proven to be important for

strained Si [10] and SiGe [11] channels. Just recently, some experimental [8] and theoretical [12] studies have indicated that the doping-induced confinement may be of great importance for the QW mobility. To date, the theory of doping effect on quantum confinement has been developed for triangular QWs [9], however, no theory for square QWs available. Thus, the goal of this paper is to provide a theory of the band-bending effect on the low-temperature transport properties of charge carriers in a single-side modulation doped infinite square QW. We develop a variational approach to the description of quantum confinement in bent-band infinite square QWs.

2. Single-Side Modulation Doped Infinite Square QW

2.1 Variational Wave Function for a Single-Side Modulation Doped Infinite Square QW

As a prototype, we are dealing with a heterostructure made of cubic crystals, which is composed of a strained well layer grown pseudomorphically along the [001] axis between two barrier ones. The well layer forms a conduction channel of width L in the region $|z| < L/2$. The sample is modulation doped in a region of thickness L_d in the surface-side barrier $z < -L/2$ and separated from the channel by a spacer layer of thickness L_s . The confinement may be plausibly described by an asymmetric wave function as follows:

$$\zeta(z) = \begin{cases} Bk^{1/2}(\cos kz)e^{-k'z} & \text{for } |z| < L/2 \\ 0 & \text{for } |z| > L/2, \end{cases} \quad (1)$$

in which B , k , and k' are variational parameters to be determined; k and k' are wave numbers in the well layer with k' quantifying the doping – induced band bending effect. The boundary conditions at the interface planes and the normalization read as follows:

$$k = \pi/L, \quad \pi B^2 \gamma_1(c)/2 = 1, \quad (2)$$

where $c = k' L$, and $\gamma_1(c)$ is in Eq.(A3), so c is the single independent variational parameter. In the absence of doping $c = 0$, this goes to the exact symmetric wave function of an ideally-square well (flat-band model) [6]. Thus, the parameter c quantifies the effect of the doping-induced band bending on the wave function.

2.2 Hartree Potential in a Single-Side Modulation Doped Infinite Square QW

The wave function of the lowest subband is obtained by minimizing the total energy per particle which is determined by the Hamiltonian

$$H = T + V_H(z), \quad (3)$$

where T is the kinetic energy, and $V_H(z)$ is the Hartree potential as a confining potential along the growth direction. The latter is created by the ionized remote impurities and charge carriers in the well in accordance with Poisson's equation

$$\frac{d^2}{dz^2} V_H(z) = \frac{4\pi e^2}{\epsilon_L} [N_I(z) - p(z)], \quad (4)$$

in which $N_I(z)$ is the bulk density of impurities (per unit volume), $p(z)$ the one of carriers, and ϵ_L is the dielectric constant of the QW. The sample is modulation doped with an impurity density N_I in a region in the top barrier from $-z_d$ to $-z_s$, where the doping positions: $z_d = L_d + L_s + L/2$ and $z_s = L_s + L/2$, so that

$$N_I(z) = \begin{cases} N_I, & \text{for } -z_d \leq z \leq -z_s \\ 0, & \text{elsewhere.} \end{cases} \quad \text{and} \quad p(z) = p_s |\zeta(z)|^2 \quad (5)$$

with p_s as a sheet carrier density. We solve Poisson's equation (4) in combination with electrostatic boundary conditions, especially the vanishing of the relevant electric field at infinity $z \rightarrow \pm\infty$. As a result, within the variational approximation with the use of the wave function from Eq. (1), the Hartree potential may be separated into two parts:

$$V_H(z) = V_I(z) + V_s(z). \quad (6)$$

The first term V_I from Eq. (6) is to be regarded as the impurity potential fixed by the doping profile, viz. the impurity density N_I and doping positions z_d, z_s ; while the second one V_s as the 2DHG potential fixed by the sheet hole density p_s and their distribution, i.e., the variational parameters.

2.3 Total Energy Per Particle in the Lowest Subband

We now turn to the total energy per particle in the ground-state subband. The expectation value for the Hamiltonian from Eqs. (3) and (6) is a function of the bending parameter c , given by

$$E(c) = \langle T \rangle + \langle V_I \rangle + \langle V_s \rangle. \quad (7)$$

The total energy per particle is given by Eq. (7), in which the average potential due to the carrier distribution is to be replaced by its half. For the kinetic energy, it holds

$$\langle T \rangle = \frac{-\hbar^2}{2m_z L^2} \frac{\pi B^2}{2} \left[(c^2 - \pi^2) \gamma_I(c) + 2\pi c \omega_I(c) \right], \quad (8)$$

where m_z is the out-of-plane carrier effective mass of the well material, γ_n and ω_n with n as an integer are simple functions of a variable defined by Eqs. (A3) and

(A4). Next, the average potential due to charged impurities can be written in terms of the dimensionless doping positions: $d = z_d/L$ and $s = z_s/L$, as

$$\langle V_I \rangle = \frac{4pe^2}{e_L} \frac{N_I L^2}{2} (d^2 - s^2). \quad (9)$$

Lastly, for the carrier potential it holds

$$\begin{aligned} \langle V_s \rangle = & \frac{4\pi e^2}{\varepsilon_L} \frac{p_s L}{4} \left\{ \pi B^2 \left[\left(2 \frac{g_-}{L} + g'_- \right) \gamma_1(c) - g'_+ + \frac{\partial \gamma_1(c)}{\partial c} \right] \right. \\ & - \frac{\pi^2 B^4}{4} \gamma_1(2c) \left[\frac{1}{c^2} + \frac{c^2 - \pi^2}{(c^2 + \pi^2)^2} + \frac{c^2 - \pi^2}{2(c^2 + \pi^2)^2} [\gamma_2(2c) - \gamma_0(2c)] \right] \\ & \left. + \frac{\pi^2 B^4}{4} \left[\frac{\pi c}{(c^2 + \pi^2)^2} [\omega_2(2c) + 2\omega_1(2c)] \right] \right\}. \quad (10) \end{aligned}$$

3. Low-Temperature Transport Lifetime

3.1 Basic Equations

In this section we are dealing with transport properties of charge carriers confined in a single-side modulation doped infinite square QW, viz., their transport lifetime τ_i .

The particles moving along the in-plane are scattered by various disorder sources which are characterized by some random fields. Scattering by a Gaussian random field is specified by its autocorrelation function in wave vector space $\langle |U(\mathbf{q})|^2 \rangle$. Here $U(\mathbf{q})$ is a two-dimensional Fourier transform of the unscreened scattering potential weighted with an envelope wave function

$$U(\mathbf{q}) = \int_{-\infty}^{+\infty} dz |\zeta(z)|^2 U(\mathbf{q}, z). \quad (11)$$

At very low temperature the charge carriers are in general expected to experience the following scattering mechanisms: (i) remote impurities (RI), (ii) surface roughness (SR) from both interfaces, and (iii) misfit deformation potential (DP) therefrom. The overall lifetime is determined by the ones for individual disorders according to the Matthiessen's rule

$$\frac{1}{\tau_{tot}} = \frac{1}{\tau_{RI}} + \frac{1}{\tau_{SR}^{(t)}} + \frac{1}{\tau_{SR}^{(b)}} + \frac{1}{\tau_{DP}^{(t)}} + \frac{1}{\tau_{DP}^{(b)}}, \quad (12)$$

with the superindex (t) referring to the top interface and (b) to the bottom one, respectively. Within the linear transport theory, the inverse transport lifetime for zero temperature is represented in terms of the autocorrelation function for each disorder by [6]

$$\frac{1}{\tau_t} = \frac{1}{(2\pi)^2 \hbar E_F} \int_0^{2k_F} dq \int_0^{2\pi} d\varphi \frac{q^2}{(4k_F^2 - q^2)^{1/2}} \frac{\langle |U(\mathbf{q})|^2 \rangle}{\varepsilon^2(q)}, \quad (13)$$

here $\mathbf{q}(q, \varphi)$ denotes the 2D momentum transfer by a scattering event in the (x - y) plane (in polar coordinates), $q = |\mathbf{q}| = 2k_F \sin(\theta/2)$ with θ as a scattering angle. The Fermi energy is given by $E_F = \hbar^2 k_F^2 / 2m^*$, with k_F as the Fermi wave number fixed by the sheet carrier density: $k_F = (2\pi p_s)^{1/2}$, and m^* as the in-plane carrier effective mass of the well. The dielectric function $\varepsilon(q)$ entering Eq. (13) takes account of the screening of a scattering potential by charge carriers. As usual, this is evaluated within the random phase approximation

$$\varepsilon(q) = 1 + \frac{q_s}{q} F_S(q) \left[1 - q/2 (q^2 + k_F^2)^{1/2} \right], \quad \text{for } q \leq 2k_F \quad (14)$$

with $q_s = 2m^* e^2 / \varepsilon_L \hbar^2$ as the inverse 2D Thomas-Fermi screening length. The screening form factor $F_S(q)$ takes account of the extension of particle states along the growth direction, defined by

$$F_S(q) = \int_{-\infty}^{+\infty} dz \int_{-\infty}^{+\infty} dz' |\zeta(z)|^2 |\zeta(z')|^2 e^{-q|z-z'|}. \quad (15)$$

The calculation of the screening form factor with the wave function given by Eq. (1) is lengthy. As a result, one may achieve an analytic expression:

$$F_S(t) = (\pi^2 B^d / 4) [S^{(u)}(t) + S^{(l)}(t)], \quad (16)$$

with $t = qL$ as the dimensionless in-plane wave number. The functions figuring here are defined as follows:

$$\begin{aligned} S^{(u/l)}(t) = & \pm \frac{1}{2(c \mp t/2)} \left[e^{\pm(c \mp t/2)} \gamma_1(c \pm t/2) - \gamma_1(2c) \right] \\ & \pm \frac{\pi}{4[\pi^2 + (c \mp t/2)^2]} [\omega_2(2c) + 2\omega_l(2c)] \\ & \mp \frac{c \mp t/2}{4[\pi^2 + (c \mp t/2)^2]} \left[2e^{\pm(c \mp t/2)} \gamma_1(c \pm t/2) + \gamma_2(2c) + 2\gamma_1(2c) - \gamma_0(2c) \right], \end{aligned} \quad (17)$$

where the upper (lower) signs refer to the subindex (u) and (l), respectively.

In the doping-free condition ($c = 0$), the above expression is simplified to the one for the flat-band model [6].

3.2 Autocorrelation Functions for Scattering Mechanisms

Remote impurity

As known, [6,13] the autocorrelation function for scattering from a random distribution of charged impurities is supplied by an integral over the doping region:

$$\langle |U_{RI}(q)|^2 \rangle = \left(\frac{2\pi e^2}{\varepsilon_L q} \right)^2 \int_{-\infty}^{+\infty} dz_i N_I(z_i) F_R^2(q, z_i), \quad (18)$$

where $N_I(z_i)$ is the three-dimensional impurity density given by Eq. (5). $F_R(q, z_i)$ denotes the form factor for a sheet of impurities in the plane z_i defined by

$$F_R(q, z_i) = \int_{-\infty}^{+\infty} dz |\zeta(z)|^2 e^{-q|z-z_i|}. \quad (19)$$

The calculation of Eq. (19) with the wave function from Eq. (1) yields

$$F_R(q, z_i) = \pi B^2 \frac{e^{qz_i}}{2} \gamma_1(c + qL/2). \quad (20)$$

However, the sample is usually subjected to thermal treatment during epitaxial growth. Therefore, one has to take into account the Coulomb repulsion between charged impurities during their diffusion, which weakens their averaged field.

Accordingly, the high-temperature ionic correlation is proven to diminish their autocorrelation function by some factor $t/(t+t_c)$, where

$$t_c = (2\pi e^2 n_I L) / (\varepsilon_L k_B T_0), \quad (21)$$

with n_I as the sheet impurity density: $n_I = (N_I)^{2/3}$, T_0 as the freezing temperature for impurity diffusion, and k_B the Boltzmann constant. Consequently, we may arrive at the following autocorrelation function for remote impurities:

$$\langle |U_{RI}(t)|^2 \rangle_c = \frac{N_I L^3}{4} \left(\frac{2\pi e^2}{\varepsilon_L} \right)^2 \frac{\pi B^2 \gamma_1(c + t/2)}{2} \frac{e^{-2st} - e^{-2dt}}{t^2(t+t_c)}, \quad (20)$$

where $\langle \dots \rangle_c$ stands for the averaging over correlated impurities.

Surface roughness

We now turn to scattering related to interface roughness, viz., surface roughness and misfit deformation potential. The former is an event which arises from

roughness-induced fluctuations in position of the potential barriers. The weighted scattering potential in wave vector space is determined by the value of the wave function at the interface planes $\zeta_{\pm} = \zeta(z = \pm L/2)$ [13]:

$$U_{SR}(q) = V_0 |\zeta_{\pm}|^2 \Delta_q, \quad (21)$$

where Δ_q denotes a Fourier transform of the interface profile. The scattering rate calculated with the use of a variational wave function might be much larger than the one calculated numerically self-consistently. For getting rid of this problem we need to establish a formula for the weighted roughness potential in terms of such quantities that are insensitive to the trial wave function, e.g., its large peak and some integral quantities on the z axis. For the wave function from Eq. (1), this peak is located at a point $z_0 = \delta L$, with $\delta = -(1/\pi) \arctan(c/\pi)$ and $|\delta| < 1/2$.

For the above set purpose, we integrate the one-dimensional Schrodinger's equation with the Hamiltonian fixed by Eqs. (3) along the growth direction from $z = 0$ to $z = \pm\infty$. With some wave function $\zeta(z)$ we may arrive at the following relations:

$$V_0 |\zeta_-|^2 = [E(c) - V_H(z_0)] \zeta^2(z_0) + \int_{-\infty}^{z_0} dz \zeta^2(z) \frac{\partial V_H(z)}{\partial z}, \quad (22)$$

$$V_0 |\zeta_+|^2 = [E(c) - V_H(z_0)] \zeta^2(z_0) - \int_{z_0}^{+\infty} dz \zeta^2(z) \frac{\partial V_H(z)}{\partial z}, \quad (23)$$

where $E(c)$ is the particle energy given by Eq. (7). From Eqs. (22) and (23), it holds for scattering from the top and bottom rough interfaces that

$$V_0 \zeta_{\mp}^2 = [E(c) - V_H(z_0)] \zeta^2(z_0) \pm \frac{4\pi e^2}{\varepsilon_L} \frac{p_s}{8} W^{(t/b)}, \quad (24)$$

where by definition:

$$\begin{aligned} W^{(t/b)} = & 4\pi B^2 g'_+ \Gamma_1(\pm c; \pm \delta) + \pi^2 B^4 \left\{ \left[\frac{I}{c} + \frac{c}{c^2 + \pi^2} \right] \Gamma_1(\pm 2c; \pm \delta) \right. \\ & + \frac{c}{2(c^2 + \pi^2)} [\Gamma_2(\pm 2c; \pm \delta) - \Gamma_0(\pm 2c; \pm \delta)] \\ & \left. \mp \frac{\pi}{2(c^2 + \pi^2)} [\Omega_2(\pm 2c; \pm \delta) + 2\Omega_1(\pm 2c; \pm \delta)] \right\}, \end{aligned} \quad (25)$$

with Γ_n and Ω_n as simple functions of two variables defined by Eqs. (A1) and (A2). The upper signs on the right-hand side of Eq. (25) refer to the top interface (t), and the lower signs to the bottom one (b). It follows from Eq. (21) that the

surface roughness scattering depends strongly on the interface profile. This is normally written as follows:

$$\langle |\Delta_q|^2 \rangle = \pi \Delta^2 \Lambda^2 F_{SR}(t), \quad (26)$$

where Δ is a roughness amplitude, and Λ is a correlation length. The form factor for surface roughness is well described by a form of Gaussian type distribution:

$$F_{SR}(t) = \exp(-t^2 \Lambda^2 / 4L^2). \quad (27)$$

Misfit deformation potential

In the pseudomorphic QW under study the well layer is assumed to be under strain. The in-plane component of the strain field in the well is fixed by a lattice mismatch as follows:

$$\epsilon_{\parallel} = (a_{\parallel} - a_0) / a_0, \quad (28)$$

where $a_{\parallel}$ and a_0 are the lattice constants of this layer in the presence and in the absence of strain. It has been demonstrated [6,10] that interface roughness produces fluctuations in the strain field. These strain fluctuations in turn induce nonuniform shifts of the band edges, and so act on the charge carriers as a scattering source. It should be stressed that the misfit deformation potentials for two kinds of carrier are quite different, viz., the one for electrons is fixed by a single normal diagonal component of the strain field [6], whereas the one for holes by all its components [11].

The roughness-induced misfit deformation potential for holes in a cubic crystal is

$$U_{DP}^{(t/b)}(q, z) = \frac{\alpha \epsilon_{\parallel}}{2} q \Delta_q e^{\mp(z \pm L/2)} \times \left\{ \frac{3}{2} [b_s(K+1)]^2 (1 + \sin^4 \varphi + \cos^4 \varphi) + \left(\frac{d_s G}{4c_{44}} \right)^2 (1 + \sin^2 \varphi \cos^2 \varphi) \right\}^{1/2} \quad (29)$$

in the well ($|z| \leq L/2$) and zero elsewhere. Here the upper and lower signs again refer to the top (t) and bottom (b) interfaces, respectively. In Eq. (29) b_s and d_s are the shear deformation potential constants of the well layer, and its anisotropy ratio is α , elastic constants K , G are given in [11].

Upon averaging this potential with the wave function from Eq. (1), we may obtain the autocorrelation function of interest in an analytic form:

$$\begin{aligned} \left\langle \left| U_{DP}^{(t/b)}(q) \right|^2 \right\rangle = & \left(\frac{\pi^{3/2} \alpha \epsilon_{\parallel} \Delta \Lambda}{4} \right)^2 \left(\frac{B^2}{L} \right)^2 \left[\frac{3}{2} [b_s(K+1)]^2 (1 + \sin^4 \varphi + \cos^4 \varphi) \right. \\ & \left. + \left(\frac{d_s G}{4c_{44}} \right)^2 (1 + \sin^2 \varphi \cos^2 \varphi) \right] F_{DP}^{(t/b)}(t), \end{aligned} \quad (30)$$

where the form factor is defined by

$$F_{DP}^{(t/b)}(t) = t^2 e^{-t} \gamma_1^2 (c \pm t/2) F_{SR}(t), \quad (31)$$

with $t = qL$ and $F_{SR}(t)$ from Eq. (27).

4. Results and Conclutions

4.1 Validity of the Model and Input Parameters

In what follows, we will use the theory developed above to study the low-temperature transport properties of single-side modulation doped infinite square QWs. As an example, the theory is illustrated for the 2DHG in a $\text{Si}_{1-x}\text{Ge}_x/\text{Ge}/\text{Si}_{1-x}\text{Ge}_x$ QWs sample, where the Ge channel is under in-plane biaxial compressive strain. We will show how to explain the recent experimental data about the dependence on channel width [3–5], and on carrier density [7, 9] of the 2DHG mobility. Thereby, we are able to identify the key scattering mechanisms for holes in the Ge channel of this heterostructure.

We now outline a discussion of the validity of the assumptions adopted in the formulation. As pointed out in [14] for strained Ge on cubic $\text{Si}_{1-x}\text{Ge}_x$ with Ge content $x \approx 0.7$ the potential barrier height is somewhat large: $V_0 \approx 300$ meV. Thus, for not narrow Ge channels ($L \approx 50$), the infinite square QW model may be acceptable as in earlier theories [9,11]. Thus, for not wide Ge channels ($L \approx 160$) and not high carrier densities ($p_s \approx 2 \times 10^{12} \text{ cm}^{-2}$), the single-subband scattering model may be acceptable.

For numerical calculation, we used the lattice constants, elastic stiffness constants, dielectric constants, and shear deformation potentials listed in [15] for Si and Ge. The corresponding constants for a $\text{Si}_{1-x}\text{Ge}_x$ alloy are estimated within the virtual crystal approximation. For strained Ge the

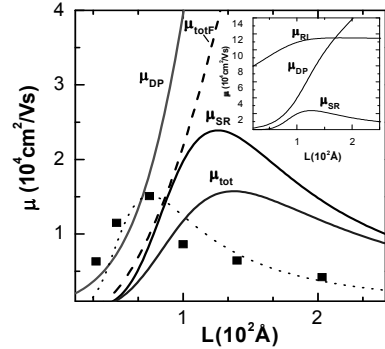


Fig. 1. Partial and total mobilities μ of holes in a $\text{Si}_{0.33}\text{Ge}_{0.67}/\text{Ge}/\text{Si}_{0.33}\text{Ge}_{0.67}$ square QW vs channel width L . The 20K experimental data [4] are marked by squares. The dotted line is total mobility of the bent-band model with $p_s = 5.10^{12} \text{ cm}^{-2}$

out of-plane hole effective mass is fixed $m_z=0.19m_e$, while the in-plane hole effective mass is supplied by measurement in [7] as an increasing function of carrier density owing to nonparabolicity of the valence band.

4.2 Numerical Results and Comparison with Experiment

To end this section, we attempt to explain some recent experimental findings about the 2DHG mobility in square Ge QWs. We first deal with the channel width dependence of the mobility for the sample studied in [4], made of $\text{Si}_{0.33}\text{Ge}_{0.67}/\text{Ge}/\text{Si}_{0.33}\text{Ge}_{0.67}$ with a lattice mismatch $\varepsilon_{||} = -0.01$. The sample was modulation doped with a thickness $L_d = 100$, a spacer $L_s = 200$. The partial and overall mobilities limited by the above scatterings are plotted at a hole density $p_s = 1 \times 10^{12} \text{ cm}^{-2}$ versus channel width L in Fig. 1, where the measured 20K data [4] is represented for a comparison.

Next, we are concerned with the carrier density dependence of the transport in the sample studied in [7], made of $\text{Si}_{0.3}\text{Ge}_{0.7}/\text{Ge}/\text{Si}_{0.3}\text{Ge}_{0.7}$. The doping is the same as in Fig. 1, but with a smaller spacer $L_s = 100$. The partial and overall mobilities limited by the diverse scatterings are plotted at a channel width $L = 75$ versus hole density p_s in Fig. 2, where the measured 8K data [7] is also represented.

From the lines thus obtained, we may draw the following conclusions:

(i) As clearly observed from Fig. 1, the calculated overall mobility may reproduce very well the observed channel width dependence of the 2DHG mobility. The key scattering mechanisms are surface roughness and misfit deformation potential, remote impurities are in general less relevant.

(ii) The channel width evolution shows up in a pronounced mobility maximum for a channel of $L_{\text{max}} \sim 130$ nearly equal to the one specified by experiment [4]. This peak was also detected by other groups [3,5] at somewhat larger L_{max} .

5. Summary

In this report we have provided a theory of the band-bending effect on the transport properties of charge carriers confined a single-side modulation-doped infinite square QW. In contrast to the earlier belief, we have shown that the peak in the channel width evolution of the mobility appears as an effect of the doping-induced band bending.

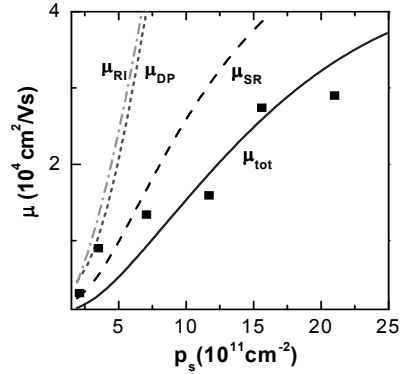


Fig. 2. Partial and total mobilities μ of holes in a $\text{Si}_{0.33}\text{Ge}_{0.67}/\text{Ge}/\text{Si}_{0.33}\text{Ge}_{0.67}$ square QW with a channel width $L = 75$ vs hole density p_s . The 8K experimental data [7] are marked by squares

6. Auxiliary Functions

These are defined as an algebraic combination of elementary functions by

$$\Gamma_n(\eta; \nu) = \frac{e^\eta - e^{-2\nu\eta}}{2\eta} + \frac{1}{2(\eta^2 + n^2\pi^2)} [(-1)^n \eta e^\eta + e^{-2\nu\eta} (n\pi \sin 2\nu n\pi - \eta \cos 2\nu n\pi)], \quad (\text{A1})$$

$$\Omega_n(\eta; \nu) = \frac{1}{2(\eta^2 + n^2\pi^2)} [(-1)^n n\pi e^\eta + e^{-2\nu\eta} (n\pi \cos 2\nu n\pi + \eta \sin 2\nu n\pi)], \quad (\text{A2})$$

$$\gamma_n(\eta) = \left[\frac{1}{\eta} + \frac{(-1)^n \eta}{\eta^2 + n^2\pi^2} \right] \sinh \eta, \quad (\text{A3})$$

$$\omega_n(\eta) = (-1)^n n\pi \frac{\sinh \eta}{\eta^2 + n^2\pi^2}. \quad (\text{A4})$$

References

1. F. Schaffler, *Semiconductor Science and Technology* **12**, 1515 (1997).
2. T. E. Whall and E. H. C. Parker, *Journal of Physics D* **31**, 1397 (1998).
3. Y. H. Xie, D. Monroe, E. A. Fitzgerald, P. J. Silverman, F. A. Thiel, and G. P. Watson, *Applied Physics Letters* **63**, 2263 (1993).
4. T. Irisawa, H. Miura, T. Ueno, Y. Shiraki, *Japanese Journal of Applied Physics* **40**, 2964 (2001).
5. R. J. H. Morris, T. J. Grasby, R. Hammond, M. Myronov, O. A. Mironov, D. R. Leadley, T. E. Whall, E. H. C. Parker, M. T. Currie, C. W. Leitz, and E. A. Fitzgerald, *Semiconductor Science and Technology* **19**, L106 (2004).
6. A. Gold, *Physical. Review. B* **35**, 723 (1987).
7. T. Irisawa, M. Myronov, E. H. C. Parker, K. Nakagawa, M. Murata, S. Koh, and Y. Shiraki, *Applied Physics Letters* **82**, 1425 (2003).
8. M. Myronov, K. Sawano, and Y. Shiraki, *Applied Physics Letters* **88**, 252115 (2006).
9. B. Rossner, D. Chrastina, G. Isella, H. von Kanel, *Applied Physics Letters* **84**, 3058 (2004).
10. R. M. Feenstra and M. A. Lutz, *Journal of Applied Physics* **78**, 6091 (1995).
11. D. N. Quang, N. H. Tung, D. T. Hien, and H. A. Huy, *Physical. Review. B* **75**, 073305 (2007).
12. D. N. Quang, N. H. Tung, V. N. Tuoc, N. V. Minh, H. A. Huy, and D. T. Hien, *Physical. Review. B* **74**, 205312 (2006).
13. T. Ando, A. B. Fowler, and F. Stern, *Reviews of Modern Physics* **54**, 437 (1982).
14. Kahan, M. Chi, and L. Friedman, *Journal of Applied Physics* **75**, 8012 (1994).
15. G. Van de Walle, *Physical. Review. B* **39**, 1871 (1989).

Nonlinear Optical Conductivity in Doped Semiconductor Superlattices Due to LO Phonon Scattering

Luong Van Tung¹, Tran Cong Phong² and Nguyen Thi Le Thuy¹

¹ Department of Physics, Dong Thap University of Education, 783 Pham Huu Lau, Cao Lanh, Dong Thap, Viet Nam

E-mail: dhsptvantung@yahoo.com

² Department of Physics, Hue University, 32 Le Loi, Hue, Vietnam

E-mail: congphong2000@yahoo.com

Abstract. Based on new theory of nonlinear optical conductivity for an electron – phonon system, we calculate line-widths for the nonlinear optical conductivity in a system of electron interacting with longitudinal optical phonons (LO) in doped semiconductor superlattices (DSSL). Our numerical results for a specific DSSL show that temperature dependence of the width is different and non-monotonous in the region of low temperature. The results are compared with other theoretical results and recent experiments.

1. Introduction

The development of low dimensional semiconductors has opened up various new fields of study in both theory and practice. One of those is studying theory of electronic transport and optical conductivity in materials in the presence of high intense electromagnetic field [1–5]. A superlattice is a low dimensional semiconductor which has preminent characteristics due to being built out of layers of different semiconductors [6, 7]. Obtaining line-widths of absorption spectrum from optical conductivity and investigating the dependence of the line-width on temperature and field shall greatly contribute to the study of transport theory and various other effects in superlattices.

The temperature dependence of the fundamental bandgap energy is an extremely important characteristic of any semiconductor material and it brings about great interest, mainly from the technological point of view [8, 9]. Some models have been proposed to describe this dependence, but the relation between the physical mechanisms involved with the processes and the parameters used in the expressions of these models still are intensively discussed. Few studies of their energy gap and linewidth variation with temperature have been published [4, 8, 9]. But, to our knowledge, there is no systematic analysis of the theoretical models used to describe the temperature dependence of the linewidth for superlattices.

This paper aims to apply a method of calculating nonlinear optical conductivity by using the state-dependent projection operator technique in many-body theory [2] in the case of DSSLs. The rest of the paper is organized as follows: In Section 2, the general theory of line-width from nonlinear optical conductivity, which has

been presented in Ref. 2, will be reviewed. Our analytic calculations of the line-width for a specific DSSL are presented in Section 3. Then, numerical results of the line-width in the DSSL and some comments on dependences of the line-width on temperature, and on external electric field are presented in Section 4.

2. Theory of Nonlinear Optical Conductivity and Line-Width

We consider a system of electrons interacting with phonons in a DSSL which is subjected by a time-dependent external electric field $\vec{E}(t) = \sum_{j=1,2,3} E_j e^{i\omega t} \vec{e}_j$. The total Hamiltonian of the system consists of the equilibrium Hamiltonian H_{eq} and the non-equilibrium Hamiltonian $H_{int}(t)$ caused by the action of external field. The equilibrium Hamiltonian H_{eq} includes the Hamiltonian of the free electron-phonon system H_d and the Hamiltonian of interacting electron-phonon system V :

$$H_{eq} = H_d + V = \sum_{\alpha} \varepsilon_{\alpha} a_{\alpha}^{\dagger} a_{\alpha} + \sum_q \hbar \omega_q b_q^{\dagger} b_q + \sum_q \sum_{\alpha, \mu} C_{\alpha, \mu}(q) a_{\alpha}^{\dagger} a_{\mu} (b_q + b_{-q}^{\dagger}) \quad (1)$$

The interaction Hamiltonian of the external field takes the form

$$H_{int}(t) = \lim_{\Delta \rightarrow 0^+} e \sum_{j=1}^3 \sum_{\alpha, \beta} (r_j)_{\alpha\beta} a_{\alpha}^{\dagger} a_{\beta} E_j e^{i\omega t} \quad (2)$$

where $a_{\alpha}^{\dagger}$ and a_{α} ($b_q^{\dagger}$ and b_q) are the creation and annihilation operators of electron in the $|\alpha\rangle$ state (phonon), e and ε_{α} are the charge and energy spectrum of the electron, $E_j(\bar{\omega}) \equiv E_j e^{i\bar{\omega}t}$, $\bar{\omega} = \omega - i\Delta$, $\Delta \rightarrow +0$. The electron-phonon interaction matrix element $C_{\alpha, \mu}(q)$ depends on the type of phonons and electron energy spectra (of course, it depends on specific structure).

When a time-dependent external electric field is applied to the sample, the time dependent density operator $\rho(t) = \rho_{eq} + \rho_{int}(t)$, where $\rho_{int}(t)$ is the perturbed term by the time dependent external field. The Liouville equation for $\rho(t)$ is

$$i\hbar \frac{\partial \rho(t)}{\partial t} = [H(t), \rho(t)] \equiv L(t) \rho(t). \quad (3)$$

here, $L(t)$ is the Liouville operator defined as $L(t)X = [H(t), X]$ for an arbitrary linear operator X . $L(t) = L_{eq} + L_{int}(t)$, where L_{eq} and $L_{int}(t)$ correspond to H_{eq} and $H_{int}(t)$, respectively.

In order to obtain $\rho(t)$, using the density operator in the Dirac picture [3], we have [2]

$$\rho_{int}(t) \equiv \rho^{(1)}(t) + \rho^{(2)}(t) + \dots + \rho^{(n)}(t), \quad (4)$$

where $\rho^{(i)}(t)$, with $i = 1, 2, 3, \dots, n$ involves $L_{int}(t)$'s n times.

Using the density operator in (4), the ensemble average [2, 4] of the i component of the current density operator $\bar{J}$ takes the form

$$\begin{aligned} \langle J_i \rangle_{ens} &= \sum_{n=1}^{+\infty} \langle J_i^{(n)} \rangle = \sum_{n=1}^{+\infty} Tr \{ J_i \rho^{(n)}(t) \} \\ &= \sum_{j=1}^3 \sigma_{ij}(\omega) E_j(\bar{\omega}) + \sum_{j,k=1}^3 \sigma_{ijk}(\omega_1, \omega_2) E_j(\bar{\omega}_1) E_k(\bar{\omega}_2) + \dots, \end{aligned} \quad (5)$$

where $\bar{\omega}_{l(2)} = \omega_{l(2)} - i\Delta$, “...” denotes terms that are from the third order upwards. $\sigma_{ij}(\omega)$ and $\sigma_{ijk}(\omega_1, \omega_2)$ are the linear and first order nonlinear conductivities, respectively. Eq. (5) will be used to calculate linear and nonlinear conductivities. In the present paper we focus on the first order nonlinear conductivity corresponding to two incident waves of frequencies ω_1 and ω_2 .

The first order nonlinear component of optical conductivity tensor is determined as [2, 4]

$$\begin{aligned} \sigma_{ijk}(\omega_1, \omega_2) &= e^2 \lim_{\Delta \rightarrow 0^+} \sum_{\alpha, \beta} \sum_{\gamma, \delta} \sum_{\xi \in} (r_j)_{\alpha\beta} (r_k)_{\gamma\delta} (J_i)_{\xi \in} \\ &\times Tr \left\{ \rho_{eq} [(\hbar \bar{\omega}_2 - L_{eq})^{-1} [(\hbar \bar{\omega}_{12} - L_{eq})^{-1} a_{\xi}^+ a_{\epsilon}, a_{\gamma}^+ a_{\delta}], a_{\alpha}^+ a_{\beta}] \right\} \end{aligned} \quad (6)$$

here, $\omega_{12} = \omega_1 + \omega_2$, L_{eq} is the Liouville operator corresponding to the equilibrium Hamiltonian and can be written as $L_{eq} = L_d + L_v$, where L_d and L_v are the Liouville operators corresponding to the Hamiltonian H_d and the scattering potential V , respectively.

Now, in order to establish an expression of nonlinear conductivity, the authors of Ref. 2 have defined the projectors P and Q as

$$PX \equiv \langle X \rangle_{\alpha\beta}^{\gamma\delta} \left[\langle a_{\xi}^+ a_{\epsilon} \rangle_{\alpha\beta}^{\gamma\delta} \right]^{-1} a_{\xi}^+ a_{\epsilon}, \quad Q \equiv 1 - P; \quad (7)$$

and after systematic calculations, the optical conductivity tensor takes the form

$$\begin{aligned} \sigma_{ijk}(\bar{\omega}_1, \bar{\omega}_2) &= e^2 \lim_{\Delta \rightarrow 0^+} \sum_{\alpha\beta} \sum_{\gamma\delta} \sum_{\xi \in} (r_i)_{\alpha\beta} (r_k)_{\gamma\delta} (J_i)_{\xi \in} \frac{(f_{\beta} - f_{\alpha})}{\hbar \bar{\omega}_2 - \epsilon_{\beta\alpha} - \Gamma_0^{\alpha\beta}(\bar{\omega}_2)} \\ &\times \left[\frac{\delta_{\xi\beta} \delta_{\delta\alpha} \delta_{\epsilon\gamma}}{\hbar \bar{\omega}_{12} - \epsilon_{\beta\alpha} - \Gamma_1^{\alpha\beta\gamma}(\bar{\omega}_{12})} - \frac{\delta_{\gamma\beta} \delta_{\epsilon\alpha} \delta_{\xi\delta}}{\hbar \bar{\omega}_{12} - \epsilon_{\delta\alpha} - \Gamma_2^{\alpha\beta\delta}(\bar{\omega}_{12})} \right] \end{aligned} \quad (8)$$

where $\Gamma_0^{\alpha\beta}(\bar{\omega})$ is the linear line-shape function (the relaxation rates) we have considered [10], while $\Gamma_1^{\alpha\beta\gamma}(\bar{\omega}_{12})$ and $\Gamma_2^{\alpha\beta\delta}(\bar{\omega}_{12})$ are the nonlinear ones that are considered here. Line-shape functions defined in Eq. (8) are complex expressions due to $\bar{\omega}_s = \omega_s - i\Delta$. The real parts and the imaginary parts of the line-shape functions are peak shift and line-width function of the absorption spectrum, respectively.

Assuming that we consider up to the second order of the scattering term (L_v) and the solutions near the resonance points, $\hbar\bar{\omega}_2 \approx \varepsilon_\beta - \varepsilon_\alpha$ or $\hbar\bar{\omega}_2 \approx \varepsilon_\delta - \varepsilon_\alpha$. Then, the two functions of the linewidth for nonlinear case are the same form. For example:

$$\begin{aligned} \gamma_1^{\alpha\beta\gamma}(\omega_{12})(f_\beta - f_\alpha) &= \text{Im}\left\{\Gamma_1^{\alpha\beta\gamma}(\omega_{12})\right\}(f_\beta - f_\alpha) = \pi \sum_q \sum_\eta |C_{\gamma,\eta}(q)|^2 \\ &\times \left\{[(1 - f_\eta + N_q)(f_\alpha + f_\beta) - 2N_q f_\eta] \delta_{\beta\eta}^+ + [2(1 + N_q)f_\alpha - (N_q + f_\eta)(f_\alpha + f_\beta)] \delta_{\beta\eta}^- \right\} \\ &- \pi \sum_q \sum_\eta |C_{\eta,\beta}(q)|^2 \left\{[(1 + N_q)f_\alpha - f_\eta(N_q + f_\alpha)] \delta_{\eta\gamma}^- - [(1 + N_q)f_\eta - f_\alpha(N_q + f_\eta)] \delta_{\eta\gamma}^- \right\} \end{aligned} \quad (9)$$

where $\delta_{\alpha\beta}^\pm = \hbar\omega_{12} - \varepsilon_{\alpha\beta} \pm \hbar\omega_q$, $f_\alpha = [\exp((\varepsilon_\alpha - \varepsilon_F)/k_B T) + 1]^{-1}$ is the Fermi-Dirac distribution function for an electron in the state α , ε_F is the Fermi level, and $N_q = [\exp(\hbar\omega_q/k_B T) - 1]^{-1}$ is the Bose-Einstein distribution function for phonons with energy $\hbar\omega_q$

We apply this result to doped semiconductor superlattices in the next sections.

3. Analytic Expression of Nonlinear Line-Width on DSSL

We use a simple model for DSSLs, in which a two-dimensional electron gas is confined by superlattice potential along the z direction and electrons are free on the x - y plane. The motion of an electron is confined in each layer of the DSSL and its energy spectrum is quantized into discrete levels in the z direction. In most cases, the interaction between the neighboring quantum wells can be neglected, i.e., the dependence of the energy on the wave vector k_z can be neglected [6]. Then, the $|\alpha\rangle$ state of an electron is determined by the index of the miniband n_α and wave vector $\vec{k}^\alpha$; $k^\alpha = \sqrt{k_\perp^2 + k_z^2}$. The wave function and the energy spectrum of the electron in the $|\alpha\rangle$ state take the following forms [7]

$$\psi_{n_\alpha, \vec{k}^\alpha}(\vec{r}) = e^{i\vec{k}_\perp \cdot \vec{r}_\perp} u_{n_\alpha}(r) \sum_{j=1}^{s_0} e^{ik_z^\alpha j d} \Phi_{n_\alpha}(z - jd), \quad \varepsilon_\alpha = \frac{\hbar^2 (k_\perp^\alpha)^2}{2m_e} + \hbar\omega_p(n_\alpha + \frac{1}{2}). \quad (10)$$

We consider electron-LO phonon interaction and $q = (0, 0, q)$. The electron-LO phonon interaction matrix element is $C_{\alpha\mu}(q) = V_q M_{n_\alpha, n_\mu}(q_z)$, where

$$|V_q|^2 = \frac{e^2 \hbar \omega_q}{2\Omega \chi} \left(\frac{1}{\chi_\infty} - \frac{1}{\chi_0} \right) \frac{q^2}{(q^2 + q_d^2)^2}, \quad M_{n_\alpha, n_\mu}(q_z) = \sum_{j=1}^{s_0} \int_0^d e^{iq_z d} \Phi_{n_\alpha}(z - jd) \Phi_{n_\mu}(z - jd) dz \quad (11)$$

with $\omega_p = (4\pi e^2 n_D / \chi m_e)^{1/2}$ as plasma frequency caused by donor impurities with concentration n_D and χ is the static dielectric permittivity; Ω is the volume of

the system, ε_∞ and ε_0 , respectively, are the optical and the static dielectric constants; $\Phi_{n_\alpha}(z)$ is the electron wave function in each individual quantum well, s_0 is the number of period and d is the period of the DSSL, q_d is the reciprocal of the Debye screening length [1], m_e is the effective mass of the electron.

Using the formula of converting summation over q and the state $|n\rangle = |n_\eta, k_\perp^\eta\rangle$ into summation over n_η and integration over $k_\perp^\eta$ for 2D-electron systems in a DSSL and applying to Eq. (9), we obtain the expression of the nonlinear line-width function (NLW):

$$\gamma_1^{\alpha\beta\gamma}(\omega_{12}) = \sum_{n_\gamma} \left\{ A_{n_\eta, n_\gamma} \left[(1 + N_q - f_{n_\eta, k_{1+}})(f_\beta - f_\alpha) \right] + A_{n_\gamma, n_\eta} \left[(N_q + f_{n_\eta, k_{1-}})(f_\beta - f_\alpha) \right] \right\} \\ - \sum_{n_\gamma} A_{n_\eta, n_\beta} \left[(1 + N_q - f_{n_\eta, k_{2-}})f_\alpha - N_q f_\alpha - (1 + N_q - f_\alpha)f_{n_\eta, k_{2+}} + N_q f_\alpha \right], \quad (12)$$

where $f_{n_\alpha, k} = 1/[1 + \exp(\varepsilon_{n_\alpha}(k) - \varepsilon_F)/k_B T]$, ε_η is the Fermi level,

$$k_{1\pm} = \left\{ (k_\perp^\beta)^2 + \frac{2m_e}{\hbar} \omega_p (n_\beta - n_\eta) - \frac{2m_e}{\hbar} (\omega_{12} \pm \omega_q) \right\}^{1/2}, \quad (13)$$

and $k_{2\pm}$ takes the same form as $k_{1\pm}$, but the $|\beta\rangle$ -state is replaced by the $|\eta\rangle$ -state,

$$A_{n_\eta, n_\mu} = \frac{1}{f_\beta - f_\alpha} \left| \sum_{j=1}^{s_0} \int dz \Phi_{n_\eta}(z - jd) \Phi_{n_\mu}(z - jd) \right|^2 \frac{m_e e^2 \omega_q}{8\hbar \chi q_d^2} \left(\frac{1}{\chi_\infty} - \frac{1}{\chi_0} \right) \quad (14)$$

Now, it can be used Eqs. (12)-(14) to compute and consider dependences of NLM on temperature, external field, and parameters of DSSLs.

4. Numerical Results of Nonlinear Line-Width in a DSSL and Discussions

In this section, we numerically calculate and plot the dependence of NLW in the nonlinear conductivity on temperature and frequency of external field for DSSL n-i-p-i of GaAs:Si/GaAs:Be [6]. For a superlattice with constant density n_D , the envelope wave function and the quantized energy levels of electrons in the potential wells coincide with good accuracy to the wave functions and the energy spectrum of the harmonic oscillator [7].

It is noted that the result cannot be put forward in a satisfactory way because no experimental data are yet available for this problem. However, some useful theoretical and experimental data on the conductivity and the line-widths were obtained for different models [8,11-14], which will be a good guide for our discussions.

Figures 1 show the temperature dependence of the NLW at three different values of the photon energy. We can see that the dependence is different and non-monotonous. This temperature dependence is identical to the experimental conductivity vs. temperature plot in [11, 12]. In the low-temperature range $T \leq 300$ K, we can see that the NLWs decrease as the temperature increases and show the dependence which is typical for the quasi-elastic electron – ripplon scattering. As mentioned above, the unusual temperature dependence of the NLM comes directly from the singular nature of the 2D electron system in DSSL. This decrease in the low-temperature range is expected because of the decrease of excited state energy [8]. In the high-temperature range $T \geq 300$ K, from the figure on the right, it is clear that as the temperature increases the temperature dependence of the NLWs becomes linear, with a slope that is determined by the electron–phonon coupling parameter [14] as it is expected [13]. This characteristic can be explained by the fact that there exists a certain value of temperature at which the phonon distribution function has a maxima [13]. In view of these, we can only expect a linear dependence of the line-width on temperature above 300 K.

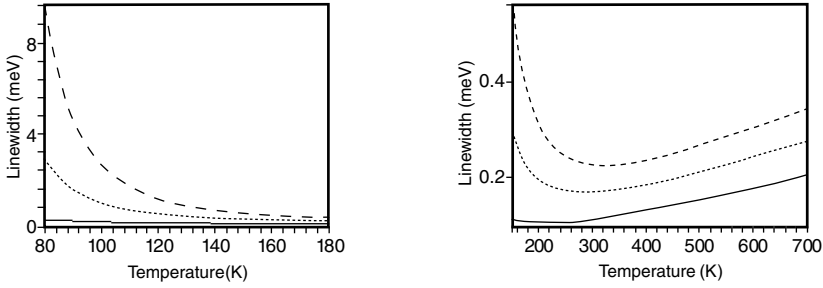


Fig. 1. Temperature dependence of NLW at three different values of the photon energy for low-temperature range (on the left) and high-temperature range (on the right). From top to bottom, photon energies correspond to 100, 80, and 60 meV.

Figure 2 shows the dependence of the nonlinear line-width on photon energy. It can be seen from the figure that the line-width increases and reaches saturate values at $\hbar\omega \geq 150$ meV. This dependence is nearly identical to calculated and experimental absorption spectra for InAs/GaInSb superlattice [11, 15].

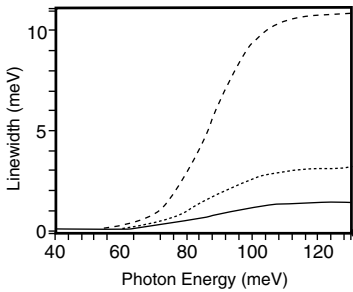


Fig. 2. Dependence of NLW on photon energy at three different values of temperature. From top to bottom, temperatures correspond to 80, 100, and 120 K. Here, $d = 80$ nm, $s_0 = 150$, $n_D = 10^{22} \text{ m}^{-3}$.

By comparing two figures for linear [10] and nonlinear cases we can estimate that the nonlinear line-width is smaller by six times than the linear one. This is one important result because it helps us estimate the convergence of series of the density matrix Eq. (4), which play an important role in the theoretical method for the calculations of nonlinear phenomena.

5. Conclusions

So far, we have presented analytical and numerical results for the line-width in nonlinear optical conductivity of a system of electrons interacting with LO-phonons in DSSL by using quantum statistical transport theory.

We have computed and plotted the dependence of the line-width on temperature and photon energy for a specific DSSL. The analytical and numerical results obtained above represent a reasonable and clear theory in the calculation of nonlinear phenomena.

By using the systematic (successive) calculation as used in this method, one can physically explain the nonlinear optical conductivity and spectral line-width. Moreover, the method can be extended for various types of low dimensional semiconductors with or without a magnetic field. In future, we will study this problem in more detailed.

References

1. N.L. Kang, D.H. Shin, S.D. Choi, *J. Kor. Phys. Soc.*, Vol. 46, 1004, 2005.
2. H.J. Lee, N.L. Kang, J.Y. Sug, S.D. Choi, *Phys. Rev. B*, Vol. 65, 195113, 2002; N.L. Kang, J.Y. Cho, S.D. Choi, *Prog. Theor. Phys.*, Vol. 96, 307, 1996.
3. J.Y. Ryu and S.D. Choi, *Phys. Rev. B*, Vol. 44, 11328, 1991.
4. N.L. Kang, Ji Y. J., H.J. Lee, S.D. Choi, *J. Kor. Phys. Soc.*, Vol. 44, 938, 2004.
5. N.L. Kang, H.J. Lee, S.D. Choi, *J. Kor. Phys. Soc.*, Vol. 42, 379, 2003.
6. K. Ploog and G.H. Dohler, *Adv. Phys.*, Vol. 32, 285, 1983.
7. A.P. Silin, *Sov. Phys. Usp.* Vol. 28, 972, 1986.
8. E.M. Lopes, J.L. Duarte, I.F.L. Dias, L.C. Pocas, E. Laureto and J.C. Harmand, *J. Phys.: Condens. Matter*, Vol. 19, 086207, 2007.
9. J.L. Johnson, L.A. Samoska, A.C. Gossard, J.L. Merz, M.D. Jack, G.R. Chapman, B.A. Baumgratz, K. Kosai and S.M. Johnson, *J. Appl. Phys.*, Vol. 80, 1116, 1996.
10. T.C. Phong, L.V. Tung, H.V. Phuc and N.T.L. Thuy, *Proceedings of 31th Nat. Conf. Theor. Phys.*, Submitted, 2006.
11. Yu.P. Monarkhaa, E. Teskea, P. Wydera, *Physics Reports*, 370, 1, 2001.
12. Yu.P. Monarkha, S. Ito, K. Shirahama, K. Kono, *Phys. Rev. Lett.*, Vol. 78, 2445, 1997.
13. T.S. Rahman, J.D. Spangler and Ah. Al-Rawi, *J. Phys.: Condens. Matter*, Vol. 14 5903, 2002.
14. I.Yu. Sklyadneva, A. Leonardo, P.M. Echenique, S.V. Ereemeev and E.V. Chulkov, *J. Phys.: Condens. Matter*, Vol. 18, 7923, 2006.
15. C. Jenner, E. Corbin, B.M. Adderley and M. Jaros, *Semicond. Sci. Technol.*, Vol. 13, 359, 1998.

The Effects of the Polarization Charges on the Quantum Lifetime of the Two-Dimensional Electron Gas in a Uniformly-Doped Heterostructure

Nguyen Viet Minh

Institute of Engineering Physics, Hanoi University of Technology, 01 Dai Co Viet Road,
Hanoi, Vietnam

E-mail: minhnv@mail.hut.edu.vn

Abstract. We present a theoretical study of the quantum confinement of the two-dimensional electron gas (2DEG) in a group-III-nitride-based single heterostructure under uniformly doping, taking into account effects arising from polarization charges and ionized dopants. By using an extended Fang-Howard wave function for the actual model of a finitely-deep triangular quantum well, we are able to derive an analytic expression for the self-consistent Hartree potential due to uniformly doping. We proved with the presence of the sheet polarization charges, electron wave function is been squeezed close to the barrier. We studied the effect of polarization charges on the quantum lifetime of the 2DEG.

1. Introduction

Two characteristic relaxation times [1] for scattering of the two-dimensional electron gas (2DEG) in a semiconductor heterostructure have been detected in recent investigations. The most frequently encountered one is the transport lifetime τ^t . This is defined as average amount of the intercollision time that an electron remains moving in a particular direction (applied electric field) in the presence of spatial inhomogeneties [2]. Another scattering time is the quantum time, τ^q . This is the average amount of the time that an electron remains in a particular momentum eigenstate in the presence of scattering. Various studies have reported on the quantum lifetime of the 2DEG in AlGaN/GaN-based heterostructure. Manfra et al. [3] are able to tune the 2DEG density from $2 \cdot 10^{11}$ to $2 \cdot 10^{12} \text{ cm}^{-2}$. They found that at low temperature (0.3 K) the quantum lifetime is an increasing function of density. Just recently, Lorenzini et al. [4] have reported the quantum life time in a high-density regime, from $2 \cdot 10^{12} \text{ cm}^{-2}$ to $2 \cdot 10^{13} \text{ cm}^{-2}$.

In the calculation of the 2DEG mobility, the quantum confinement is of major importance. Therefore, in physics literature there have been introduced models for confinement of the 2DEG in heterostructures based on various confining sources. It was shown [5] that in heterostructures made from III-nitride and their alloys, there exists a sheet density of positive polarization charges bound to the interface. These charges may give rise to remarkable modifications in the confining potential.

There are two kinds of doping: modulation and uniform. The former is often at a high doping level ($N_D \geq 10^{18} \text{ cm}^{-3}$), while the latter is at a low one ($N_D \leq 10^{17} \text{ cm}^{-3}$). However, it should be noted that in most existing quantum lifetime theories one has been interested in the uniform doping merely as a scattering mechanism rather than a confining source for electrons in the QW. Therefore, at a low doping level ($N_D \leq 10^{16} \text{ cm}^{-3}$), this is usually ignored. Thus, in this contribution we will involve uniform doping in theory, especially, as a confining source for the 2DEG. We derive analytic expressions for the parts of the confining potential, which are induced by polarization charges and ionized dopants. We show the effects of the polarization charges on quantum lifetime of 2DEG in AlGaIn/GaN heterostructure.

Recently it has been pointed out [6-9], that in actual lattice-mismatched heterostructure interface roughness gives rise to strain fluctuations in both strained and relaxed epilayers. These fluctuations in turn produce random fields: misfit piezoelectric and misfit deformation potentials acting on electron moving in plane [7, 8]. So, we will include them in the calculation of the quantum lifetime in wurtzite-nitride heterostructures.

2. The 2DEG in a Heterostructure of Finite Depth

We will be dealing with an AlGaIn/GaN sample, which is composed of an AlGaIn layer grown pseudomorphically on a GaN layer. The crystal reference system is such that the z axis is opposite to the growth direction [0001], and $z = 0$ defines the interface plane between the AlGaIn barrier ($z < 0$) and the GaN well ($z > 0$). It is assumed that the AlGaIn layer is under tensile strain, while the GaN layer is relaxed.

The piezoelectric polarization is generated in the strained AlGaIn layer. The polarization charges are found located in an extremely narrow region of the AlGaIn barrier near to the interface [11], and their density σ is positive for all values of the Al content. The total polarization in a given layer is simply the sum of the piezoelectric and spontaneous polarizations [8]. They attract free electrons, facilitating their transfer to form a 2DEG in GaN well. The polarization charges in turns create an electric field. The potential of an electron of charge $-e$ in this field is fixed by their areal density as:

$$V_{\sigma}(z) = \frac{2\pi e\sigma}{\epsilon_L} |z| \quad (1)$$

where ϵ_L is the dielectric constant of the heterostructure. It is clearly seen from Eq. (1) that the polarization-induced electric field is varying along the growth direction, but, it remains unchanged along the in-plane. Therefore this field can exert an influence on the quantum confinement rather than on the 2D motion of charge carriers. In other words, this field exhibits no source of scattering of 2D electron.

As usual for the electrons confined in the channel layer [2, 10], we assume a triangular QW located along the growth direction. For the triangular QW in an AlGaIn/GaN heterostructure, Poisson-Schrodinger simulations [12] revealed that the electron distribution has a significant penetration depth into the barrier.

Therefore, we must in general adopt the realistic model of finitely deep wells. It has been shown [13-15] that for a finitely deep triangular QW this may be very well described by a modified Fang-Howard wave function proposed by Ando [13]

$$\zeta(z) = \begin{cases} A\kappa^{1/2}\exp(\kappa z/2) & \text{for } z < 0 \\ B\kappa^{1/2}(kz+c)\exp(-kz/2) & \text{for } z > 0 \end{cases}, \quad (2)$$

in which A , B , c , k , and κ are variational parameters to be determined. Here, k and κ are half the wave numbers in the well and the barrier, respectively. A , B and c are dimensionless parameters given in terms of k and κ through boundary conditions at the interface plane $z = 0$ and the normalization. These read as [14, 15]:

$$\begin{aligned} A\kappa^{1/2} &= B\kappa^{1/2}c, \\ A\kappa^{3/2} &= B\kappa^{3/2}(1-c/2), \\ A^2 + B^2(c^2 + 2c + 2) &= 1, \end{aligned} \quad (3)$$

The wave function of the lowest subband is obtained by minimizing the total energy per electron, which is determined by the following Hamiltonian:

$$H = T + V_{\text{tot}}(z) \quad (4)$$

where T is the kinetic energy and $V_{\text{tot}}(z)$ is the effective confining potential along the growth direction. The latter arises from all possible sources, viz. barrier potential $V_b(z)$, polarization charges $V_\sigma(z)$, Hartree potential created by ionized donors, and electronic cloud $V_H(z)$:

$$V_{\text{tot}}(z) = V_b(z) + V_\sigma(z) + V_H(z). \quad (5)$$

Lastly, $V_H(z)$ is the Hartree potential induced by ionized donors and the electronic cloud in QW and is obtained from solving the Poisson equation:

$$\frac{d^2}{dz^2} V_H(z) = \frac{4\pi e^2}{\epsilon_L} [N_I(z) - n_s(z)]. \quad (6)$$

within the variation approximation with the use of the wave function from Eq. (2), the Hartree potential may be separated into two parts: the donor potential determined by donor profile $V_I(z)$, and the self-consistent potential $V_S(z)$ fixed by the sheet density of electron n_s and the shape of their contribution, i.e., the variational parameters:

$$V_H(z) = V_I(z) + V_S(z). \quad (7)$$

The total energy per electron of the 2DEG is evidently supplied by

$$E_0(k)/N = \langle T \rangle + \langle V_b \rangle + \langle V_\sigma \rangle + \langle V_I \rangle + \frac{1}{2} \langle V_s \rangle \quad (8)$$

Then, the requirement of minimization of this total energy with respect to the wave vector in the well yields wave vector k that depend on the density of polarization charge.

3. Low-Temperature Quantum Lifetime

Quantum Lifetime. In what follows we are concerned with wurtzite AlGaIn/GaN heterostructure at very low temperature. It was indicated [16, 17] that the sheet polarization charges in an AlGaIn/GaN heterostructure may enable a 2DEG of very high density ($n_s \sim 10^{13} \text{cm}^{-2}$). Under such a high carrier density the multiple scattering effects were found [18] to be negligibly small, so that we may adopt the linear transport theory as a good approximation. The inverse quantum lifetime in term of the autocorrelation function for each disorder follows as:

$$\frac{1}{\tau^q} = \frac{1}{2\pi\hbar E_F} \int_0^{2k_F} dq \frac{2k_F}{(4k_F^2 - q^2)^{1/2}} \frac{\langle |U(\mathbf{q})|^2 \rangle}{\varepsilon(q)^2}. \quad (9)$$

Here $q = |\mathbf{q}|$, with $\mathbf{q}$ as a 2D wave vector in the interface plane, $E_F = \hbar^2 k_F^2 / (2m^*)$ is the Fermi energy with k_F as the Fermi wave number fixed by the electron density.

At very low temperature, the carrier are assumed to primarily occupy the ground-state subband, and the scattering processes limiting their quantum lifetime occur mainly within this subband. Thus, the autocorrelation function $\langle |U(\mathbf{q})|^2 \rangle$ entering Eq. (9) is for an unscreened scattering potential with the lowest-subband wave function from Eq. (2). The phonon scattering in the system under study is clearly negligibly weak. Moreover, at rather low doping level ($N_D < 1.10^{16} \text{cm}^{-3}$) the impurity scattering is of minor importance. Therefore, the electron in uniformly-doped AlGaIn/GaN sample are expected to experience the following possible sources of scattering: (i) surface roughness, (ii) roughness-induced piezoelectric charges, (iii) roughness-induced deformation potential, and (iv) alloy disorder. The overall quantum lifetime is then determined by the ones for individual disorder according to Matthiessen's rule:

$$\frac{1}{\tau_{\text{tot}}^q} = \frac{1}{\tau_{\text{AD}}^q} + \frac{1}{\tau_{\text{SR}}^q} + \frac{1}{\tau_{\text{PE}}^q} + \frac{1}{\tau_{\text{DP}}^q} \quad (10)$$

The dielectric function $\varepsilon(q)$ figuring in Eq.(9) allows for the screening of scattering potential by the 2DEG. Within the random phase approximation, this is given at zero temperature by [10].

$$\epsilon(q) = 1 + \frac{q_{TF}}{q} F_s(q/k) [1 - G(q)] \quad \text{for } q \leq 2k_F \quad (11)$$

where $q_{TF} = 2m^* e^2 / \epsilon_L \hbar^2$ is the inverse 2D Thomas-Fermi screening length, with ϵ_L as the dielectric constant of the sample.

The screening formfactor $F_s(q/k)$ in Eq. (11) accounts for the extension of the electron distribution along the growth direction. With the use the lowest-subband wave function from Eq. (2), this is estimated to be [7, 15]

$$\begin{aligned} F_S(t) = & \frac{A^4 a}{t+a} + 2 A^2 B^2 a \frac{2 + 2c(t+1) + c^2(t+1)^2}{(t+a)(t+1)^3} \\ & + \frac{B^4}{2(t+1)^3} [2(c^4 + 4c^3 + 8c^2 + 8c + 4) + t(4c^4 + 12c^3 \\ & + 18c^2 + 18c + 9) + t^2(2c^4 + 4c^3 + 6c^2 + 6c + 3)]. \end{aligned} \quad (12)$$

here, we introduced dimensionless wave numbers (t) in the interface plane and the barrier (a) by the definitions

$$t = q/k, \quad a = \kappa/k. \quad (13)$$

Finally, the function $G(q)$ appears in Eq. (7) to allow for the local field corrections associated with the many-body interaction in the 2DEG. Within Hubbard's approximation, in which merely the exchange effect is included, it holds [19]

$$G(q) = \frac{q}{2(q^2 + k_F^2)^{1/2}}. \quad (14)$$

Scattering Mechanisms

Surface Roughness. We are treating scattering from a rough potential barrier. The scattering potential is due to roughness-induced fluctuation in the position of the potential barrier given by [10]

$$U_{SR}(\mathbf{q}) = V_0 |\zeta(0)|^2 \Delta_q \quad (15)$$

where V_0 is potential barrier height and Δ_q denotes a Fourier transform of the interface roughness profile. $\zeta(0)$ is given by [8]

$$V_0 |\zeta(0)|^2 = \langle V'_\sigma \rangle + \langle V'_l \rangle + \langle V'_s \rangle. \quad (16)$$

which $V' = \partial V(z)/\partial z$. Next, by putting Eq. (16) into Eq. (15), we arrive at the autocorrelation function for surface roughness:

$$\langle |U_{SR}(\mathbf{q})|^2 \rangle = \left| \langle V'_\sigma \rangle + \langle V'_l \rangle + \langle V'_s \rangle \right|^2 \langle |\Delta_{\mathbf{q}}|^2 \rangle \quad (17)$$

Roughness-Induced Piezoelectric Charge. In wurtzite nitride heterostructures, surface roughness give rise to strain fluctuations in both strained and relaxed layer [8]. These induce fluctuating densities of piezoelectric charges. The charges create relevant random electric field and act as scattering sources on the motion of electrons in-plane [8].

The autocorrelation function for scattering by roughness-induced misfit piezoelectric (index PE) charges is supplied by [8]

$$U_{PE}(\mathbf{q}) = \frac{\pi \alpha \epsilon_{\parallel} eQ}{\epsilon_L} F_{PE}(\mathbf{q}/k) \Delta_{\mathbf{q}} \quad (18)$$

where $\epsilon_{\parallel}$ is the lattice mismatch, and α denote the anisotropy ratio as a measure for the deviation of hexagonal symmetry of wurtzite crystal from isotropy. We introduced a material parameter characteristic of the well defined in term of its elasticity coefficients c_{ij}^w and piezoelectric constants e_{ij}^w by

$$Q = \frac{C_b}{c_{33}^b} \left[\frac{e_{15}^w}{c_{44}^w} + \frac{e_{31}^w(c_{33}^w + 2c_{13}^w) - e_{33}^w(c_{11}^w + c_{12}^w + c_{13}^w)}{C_w} \right] \quad (19)$$

where

$$C_{\lambda} = c_{33}^{\lambda}(c_{11}^{\lambda} + c_{12}^{\lambda}) - 2(c_{13}^{\lambda})^2 \quad (20)$$

with $\lambda = b, w$ as the labels for the well and barrier layers, respectively.

The form factor in Eq. (18) is expressed as a function of the dimensionless wave number in Eq. (13). Then

$$F_{PE}(t) = \frac{A^2}{2} \frac{a}{t+a} + \frac{B^2}{2} \left\{ \frac{2}{(t+1)^3} + \frac{2c}{(t+1)^2} + \frac{c^2}{(t+1)} + 2t \left[\frac{6}{(t+1)^4} + \frac{4c}{(t+1)^3} + \frac{c^2}{(t+1)^2} \right] \right\} \quad (21)$$

Roughness-Induced Deformation Potential. Further, strain fluctuations also induce nonuniform shifts of the band edges. The roughness-induced misfit deformation potential exists in both the well and the barrier layers and decays exponentially far away from the interface [20, 7, 9]. The roughness-induced deformation potential (index DP) for the electron is determined by fluctuations of a diagonal strain component $\Delta \epsilon_a$ according to [21]:

$$U_{DP} = \Xi_d \Delta \epsilon_a \quad (22)$$

where Ξ_d is the combined dilational component of the deformation potential for the conduction band. Since the deformation potential is of short range, and the 2DEG is located mainly in the well, we reasonably take into account the relevant scattering merely in this layer.

On the substitution of roughness-induced fluctuations [22] into Eq. (22) and then average by mean of the wave function from Eq. (2) we may find the following autocorrelation function for roughness-induced deformation potential [8]

$$\langle |U_{DP}(\mathbf{q})|^2 \rangle = \left[\frac{\alpha \epsilon_{||} \Xi_d \Delta \Lambda}{2} \frac{C_b}{c_{33}^b} \frac{c_{11}^w + c_{12}^w + c_{13}^w}{C_w} q F_{DP}(t) \right]^2 \langle |\Delta \mathbf{q}|^2 \rangle \quad (23)$$

where the form factor is given by

$$F_{DP}(t) = B^2 \left[\frac{2}{(t+1)^3} + \frac{2c}{(t+1)^2} + \frac{c^2}{(t+1)^3} \right]. \quad (24)$$

Alloy Disorder: The autocorrelation function for scattering by alloy disorder located in the AlGa_xN barrier is supplied by [9,13]

$$\langle |U_{AD}(\mathbf{q})|^2 \rangle = x(1-x) u_{al}^2 \Omega \int_{-L_b}^0 dz \zeta^4 \quad (25)$$

where x is the Al content of the alloy layer, L_b is its thickness, and u_{al} is the alloy potential assumed to be close to the conduction band offset between AlN and GaN ($u_{al} \approx \Delta E_c(1) = 2.03\text{eV}$). The volume of a hexagonal unit cell is $\Omega = 3^{1/2} a(x)^2 c(x)/2$, with $a(x)$ and $c(x)$ as the lattice constant of the alloy.

By mean of Eq. (2) for the lowest-subband wave function, this is written in terms of the barrier wave number κ as follows:

$$\langle |U_{AD}(\mathbf{q})|^2 \rangle = x(1-x) u_{al}^2 \Omega \frac{A^2 \kappa}{2} (1 - e^{-2\kappa L_b}). \quad (26)$$

4. Results and Conclusions

In this section, we are trying to apply the presented theory to study the effects of the polarization charges on the quantum lifetime of electrons in Al_xGa_{1-x}N/GaN heterojunctions. The effective electron masses of GaN are for the growth direction $m_z = 0.18 m_e$ [23] and for the in plane $m^* = 0.228 m_e$ [24]. We are examining the key parameters to which the calculation of the quantum confinement, i.e., the electron distribution in Al_xGa_{1-x}N/GaN heterostructures, is sensitive. First, the potential barrier is normally assumed to be equal to the conduction band offset between the Al_xGa_{1-x}N barrier and the GaN well, $V_0 = \Delta E_c(x)$, which depends on the Al content x as

$$\Delta E_c(x) = 0.75 [E_g(x) - E_g(0)] \quad (27)$$

in which

$$E_g(x) = 6.13x + 3.42(1-x) - x(1-x) \text{ eV} \quad (28)$$

Secondly, some recent experimental and theoretical investigation [25] suggested that the measured spontaneous polarization charge density may be very small, therefore we adopt the measured value of this charge density of AlN reported in Ref. [26], $\sigma_{sp}(\text{AlN}) = 0.044 \text{ C/m}^2$. Then

$$\sigma(x) = 0.011 \times -2 \frac{a(x) - a(0)}{a(0)} [e_{31}(x) - e_{33}(x) \frac{c_{13}(x)}{c_{33}(x)}] \quad (29)$$

(in units of C/m^2).

We are examining input parameters based the recent experimental data [4] about the 2DEG quantum well made from GaN of thickness $L_w = 4.7 \cdot 10^4 \text{ \AA}$ and a barrier from AlGaN of thickness $L_b = 210 \text{ \AA}$ and an Al content $x = 0.23$. We carried out the calculation for standard Fang-Howard wave function $\zeta(z)$ along the growth direction in presence and absence of the polarization charges. Further, we calculated the quantum lifetime τ^q due to SR, PE, DP, and AD scattering, and the for the total quantum lifetime in presence and the absence of the polarization charges. From calculation results obtained, we may draw the following conclusions:

- (i) With the presence of the sheet polarization charges, electron wave function is been squeezed close to the barrier, which mean it is close to the key scattering sources.
- (ii) The total quantum lifetime of these 2DEG in presence of polarization charges is decreased in comparison with the one in absence of polarization charges. This is because of the presence of the sheet polarization charges, electron wave function is squeezed close to the barrier. There are the key scattering sources. Scattering decreased the quantum lifetime of 2DEG.
- (iii) In our calculation results, surface roughness, piezoelectric and alloy disorder scatterings are most important in limiting quantum lifetime in presence and also in absence of polarization charges. In Fig. 3 and Fig. 4, two most important scattering mechanism are shown as examples: surface roughness, and piezoelectric scattering. Another example given in [27], in which surface roughness and alloy disorder are predominant effects.

To summarize, in this contribution we have theoretical studied the effects of the polarization charges on the quantum lifetime of the two-dimensional electron gas in a uniformly-doped AlGaIn/GaN heterostructure. We take into account the effects of the polarization charges on the wave function of electrons and have calculated the total quantum lifetime of the 2DEG due to all possible scattering mechanisms and quantum lifetime of each scattering mechanisms. We find that SR, PE and AD scattering dominate the quantum lifetime.

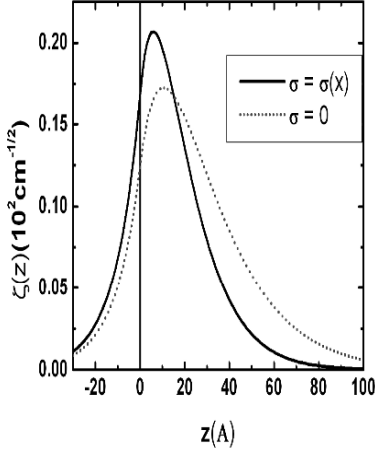


Fig. 1. The wave function of the 2DEG for $\sigma = \sigma(x)$ (solid line), and $\sigma = 0$ (dotted)

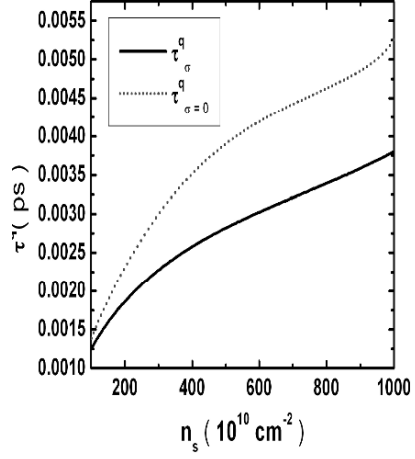


Fig. 2. The quantum lifetime vs. the carrier sheet density n_s for $\sigma = \sigma(x)$ (solid line), and $\sigma = 0$ (dotted)

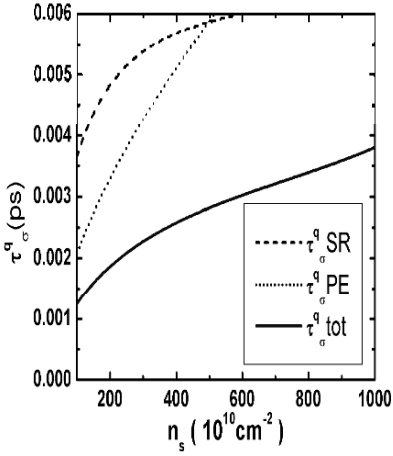


Fig. 3. The total quantum lifetime and quantum lifetime (SR, PE) in presence of polarization charges

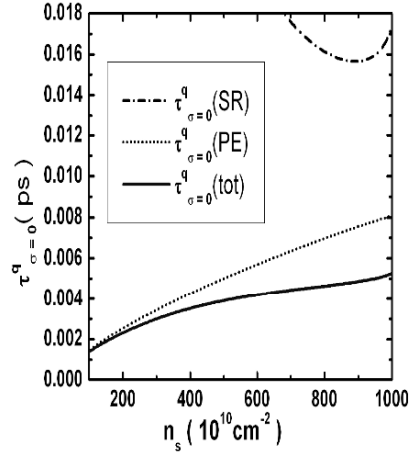


Fig. 4. The total quantum lifetime and quantum lifetime (SR, PE) in absence of polarization charges

References

1. L. Hsu and W. Walukiewicz. Appl. Phys. Lett. 80, 2508, 2002.
2. M.J. Manfra, S.H. Simon, K.W. Baldwin, A.M. Sergent, K.W. West, R.J. Molnar, and J. Caissie, Appl. Phys. Lett. 85, 5278, 2004.
3. P. Lorenzini, Z. Bougrioua, A. Tiberj, R. Tauk, M. Azize, M. Sakowicz, K. Kaprierz, and W. Knap, Appl. Phys. Lett. 87, 232107, 2005.
4. Bykhovski, G. Gelmont, and M. Shur J. Appl. Phys. 74, 6734, 1993
5. R.M. Feenstra and M.A. Lutz, J. Appl. Phys. 78, 6091, (1995)
6. D.N. Quang, V.N. Tuoc, N.H. Tung, and T.D. Huan, Phys. Rev. Lett. 89, 077601, 2002. Phys. Rev. B 68, 153306, 2003.
7. D.N. Quang, V.N. Tuoc, N.H. Tung, N.V. Minh, and P.N. Phong, Phys. Rev. B 72, 245303, 2005
8. D.N. Quang, V.N. Tuoc, T.D. Huan, and P.N. Phong, Phys. Rev. B 70, 195336, 2004.
9. T. Ando, A.B. Fowler, and F. Stern, Rev. Mod. Phys. 54, 437, 1982.
10. M. Mokroc, F. Hamdani and A. Salvador, in Gallium Nitride (GaN) Semiconductor and semimetals Vol. 50, edited by J.I. Pankove and T.D. Moustakas (Akademic, San Diego, p. 193, 1998
11. T.H. Yu and K.F. Brennan, J. Appl. Phys. 89, 3827, 2001
12. T. Ando, J. Phys. Soc. Jpn. 51, 3893 (1982); 51, 3900, 1982.
13. G. Bastard, Wave Mechanics Applied to Semiconductor Heterostructures (Les Editions de Physique, Paris, 1988.
14. Y. Okuyama and N. Tokuda, Phys. Rev. B 40, 9744, 1989.
15. L. Hsu and W. Walukiewicz, J. Appl. Phys. 89, 1783, 2001
16. P.M. Asbeck, E.T. Yu, S.S. Lau, G.J. Sullivan, J. Van Hove, and J. Redwing, Electron. Lett. 33, 1230, 1997
17. A. Gold and W. Gotze, J. Phys. C 14, 4049 (1981); Phys. Rev. B33, (1986) 2495, 1986.
18. M. Johnson, J. Phys. C 9, 3055, 1976.
19. R. M. Feenstra and M. A. Lutz, J. Appl. Phys. 78, 6091, 1995.
20. S. Chichibu, A. Shikanai, T. Azuhata, T. Sota, A. Kuramata, K. Horino, and S. Nakamura, Appl. Phys. Lett. 68, 3766, 1996.
21. D.N. Quang, V.N. Tuoc, N.H. Tung, N.V. Minh, and P.N. Phong, Phys. Rev. B 72, 115337, 2005.
22. M. Suzuki, T. Uenoyama, and A. Ynase, Phys. Rev. B 52, (1995) 8132
23. L.W. Wong, S.J. Cai, R. Li, K. Wang, H.W. Jang, and M. Chen, Appl. Phys. Lett. 73, 1391, 1998.
24. L. Hsu and W. Walukiewicz. J. Appl. Phys. 89. 1783, 2001.
25. S.H. Park and S.L. Chuang, Appl. Phys. Lett. 76, 1981, 2000
26. N.H. Tung and N.V. Minh, Proceeding of the International Conference on Engineering Physics, Ha noi, October 9-12, 287, 2006.

Possible T_C Superconducting Enhancement in Q2D Materials by Incommensurate Structural Phase Transition

Do Tran Cat¹ and Ong Phuong Khuong²

¹ Institute of Engineering Physics, Hanoi University of Technology, Dai Co Viet Road 1, Hanoi 10004, Vietnam

E-mail: stacoproft@hn.vnn.vn

² Institute of High Performance Computing, 1 Science Park Road, #01-01 The Capricorn Singapore Science Park II, Singapore 117528

Abstract. It is shown that low dimensional electron systems in a deformable lattice are unstable against a lattice modulation at the Fermi wave vector only when there is half-filling of the conductive band (no doping: $n = 0$). When there is doping ($n \neq 0$), the phase transition is metal-semimetal, the gap appears at a wave vector that is different from the Fermi-wave vector and an incommensurate structural phase transition takes place. This phase transition plays an important role in the formation of electron (or hole) bags, in the considerable increase of carrier DOS near the Fermi level and in the change of Cooper pair wave character that may lead to enhancement of superconducting T_C in Quasi-two dimensional (Q2D) materials. The start of our study is that when the doping n is different from zero the nesting vector is different from (π, π) and defined by minimizing the energy of the system. By the method of Green 's functions for the charge density wave and the Cooper pair we found a system of equations describing the phase transition properties of Q2D materials, including superconductivity. A rough estimate of T_C gives agreement to experiments.

1. Introduction

Quasi-two dimensional (Q2D) materials, especially magnetic system of perovskite-type and high T_C superconductors of cuprate-type have attracted many scientists, recently, because of their special properties. In general, the structural, electronic and magnetic properties of Q2D systems change with charge carrier doping. Theoretical studies show that these changes are because of a lattice instability and this causes the formation of energy gaps at some parts of the Fermi surface when the nesting condition is satisfied. However, the consequence that the energy gap exists with the nesting wave vector $Q = (\pi, \pi)$ is realized only in the undoped case. In the doped case the energy gap Δ increases and attains a maximum (corresponding to this, the energy of system becomes minimum) with exciton pairs with $Q \neq (\pi, \pi)$ and a structural phase transition takes place.

For example, band calculations for the La_2CuO_4 compound showed strongly two-dimensional characteristics and rather perfect nesting of the Fermi surface [1,2]. Nesting leads to a Fermi surface instability and causes a lattice distortion. An energy gap is formed at the Fermi surface as a consequence and this turns the

material into an insulator [3]. Differently from one-dimensional materials nesting in Q2D materials takes place only in a part of the Fermi surface. The band calculations for La_2CuO_4 and $YBa_2Cu_3O_7$ [4, 5] showed also that nesting of Fermi surfaces seems to be associated with structural (charge density wave, CDW) and antiferromagnetic (AF) transitions in $La_{2-x}M_xCuO_4$ [6, 7]. In $La_{2-x}M_xCuO_4$ the nesting vector corresponds to a dimerization of the period. In real systems, e.g. superconducting ceramics with increasing of doping concentration, the nesting of Fermi-surface sections is dominant only in certain directions of the k-space. Neutron scattering studies [8] have also shown that in the $La_{2-x}(Ba; Sr)_xCuO_4$ compound when $n = 0$ the nesting vector is $\vec{Q} = (\pi, \pi)$ and the compound is an insulator. However, when it is diluted by Ba or Sr which deteriorates the nearly perfect nesting situation, an incommensurate splitting of the inelastic magnetic scattering peaks in the $La_{2-x}Sr_xCuO_4$ compound appears.

The result mentioned above can be explained as follows: when there is no doping ($n = 0$) the existence of a lattice modulation at the wave vector, for example, in some x-direction Q_x equal to twice the Fermi-wave vector ($2k_F$) leads to an electron pairing $\langle a_k^+ a_{k+2k_F} \rangle$, where a_k is the electron annihilation operator. In this case $Q_x = 2k_F = \pi$, the period of energy spectra of electrons decreases twice and the gap appears at the Fermi level. When $n \neq 0$ such electron pairing leads to the existence of a gap at a wave vector different from the Fermi-wave vector (see Fig. 1).

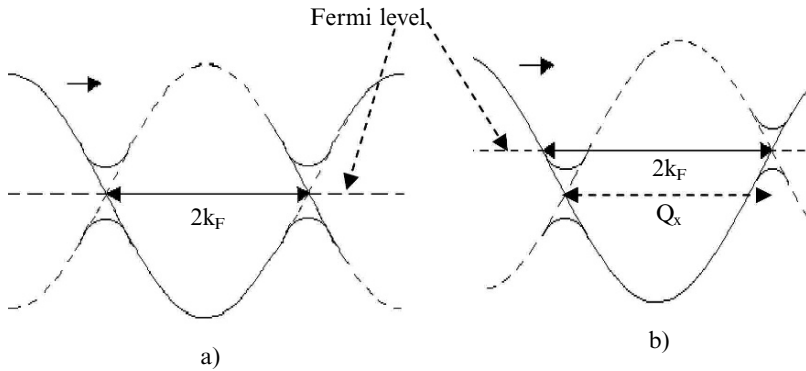


Fig. 1. Formation of gaps: a) in the undoped case: $Q_x = 2k_F = \pi$; b) in the doped case: $Q_x \neq \pi$

In the model suggested in this paper, the nesting situation leads to existence of excitons with a charge-density wave. The exchange of two intra- and inter-sublayer electrons by excitons and phonons can lead to their attraction [9].

The phase transitions play an important role in the formation of electron (or hole) bags and for the considerable increase of carrier density of state (DOS) near the Fermi level, which together with the interference of the charge density

wave and Cooper pair wave as in the three dimensional system [10] leads to the enhancement of the superconducting T_C in Q2D systems.

2. Model Hamiltonian and Green's functions

To reflect all features mentioned above , the Hamiltonian is given by [9]:

$$H = H_{el} + H_p + H_{el-el} + H_{el-p} \quad (1a)$$

with

$$H_{el} = \sum_{\vec{k}, \sigma} \varepsilon(\vec{k}) a_{\sigma}^+(\vec{k}) a_{\sigma}(\vec{k}) \quad (1b)$$

$$H_p = \sum_{\vec{q}} \omega_{\vec{q}} (b_{\vec{q}}^+ b_{\vec{q}} + \frac{1}{2}), \quad (1c)$$

$$H_{el-el} = \frac{1}{2} \sum_{\substack{\vec{k}_1, \vec{k}_2, \vec{q} \\ \sigma_1, \sigma_2}} \lambda a_{\sigma_1}^+(\vec{k}_1 + \vec{q}) a_{\sigma_2}^+(\vec{k}_2 - \vec{q}) a_{\sigma_2}(\vec{k}_2) a_{\sigma_1}(\vec{k}_1) \quad (1d)$$

and

$$H_{el-p} = \sum_{\vec{k}, \vec{q}, \sigma} g a_{\sigma}^+(\vec{k}) a_{\sigma}(\vec{k} + \vec{q}) (b_{\vec{q}}^+ + b_{-\vec{q}}) \quad (1e)$$

where λ is the coupling constant characterizing the screened Coulomb interaction.

$$\varepsilon(\vec{k}) = \mu - (\cos k_x + \cos k_y) \quad (2)$$

is the 2D-energy spectrum in the tight binding approximation. We note that in the Hamiltonian (1) the energy is used in units of the lower conduction band edge. $a_{\sigma}(\vec{k})$ and $b_{\vec{q}}$ are annihilation operators of electron (with spin σ , wave vector $\vec{k}$) and phonon (with wave vector $\vec{q}$) respectively, μ is the shift of the chemical potential from the half filling level and g is electron-phonon interaction constant.

In order to solve this problem with this Hamiltonian we introduce the following Green's functions as in quasi-one-dimensional systems [11]:

$$G_1(\vec{k}, t) = \langle T a_{\sigma}^+(\vec{k}, t) a_{\sigma}(\vec{k}, 0) \rangle, \quad (3a)$$

$$G_2(\vec{k}, \vec{Q}, t) = \langle T a_{\sigma}^+(\vec{k} - \frac{\vec{Q}}{2}, t) a_{\sigma}(\vec{k} + \frac{\vec{Q}}{2}, 0) \rangle, \quad (3b)$$

$$F_1(\vec{k}, t) = \langle T a_{\sigma}(-\vec{k}, t) a_{-\sigma}(\vec{k}, 0) \rangle, \quad (3c)$$

$$F_2(\vec{k}, \vec{Q}, t) = \langle Ta_\sigma(-\vec{k} + \frac{\vec{Q}}{2}, t) a_\sigma(\vec{k} + \frac{\vec{Q}}{2}, 0) \rangle, \quad (3d)$$

The appearance of the function $F_2(\vec{k}, \vec{Q}, t)$ is due to the excitonic pairing $G_2(\vec{k}, \vec{Q}, t)$. By solving the equations of motion for these Green's functions we can obtain the system of equations describing the material properties of interest.

3. The State with Excitonic Pairing and Structural Phase Transition

In the mean field approximation with singlet excitonic pairing without superconductivity we find the following self-consistent equations for the gap and the shift of chemical potential :

$$1 = \sum_{\vec{k}} \frac{\lambda_1}{4E} \left\{ th\left(\frac{E + \delta}{2T}\right) + th\left(\frac{E - \delta}{2T}\right) \right\} \quad (4)$$

and

$$n = \frac{1}{4} \sum_{\vec{k}} \left\{ th\left(\frac{E + \delta}{2T}\right) + th\left(\frac{E - \delta}{2T}\right) \right\} \quad (5)$$

where $n = (2N/N_0) - 1$ is the shift of relative carrier concentration from the half filling state (considered as doping), N_0 is the carrier number of the filled band: $N_0 = \sum_{\vec{k}, \sigma} 1$, and T is the temperature in energetic units. The carrier concentration N is determined by the Green's functions via

$$N = \frac{1}{2} T \sum_{\vec{k}, \omega_m} \left[G_1\left(\vec{k} + \frac{\vec{Q}}{2}, \omega_m\right) + G_1\left(\vec{k} - \frac{\vec{Q}}{2}, \omega_m\right) \right] \quad (6)$$

where $\omega_m = \pi T(2m + 1)$, m is an integer.

$$E = \sqrt{(\vec{s} \cdot \vec{B})^2 + |\Delta|^2} \quad (7a)$$

$$\delta = \mu - \vec{c} \cdot \vec{A} \quad (7b)$$

$$\vec{s} = \left(\sin \frac{Q_x}{2}, \sin \frac{Q_y}{2} \right) \quad (7c)$$

$$\vec{c} = \left(\cos \frac{Q_x}{2}, \cos \frac{Q_y}{2} \right) \quad (7d)$$

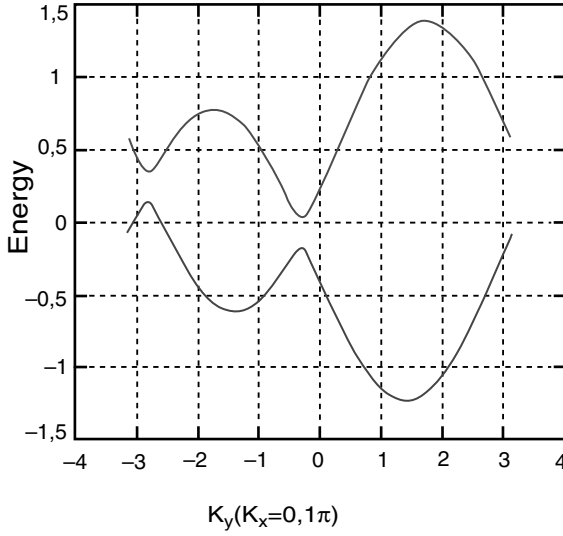


Fig. 2. Electron excitation spectrum for $\lambda_1=0.025$; $n = 0.2$

$$\vec{A} = (\cos k_x, \cos k_y) \quad (7e)$$

$$\vec{B} = (\sin k_x, \sin k_y) \quad (7f)$$

The excitation spectrum (for one direction, for example y)

$$\omega_{\pm} = \mu - \vec{c}\vec{A} \pm \sqrt{(\vec{s}\vec{B})^2 + \Delta^2} \quad (8)$$

is shown in Fig. 2. The carrier filled region's width in Fig. 2 is equal to c_y , which signifies the correlation of the nesting vector with doping n .

The nesting vector $\vec{Q}$ is defined by the minimized energy of the system

In case of $\lambda_1=0.025$; $T=0.01$ the results are these:

$$\mathbf{Q}_1 = (\pi, \pi - 0.095\pi), \mathbf{Q}_2 = (\pi - 0.095\pi, \pi) \text{ for } n = 0.01;$$

$$\mathbf{Q}_1 = (\pi, \pi - 0.098\pi), \mathbf{Q}_2 = (\pi - 0.098\pi, \pi) \text{ for } n = 0.03;$$

$$\mathbf{Q}_1 = (\pi, \pi - 0.1\pi), \mathbf{Q}_2 = (\pi - 0.1\pi, \pi) \text{ for } n = 0.05.$$

The order parameter $\Delta(\vec{Q})$ is defined as

$$\Delta(\vec{Q}) = -T\lambda_1 \sum_{\vec{k}, \omega} G_2(\vec{k}, \vec{Q}, \omega) \quad (9)$$

λ_1 is the renormalized interaction constant:

$$\lambda_1 = \lambda + 4|g|^2/\omega_Q. \quad (10)$$

For $n = 0.05$ the plot is shown in Fig. 3. We see that when the doping content n increases Q will deviate and move away from (π, π) . This can take us to the conclusion that the lattice structure of the host Q2D material has changed with doping. By fixing n and λ_1 and change T we obtained interesting results as follows: There exists a temperature T_{str} at which the structural phase transition takes place. When the doping content n increases T_{str} is also increased.

This is shown by the relationship of the chemical potential to T in Fig. 4. Figure 4 shows that when temperature T increases in the range $T < T_{str}$ the chemical potential μ increases. This is clear because the increase of temperature leads to the increase of energy of atoms in the materials. However, from Fig. 4 the chemical

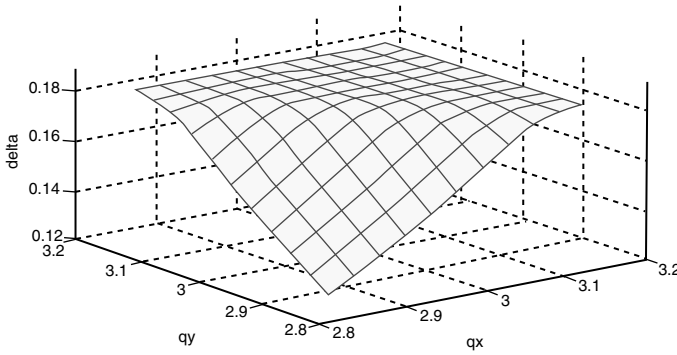


Fig. 3. The plot of the gap (“delta”) $\Delta = \Delta(Qx, Qy)$ with $\lambda_1 = 0.025$; $n = 0.05$; $T = 0.01$

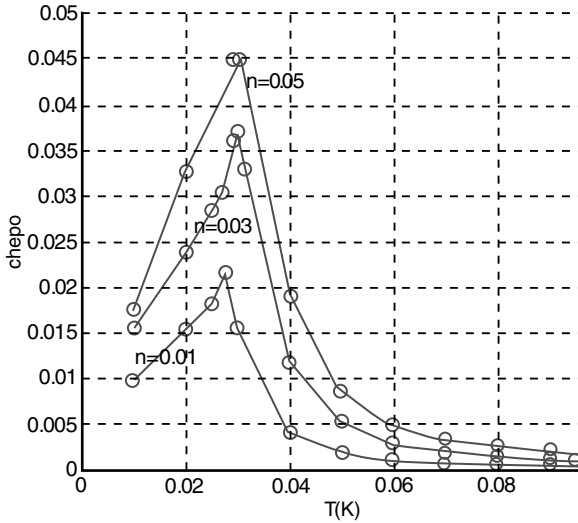


Fig. 4. Plot of chemical potential (“chepo”) $\mu = \mu(T)$ with $n = 0.01$; 0.03 ; 0.05 , $\lambda_1 = 0.025$

potential μ attains a maximum at T_{str} , where $Q = (\pi, \pi)$ and the lattice recovers to the initial state with which the average deviation $\langle u \rangle$ of atoms from equilibrium positions is equal to zero. Because of this, the half filling level has changed; not just as in the case of lattice deformation with $\langle u \rangle \neq 0$. In the range $T > T_{str}$ an increase of temperature T leads to a decreasing Δ (Fig. 5), and because the doping n is fixed, μ will be decreased.

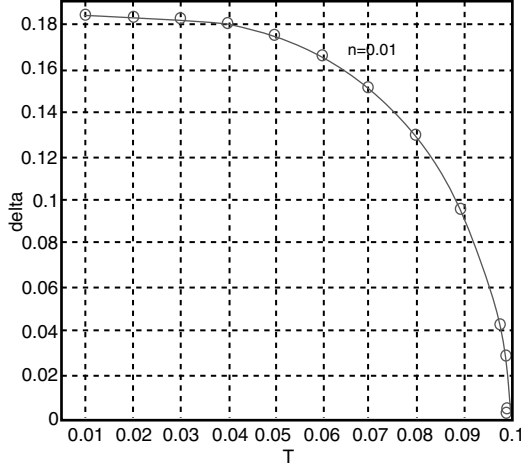


Fig. 5. Plot of the gap (“delta”) $\Delta = \Delta(T)$ with $n = 0.01$; $\lambda_1 = 0.025$; $T_N = 0.09985475$

4. Possibility of Superconducting T_C Enhancement

The system of equations for the superconducting phase transition temperature T_C is obtained from (1)-(3) by solving the equations of motion for all Green’s functions (3). We have

$$1 = \sum_{\vec{k}} \frac{\lambda_1}{4E} \left[th \frac{E + \delta}{2T_c} + th \frac{E - \delta}{2T_c} \right], \quad (11a)$$

$$1 = -\frac{1}{4} \sum_{\vec{k}} \lambda_2 \left[\frac{th \frac{E + \delta}{2T_c}}{E + \delta} + \frac{th \frac{E - \delta}{2T_c}}{E - \delta} \right], \quad (11b)$$

$$n = \frac{1}{4} \sum_{\vec{k}} \left[th \left(\frac{E + \delta}{2T_c} \right) + th \left(\frac{E - \delta}{2T_c} \right) \right] \quad (11c)$$

Here

$$\lambda_2 = \lambda^* + 2\lambda^2 \Pi + 2|g|^2 D, \quad (12a)$$

Π and D are described by the electron loop and the phonon Green's function, respectively; λ^* is the weakened Coulomb interaction:

$$\lambda^* = \lambda / (1 + \lambda \ln 1/\omega_o), \quad (12b)$$

ω_o is the exciton cut-off energy in units of the conduction band edge.

Δ_o and S_o are introduced as order parameters for exciton pairing and for Cooper pairs, respectively, when they exist separately, then

$$1.76T_{c0} = S_o = 2\omega_D \exp(-\pi^2/\lambda_2), \quad (13a)$$

$$\Delta_o = 2\omega_o \exp(-\pi^2/\lambda_1). \quad (13b)$$

ω_D is the Debye energy in units of the conduction band edge.

In the limit of $\Delta_o \gg S_o$; $T_{c0} \ll n$, we have an expression for the estimate of T_c :

$$\frac{T_c}{T_{c0}} = \frac{1}{4\gamma^2} \exp[g_o(16\gamma^2 + \frac{4\gamma}{3} - \frac{2}{5})] \quad (14)$$

where $\gamma = \Delta_o/n$;

$$g_o = \ln(\Delta_o/S_o). \quad (15)$$

The maximum of T_c/T_{c0} is obtained with doping and then

$$\gamma = \frac{1}{4g_o} \left(\frac{1}{12} + \sqrt{\frac{1}{144} + g_o^{-1}} \right)^{-1}. \quad (16)$$

In order to roughly estimate T_c we assume $\mathcal{E}_o = 2\text{eV}$; $\Delta_o/S_o = 50$. Then for $T_{c0} = 5\text{K}$ and 10K we get $T_c = 81\text{K}$ and 163K respectively. It is clear that the exciton pairing increases considerably the superconducting T_c . The value of doping n used in (16) is equal to 0.20, therefore $c_i = 0.0996$ ($i=x$ or y). So, the stable state and the maximum value of T_c correspond to the magnitude of Q which is different from (π, π) . In dependence of the doping the maximum of T_c is due to two effects: firstly, doping favours the superconductivity, secondly, it weakens the excitonic pairing. The enhancement of superconducting T_c is due to the increase of carrier DOS near the Fermi level and the interference of the charge-density wave and Cooper-pair wave like in three-dimensional systems [10].

Acknowledgements

This work is financed by the Fundamental Science Research Project, No. 4.043.06, from Ministry of Science and Technology (MIST) of Vietnam.

References

- 1 L.F. Mattheis, Phys. Rev. Lett. 58, 1028 (1987)
- 2 J. Yu, A.J. Freeman, and J.H. Xu, Phys. Rev. Lett. 58, 1035 (1987)
- 3 J.D. Jorgensen et al., Phys. Rev. Lett. 58, 1024 (1987)
- 4 L.F. Mattheis and D.R. Haman, Phys. Rev. Lett. 60, 2681 (1988)
- 5 J. Yu, S. Massida, A.J. Freeman, and D.D. Koeling, Phys. Lett. A. 122, 203 (1987)
- 6 D.M. Paul et al., Phys. Rev. Lett. 58, 1976 (1987)
- 7 T. Fujita et al., J. Appl. Phys. 26, L368 (1987)
- 8 B.O. Wells, Y.S. Lee, M.A. Kastner, R.J. Christianson, R.J. Birgeneau, K. Yamada, Y. Endoh, G. Shirane, Science 277, 1067 (1997)
- 9 D.T. Cat, M.S. Li and N.M. Duc, Proc. of the European conference on high T_C TFSC. 1989, Ustron, Poland.
- 10 A.I. Rusinov, Do Tran Cat and Iu.V. Kopaev. Zh. Eksper. Teor. Fiz. 65, 1984, (1973)
- 11 Do Tran Cat, Acta Phys. Pol. A, vol. 74, p. 465, 1988; Problems of physical kinetics and solid state physics. p. 133, Kiev, 1990.

Compressed Electron Distribution in the Nanostructure

Nguyen Van Tri

Institute of Engineering Physics, Hanoi University of Technology
PCHT, C2-101, Dai hoc Bach khoa, 1 Dai Co Viet, Hanoi, Vietnam
E-mail: nvtri@mail.hut.edu.vn

Abstract. Two very peculiar effects of ESR spectral intensity have been revealed in numerous different material and biological matters possessing a prominent nano-ordering. And on the basis of the experimental results, a new conception called “Compressed Electron Distribution” in the nanostructure is suggested, so that the revealed phenomena as well as their nanomechanisms can be interpreted.

1. Introduction

The existence of functional structures of nanometer dimensions is not new, in fact they have existed on earth as long as life itself. Such structures as nanoparticles themselves had been studied long before the words *nanoparticle* and *nanotechnology* were coined. A nanoparticle, or generally a nanosystem, may be considered as a nanoscaled aggregate of atoms viewed as a subdivision of a bulk material and it is structuredly distinct from the bulk material [1].

The nanostructures exist everywhere in nature and industry. They can persist in different real forms of condensed matter such as the particles (grains) in a bulk nanostructured material, the basic units in a disordered solid, the modulated or composited structural units in aperiodic materials, the individual nanoparticles localized in functional materials (donors, acceptors, deep traps, metal clusters, ...). Especially, many biological materials are classified as nanoparticles. They play the decisively important roles in all processes of life.

The *nanoworld* is of quantum nature and a peculiar “kingdom” between the macroscopic world and the atom – the building stone of matter. Evidently, the structure and the behaviour of electron in the nanosystem can be strongly influenced by the nanosized constitution and thereby completely changes [1-3].

The functional nanostructures or the called “active centers” persisting in a material or a living body, in most cases, are the perturbed nanosystems that show *odd electrons* that are responsible for the specific feature of the material or the particular activity of the living body. These informative quantum electronic systems themselves are the fundamental and very convincing study-objects of electron spin resonance (ESR). For that reason, ESR can offer efficient help for studying the elementary dynamic processes in condensed matters. From the experimental results with ESR in combination with other methods on different real materials and biomedical systems of nano-level, numerous special complexes of odd electrons and their unusual structures and behaviours very distinct from the ones in the normal crystalline materials have been revealed and partly reported in some preceding publications by the author, e.g. [4-8, 12].

In this paper, two peculiar spectral effects revealed in different nanostructured material and biological matters, the new conception “compressed electron distribution” in the nanostructure and its applications will be reported and discussed.

2. Experimental Results

The new and very peculiar ESR spectral effects, namely the *compression of the spectral intensity* and the *pumpless emission of radiation*, outstandingly occur in those matters possessing a prominent nano-range ordering. The ESR measurements were performed on an ERS-220 standard electron resonance spectrometer system with the sensitivity of 10^{10} spin/G. The sample temperature was automatically controlled at different values with the accuracy of ± 1 K.

In the effect of compression of the spectral intensity, the whole intensity of a line group is climaxedly concentrated into only an individual line. This phenomenon has been distinctly observed in amorphous SiO_2 thin films, glasses, and especially in biological tissues such as natural fibers, soya, ananas, kidney, etc. In figure 1 a typical example concerning the line group of the called complex C in SiO_2 materials is shown. From a high-melting glass after special supplemental thermo-treatments for improving the amorphous state (Fig. 1a), the line C5 arises extremely strongly, and all the rest lines become very feeble. But from a low-melting glass (Fig. 1b), the strong line is changed to C2.

The effect of stimulated emission of radiation without pumping has been distinctly observed in some cases of an excellent nano-range ordering in special disordered materials and biological tissues. Some typical examples are given in Figure 2 and Figure 3. Figure 2 presents the occurrence of the emission line from the “dangling bond” center Si^{3+} in an amorphous SiO_2 thin film at the temperature $T_c \approx 103$ K. And Figure 3 – from the “labile sulfur” center S^* in a living tissue of upper kidney gland at the temperature $T_c \approx 153$ K.

In the normal ESR technique, under action of microwave of resonant frequency ν , the effective transitions of the ensemble of the spin centers in a measurement sample only can be a characteristic stimulated absorption with the absorption lines as registered in Figure 2a, 2b and Figure 3a, 3b. But the surprise in these experiments is that around a certain temperature, here called critical temperature, an *inverted line*, i.e. a *Stimulated Emission Line* of the same resonant frequency ν rather suddenly appears (registered as $\mathbf{A}^*$ and $\mathbf{R}_\bullet^*$ in Fig. 2c, 3c) *without any pumping* for producing *population inversion* by an outside source. As it is well known, the population inversion is the first prerequisite for the action of a LASER.

An *emission line* in X-band from the dangling bond center $\text{A}(\text{Si}^{3+})$ also has been clearly observed in a low-melting glass at the critical temperature $T_c = 1.6$ K with the effective spectroscopic splitting factor or the g-factor $g(\text{A}) = 1.9995$ and the full width between the peaks or the peak-peak width $\Delta H_{pp} = 3.27$ G. Similarly, the experiment showed that an *emission line* in X-band from the complex $[\text{Fe-S}]$ in wild natural ananas can very strongly happen at a rather high critical temperature, namely at $T_c \approx 313$ K nearby the vegetable body temperature. It is very

Fig. 1. Occurrence of an individual strong line of the spin complex C in a high-melting glass (a) and a low-melting glass (b) after special supplemental treatments for improving amorphous state. ESR recorded at $\nu = 9.5$ GHz, $T = 300$ K with first (b1) and second (a1, a2, a3, b2) derivative. a1) Initial sample (polycrystalline). a2), a3) The sample after special thermo-treatments, the line C5 appears extremely strongly occupying 92% of the total intensity of the group. b1), b2) In glass (b) the line C2 occupies over 95% of the the total intensity

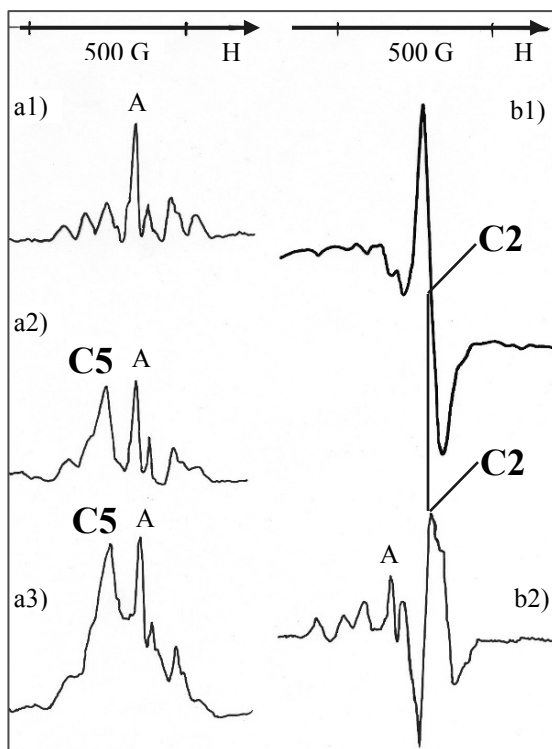


Fig. 2. The occurrence of the *stimulated emission line* (A^*) from “dangling bond” Si^{3+} (spin center A) in an amorphous SiO_2 thin film CVD-produced on silicon: a) Almost only the absorption line A appears, b) The absorption lines A (from Si^{3+}) and B_1, B_2 (from the coupled pair $\text{Si}^{3+} - \text{Si}^{3+}$) merge, c) The *emission line* A^* and the absorption lines $B_1 - B_2$ merge. $\nu = 9.5$ GHz, $g(A) = g(A^*) = g(\text{Si}^{3+}) = 1.9980$, $\Delta H_{pp}(A, 300 \text{ K}) = 4.5 \text{ G}$; $\Delta H_{pp}(A^*, 103 \text{ K}) = 2.1 \text{ G}$. Spin number: $N = 10^{14} - 10^{15} \text{ cm}^{-3}$. Splitting $B_1 - B_2 = 21.3 \text{ G}$ is also used as abscissa scale for magnetic field H

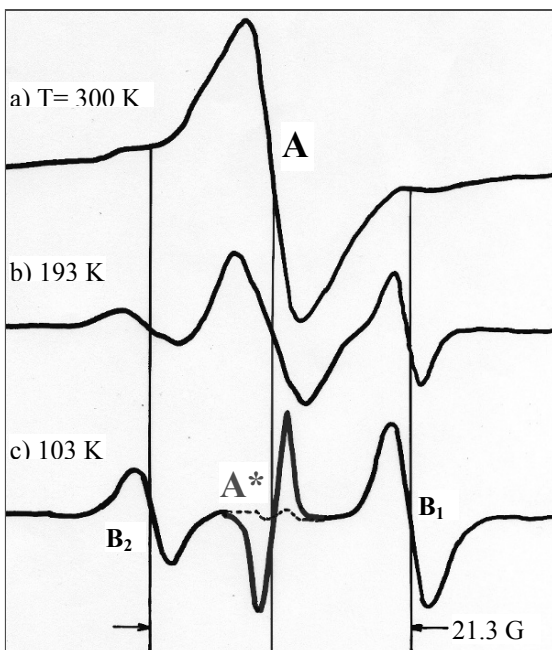
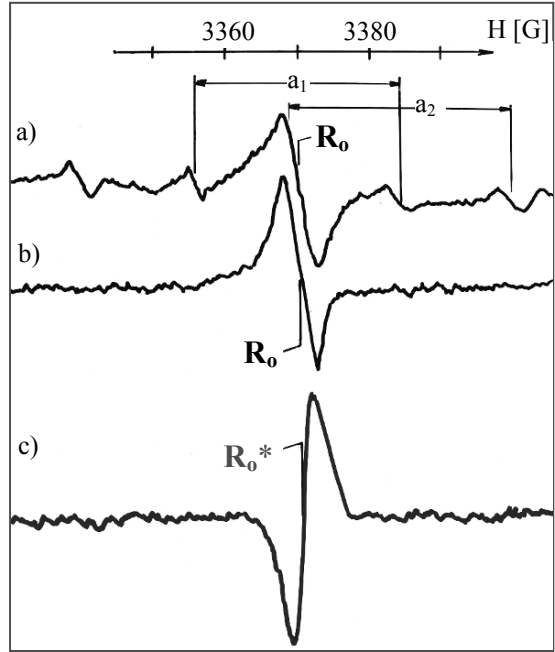


Fig. 3. The occurrence of the *stimulated emission* line (R_0^*) from the “labile Sulfur” (spin center S^*) in a living tissue of upper kidney gland at the temperature $T_c \approx 153$ K. a) and b) $T > 153$ K: R_0 is the absorption line of S^* . The four weak lines of the Hyperfine Structure (HFS) are due to the non-equivalent interaction of some electron spin S^* with the nuclear spins of the two Fe ions in the functional structure of the (2Fe-2S) protein of kidney gland. c) $T \approx 153$ K: The *stimulated emission* line (R_0^*) from the labile Sulfur S^* appears. ESR recorded in X- band ($\nu = 9.5$ GHz) at $T \geq 153$ K.



remarkable that at this critical temperature the fiber suddenly shows a peculiar maximum point of conductivity, while at other temperatures it is highly insulative. This phenomenon should be detailedly reported in a next publication.

3. Model and Application. Discussion

3.1 Conception of the Compressed Distribution in the Nanostructure

In a paramagnetic sample of normal crystalline structure, the spin centers obey the thermodynamic Boltzmann distribution (Fig. 4a). Hereby the effective induced transition between the two levels always results in an absorption and the spectral intensity distribution is smooth.

In a nanosystem (nanoparticle or “quantum dot”), the odd electrons can be considered as quasi-free electrons (QFEs) moving in a nano resonant cavity (NRC) constituted by the boundary planes of its definite geometry. Contrary to the case of a normal crystalline matter, the sole quantum state of the QFE in the NRC only can be a standing wave, in which the wavelength of the QFE must fulfil the following resonance condition:

$$n \frac{\lambda}{2} = d, \quad n = 1, 2, 3, \dots \quad (1)$$

The ground wave state corresponds to

$$n = 1, \text{ and } \lambda = 2d \quad (2)$$

where d is the longest extension distance between both parallel planes of the NRC.

The stationary eigen functions in the ground states of the QFEs in the NRC in the one-dimensional representation are given by the standing waves

$$\psi_a(x) = A \cos kx, \text{ and } \psi_b(x) = A \sin kx \quad (3)$$

where

$$k = \frac{2\pi}{\lambda} = \frac{\pi}{d} \quad (4)$$

is the sole allowed value of the wave parameter (wavevector). It is especially remarkable that for the case of a crystalline matter this value of k is forbidden.

However, the arguments discussed above only are the preliminaries and rest on the crude approximation. A more refined treatment of the motion of QFEs in a nanostructured matter must take the interactions between these electrons and the lattice into account, by which the energy level corresponding to an eigen function (3) occurs in an energy band around the resonance peak at the middle energy E_0 of the NRC.

On the other hand, the natural reaction of the NRC is just compressing all allowed states of the QFE as nearest as possible to the middle level E_0 of the energy band (Fig. 4b). This peculiarity leads to the “Compressed Distribution” in the nanostructure. From the resonant character, it can be assumed that this compressed distribution of the QFE states in an energy band in the nanostructure approximately shows a normal Gauss form (Fig. 5) with

$$n(E) = \frac{1}{\Delta\sqrt{2\pi}} \exp\left[-\frac{(E - E_0)^2}{2\Delta^2}\right] \quad (5)$$

where Δ^2 is the mean square fluctuation. Evidently, this distribution of the states of QFEs in the nanostructure is quite different from the one after the “ k^2 -rule” of the normal crystalline matter. Certainly, this emergent distinction can lead to some peculiarities of the nanostructured matter.

The general natural fluctuation of the parameter of short-range order in real non-crystalline state of matter is of 10^{-2} [9, 10]. Therefrom it may be initially evaluated that the full width at half maximum (FWHM) of the compressed distribution curve vs energy is of order of $10^{-4} - 10^{-3}$ eV. However, its abruptest area is very narrow and may contain *only one ESR transition line*.

3.2. The Climax-compression of the Spectral Intensity into an Individual Line

As an example, this effect on the line group of the spin complex C in silica glasses (Fig. 1.) is illustrated in the diagrams Figure 6 and Figure 7.

The careful ESR measurements showed that in the case of two Si-vacancies being on a [Si-O-Si]-bridge the six unpaired electrons from the O^- ions in a nano-system containing two $SiO_{4/2}$ basic units can be favourably combined into a superexchange coupled spin complex C (or “ $6O^-$ ”) with the resultant spin $S = 6/2$. This complex provides in the whole 12 ESR lines, where the multiple of the ground quantum state $S = 3$ includes 6 lines: C1, C2, C3, C4, C5 and C6. In figure 7a and Figure 7b, the diagrams of the energy levels, the ESR transitions and the ESR lines of the multiple $S = 3$ are described. The energy level and ESR transition diagrams for the both cases are entirely the same, but their positions of the initial energy (i.e., the energy at the applied magnetic field $H = 0$) of the spin center

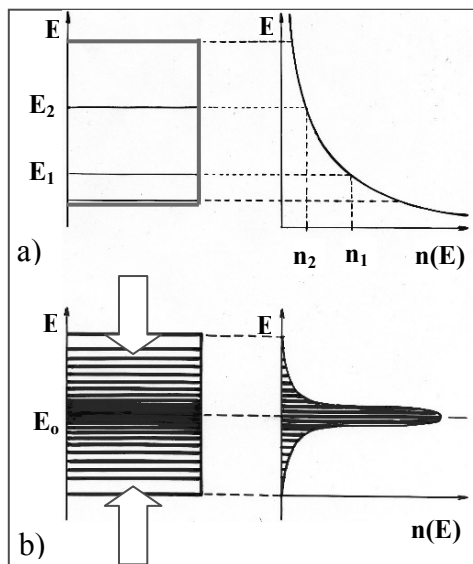


Fig. 4. Distribution of state density and the distribution function $n(E)$ in a normal crystalline structure (a) and in a nanostructure (b). The left parts are simplified sketches of the levels in an energy band. The two big arrows imagine the natural reaction of the NRC leading to the “compressed distribution”

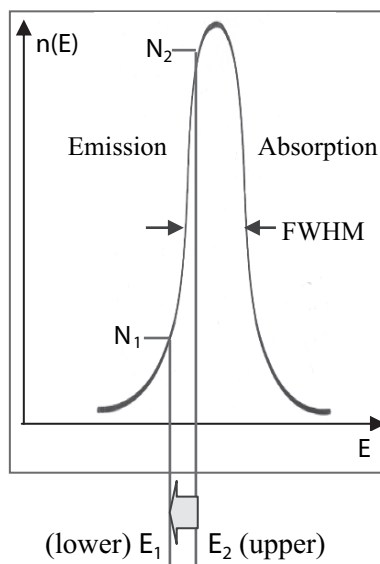


Fig. 5. Illustration of the course of the compressed distribution in the nanostructure, by which an intensive induced absorption on its right abrupt slope and a intensive emission on its left abrupt slope can take place

Fig. 6. Structure of the Complex C:

Dashed circle: Si-vacancy

○ : O^{2-} ion

● : O^- ion with an odd electron

H: Hydrogen (or Natrium, Kalium, Lithium, ...) ion

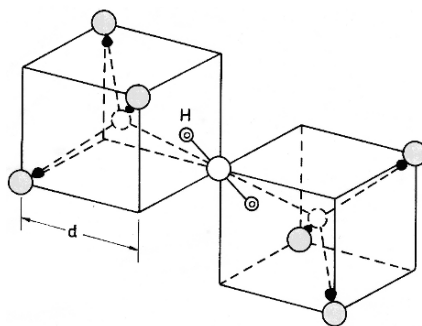
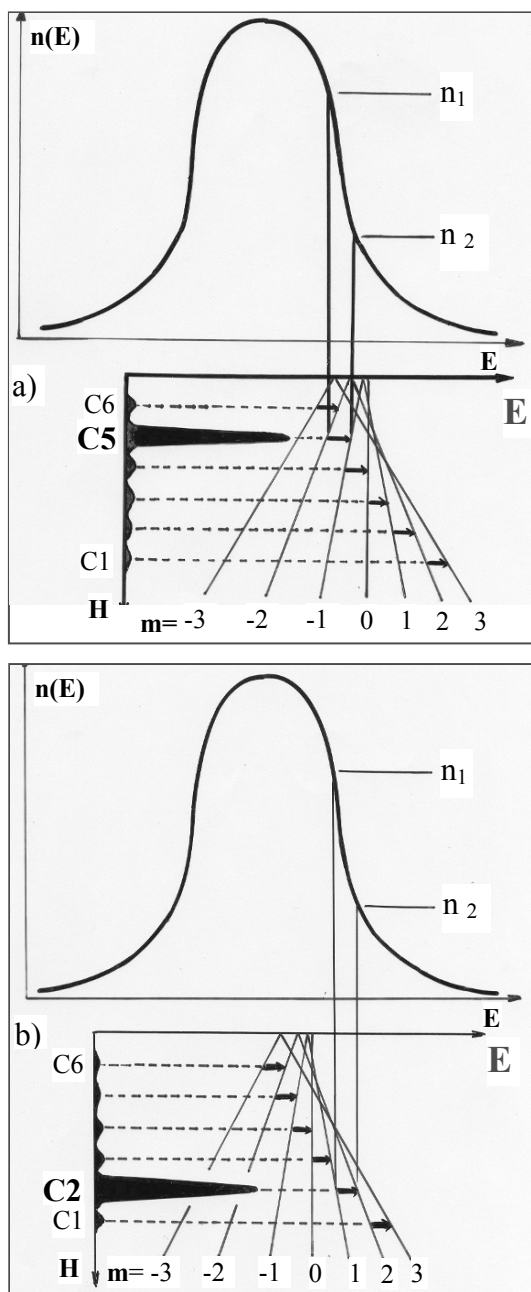


Fig. 7. Interpretation of the effect of compression of the spectral intensity into an individual line of the coupled spin complex C: a) in a high-melting and b) in a low-melting glass. The diagrams of the energy levels of the spin complex in dependence on the applied magnetic field H , the ESR transitions and the six corresponding absorption line positions C1 – C6 of the multiple $S = 3$ are described together with the curve of the compressed distribution in the nanostructure.

The energy level and ESR transition diagrams for the both cases are entirely the same, only their positions of the initial energy (at $H = 0$) of the spin complex are different:

In the high-melting glass (Fig. 7a), the initial energy is higher, only the C5 transition can fall into the abruptest area of the right slope of the compressed distribution curve and obtains an enormous population difference ($n_2 - n_1$).

But in the low-melting glass (Fig. 7b), the initial energy is lower, thereby only the C2 transition can fall into the abruptest area of the right slope of the compressed distribution curve (complex C) are different. In the high-melting glass (Fig. 7a), the initial spin energy is higher, thereby only the C5 transition can fall into the abruptest



area of the right slope of the compressed distribution curve and obtains an enormous population difference ($n - n$), that causes the extremely high intensity of the line C5. But in the low-melting glass (Fig. 7b), the initial spin energy is lower. The whole energy level system moves down so that the C2 transition can fall into the abruptest area of the right slope of the compressed distribution curve, that causes now the extremely high intensity of the line C2.

3.3. The Stimulated Emission of Radiation without Pumping

As an illustration. example, the stimulated emission line from spin center A (Si^{3+}) in amorphous SiO_2 whose experimental result already presented in Figure 2 is interpreted by the diagram in Figure 8 below.

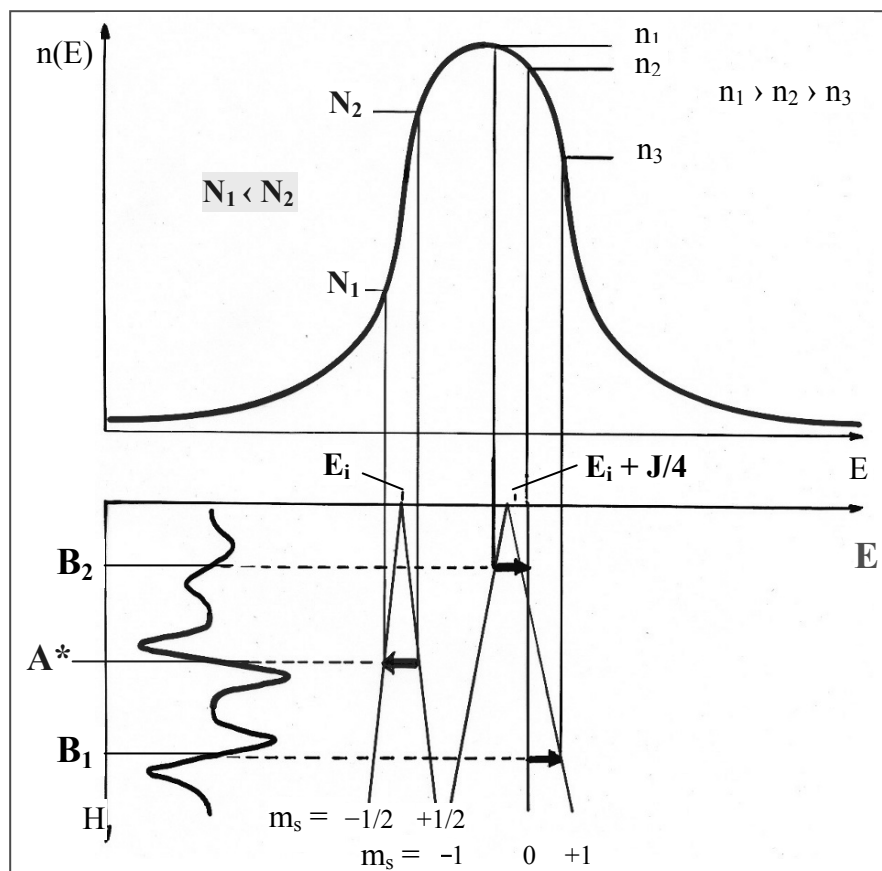


Fig. 8. Interpretation of the effect of stimulated emission of radiation without pumping (line A*) from the center Si^{3+} in amorphous SiO_2 at $T_c \approx 103$ K (s. also Fig. 2)

The well known center A (Si^{3+}) together with the center B ($[\text{Si}^{3+} - \text{Si}^{3+}]$ coupled pair) in SiO_2 materials has been studied for a long time. Their eigen values with the quantum states $m_s(\text{A}) = \pm 1/2$ and $m_s(\text{B}) = \pm 1, 0$ can be simplified described as follows

$$\begin{aligned} E(\text{A}, \pm \frac{1}{2}) &= \pm \frac{1}{2} g \beta H, \\ E(\text{B}, \pm 1) &= + \frac{1}{4} J \pm g \beta H - \frac{1}{8} \frac{g^2 \beta^2}{r^3}, \\ E(\text{B}, 0) &= + \frac{1}{4} J + \frac{1}{4} \frac{g^2 \beta^2}{r^3}, \end{aligned} \quad (6)$$

where J is the exchange integral of the coupled pair B; its measured value is of about 90 cm^{-1} ($\cong 1.2 \times 10^{-2} \text{ eV}$ or 130 K), g – g -factor of the center A, β – the Bohr magneton, H – the applied magnetic field and r – the pair distance. In figure 8 there are shown the diagrams of the energy levels, the ESR transitions and the first derivative spectral lines.

The initial energy of the center B is higher than the one of the center A, the difference is of $J/4$. The key is that, at the critical temperature $T_c \approx 103 \text{ K}$, whereas the energy levels and the corresponding ESR transitions of center B is lying on the absorption slope, the ones of the center A fall into the abrupt area of the emission slope of the *compressed distribution*. For this reason, at the temperature T_c the *emission line A** from the center A and the two absorption lines B_1 - B_2 from the center B can be together observed. The outstanding *Stimulated Emission Line A** appears without any pumping by an external source.

Furthermore, the distribution of the spectral intensity of the absorption group B in amorphous SiO_2 is also very peculiar, contrarily to the case of crystalline SiO_2 , the line B_1 becomes very much more intensive than B_2 . This phenomenon can be explained by the diagram with the compressed distribution curve (Fig. 8).

The existence of the center A (Si^{3+}) in Si- SiO_2 materials is not new. But, the effect of stimulated emission of radiation without pumping from A(Si^{3+}) in the amorphous/nanostructured SiO_2 is new. As above-mentioned, some other distinguished examples of this effect also have been revealed such as from low-melting glass, from upper kidney gland tissue, from natural vegetable fiber tissue. This effect can be considered as a new paramagnetic MASER mechanism, in which *the active medium* is a nanostructured matter, *the stimulating signal* is a microwave and the *population inversion* is established not by artificial means (pumping), but by the compressed distribution already naturally persisted inside the nanostructure of the active medium.

That may be to say, a new and peculiar type of “NATURAL MASERS” is discovered, although the other natural masers have been known for several decades. This naturally occurring maser action is frequently found in clouds of molecular gases in our galaxy where water or other molecules amplify radiation from stars [11].

The sudden changes of the conductivity in some nanostructured materials, e.g., in amorphous silicon [12], in semiconductive phase of YBCO compounds [8], etc. can be considered as an other important proof of the compressed distribution.

4. Conclusion

The effect of climax-compression of the spectral intensity into an individual line and the effect of stimulated emission of radiation without pumping (a new type of natural maser) have been experimentally revealed in numerous material and biomedical objects. The effects outstandingly occur in those matters possessing a prominent nanorange ordering. The achieved results can be explained as to originate only from a peculiarity of the population distribution of the dynamical electrons in the nanostructure, very distinct from the one in the normal crystalline materials I call this distribution “Compressed Electron Distribution” in the nanostructure. On the basis of this conception, the revealed effects and their nano-mechanisms have been satisfactorily interpreted. These new and very peculiar effects and their real applications will be furthermore investigated.

Acknowledgments

This research was supported by the National Basic Research Program in Natural Sciences, the Hanoi University of Technology and the Technische Universitaet Ilmenau. The author especially thanks Prof. K.-H. Gothe, Dr. G. Hartung, Dipl.-Ing. M. Siegmund, Mrs. K. Schiller, Institut fuer Physik, Technische Universitaet Ilmenau and the collaborators of the Laboratory of Magnetic Resonance – Electron Physics, Hanoi University of Technology, for their very helpful scientific suggestions and experimental activities.

References

1. Poole, Charles P., Frank J. Owens, Introduction to Nanotechnology, USA and CANADA, WILEY- INTERSCIENCE, 2003.
2. Boeing Niels, Nano? ! Die Technik des 21. Jahrhunderts, Rowohlt - Berlin, 2004.
3. Wolf, Edward L., Nanophysics and Nanotechnology, WILEY-VCH, 2005.
4. Nguyen Van Tri, in: Microstructural Investigation and Analysis, p. 47-51, WILEY-VCH, 2000.
5. Nguyen Van Tri et al., in: EPR in the 21st Century: Basics and Applications to Material,
6. Life and Earth Sciences (Kawamori A., Yamauchi J., Ohta H., eds.), p. 412-417,
7. ELSEVIER, 2002.
8. Nguyen Van Tri et al., J. Ferroelectrics, Vol. **250**, p. 265-269, Gordon and Breach Science Publishers (2001).
9. Nguyen Van Tri, J. Ferroelectrics, Vol. **250**, p. 385-389, Gordon and Breach Science Publishers (2001).
10. Nguyen Van Tri, J. Ferroelectrics, Vol. **305**, p. 141-145, Taylor & Franncis Inc. USA, (2004).
11. Kliava J., Review Article, Phys. Stat. Sol. (b), Vol. **134**, p. 411-426, (1986).
12. Kittel Ch, Introduction to Solid State Physics, John Wiley & Sons, Inc., 1986.
13. Marvin J. Weber, Handbook of Laser Wavelengths, CRC Press, Boca Raton - Boston - London - New York - Washington, D.C., 1999.
14. Nguyen Van Tri, Proc. of the 4th National Conference on Physics, 548-557, (1994).

Time and Space Resolved Studies on Metallic Nanoparticles

D. Bayer¹, J. Lange¹, C. Wiemann³, M. Rohmer¹, M. Bauer² and M. Aeschlimann¹

¹ Department of Physics, University of Kaiserslautern, 67663 Kaiserslautern

² Institut für Experimentelle und Angewandte Physik, Universität Kiel, 24118 Kiel

³ Forschungszentrum Jülich, Institut für Festkörperforschung (IFF), Elektronische Eigenschaften, 52425 Jülich

Abstract. The dynamics of laser-excited electronic excitations (localized surface plasmons) in spherical Ag nanoparticles is studied by phase and time resolved two photon photoemission (TR-2PPE) and photoelectron emission microscopy (TR-PEEM). A two-dimensional array of nearly identical, parallelly oriented particles is deposited lithographically on a transparent ITO covered glass substrate. We are able to show that the parallel acquisition mode of the PEEM enables us to resolve local variations in the ultrafast electron dynamics in the nanoparticles with an accuracy of 1fs and a lateral resolution in the nanometer regime. A qualitative interpretation of the mapped inhomogeneities in the local electron dynamics is provided.

1. Introduction

In noble metal nanoparticles collective electronic oscillations – so-called particle plasmons or localized surface plasmons (LSP) – can be excited by electromagnetic waves. Therefore they are detectable as pronounced resonances in the scattering and absorption cross-section, commonly located in the visible or UV part of the spectrum [1]. The resonance frequency of the plasma oscillation is determined by the dielectric properties of the metal and the surrounding medium as well as by the particle size and shape [1, 2, 3]. The collective oscillation can be interpreted as a displacement of the electrons in the particle against the positively charged background of the atomic nuclei. Resonant excitation of this collective charge oscillation causes a large enhancement of the local field inside and near the particle [4, 5] which dominates the linear and nonlinear response of the particles to the light field. The field enhancement caused by the electron oscillation is thought to be responsible for the enhancement of non-linear optical effects such as surface-enhanced Raman scattering (SERS) [6], surface second harmonic generation [7, 8] and multiphoton photoemission [9-12]. In recent years the promising research field of plasmonics and ultrafast nanooptics has emerged, exploiting the high potential of plasmons to concentrate and channel light into subwavelength structures of nanoscopic circuits [13].

While the spectral positions of the resonances of particle plasmon excitations as a function of particle size, shape and dielectric properties are well understood [1-4], the ultrafast dynamics of these collective electronic excitations have remained a highly interesting topic to be studied in more detail. To understand the dynamics, it is essential to investigate the mechanisms relevant for the loss of phase coherence between the electrons contributing to the collective excitation (dephasing).

Photoemission electron microscopy (PEEM) in combination with nonlinear photoemission, in particular two photon photoemission (2PPE), has emerged as a versatile tool to study plasmonic excitations. As the photoemission yield is governed by the local electric field distribution it can be employed as a direct probe of the plasmon induced field enhancement. For instance, Cinchetti et al. [14] used 2P PEEM to map the lateral distribution of optical near fields in the vicinity of plasmon resonant structures.

A highly promising aspect of two-photon photoemission electron microscopy with respect to questions of the dynamical behaviour of plasmonic excitations is the option to employ the technique in a time-resolved stroboscopic mode (TR-PEEM) with a temporal resolution below 10 fs [15, 16]. In combination with the PEEM lateral resolution of sub 50 nm [17], this allows us to directly monitor the spatio-temporal dynamics of the local field distribution associated with the excitation and decay of localized plasmon modes. Further enhancement of the time resolution can be achieved by stabilizing the pump-probe setup with sub-wavelength accuracy by interferometric methods. In this way, accurate information on the relative phase of the plasmon mode to an oscillating reference field such as the driving external light field can be obtained [11]. The combination of laterally and temporally high resolving methods allows one to obtain a complete picture of the near-field dynamics associated with plasmon excitations in low-dimensional nanostructures.

In this paper we present a study of a two-dimensional array of identically prepared, parallelly oriented particles deposited lithographically on a transparent ITO substrate by phase and time resolved two photon photoemission (TR-2PPE) and photoelectron emission microscopy (TR-PEEM). This combined technique allows to study spatial variations in the local electron dynamics. Furthermore, by mapping the spatio-temporal evolution of the 2PPE-yield within a single particle we are able to follow the phase-propagation of a localized surface plasmon mode through a particle on a sub-femtosecond time-scale. This illustrates how the phase-control of a laser field allows manipulating the local field-distribution in nanoscopic systems.

2. Experimental Methods

The experimental method used to investigate the dynamics of the optically induced electronic excitations is time resolved two photon photoemission (TR-2PPE) [18]. This pump-probe technique permits a direct measurement of dynamical properties of electronic excitations in the time domain with a resolution of a few femtoseconds. The principle is shown schematically in figure 1. Photoemission takes place via a two-step process. Absorption of a first photon with energy below the work function leaves the system in an excited state which will decay after a characteristic average lifetime T_1 . If a second photon is absorbed within this time interval, a photoelectron is emitted

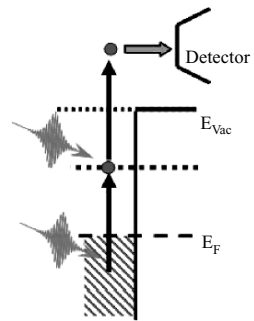


Fig. 1. Excitation scheme of the 2PPE process

from the sample surface and can subsequently be detected. An energy analyzer can be employed to address a specific intermediate energy level. The population decay time of the intermediate state is measured by an autocorrelation technique. In our setup the frequency-doubled output of a Ti:Sapphire oscillator provides ultrashort pulses (<20 fs) with a photon energy of 3.1 eV. A Mach-Zehnder interferometer is used to prepare a pair of identical pump-probe pulses with variable time delay. Measurement of the photoemission signal while scanning the temporal delay between pump and probe pulse results in an autocorrelation trace which contains an exponentially decaying contribution which is directly related to the population decay time T_1 of the intermediate excitation state.

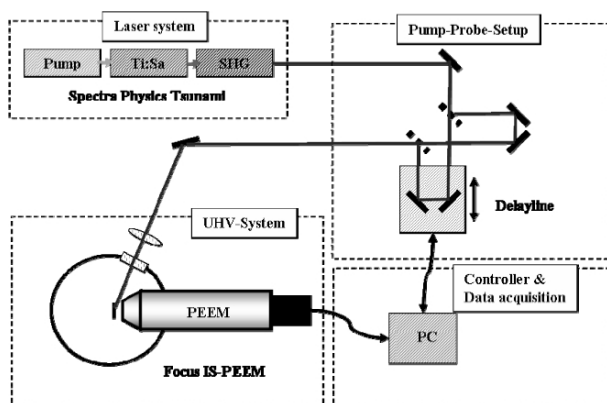


Fig. 2. Setup for the space and time resolved two-photon photoemission experiment (TR-PEEM)

The extension to a space and time resolved 2PPE set-up (TR-PEEM) is shown in figure 2. The PEEM serves as a 2D-electron detector that maps the lateral photoelectron distribution from the sample surface. A more detailed description of the employed PEEM system can be found in reference [15, 19]. For a full pump-probe scan, the delay between the two pulses is varied in small steps (typically $\Delta t = 1$ fs)

and for each step a PEEM image is taken. This results in a series of images containing a correlation trace for each pixel. Thus we obtain information on the dynamical behavior of the electron system at the sample surface (decay time T_1 of the intermediate state) with the spatial resolution of the PEEM.

To further improve the time resolution, a phase-resolved PEEM setup has been realized. The Mach-Zehnder interferometer has been modified as depicted in figure 3a. Here, the probe is delayed with respect to the pump by a piezo-driven optical delay stage enabling relative positioning of both interferometer arms with 20 nm accuracy. This corresponds to a temporal delay between the respective laser pulses travelling through the different arms of 67 attoseconds. To guarantee this extremely high resolution, the optical pathway is calibrated by monitoring the interference signal from a frequency stabilized HeNe laser [20]. The performance of phase-resolved as well as phase-averaged 2PPE has been tested on a polycrystalline tantalum film (see figure 3b, photon energy 3.1 eV). The oscillation fringes due to the interference between pump- and probe- pulse are well resolved, i.e., the accurate reproduction and periodicity of these measurements over the entire temporal delay proves the position stability of our setup. Note that the phase-integrated correlation trace can be obtained from the phase-resolved signal by time-averaging.

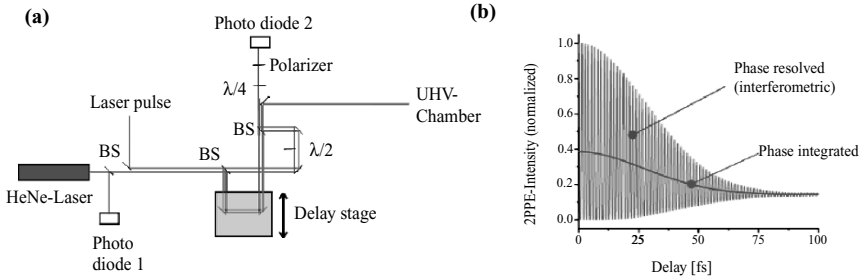


Fig. 3. a) Setup of a phase resolving high resolution Mach-Zehnder interferometer. b) The performance of the interferometer has been checked by lateral integrating phase- and time-resolved 2PPE measurements on a polycrystalline tantalum sheet.

The investigated 2D silver nanoparticles array is prepared by electron beam lithography [21] on an ITO (indium-tin oxide) covered glass substrate. As the optical properties, especially the position and width of the LSP- resonance critically depend on the shape, size and distance between two neighboring particles, the sample is designed to fit the setup conditions. Hence, the LSP resonances are tuned to fundamental and second harmonic of the used Tisapphire laser (1.55 eV and 3.1 eV). the SEM (Scanning Electron Microscope) image in figure 4 shows the homogeneity of the silver particles.

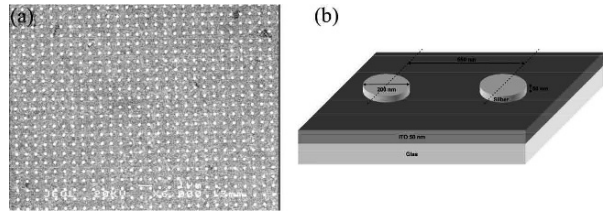


Fig. 4. a) SEM image of the used array of spherical Ag nanoparticles. b) The dimensions of the nanoparticles (diameter 200 nm, height 50 nm, grating constant 650 nm).

3. Results and Discussion

The spectral position of the LSP resonance critically depends on the dimensions, shape and material of the nanostructure as well as the dielectric constant of the surrounding [1-3]. The spectral response of the prepared silver nanocylinders can be well reproduced by calculations based on the model of reference [22]. The material properties are taken into account by using the measured dielectric function of silver and an average value for the surrounding. The model also includes the known geometry of the cylinders as well as a broadening of the resonance due to radiation damping and retardation effects. Figure 5 presents a calculated (a) and a measured (b) extinction spectrum of the used 2D silver nanodot array. The extinction spectroscopy performed through an optical microscope (Zeiss Axioskop with integrated microspectrometer MMS1) is only sensitive to the in-plane (x and y) resonances of the particles because of the setup geometry

(normal incidence). A comparison of the calculated and the measured spectrum shows a good agreement of resonance position and width. Therefore, we conclude that the model is also reliable in predicting the properties of the perpendicular resonance which is not accessible by our extinction spectroscopy setup, but crucial for the 2PPE-excitations discussed below. Simulation and spectroscopy as characterization tools enable us to create samples with perfectly adapted properties to perform LSP dynamics investigations with two photon photoemission.

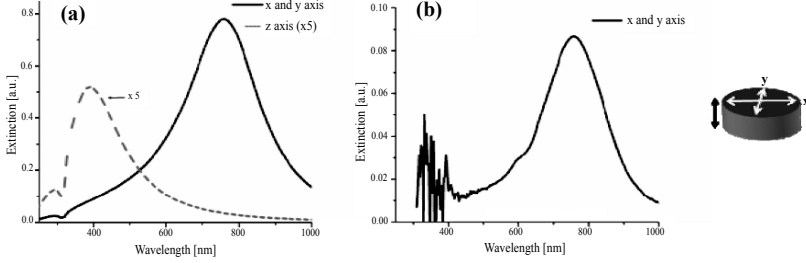


Fig. 5. Calculated (left) and measured (right) extinction spectra for square 2D arrays (grating constant 650 nm) of cylindrical Ag nanoparticles (diameter 200 nm, height 50 nm) on an ITO coated quartz substrate depicted in the SEM image (figure 4)

The connection between 2PPE and LSP is mediated by the internal electric field that is responsible for the photoemission. A resonantly excited LSP causes a high field enhancement resulting in a high photoemission yield as schematically shown in figure 6. The external (laser) field resonantly drives the plasma oscillation of the electrons inside the silver particles. The induced polarisation gives rise to an additional electric field which is superimposed on the light field. The modification of the internal field relative to the external laser field with respect

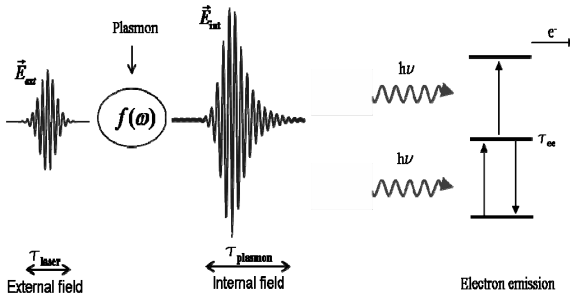


Fig. 6. Influence of the LSP resonance on the amplitude and duration of the incident laser pulse. Finally, the internal field induces optical transitions leading to the two photon photoemission process

to amplitude and phase can be described by a frequency dependent complex field enhancement factor $f(\omega)$ [23].

Since the photoemission signal is directly proportional to the fourth power of the internal field $j_{2PPE}(\vec{r}) \propto |\vec{E}_{int}|^4$, the electron yield is a highly sensitive probe of the field enhancement due to the LSP resonance.

Figure 7 shows a PEEM image of the particle array (2PPE) and the corresponding 2D lifetime map, which was generated by extracting the full width at half maximum (FWHM) of the correlation curves of each pixel, from a series of over 100 PEEM images at different

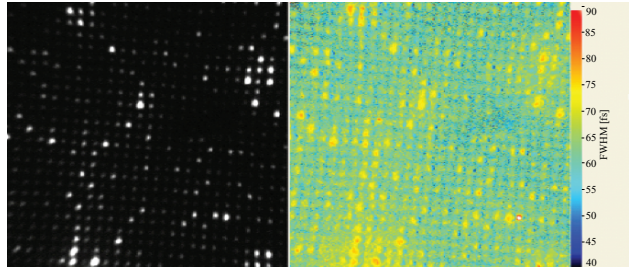


Fig. 7. PEEM image (left) and the corresponding lifetime map (FWHM of the autocorrelation curves)

pump probe time delays (phase-averaging mode). However, in this case the interparticle brightness variations as seen in figure 7 are dominated by defect-induced indirect transitions and are discussed in more detail in Ref. [10]. The properties of the particles' plasmon resonances are not affected by this effect, yet it is of course to be included in the analysis of the time resolved data, which will be discussed next.

The lifetime map visualizes the lateral variations in the electron dynamics in colour coding. Red tones correspond to high FWHM values, indicating long decay times, while blue tones are associated with faster decay. We note a certain correlation between brightness in the 2PPE image and the FWHM values of the lifetime map: Particles appearing bright in the 2PPE image tend to exhibit longer average decay times in the lifetime image. This effect must obviously be related to the defect induced transitions. The involved intermediate single-electron states on the one hand give rise to a higher overall transition probability and a higher photoemission yield, on the other hand they show longer decay times. The underlying plasmon dynamic can be extracted by a detailed inspection of a single nanoparticle.

The dynamic processes associated with a plasmon excitation in a single particle can be studied in further detail if the phase-resolved setup is employed. The image sequence in figure 8 shows the plasmon dynamics in a single particle. The time interval between two images is 0.13 fs. A clear variation in the contrast within the area of the nanoparticle in the sub fs time-scale is detectable.

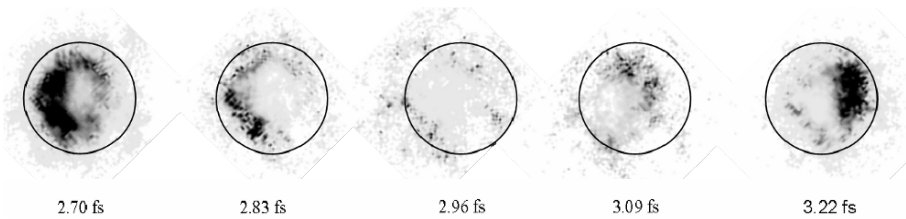


Fig. 8. The image sequence shows one Ag nanodot (diameter 200 nm) at different time delays: The phase resolved 2PPE is highlighting the local variation in the collective electron dynamics of a single nanoparticle

The result can be explained in the following way: The electric field amplitude is determined by the phase delay $\Delta\phi(\tau)$ between pump and probe laser pulse as adjusted by the Mach-Zehnder interferometer, as well as the polarization field of the particle plasmon which is oscillating at its resonance frequency. Due to oblique incidence from the right, we expect the laser light to couple at first to the LSP-mode at the right edge of the particle. Here external (laser) field and internal (plasmon) field attain a fixed phase relation. Since the propagation velocity of external and internal field vary, a position dependent phase lag between the two field components is acquired as the plasmon excitation travels through the particle. The particle internal structure visible in a single PEEM image of figure 8 is a residual of the varying interference between the external light field and the particle internal LSP-field, directly connected to the plasmon phase.

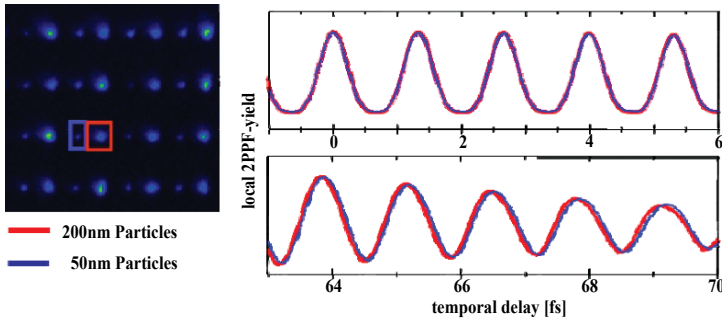


Fig. 9. The left PEEM image shows an array of Ag nanoparticles alternating 200 nm and 50 nm in diameter. The right side shows a comparison of a 50 nm and a 200 nm dot at different delay times: At time zero (temporal overlap of pump and probe pulse) and at large temporal delay of about 66 fs

Using the phase resolved (interferometric) setup providing a temporal precision in the pump-probe delay of better than 70 attoseconds the dynamics of a plasmon excitation in different nanoparticles can be directly compared in real time. Figure 9 shows the measurement of a 2D array of silver nanodots with diameters of 50 nm and 200 nm respectively. Comparing the interferograms of two neighboring particles at time zero and around 66 fs later, the phase of the neighbouring particles are delayed with respect to each other. The parallel data acquisition by the PEEM allows us to exclude any systematic errors. The phase difference in figure 9 can be explained as follows: At time zero the incident laser pulse forces the internal LSP mode to oscillate with the laser pulse frequency. Because of the limited pulse width of the laser and the finite lifetime of the LSP, the LSP starts to oscillate at its eigenfrequency resulting in a phase shift at higher pump-probe delays.

4. Conclusion

By combining a femtosecond time-resolved pump-probe method and PEEM we demonstrated that time- and spacially-resolved spectromicroscopy is a powerful tool to image local plasmon dynamics in real time that provides information about the internal dynamics of plasmon excitations in nanostructured materials. The

presented technique uses the advantage of parallel data acquisition in order to avoid any systematic errors. This offers the opportunity to investigate coupling effects between different neighbouring nanostructures in the sub fs time scale.

Acknowledgements

The authors thank the Nano-Bio Center at the University of Kaiserslautern for their support in preparing the silver nanoparticle samples. This work was supported by the Deutsche Forschungsgemeinschaft through SPP 1093.

References

1. G. Mie, Ann. Phys. 25, 377 (1908)
2. U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters*, Springer Series in materials Science, Vol. 25, (Springer, Berlin 1995)
3. C. F. Bohren, D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, Wiley New York (1983)
4. J.P. Kottmann, O. J. F. Martin, Opt. Lett. 26, 1096-1098 (2001)
5. J.P. Kottmann, O. J. F. Martin, Optics Express 8, 655-663 (2001)
6. M. Moskovits, Rev. Mod. Phys. 57, 783-826 (1985)
7. H.J. Simon, Zhan Chen, PRB 39, 3077-3085 (1989)
8. A. Bouhelier, M. Beversluis, A. Hartschuh, and L. Novotny, PRL 90, 013903 (2003)
9. M. Scharfe, R. Porath, T. Ohms, M. Aeschlimann, J.R. Krenn, H. Dittelbacher, F.R. Aussenegg, A. Liebsch, Appl. Phys. B 73, 305-310 (2001)
10. C. Wiemann, D. Bayer, M. Rohmer, M. Aeschlimann, M. Bauer, Surf. Sci., in print
11. J. Lange, D. Bayer, M. Rohmer, C. Wiemann, O. Gaier, M. Aeschlimann, M. Bauer, Proc. SPIE 6195, 61950Z (2006)
12. M. Rohmer, F. Ghaleb, M. Aeschlimann, M. Bauer, H. Hövel, European Physical Journal D, in print
13. M. Salerno, J.R. Krenn, B. Lamprecht, G. Schider, H. Ditlbacher, N. Féridj, A. Leitner, F.R. Aussenegg, Opto-Electronics Review 10, 217-224 (2002)
14. M. Cinchetti, A. Gloskowskii, S. A. Nepjiko, G. Schönhense, Appl. Phys. Lett. 95, 047601 (2005)
15. O. Schmidt, M. Bauer, C. Wiemann, R. Porath, M. Scharfe, O. Andreyev, G. Schönhense, M. Aeschlimann, Appl. Phys. B 74, 223-227 (2002)
16. A. Kubo, K. Onda, H. Petek, Z. Sun, Y.S. Jung, H.K. Kim, *Nano Lett.* 5, 1123 (2005)
17. M. Aeschlimann, M. Bauer, D. Bayer, T. Brixner, F.J. García de Abajo, W. Pfeiffer, M. Rohmer, C. Spindler, F. Steeb, Nature 446, 301 (2007)
18. C.A. Schmuttenmaer, M. Aeschlimann, H.E. Elsayed-Ali, R.J.D. Miller, D.A. Mantell
19. W. Swich, G. H. Fecher, Ch. Zieten, O. Schmidt, G. Schönhense, K. Grzelakowski, C. M. Schneider, R. Frömten, H. P. Oepen, and J. Kirschner, J. Elec. Spec. Rel. Phenom. 84, 171 (1997)
20. M.U. Wehner, M.H. Ulm, and M. Wegener, Optics Lett. 22, 1455-1457 (1997)
21. A. Hohenau, H. Ditlbacher, B. Lamprecht, J.R. Krenn, A. Leitner, F. Aussenegg, Microelectronic Engineering 83, 1464-1467 (2006)
22. H. Kuwata, H. Tamaru, K. Esumi, K. Miyano, Appl. Phys. Lett. 83, 4625- 4627 (2003)
23. M. Mersdorf, C. Kennerknecht, W. Pfeiffer, Phys. Rev. B 70, 193401 (2001)

Ultra-small One-Dimensional Metallic Nanostructures

H. Pfnür

Institut für Festkörperphysik, Abteilung Oberflächen,
Leibniz Universität Hannover,
Appelstr. 2, D-30167 Hannover, Germany
e-mail: pfnuer@fkpuni-hannover.de

1. Introduction

Confinement of electrons in low-dimensional structures induces intriguing transport phenomena and electronic properties. This is already seen in metallic layers, which represent prototypes for the observation of quantum size effects (QSE) [1]. Especially for metallic Pb layers, quantum well states are responsible for the formation of “magic” island heights [2]. Multiple changes of sign as a function of layer thickness in the Hall coefficient for Pb layers on Si(111) [3] turn out to be due to the thickness dependent formation of the two-dimensional band structure, and are thus also related to the QSE.

Extreme confinement happens in one-dimensional (1d) objects resulting in enhanced electron correlation. Therefore, 1d conductors are expected to have properties deviating from a Fermi liquid [4]. A very flexible way to create 1d conductors is to use vicinal surfaces and the adsorption of submonolayers of metals on semiconductor substrates. E.g., Ag and Au on vicinal Si(111) surfaces form chain structures at submonolayer coverages that exhibit localized states perpendicular to the chain direction [5, 6, 7]. However, these weakly interacting systems often undergo instabilities, e.g. Peierls- or Mott-Hubbard driven phase transitions into insulating states at low temperature (see, e.g., [8]). In addition, the 1d character of electronic transport is rarely established.

In order to carry out such measurements, the key prerequisite is the generation of reliable contacts, which allow testing of the conductive properties of nanowires, in the limit of ultra-small separations of single molecules, and the control of their functionalities. Because molecule and leads must be considered as an entity [9, 10], the local structure, in particular the bonding of a molecule to the metallic contacts, crucially determines the conductive properties of these quantum mechanical objects in case of strong coupling. Therefore, the control of the complete atomic arrangement in the vicinity of the contact on the atomic scale is necessary in order to reach a more complete understanding of contact properties.

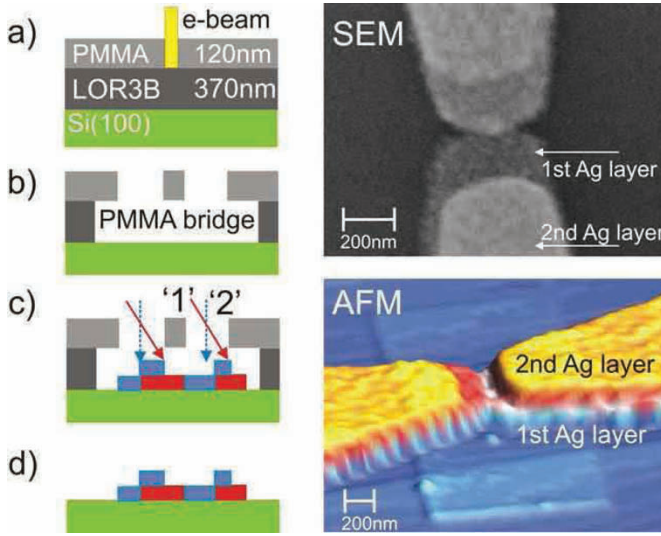


Fig. 1. Generation of ultrasmall nanocontacts Left: a) Side view of the double layer PMMA/LOR3B resist structure, b) after e-beam exposure and development c) Ag evaporation at various angles for controlled thickness variation of Ag layers d) after removal of resist. Top right: top view of the resulting Ag layer structure in SEM, bottom right: perspective view of the same structure taken with AFM

We have used two different approaches to generate contacts. One is to use TiSi_2 pads on Si single crystalline substrates, generated by e-beam lithography in Polymethylmethacrylate (PMMA). Ti is evaporated onto the developed structure, and after lift-off and careful removal of all traces of PMMA these structures are put into UHV, where the reaction to TiSi_2 takes place at around 650°C [11]. The formation of large step bunches during reaction can be avoided by a built-in concentration gradient at the edges of the pads [12]. UHV e-beam lithography is then used to write wire-like structures directly into ultra-thin SiO_2 after oxidation of the whole surface in UHV [11, 13]. These can be used to form metallic wires after evaporation of appropriate metals [14]. Typical structural sizes are below 20 nm, but in combination with self-organised step structures can be as low as 5 nm [15].

In the first part of this paper we concentrate on a second approach for contact formation by use of Ag layers on Si(100) that wet the Si surface. We show that we are able to produce structures with gaps in the range between 5 nm and below 1 nm. In addition, these structures are thin enough and laterally open so that they are completely accessible to a scanning tunneling microscope (STM) for local control. We also demonstrate that they can be successfully used to contact small molecules.

The second part of the paper is devoted to the exploration of conditions for one-dimensional conductance in a layer of strongly coupled Pb wires on

a vicinal Si(557) surface. For contacting, TiSi_2 pads on Si single crystalline substrates are used. Here we show that Pb on this surface is able to refacet the surface after appropriate annealing, and that this refacetting is crucial for defining conditions of 1d conductance.

2. Molecular Contacts

Using electron beam lithography (EBL) nanostructures were written into a PMMA/LOR3B resist structure, which was spin coated onto the Si(100) wafer. The wafer was cleaned before by O_2 -plasma etching. A schematic drawing of the writing and evaporation process is shown in Fig. 1. The thickness of the PMMA/LOR3B structure used for our samples was 120nm and 370nm, respectively (see Fig. 1a). The writing was done using a JEOL 5900 SEM in combination with a RAITH lithography system.

After etching the structure in the LOR3B layer is laterally larger than the openings in the upper PMMA layer. This effect allows fabrication of a 250 nm wide *nanobridge of PMMA* above the Si(100) surface, which was used as a shadow mask during the Ag evaporation (see Fig. 1b). The evaporation of Ag, controlled by a microbalance, was carried out under UHV conditions while the substrate was kept at 100 K. Changing the angle of the Ag flux from the evaporator, vertically structured Ag-wires are fabricated. After removal of the resist, a three-dimensional Ag structure is obtained with a thin central part, which is subsequently thinned and opened in a controlled electromigration (EM) experiment. An SEM image of the final structure with the typical size (after removal of the residual resist) is shown in the top right part of Fig. 1, whereas the bottom shows the same structure in AFM. The dimensions of the wires are limited by the stability of the free-standing nanobridge and the etching rate within the LOR3B. The thickness of the Ag films in the center was varied between 2nm–15nm. Notice the minimal thickness in the center can be as low as 2nm, i.e. around 7 monolayers.

The gap itself was generated using a feedback-controlled electromigration technique. A systematic test of different contacts has shown that both the geometry in the vicinity of the narrowest part, as well as temperature of the sample (here it was cooled to ℓN_2 temperatures) are important parameters for the fabrication of reliable gap openings of a few Å at the narrowest part of the structure. Depending on the geometry of the initial structure the final tunneling resistances obtained for different samples after EM vary between 0.2 and 10 MΩ, i.e. the tunneling gaps are between 5 Å and 5 nm [16]. The resistance of the Si(100) sample itself is an order of magnitude larger, as reference measurements have shown on non-processed Si(100) samples. These gaps can be closed reversibly just by slowly warming up the samples to room temperature. More details about the procedures to fabricate these contacts can be found in [17].

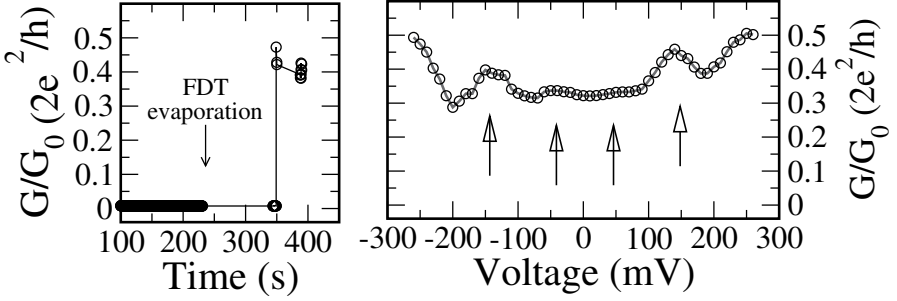


Fig. 2. left: measured current across nanocontact during adsorption of ferrocenedithiol. right: Derivative of the measure IV-curve after the jump in resistance has occurred.

These gaps can be used to contact individual molecules, as shown in Fig. 2. Ferrocenedithiol (FDT, $C_{10}H_{12}S_2Fe$, length 9 Å) [18] was evaporated thermally out of a ceramic crucible until a stepwise increase in conductance was detected. The conductance curve during evaporation is shown in the left part of Fig. 2. The original gap resistance $R=200\text{ k}\Omega$ indicates a gap of less than 1nm. Approximately 10 seconds after the voltage of 300 mV for monitoring the resistance has been turned on again the conductance switches to $0.4\text{ }G_0$ ($G_0 = 77.5\mu S$), indicating a field induced capturing of a molecule in between the contacts.

The I-V curves taken with a molecule between the contacts contains a structure, which is more clearly visible as peaks at ± 50 and at $\pm 140\text{ meV}$ in the derivative shown in the left part of Fig. 2. These peaks correspond well to typical vibrational energies of the FDT molecule [19]. Since these peaks are seen in the first, not in the second derivative, it is clear that they are not correlated with the opening of new channels in the conductance, but are more likely due to a resonance effect [20].

3. Pb wires on Si(557): conditions for 1d conductance

3.1 Observation of 1d Conductance

Recently [21], we discovered that at coverages close to one monolayer of Pb, a quasi one-dimensional conductance can be obtained on a vicinal Si(557) surface after annealing the layer close to desorption temperatures. The experimental result, obtained by using a modified 4-point technique with 8 contacts on a macroscopic sample (size $15 \times 15\text{ mm}$) with $TiSi_2$ contacts (see above), is shown in Fig. 3.

As seen in this figure, there is an abrupt, but reversible change in conductance close to 80 K. It ranges from activated conductance at higher temperatures with weak anisotropy to strong anisotropy at lower temperature, and

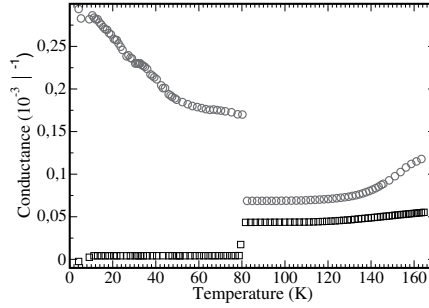


Fig. 3. Measured conductance after adsorption of 1.3 ML (i.e. one physical monolayer) of Pb on Si(557) and annealing to 640 K. For the data points marked by circles, the current direction was parallel, for those marked by squares perpendicular to the steps.

essentially insulating behaviour perpendicular to the steps of the surface. Surprisingly, and in contrast to all other examples of 1d conductance discussed so far in the literature, this system is metallic at low temperatures in the direction parallel to the step edges, and there is no indication for any kind of instability as a function of temperature in the measured conductance down to 4 K.

3.2 Pb-induced Changes of Step Morphology Close to Monolayer Coverage

This interesting behaviour must be caused by structural and/or electronic changes, which will be discussed in the following. These changes became most obvious in a systematic LEED investigation carried out in our group recently [22]: In Fig. 4a) the LEED pattern of the clean (557) surface is seen. It consists of a regular sequence of small (111) and (112) terraces [23]. Marked are the integer order spots of the small (111) terraces. The multiple spots in between correspond to this regular array of steps with a periodicity of 5.7 nm. Also visible are streaky (7×7) spots, which are due to the small (111) oriented terraces, and streaks at half order positions. These indicate a period doubling at the step edges.

This step morphology changes dramatically, when Pb is adsorbed at concentrations between 1.2 and 1.4 monolayers (ML, referenced to the Si density of surface atoms) onto this surface and annealed to temperatures above 600 K. The result at a coverage of 1.3 ML is shown in Fig. 4b). As seen there, the average step separation has changed dramatically. From the distance of the spots between those marked (00) and (01) we deduce an average Pb-induced step separation of 4.67 Si lattice constants. This corresponds to formation of a (223) oriented facet, which has a higher step density than the original (557) surface. Occasional formation of steps in the opposite direction can compensate for the higher step density in order to maintain the macroscopic surface

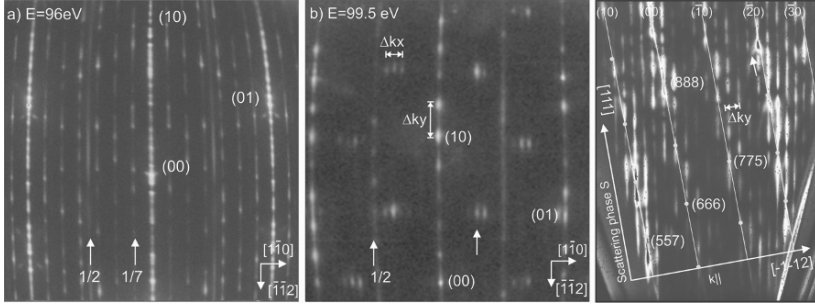


Fig. 4. a) LEED pattern of the clean Si(557) surface. b) after adsorption of 1.3 ML of Pb and annealing above 600 K, c) k-space mapping of along the line from (00) to (10) (central vertical line of spots in b)

orientation. These, however, are not periodic, and are therefore not visible in LEED. This Pb induced step array is not a minority species on the surface, as seen in Fig. 4c), where k-space mapping is shown, i.e. we plot a sequence of line scans along the line from (00) to (01) as a function of electron beam energy (or equivalently: k_z). The bright rods of the resulting two-dimensional Ewald construction show that the macroscopic surface is now covered by (223) facets. Weak rods of (111) oriented terraces, inclined by 11.42° with respect to (223), indicate that only a small fraction of this surface is covered by them. This periodic step structure is stable up to 80 K. LEED observations therefore were always made at lHe temperatures after annealing the layers.

Remarkably, variation of the average Pb concentration by only 0.2 ML, namely from 1.2 to 1.4 ML, if annealed once to high temperatures, allows tuning of the step density with facets starting with the (112) orientation at 1.2 ML, followed by the (335) orientation at 1.24 ML. At 1.27 ML the (223) facet appears, which turned out to be the most stable. It exists at Pb concentrations above 1.27 ML up to saturation of the physical monolayer close to 1.4 ML. Once the (7×7) structure is destroyed, annealing temperatures of only 180 K suffice to rearrange the surface. The homogeneously stepped (557) surface turned out to be stable only for annealing temperatures up to 80 K at a Pb concentration close to 1.35 ML. At higher annealing temperatures it irreversibly transforms into (223) facets. A schematic of the step structures found is given in Fig. 5.

3.3 Electronic properties

As mentioned, reversible switching between 1d and 2d conductance is observed for a Pb concentration of 1.3 ML. At this concentration the (223) facets are stabilized. The corresponding average terrace width turns out to be crucial for 1d conductance. In section 3.2 we showed that Pb at these coverages (and at temperatures below 80 K) is able to restructure the whole surface and to

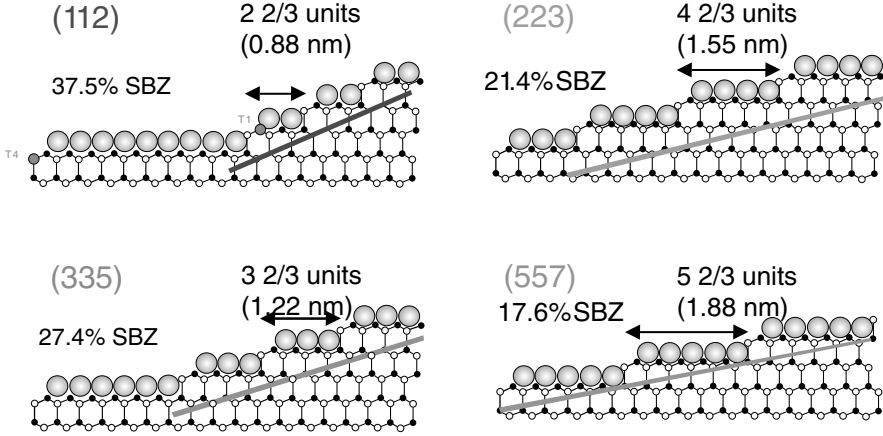


Fig. 5. Observed Pb induced step densities on Si(557) after annealing to 600 K at Pb concentrations between 1.20 ML (top left, (112) facet), 1.24 ML (bottom left, (335) facet), 1.30 ML (top right, (223) facet) and 1.35 ML ((557) facet).

establish order with various types of facets depending on Pb concentration. This means that generation and annihilation of steps is triggered by changes in Pb concentration on the surface. This can only happen due to strong interactions between the Pb wires on each terrace. We thus have a strongly coupled system, which is anisotropic due to the low symmetry of the surface, but one-dimensional behaviour cannot be expected a priori for such a system.

This is indeed what we found in recent angular resolved photoemission (ARPES) measurements [24]. Pronounced dispersion is seen in both directions, in particular in the direction normal to the steps. An example of the photoemission intensity close to the Fermi energy as a function $k_{\perp}$ at $k_{\parallel} = 0.24 \text{ \AA}^{-1}$ is shown in the left part of Fig. 6. A detailed analysis reveals that only bands associated with (Pb modified) surface states have intensity close to the Fermi level (E_F), whereas valence band states of Si reach their maximum close to $E_F - 0.3 \text{ eV}$. A characteristic repetition of bands can be also seen, which is due to the periodicity introduced by the steps. The connecting vector is marked by yellow arrows. Its length $2\pi/d$ with the characteristic terrace length d corresponds exactly to $d = 4\frac{2}{3}a_0$, in agreement with our findings above (see also schematic in the right part of Fig. 6).

Further inspection of the ARPES data reveals that for exactly this step separation the condition $2k_F = 2\pi/d$ is fulfilled in the direction normal to the steps (red arrow in Fig. 6). Thus the topmost band is completely filled in this direction leading to strong Umklapp scattering, to Fermi nesting and to gap opening of a gap of $\approx 30 \text{ meV}$. Only states close to $k_x = 0$ cross the Fermi level and lead to the 1d conductance observed at temperatures below 80 K. Fermi nesting is removed by warming up above this temperature due to changes in the average step separation coupled with disordering of the

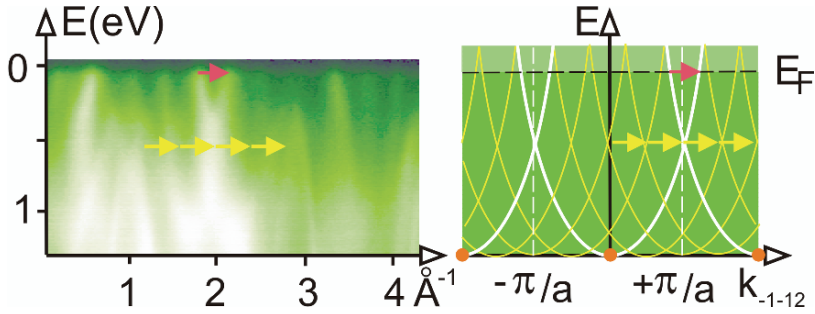


Fig. 6. left: Angular resolved photoemission data in the direction normal to the steps after adsorption of 1.3 ML of Pb on Si(557). b) Schematic of the Umklapp process leading to insulating behaviour in this direction (for details, see text).

regular step structure. This explains the reappearance of slightly anisotropic two-dimensional conductance above this temperature.

Concluding this section, 1d conductance in the example discussed here is the consequence of strong coupling between individual Pb wires on the small terraces. As a consequence, none of the instabilities typical for 1d systems is seen. In contrast to most known 1d conductors, our system is a metallic conductor at *low* temperatures that does not undergo any Peierls transition to an insulating state.

Acknowledgements

It is a pleasure to acknowledge the fruitful collaboration and stimulating discussions with all coworkers in my group, in particular with C. Tegenkamp, M. Czubanowski, G. Gardinowski and J. Schmeidel. I also thank K. Horn, T. Otha, J. McChesney and E. Rotenberg for their contributions to the ARPES measurements.

References

1. J.H. Dil, T.U. Kampen, B. Hülßen, T. Seyller, and K. Horn, Phys. Rev. B **75**, 161401(R) (2007)
2. V. Yeh, L. Berbil-Bautista, C.Z. Wang, K.M. Ho, and M.C. Tringides, Phys. Rev. Lett. **85**, 5158 (2000).
3. I. Vilfan and H. Pfnür, Eur. Phys. J. B **36** 2817 (2003)
4. J. Voit, Rep. Prog. Phys. **58**, 977 (1995).
5. J.R. Ahn, H.W. Yeom, H.S. Yoon, and I.-W. Lyo, Phys. Rev. Lett. **91**, 196403 (2003).
6. J.N. Crain, A. Kirakosian, K.N. Altmann, C. Bromberger, S.C. Erwin, J.L. McChesney, J.-L. Lin, and F.J. Himpsel, Phys. Rev. Lett. **90**, 176805 (2003).
7. J.N. Crain and F.J. Himpsel, Appl. Phys. A **82**, 431 (2006).

8. J.R. Ahn, J.H. Byun, H. Koh, E. Rotenberg, S.D. Kevan, H.W. Yeom, *Phys. Rev. Lett.* **93**, 106401 (2004).
9. R. Liu, S.-H. Ke, W. Yang, and H.U. Baranger, *J. Chem. Phys.* **124**, 24718 (2006)
10. K.-H. Müller, *Phys. Rev. B* **73**, 45403 (2006).
11. V. Zielasek, T. Block, H. Pfnür, *Rev. Adv. Mat. Sci.* **8**, 1 (2004).
12. J. Roenspies, T. Block, H. Pfnür, to be published.
13. S. Fujita, S. Maruno, H. Watanabe, M. Ichikawa, *J. Vac. Sci. Technol. B* **16**, 2817 (1998)
14. H. Pfnür, V. Zielasek, C. Tegenkamp, T. Block, Z. Kallassy, *Materials Science (Poland)* **23**, 861 (2005).
15. T. Block, H. Pfnür, *J. Appl. Phys.* **103**, 064303 (2008).
16. C. Kergueris, J.-P. Bourgoin, S. Palacib, D. Esteve, C. Urbina, M. Magoga, and C. Joachim, *Phys. Rev. B* **59**, 12505 (1999); K. Hansen and M. Brandbyge, *J. Appl. Phys.* **95**, 3582 (2004).
17. G. Gardinowski, J. Schmeidel, H. Pfnür, C. Tegenkamp, *Appl. Phys. Lett.* **89**, 063120 (2006).
18. M. Vollmann, H. Butenschön, *C. R. Chimie* **8**, 1282 (2005).
19. Bodenheimer et.al. *Chem. Phys. Lett.*, **3**, 715(1969).
20. W.H.A. Thijssen, D. Djukic, A.F. Otte, R.H. Bremmer, and J.M. van Ruitenbeek, *Phys. Rev. Lett.* **97**, 226806 (2006)
21. C. Tegenkamp, Z. Kallassy, H. Pfnür, H.-L. Günter, V. Zielasek, M. Henzler, *Phys. Rev. Lett.* **95**, 176804 (2005); C. Tegenkamp, Z. Kallassy, H.-L. Günter, V. Zielasek, H. Pfnür, *Eur. Phys. J. B* **43**, 557 (2005).
22. M. Czubanowski, A. Schuster, S. Akbari, H. Pfnür, C. Tegenkamp, *New J. Phys.* **9**, 338 (2007); C. Czubanowski, C. Tegenkamp, H. Pfnür, *Phys. Rev. B* **77** (2008) 174108
23. C. Tegenkamp, H. Pfnür, *Surf. Sci.* **601**, 2641 (2007).
24. C. Tegenkamp, T. Ohta, J.L. McChesney, H. Dil, E. Rothenberg, H. Pfnür, K. Horn, *Phys. Rev. Lett.* **100**, 076802 (2008)

Synthesis and Optical Properties of Colloidal CdS/CdSe/CdS Quantum Wells

Le Ba Hai¹, Nguyen Xuan Nghia¹, Pham Thu Nga², Vu Duc Chinh², Pham Thuy Linh² and Nguyen Thi Thu Trang¹

¹Cooperman Laboratory, Institute of Materials Science, Vietnamese Academy of Science and Technology, 18 Hoang Quoc Viet, Hanoi, Vietnam

²Laboratory for Materials and Engineering of Fibre Optics, Institute of Materials Science, Vietnamese Academy of Science and Technology, 18 Hoang Quoc Viet, Hanoi, Vietnam

Abstract. Colloidal CdS/CdSe/CdS quantum wells were synthesized from TOPSe and cadmium oleate in octadecene, a non-coordinating solvent. Absorption, emission, and Raman scattering spectra of colloidal CdS/CdSe/CdS quantum wells with different thickness of CdSe well were investigated. The effect of thickness of CdSe well on the optical and vibrational properties of colloidal CdS/CdSe/CdS quantum wells was discussed. The experimental results provide further evidence for the existence of quantum dot-quantum well structures in CdS/CdSe/CdS type materials.

1. Introduction

Semiconductor quantum dots (QDs) have been studied for over two decades. They are interesting from the point of view of basic physics since the carriers are confined to an essentially ‘zero’-dimensional structure. The efficient luminescence observed in some of these crystallites makes them promising candidates for use in optoelectronic devices. Further, the inexorable drive towards smaller and ever smaller devices makes them technologically significant. Besides the size miniaturization, surface effects are also known to influence the optical properties of these nanometre particles. To suppress surface effects, inorganic passivation has been utilized where the nanocrystals have been covered with a high-band-gap material [1].

The latter materials are composed of an internal semiconductor core that is coated with a shell of a different semiconductor material. Examples are the CdS core coated with a ZnS shell [2] and the CdSe core coated with ZnS or CdS shells [3-5]. Furthermore, there were reports on the synthesis of new and promising hetero-quantum dots (CdS/CdSe/CdS and CdS/HgS/CdS) consisting of CdS core in CdSe or HgS shell protected with outer cladding layers of CdS [6-8]. The wide band gap of CdS (2.5 eV) and narrow band gap of CdSe (1.74 eV) cause a localization of the electrons and holes within the CdSe internal layer. CdSe shell acts as a quantum well (QW) and the entire system as a quantum dot-quantum well (QDQW) [8].

In this paper we present the synthesis and optical properties of CdS/CdSe/CdS QDQW structures from TOPSe and cadmium oleate in octadecene, a non-coordinating solvent.

2. Experimental Methods

Chemicals. Cadmi Oxide (CdO), oleic acid (OA), sulfur (S), selen (Se), octadecene (ODE), tri-n-octylphosphine (TOP).

Synthesis. The synthesis route of the presented colloidal CdS/CdSe/CdS QWs can be separated in three main steps:

Step A: Growth of CdS core. A mixture of CdO, OA and ODE was heated to 300°C. A solution of S in ODE was injected into this hot solution and the reaction was allowed to cool to 250°C for 30 min to grow CdS core [9]. Aliquots were taken for the optical absorption measurements. The CdS core size was estimated from the first exciton peak position of the absorption spectrum.

Step B: The growth of CdSe well was achieved by following the established successive ion layer adsorption and reaction (SILAR) method [10]. For a typical SILAR process, the Cd injection solution (CdO dissolved with OA in ODE) and the Se injection solution (Se powder dissolved with TOP in ODE) were injected in an alternate fashion at 185°C. The quantity of well precursors added into the growth solution for each monolayer was based on the size of the nanocrystal templates, the concentration of the core nanocrystals in the solution, and the lattice constants of the crystal system [6].

Step C: The formation of CdS/CdSe/CdS QWs was achieved by alternating injections of Cd and S precursor solutions after growth of the quantum shells by using OA as the ligand. It was found that a higher reaction temperature (230–240°C) was necessary for the formation of the outer CdS layers than for the CdSe layers [6].

Removing free OA and unreacted Cd precursor by extracting with methanol purified the resulting colloidal QWs. They were then dispersed in ODE for measuring the absorption and PL spectra. CdS/CdSe/CdS QW samples were isolated from the solution by the centrifugation and then dried for Raman scattering measurement.

Measurements. The optical absorption spectra were recorded using Cary 5000 UV-Vis-NIR spectrometer (Varian). The photoluminescence (PL) spectra were measured by MicroSpec 2300i spectrometer using 325 nm excitation lines of He-Cd laser. The Raman scattering spectra were obtained in the back scattering configuration by LABRAM-1B (Jobin Yvon) with 632.8 nm excitation line of He-Ne laser. All the optical measurements were performed at room temperature.

3. Results and Discussion

Figure 1 shows the absorption spectra of typical CdS core, CdS/CdSe and CdS/CdSe/CdS structures. The energy schema of QW was determined from the differentiated absorption spectrum of CdS/CdSe/CdS structure as shown in Fig. 1. The absorption edges of the CdS core, CdSe well and outer CdS shell are shifted towards a lower wavelength region in comparison with those of the respective bulk crystals. These shifts were attributed to quantum confinement effect of the

carriers in CdS core and CdSe layer of CdS/CdSe and CdS/CdSe/CdS structure. It was found that the first absorption peak of the CdS core is shifted to longer wavelengths (~ 4 nm) after the coating by the CdSe well layer.

The PL spectra of CdS core, CdS/CdSe and CdS/CdSe/CdS structures were compared in Fig. 2. The emission bands in the longer wavelength region were caused by the surface states and/or the structural defects. In the shorter wavelength region the emission peak position of CdS/CdSe structure shifts towards a longer wavelength side in comparison with that of CdS core. Simultaneously, the PL intensity strongly increases when CdS/CdSe structure was covered by the outer CdS shell. The obtained results confirmed the formation of CdS/CdSe/CdS QDQW structure: CdS core was covered by CdSe layer and then by the outer CdS shell.

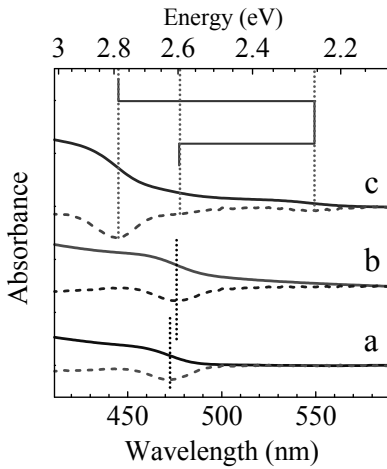


Fig. 1. Absorption spectra of CdS core (a), CdS/CdSe (b) and CdS/CdSe/CdS (c) structure. The dashed curves are the differentiated absorption spectra

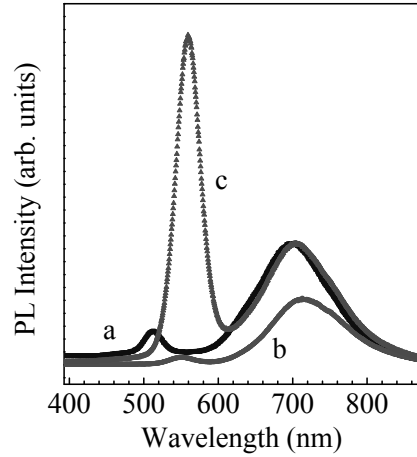


Fig. 2. PL spectra of CdS core (a), CdS/CdSe (b) and CdS/CdSe/CdS (c) structure

The thickness of CdSe layer was estimated based on the extinction coefficient. The extinction coefficient of the CdSe well was determined by the absorbance and the molar concentration of the particles in the solution from Beer's law [11]. The absorbance of the CdSe layer is to be determined from the peak position of the first absorption peak. Since this peak was not expressed its first derivative was used instead [12] as shown in Fig. 1.

The extinction coefficient per mole of the nanocrystals at the first absorption feature position was found to be approximately proportional to the well thickness for a given sized CdS core [6]. The size of CdS core was estimated from the absorption spectrum by Brus expression [13]:

$$E(R) = E_g + \frac{\hbar^2}{2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \frac{\pi^2}{R^2} - 1.786 \frac{e^2}{\epsilon R} - 0.248 E_{Ry} \quad (1)$$

where $E(R)$ is the band gap energy of CdS core; m_e^* , m_h^* is the effective mass of electron and hole, respectively; E_g is the band gap energy of bulk CdS crystal; R is the radius of the core; E_{Ry} is the effective Rydberg energy and ϵ is the dielectric constant.

The dependence of the extinction coefficient on the CdSe well thickness could be determined for a given sized CdS core using the linear interpolation.

Figure 3 shows typical absorption spectra of the colloidal CdS/CdSe/CdS QWs with the different thickness of CdSe layer (in unit of monolayer (ML)). The absorption edge shifts to the longer wavelength with increasing the thickness of CdSe layer in the QDQW structure.

Figure 4 presents the PL spectra of the colloidal CdS/CdSe/CdS QWs with the different thickness of CdSe layer. The PL peak positions vary in the range of 495–580 nm in dependence on the thickness of CdSe well layer. The full width at half maximum (FWHM) is in the range from 25 to 35 nm, indicating relatively narrow distribution of size.

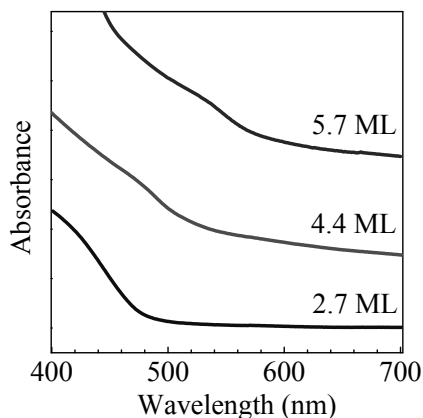


Fig. 3. Absorption and PL spectra of CdS/CdSe/CdS QDQW structure with the different thickness of CdSe layer

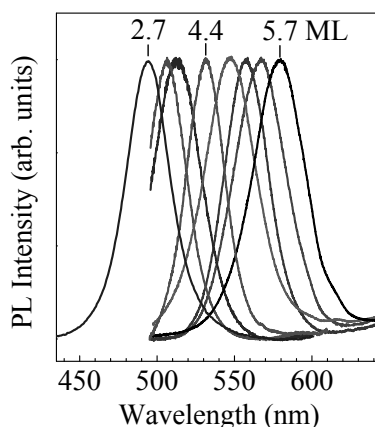


Fig. 4. PL spectra of synthesized colloidal CdS/CdSe/CdS QDQWs

The PL spectra of the colloidal CdS/CdSe/CdS QDQWs in the solution at various excitation intensities were investigated by using 488 nm excitation line of Ar^+ laser. The position and FWHM of the PL peaks for the given sample do not change noticeably with increasing laser power. However, the emission intensity increases with increasing excitation power (Fig. 5). The PL emission intensities as a function of the excitation power density are depicted in Fig. 6. The PL intensity exhibits a linear increase with excitation power in the low power density range up to approximately 2.8 W/cm^2 . At the higher power density, the PL intensity still linearly increases with pump power but with a lower angle coefficient as seen in Fig. 6. Using the relation $I \sim \text{Power}^K$, the obtained values of K are 1.0 and 0.75. It is possible that the emission rate of the QWs at low power density ($< 2.8 \text{ W/cm}^2$) is limited by the carrier generation rate (as determined by the excitation density) rather than the spontaneous emission lifetime of the QWs. At higher pump

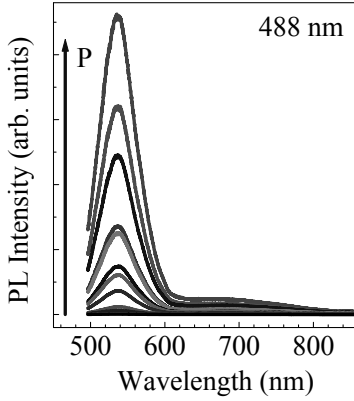


Fig. 5. The evolution of PL spectra of colloidal QWs with increasing excitation power density. The arrow shows the increase of excitation power density

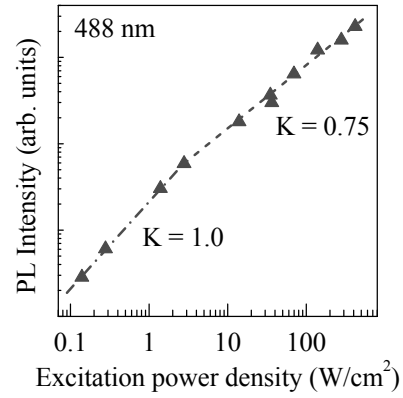


Fig. 6. The dependence of the emission intensity of colloidal CdS/CdSe/CdS QWs on the excitation power density

intensities, the emission rate is determined by the pump power, as well as the radiative lifetime of the QWs [14].

Figures 7a and 7b present the Raman spectra of CdS/CdSe and CdS/CdSe/CdS structures, respectively. Strong scattering due to the longitudinal optical (LO) phonon mode of the well and outer shell was observed. The LO peaks were shifted to lower frequency side in comparison with those of bulk CdSe (211 cm^{-1}) and CdS (306 cm^{-1}) crystals. In addition, these peaks were broadened asymmetrically in the low frequency part. This feature is related to quantum confinement of phonons in the low dimension semiconductors [15].

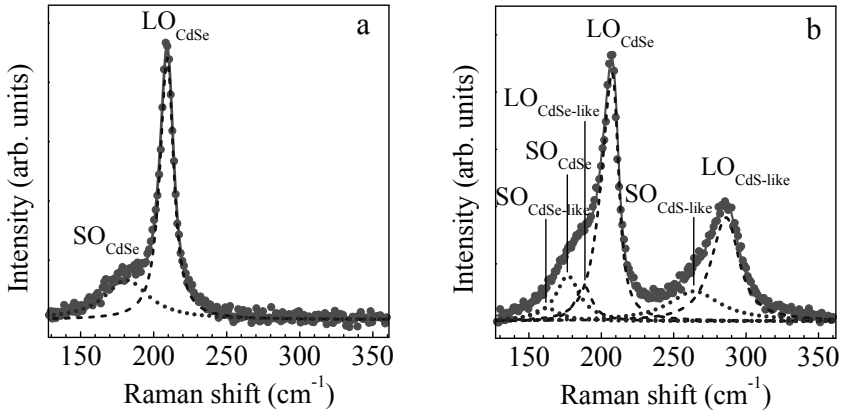


Fig. 7. Raman spectra of CdS/CdSe (a) and CdS/CdSe/CdS (b) structures. The spectra are fitted by applying the phonon confinement model of Campbell and Fauchet for LO modes (dashed lines) and Lorentzian function for SO modes (dash-dotted lines)

As seen in Fig. 7, there is a shoulder in low energy part of LO phonon contributing to the asymmetric lineshape of these peaks. This shoulder is assigned to the surface optical (SO) phonon mode [16]. In addition, the LO peak of the outer shell is at 286 cm^{-1} , which is very far from that of the bulk CdS crystal. This indicates that the outer shell of QDQW structure is not CdS, but $\text{CdS}_{1-x}\text{Se}_x$. It is possible that unreacted Se precursor leads to the formation of the outer $\text{CdS}_x\text{CdSe}_{1-x}$ shell.

In order to determine the thickness of CdSe well and outer $\text{CdS}_{1-x}\text{Se}_x$ layer in the heteronanostructures, the experimental Raman spectra were fitted by applying the phonon confinement model of Campbell and Fauchet [17] for LO_{CdSe} and LO_{CdSSe} mode. The intensity of LO mode $I_{\text{LO}}(\omega)$ is given by:

$$I_{\text{LO}}(\omega) = A \int_0^{q_{\text{max}}} \frac{dq |C(0, q)|^2}{[\omega - \omega(q)]^2 + \left(\frac{\Gamma}{2}\right)^2} \quad (2)$$

The LO lines was fitted with a combined shape $I(\omega) = I_{\text{LO}}(\omega) + I_{\text{SO}}(\omega)$, where $I_{\text{SO}}(\omega)$ is taken to be a Lorentzian function:

$$I_{\text{SO}}(\omega) = \frac{B\Gamma_{\text{SO}}}{(\omega - \omega_{\text{SO}})^2 + \Gamma_{\text{SO}}^2} \quad (3)$$

with ω_{SO} and Γ_{SO} are the peak position and the half width at half maximum (HWHM) of the SO mode, respectively.

The experimental Raman spectrum is fitted by the least square method using Matlab program. The Raman scattering intensity $I(\omega)$ is determined as a function of ω ; t , Γ , ω_{SO} , Γ_{SO} , A and B are the fitting parameters. Keeping in mind the simultaneous presence of the $\text{LO}_{\text{CdSe-like}}$ and $\text{LO}_{\text{CdS-like}}$ modes in the Raman spectrum of $\text{CdS}_{1-x}\text{Se}_x$ layer, we have attempted to fit the LO line of the outer shell with a combined shape of $\text{LO}_{\text{CdSe-like}}$ and $\text{LO}_{\text{CdS-like}}$ phonon modes.

The best fitting results for the Raman spectra of the CdS/CdSe and CdS/CdSe/CdS structure are shown by the solid lines in Figs. 7a and 7b, respectively. LO_{CdSe} , $\text{LO}_{\text{CdSe-like}}$ and $\text{LO}_{\text{CdS-like}}$ phonon modes are shown by dashed lines; a SO_{CdSe} , $\text{SO}_{\text{CdSe-like}}$ and $\text{SO}_{\text{CdS-like}}$ surface phonon modes by dotted lines. The thickness of the CdSe layer in the CdS/CdSe structure is about 7 ML. The thickness of the CdSe well and outer $\text{CdS}_{1-x}\text{Se}_x$ shell layer in CdS/CdSe/CdS structure are about 6 and 5 ML, respectively. The obtained thickness of CdSe well is in good agreement with that determined from absorption spectrum (the uppermost curve in Fig. 3). It is seen that the thickness of CdSe layer decreases after the coating of the CdS/CdSe structure by the outer shell. Practically, the shift of LO_{CdSe} peak of CdS/CdSe/CdS structure to lower frequency side in comparison with that of CdS/CdSe structure is due to the effect of the stress in the CdS/CdSe/CdS structure on the CdSe sandwich layer [18].

4. Conclusions

In summary, the colloidal CdS/CdSe/CdS quantum wells with different thickness of the CdSe well layer were synthesized by SILAR method. Their absorption, emission and Raman scattering spectra were investigated. The blue shift of the absorption edge and PL emission peak due to the size effect was observed. Similarly, the phonon confinement in colloidal quantum wells caused the shift of LO_{CdSe} , $LO_{CdSe-like}$ and $LO_{CdS-like}$ phonon lines toward lower frequency side in comparison with those of the bulk CdSe and $CdS_{1-x}Se_x$ semiconductors. The average thickness of the CdSe well layer determined by the absorption and Raman spectra are in good agreement. The dependence of PL emission intensity on the excitation power density shows two linear relationships with the different angle coefficients related to the different emission rates. The experimental results provide further evidence for the existence of quantum dot-quantum well structures in CdS/CdSe/CdS type materials. The unique properties of the colloidal quantum wells may have promising applications in optical devices such as LEDs and lasers.

Acknowledgements

This work was supported by the Vietnamese Fundamental Research Foundation. The experiments were performed at National Key Laboratory (Institute of Materials Science, Vietnamese Academy of Science and Technology).

References

1. V. Ranjan and V.A. Singh, *J. Phys.: Condens. Matter.* **13**, 8105, 2001.
2. J.S. Steckel, J.P. Zimmer, S. Coe-Sullivan, N.E. Stott, V. Bulovic, and M.G. Bawendi, *Angew. Chem. Int. Ed.* **43**, 2154, 2004.
3. B.O. Dabbousi, J. Rodriguez-Viejo, F.V. Mikulec, J.R. Heine, H. Mattoussi, R. Ober, K.F. Jensen, and M.G. Bawendi, *J. Phys. Chem. B* **101**, 9463, 1997.
4. D.V. Talapin, A.L. Rogach, A. Kornowski, M. Haase, and Weller, *Nano Lett.* **1**, 207, 2001.
5. J. Li, Y.A. Wang, W. Guo, J.C. Keay, T.D. Mishima, M.B. Johnson, and X. Peng, *J. Am.Chem. Soc.* **125**, 12567, 2003.
6. D. Battaglia, J.J. Li, Y. Wang, and X. Peng, *Angew. Chem. Int. Ed.* **42**, 5035, 2003.
7. M. Braun, C. Burda, and M.A. El-Sayed, *J. Phys. Chem.* **105**, 5548, 2001.
8. H.E. Porteanu, E. Lifshitz, M. Pflughoefft, A. Eycmuller, and H. Weller, *phys. stat. sol. (b)* **226**, 219, 2001.
9. W.W. Yu, and X. Peng, *Angew. Chem.* **114**, 2474, 2002.
10. A.U. Ubale, R.J. Dhokne, P.S. Chikhlikar, V.S. Sangawar, and D.K. Kulkarni, *Bull. Mater. Sci.* **29**, 165, 2006.
11. W.W. Yu, L. Qu, W. Guo, and X. Peng, *Chem. Mater.* **15**, 2854, 2003.
12. V. Protasenko, D. Bacinello, and M. Kuno, *J. Phys. Chem. B* **110**, 25322, 2006.
13. L.E. Brus, *J. Phys. Chem.* **90**, 2555, 1986.
14. J. Xu, D. Battaglia, X. Peng, and M. Xiao, *J. Opt. Soc. Am. B* **22**, 1112, 2005.

15. A. Tanaka, S. Onari, and T. Arai, Phys. Rev. B **45**, 6587, 1992.
16. A.V. Baranov, Phys. Rev. B **68**, 165306, 2003.
17. H. Campbell, P.M. Fauchet, Solid State Commun. **58**, 739, 1986.
18. R.W. Meulenberg, T. Jennings, and G.F. Strouse, Phys. Rev. B **70**, 235311, 2004.

Preparation and optical properties of one dimensional nano hydroxides and oxides

Lam thi Kieu Giang¹, Nguyen Vu¹, Dinh Xuan Loc¹, Man Hoai Nam¹, Gyu- Chul Yi², Tran Kim Anh¹ and Le Quoc Minh^{1,3}

¹ Institute of Materials Science, Vietnamese Academy of Science and Technology, 18 Hoang Quoc Viet Road, Cau Giay Distr., Hanoi, Vietnam
Email: anhtk@ims.vast.ac.vn

² Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790- 784, Korea

³ College of Technology, Vietnam National University, Hanoi, Vietnam

Abstract. The Yttrium hydroxide nanotubes and nanorods as well as the ZnO nanorods and nanowires were prepared by different methods. $Y(OH)_3$ nanotubes and nanorods were synthesized by polyol – mediation via the metastable precursor YCl_3 , PEG and were studied by FE SEM and XRD. The influence of the polymer molecular weights of PEG and the temperature were studied in detail. These results show that the first stage is nanorods, then it is followed by the formation of nanotubes. The outer diameter of the tubes is about 150 nm to 600 nm and interior hollow is in the range between 100 nm to 300 nm. The length of the rods and the tubes is up to several micrometers. We have found that the synthesis temperature, reaction rate and molecular weight of PEG induce the change in shape of obtained nanotubes from a cylindrical to a hexagonal appearance. The growth process of the nanotubes may be performed through three stages: first complexing the PEG polymer with $Y(NO_3)_3$, then hydrolysis for forming $Y(OH)_3$ nanorods and finally diffusion-controlled developing of $Y(OH)_3$ nanotubes. The ZnO nanorods were prepared by Chemical Vapor Deposition (CVD) and Metal Organic Chemical Vapor Deposition (MOCVD) method, respectively. Aligned growth of ZnO nanorods has been successfully prepared. The nanorods have the diameters of about 50 nm and the length of about 1.12 micrometers. The influence of the temperature is investigated. The luminescent spectra (excited by Cd-He laser at 325 nm) of ZnO nanorods at 10 K- 300 K was measured and investigated. The sharp peak is assigned to an exciton bound to a neutral donor.

Keywords: nanotubes, nanorods from $Y(OH)_3$, ZnO, PEG-polymer mediated synthesis, MOCVD, CVD

1. Introduction

Since carbon nanotubes have been discovered in 1991 till now, 1-dimensional (1-D) nanostructural materials have gained much of interests in material science. Rather than other low-dimensional nanomaterials like 0-dimensional quantum dots, which have been applied in the manufacture of nano-scale devices (quantum lasers, transistors, sensors, probes... etc.), or quantum wells, which have applications mainly in semiconductor physics, 1-D nanostructural materials are

accompanied with many peculiar and interesting applications in physics and devices manufacture. Due to their intrinsic anisotropic structure, 1-D nanostructures have been of interest in research and development of applications in manufacturing of functional materials, in optoelectronics and electronics, electromechanics, etc. [1-5].

There are many methods which have been developed to fabricate 1-D nanostructures like template-directed methods, growth of 1-D nanostructures from different phases and/or solutions, self-assembling methods, etc. [6, 7]. However, many of these methods are costly either in price or in time. In this paper, we present the fabrication of 1-D nanostructures of $Y(OH)_3$ –by using a polyol-mediated method. We have used the length of CH_2 links and hydrogen binding ability of PEG polymer and dynamic conditions to control the formation process of 1-D nanostructures of $Y(OH)_3$. The $Y(OH)_3$ – nanotubes could be converted to Y_2O_3 by using a special treatment at higher temperature.

The oxide lattice has proved to be an excellent host material for some of the most powerful laser built. The Y_2O_3 is characterized by low phonon frequencies which makes non-radiative relaxation of the excited states inefficient. ZnO nanorods also provide new opportunities for fundamental studies and applications. Especially in the last 10 years, major interests are focused on 1-dimensional nanostructures with hollow interior due to their peculiar and fascinating physical and chemical properties. Those are quite anomalous and interesting and show new phenomena in the field of material science. The low-dimensional structures such as nanowires, nanorods, nanotubes or nanobelts have been fabricated and studied by many research groups. ZnO nanorods have enhanced luminescence properties compared to other 1-dimensional nanostructures, and opened novel applications such as making new luminescence devices, new generation of displays and monitors, manufacturing of functional materials, new kinds of biosensors, emission labels in biology etc. In this paper we present two nanostructures of current interest. The first part deals with 1-D nanostructures of $Y(OH)_3$. The second part is about the preparation and the optical properties of ZnO nanorods and ZnO nanowires, which were prepared by Chemical Vapor Deposition (CVD) and Metal Organic Chemical Vapor Deposition (MOCVD).

2. Experiment

All used chemicals like NaOH, PEG with different molecular weight, $Y(NO_3)_3$, etc. were of analytical grade, with high purity (>99.9%) and used as received without further purification. Deionized water was used throughout. The micro autoclave instrument (MMM Med center Einrichtungen GmbH) allows the control of all heating processes by a programme in time and temperature; the minimum increment/decrement is $1^\circ C$.

The synthesis of Yttrium hydroxide nanorods and nanotubes were based on the preparation of colloidal hydroxide precipitates at room temperature and the subsequent hydrothermal treatment at $120-200^\circ C$ and reaction time from 16 to 50h.

Yttrium Nitrate and PEG ($M_w = 4000$) are mixed up and added by water with a desired concentration. The obtained mixture then is stirred continuously for 1h at

room temperature. Alkali hydroxide of 10% solution is used for pH control in order to reach a suitable pH value in the range of 8 to 14. The stirring is carried out for an additional half hour and then the mixture is filled into a Teflon container and put into the autoclave. The temperature of autoclave is maintained at the different temperatures from 120 to 200°C. The reaction time was lasted from 16 h to 50 h. The reaction product is cooled to room temperature. Then cleaning process of the obtained product is done by ultrasonic vibration, centrifugal separation and washing in de-ionized water. The product is dried at 60°C in air.

The morphology of the obtained product has been investigated by a FESEM (Hitachi at VAST) and a TEM (JEM- 1010 at National Institute of Hygiene and Epidemiology) instrument. The phase structures were revealed by X-ray diffraction measurements carried out on XRD systems Siemens D5000, D5005.

3. Results and Discussion

1. Construction of different one-dimensional nanoformations of yttrium hydroxide and yttrium oxide

XRD patterns have shown that most of the obtained products under these experimental conditions have hexagonal [$P6_{3/m}$] structures and the lattice constants got from calculation are $a = 6.2793$ and $c = 3.5472$. These values are highly compatible with standard ones ($a = 6.268$ and $c = 3.547$, 24-1422). Figure 1 shows the reflection patterns of $Y(OH)_3$ at 190°C.

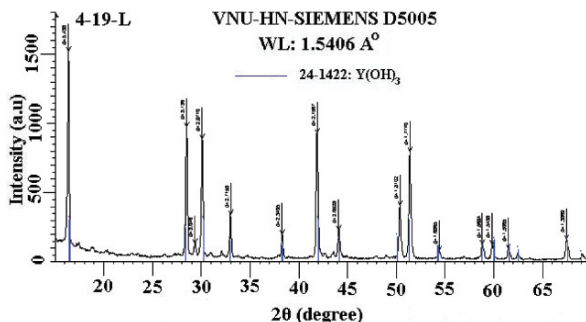


Fig. 1. XRD patterns of $Y(OH)_3$ nanorods and nanotubes at 190°C.

The morphology of $Y(OH)_3$ nanotubes has been investigated by FESEM and the result is shown in Figure 2.

In this synthesis one is able to control the morphology and dimensions of 1-D nanostructures by controlling dynamic condition of the process. When using small weight molecular-dimmed, diethylenglycol (DEG), the heating process can be performed only at 180°C to obtain spherical nanoparticles of Y_2O_3 with 5nm in size. However, with larger M_W of polymer chains ($M_W=4000$) and changing the pressure of the solution, the obtained products are 1-D nanostructures such as rods (at 170–180°C) and tubes (at 190–200°C) with diameters of 50–600 nm and

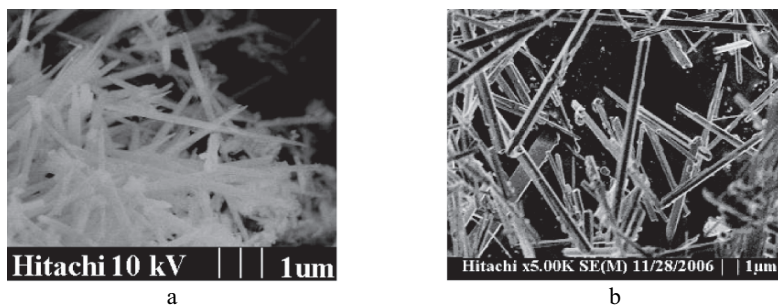


Fig. 2. FESEM images of $\text{Y}(\text{OH})_3$ nanorods and nanotubes which are prepared at the different temperatures. (a: 180°C; b: 190°C)

lengths of about tens μm . Ends of these nanotubes are opened and have hexagonal shape with inner diameters in the range of (150–300 nm) and outer ones in the range of (400–600 nm). Especially there is a change in the shape of the nanotubes from cylindrical cross-section to hexagonal one when temperature steps from 190°C to 200°C. XRD patterns show that obtained 1-D nanostructures of $\text{Y}(\text{OH})_3$ are in hexagonal phase [P63/m] with lattice constants $a = 0.6248 \text{ nm}$ and $c = 0.3525 \text{ nm}$. This is satisfied with the original values.

2. Formation mechanism of the $\text{Y}(\text{OH})_3$ nanotubes

The tubular shape of the obtained products were found by HRTEM and TEM investigations. The growth and formation processes of $\text{Y}(\text{OH})_3$ nanotubes have been studied by investigation of the samples at different conditions (120–200°C, 24–30h) and from the result, it can be concluded that the growth process of 1-D nanostructures may be performed as follows: the first stage is formation of metastable complexes between Y^{3+} and PEG in which, OH^- substitutes NO_3^- to form $\text{Y}(\text{OH})_3$. When the concentration of ions was high enough, they would aggregate to form small clusters or so-called growing nuclei through a homogeneous nucleation. Because of their antistrophic hexagonal structure, there was a tendency to grow into $\text{Y}(\text{OH})_3$ nanorods. In order to form perfect crystals, generally, it is needed to have reversible routes between nuclei at the surface and those in liquid phase. This condition allows the nuclei easily occupied suitable locations for crystallization in large scales, and controlling of adding rate of nuclei is essential to obtain crystals with homogeneous phase structure and shape. When the crystal has grown, dynamic diffusion will occur from the surface to the growing regions and become under saturation the central part of each nanorod. So when the consumption of $\text{Y}(\text{OH})_3$ reaches the end, it is naturally that nanotubes were formed as a result of dynamic diffusion. This growth process can be considered as a diffusion-controlled process. There are two directions of diffusion: radial diffusion and parallel diffusion [2]. The change from cylindrical shape to hexagonal shape occurs at a certain temperature can be explained as follows: at that temperature, the rate of parallel diffusion was at critical value.

3. ZnO nanorods morphology and photoluminescence

One-dimensional semiconductor nanorods and nanowires have attracted increasing interest due to their novel physical properties and diversity for potential electronic and photonic device applications [8-10]. ZnO nanorods were grown on Si (100) and Al_2O_3 (0001) substrates using metal organic chemical vapor deposition (MOCVD). The crystal structure and orientation of the ZnO nanorods was investigated by X-ray diffraction (XRD) including a θ -2 θ scan. The morphology of the samples was analyzed using field emission scanning electron microscopy (FE-SEM) equipped with a 4 axis motorized stage. The optical properties were investigated at room temperature and at low temperature.

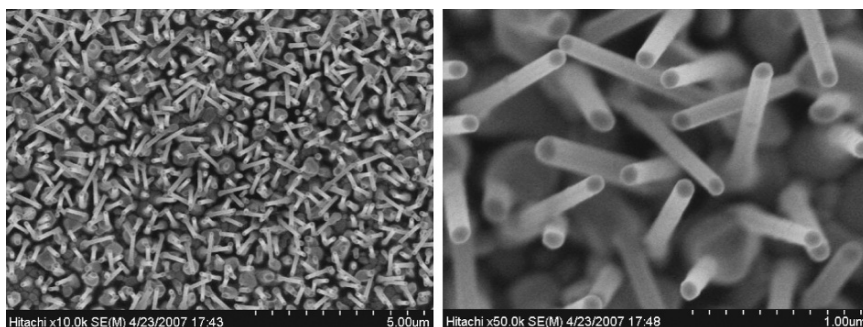


Fig. 3. FE-SEM images of ZnO sample prepared by CVD method 800°C 30 min.

Figure 3 presents FE-SEM images of ZnO sample prepared by the CVD method (800°C, 30 min.). Size and length of the nanorods depend on temperature and time as well as the method MOCVD or CVD, the distance between Zn nanopowder to the substrate, speed of argon flux, Au or Pt deposition on the Si wafer. The detail results will be presented in our other paper. In Figure 4 one can see images of FE-SEM ZnO nanorods prepared by MOCVD, sapphire substrate (left), ZnO nanorods at tempered 500°C for 1 hour (right).

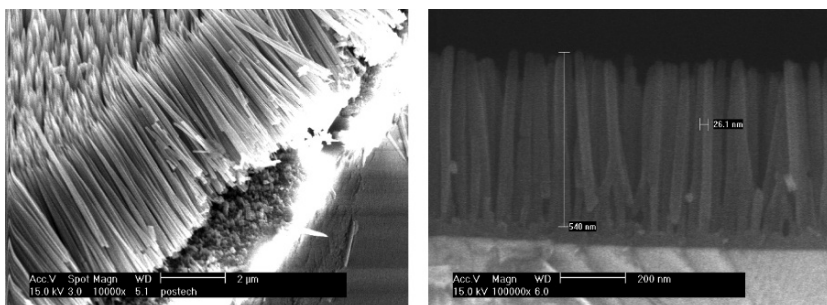


Fig. 4. FESEM ZnO nanorods MOCVD on sapphire substrate (left) and ZnO nanorods at 500°C for 1 hour (right)

The photoluminescent (PL) spectra were studied by using a Spectrapro 2300 monochromator as the dispersive unit, a Pixies 256 CCD as the detector, and a Kimmon He-Cd Laser (325 nm) as the excitation source. At room temperature a broad peak was observed at 3.312 eV with a low excitation intensity of 10 W/cm². This peak is attributed to the exciton transition bound to neutral acceptors or donor [11]. For the ZnO nanorods sample prepared by MOCVD at 500°C, with a growth time of 60 minutes, the PL spectra at low temperature (10 K) show peaks of 3.3473 eV, 3.3213 eV, 3.30186 eV, 3.2079 eV and 3.1113 eV [12]. Temperature dependance was observed in the range of 10 K to 300 K.

PL spectra of ZnO nanorods on sapphire substrate grown at 500°C for 1 hour by MOCVD and of ZnO sample prepared by CVD method at 800°C for 30 minutes were presented in Figure 5.

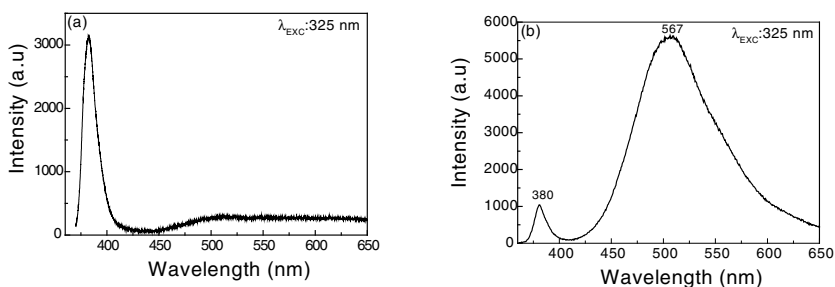


Fig. 5. PL spectra of ZnO Nanorods on sapphire substrate grown at 500°C for 1 hour by MOCVD (a) and ZnO sample prepared by CVD method 800°C 30 min. (b)

4. Conclusions

1-D nanostructures of $\text{Y}(\text{OH})_3$ with different constructions have been fabricated using a high efficient and high productivity synthesis method in polymer solutions of PEG. The obtained nanotubes have single-crystalline structure, open ends and hexagonal cross-sections with the sizes. Nanotubes have been obtained through heat treatment processes; the products were in hexagonal phase structure [P63/m] with lattice constants $a = 0.6248 \text{ nm}$ and $c = 0.3525 \text{ nm}$.

From the experimental results and current literatures, we propose the growth mechanism to forming these nanostructures is suggested as a three-stage process. Firstly, the complex is formed by PEG polymer and Yttrium Nitrate; the second step is formation of $\text{Y}(\text{OH})_3$ nanorods and the third one is developing $\text{Y}(\text{OH})_3$ nanotubes when the temperature increases. The growth mechanism of these nanostructures can be understood and explained as a three-stages process includes complexation of PEG and Yttrium Nitrate, formation of $\text{Y}(\text{OH})_3$ nanorods and, developing nanotubes, finally.

In this paper, we have briefly presented an effective route to synthesize ZnO nanorods. We have obtained ZnO nanorods with diameters in the range from 20 - 50 nm via MOCVD. The length is about 540 nm to 1.12 micrometer. ZnO

nanorods have strong luminescence in blue region. ZnO/ZnMgO nanomaterials are also prepared. We have successfully prepared ZnO nanomaterials by CVD method and studied FE-SEM images and optical properties.

Acknowledgements

We thank the financial support from the Vietnam-NSF on Physics Science, Basic research programmes CB 19, CB 20 and Key Laboratory of Electronic Materials and Devices.

References

1. Y. P. Fang, A. W. Xu, L. P. You, R. Q. Song, J. C. Yu, H. X. Zhang, Q. Li, H. Q. Liu, *Adv. Funct. Mater.*, Vol. 13, No. 12, December, (2003), 955- 960.
2. Q. Tang, Z. Liu, S. Li, S. Zhang, X. Liu, Y. Qian, *Journal of Crystal Growth*, Vol. 259 (2003), 208-214.
3. X. Wang, X. Sun, D. Yu, B. Zou, Y. D. Li, *Adv. Mater.*, Vol. 15, No. 17, September 3 (2003), 1442 – 1445.
4. T. Kim Anh, L.T. Kieu Giang, N. Vu, M. Hoai Nam, David Hui and L. Quoc Minh, *Proceedings of ICCE 14*, Colorado, USA, 2-8 July, 2006, 666-669.
5. J. Zhang, Z. Liu, J. Lin, J. Fang, *Crystal Growth & Design*, Vol. 5, No. 4, (2005), 1527-1530.
6. X. Wang, Y. D. Li, *Chem. Eur. J.*, Vol. 9, (2003), 5627-5635.
7. Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, *Adv. Mater.* Vol. 15, No. 5, March 4, (2003), 353 – 389.
8. Cai-Ling Xu, Dong-Huan Qin, Hua Li, Yun Guo, Tao Xu, Hu-Lin Li, *Materials Letters* **58** (2004) 3976 – 3979.
9. K.Yamamoto, K. Nagasawa and T. Ohmori, *Physica E: Low-dimensional Systems and Nanostructures*, June 2004.
10. Gyu –Chul Yi, Chunrui Wang and Won Il Park, *Semicond.Sci.Technol.* **20** (2005) S22-S34.
11. M. Hoai Nam, D. Xuan Loc, N. Thanh Ngan, L. T Cat Tuong, N. Vu, L.Quoc Minh, T. Kim Anh, *Proceedings of the 1st IWOFM-3rd IWONN Conference*, Halong, 2006, 703-705.
12. T.Kim Anh, L.T.Kieu Giang, L.D Tuyen, N.Vu, M.Hoai Nam, L.T Cat Tuong, N.Thanh Ngan, N.Huu Quan, L.Quoc Minh, *Proceedings of the 1st IWOFM-3rd IWONN Conference*, Halong, 2006, 424-427.

Hydrothermal Synthesis and Photocatalytic Properties of TiO₂ Nanotubes

D.D. Vuong, D.T.N. Tram, P.Q. Pho, and N.D. Chien

Institute of Engineering Physics, Hanoi University of Technology, Hanoi, Vietnam

E-mail: vuongdd-iep@mail.hut.edu.vn

Abstract. TiO₂ nanotubes (TNTs) were prepared by a hydrothermal treatment method at low temperatures. The source materials, annealing temperature and hydrothermal treatment time play important roles in the morphology, structure and photocatalytic behavior of TiO₂ nanotubes. The scanning electron microscopy (SEM) and the transmission electron microscopy (TEM) images indicate that the diameter of the nanotubes is 10–20 nm. The experimental results show that the morphology and structure of the nanotubes is thermally unstable. The photocatalytic activities of the TiO₂ nanotubes were also characterized by the decolorization of methylene blue under UV radiation.

1. Introduction

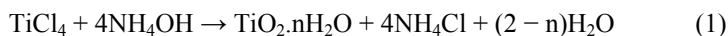
Titanium oxide is an n-type semiconductor and a typical photocatalyst, attracting much attention from both fundamental and practical viewpoints. It has been used in many industrial areas including environmental purification, antibacterial, solar cells, gas sensors, pigments and cosmetics [1,2]. To explore novel approaches for the nanostructured titania of various nature with the control of as well the particle size in nanometer-scale and the morphology is quite interesting, since the performance of titania in its various applications depends on its crystalline phase state, dimensions and morphology [3]. TiO₂ nanotubes are a novel and an intensively studied class of structurally organized, nanosized materials, having potentially a wide area of applications. Titania nanotubes of different geometrical shapes and microstructures have been fabricated by various methods, like sol–gel, anodization, electrodeposition, sonochemical deposition, or other methods involving the chemical treatment of fine titania particles [4–6]. Referring to [7] TiO₂ nanotubes with diameters of 70–100 nm were produced through a sol–gel processing. Zhao Jianling et al. [8] fabricated titanium oxide nanotube arrays by anodic oxidation. Here the nanotubes had an inner diameter of 100 nm and the length of 200 nm. Kasuga et al. [9,10] reported the first evidence that titanium oxide nanotubes with the diameter of 8 nm and length of 100 nm could be obtained via chemical treatment. Recently, it is shown that for TiO₂ nanotubes produced by the method of alkali hydrothermal treatment, the possible mechanisms of nanotube formation is based on the key stage of wrapping of intermediate multilayered titanate nanosheets. The driving force for wrapping is considered to be the mechanical stress arising during crystallisation/dissolution.

In this paper, we report the preparation of titanium oxide nanotubes by a hydrothermal soft-chemical process. By this method, we can easily control a

variety of parameters such as temperature, pressure, process time, concentration of chemical species, concentration of the solutions, pH and starting compounds. The relationship between the particle morphology, the phase composition, the properties of the products, and the processing parameters is discussed. It is also found that these nanoparticles can be shape-controlled by the hydrothermal temperature and the crystallization of TiO_2 precursors.

2. Experimental Procedure

Titanium hydroxide precipitates were obtained by adding ammonia solution dropwise to the aqueous TiCl_4 solution.



The resulting precipitate was washed thoroughly by repeating the procedures of suspending the gel into deionized water and collecting it back by filtration or centrifugation to remove Cl^- . The obtained precipitates (wet gel) were divided into four batches. The first batch was directly digested in a 10M NaOH solution at 150°C for 20h. The remaining ones were dried and heat-treated at 450°C , 500°C or 600°C for 3h to obtained TiO_2 powders. These powders were mixed with 10M NaOH solution, followed by hydrothermal treatment in an autoclave at 150°C for 20h.

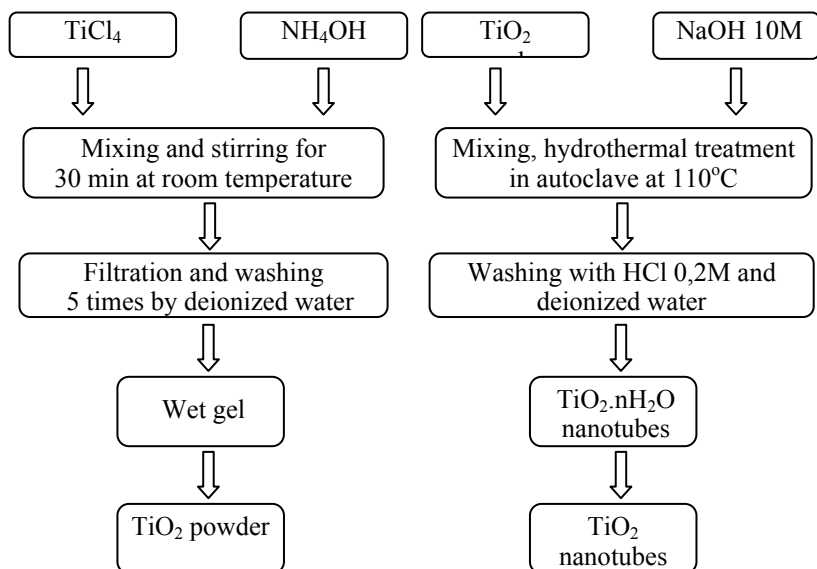


Fig. 1. Diagrams of preparation TiO_2 nanoparticles and TiO_2 nanotubes

The treated powders were washed thoroughly with deionized water and a 0.2M HCl aqueous solution until the pH value of the washing solution was lower than 7 and the solid had a white color. The precipitates were further washed by deionized water and dried at 100°C for 24h. After that, the obtained powders were calcined at high temperatures for studying the effects of calcination conditions on the morphology and structures of the material.

The crystals of the prepared precursors and the products were analyzed by powder X-ray diffractometer (Bruker D8 Advance) using CuK α radiation ($\lambda = 1.54056\text{\AA}$). Inspection of the morphology and characterization of the powders and the nanotubes were performed by a transmission electron microscopy (JEOL JEM-100CX) and field emission scanning electron microscopy (FESEM - Hiatchi S4800). The TEM investigation was performed at 80kV. The samples for TEM observation were ultrasonically dispersed in ethanol and a drop of this solution was then placed onto a carbon film supported copper grid.

Photocatalytic activity of the specimens was evaluated by measurement of degradation of methylene blue. Photocatalytic degradation of methylene blue was performed as follows: A Pyrex reactor with the size 30 mm lengths, 60 mm width and 10 mm thickness contained 200 ml of an aqueous solution of MB, 0.05 mM, and 0.5 g catalyst. The reactor was illuminated with UV-irradiation (15 W) with a dominant wave length in the range of 300 nm $\div$ 400 nm. The degradation was monitored by sampling 2 ml at various time intervals, while the absorbance was measured on a UV-visible double beam spectrophotometer.

3. Results and Discussion

3.1 Preparation of TiO₂ Nanopowders

The wet gel (titanium hydroxide) was synthesized by hydrolyzing titanium chloride with ammonia. The structures of the powders after drying at 100°C for 24h and heat treatment at high temperature are shown in figure 2. The XRD patterns of the

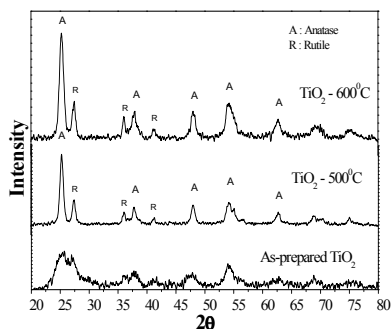


Fig. 2. XRD patterns of TiO₂ after drying and heat treatment at 500°C and 600°C for 3h

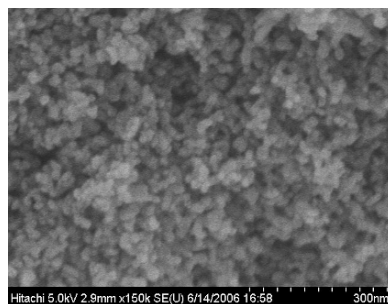


Fig. 3. FESEM image of the surface of TiO₂ nanopowder after heat treatment at 600°C for 3h

powders after calcination at 500°C and 600°C indicate that the nanoparticles are well-crystallised anatase titania with a minor rutile phase. FESEM image of the TiO₂ powder after calcination at 600°C for 3h shows that these nanoparticles are spherical with an average size of around 20 nm (figure 3).

3.2 Preparation of Titanate Nanotubes

In a typical nanotube preparation, a weighted precursor material tantamount with 1g of TiO₂ was mixed with 10 ml of 10M NaOH solution, followed by hydrothermal treatment of the mixture at 150°C in a 30 ml Teflon-lined autoclave for a desired time. The effects of starting material and post treated temperature of the powders after hydrothermal treatment on the structure and morphology of the products were investigated.

3.2.1. Effects of Starting Materials on the Formation of TiO₂ Nanotubes

As we have known, the starting materials of TiO₂ play an important role in fabricating the TNTs. Figure 4 shows the FESEM image of TiO₂ powder collected from a titanium hydroxide mixing with sodium solution and a hydrothermal treatment at 150°C for 20h. It has been shown that the TiO₂ nanotubes with the diameter of 10 nm and the length in the range of 50–70 nm were observed. For the sample derived from commercial TiO₂ nanopowder (P25 - anatase), the surface morphology of the powder show that various morphologies were obtained (figure 5). The typical structure was fibrillar. The length of the fibrillar titania is about several micrometer and the diameter is in the range of 50–300 nm.

The wet gel was dried and calcined at high temperature to obtain TiO₂ nanopowder. FESEM images of as-prepared TiO₂ nanotube derived from TiO₂ nanopowder after calcination at 500°C for 3h were shown in figure 6. In this case, the length of as-prepared TiO₂ nanotubes is about several hundred nanometers and the diameter is about 15 nm. Figure 7 shows TEM images of as-prepared TiO₂ nanotubes synthesized from in-house TiO₂ nanopowder after heat treatment at 500°C and hydrothermal treatment at 150°C for 20h and further calcination at 500°C for 1h.

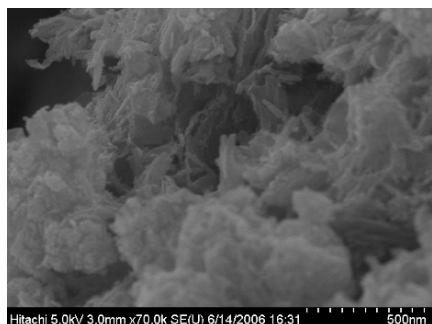


Fig. 4. FESEM image of TiO₂ nanotubes derived from wet gel and hydrothermal treatment at 150°C for 20h

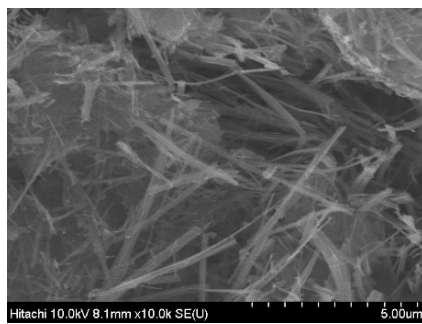


Fig. 5. FESEM image of TiO₂ nanotubes derived from commercial TiO₂ (P25) and hydrothermal treatment at 150°C for 20h

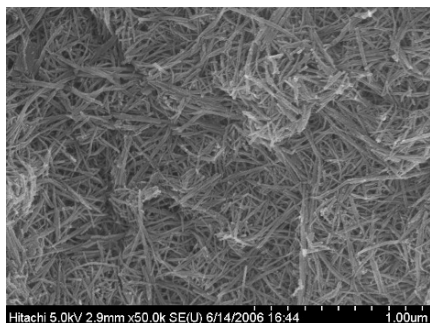


Fig. 6. FESEM image of as-prepared TNTs derived from in-house TiO₂ after calcination at 500°C and hydrothermal treatment at 150°C for 20h

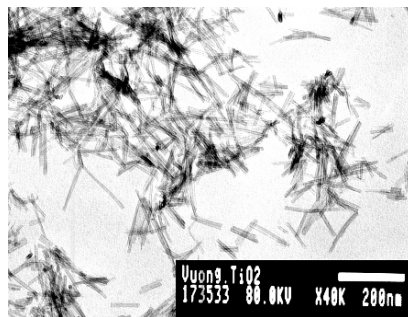
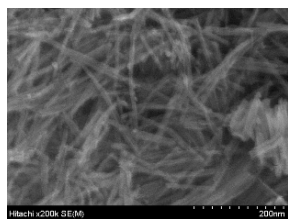


Fig. 7. TEM image of TNTs synthesized at 150°C and further calcined at 500°C for 1h

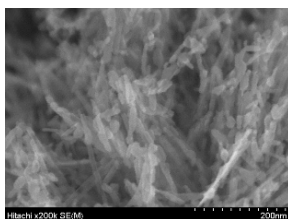
Due to our experimental results, the titania nanotubes derived from in-house TiO₂ nanopowder form nanotubes of better quantity as the ones built by commercial TiO₂ (p25) or directly from wet gel. In the following sections, we discuss the effects of annealing temperature on the properties of TiO₂ nanotubes.

3.2.1. Effects of Annealing on the Structure and Surface Morphology of TiO₂ Nanotubes

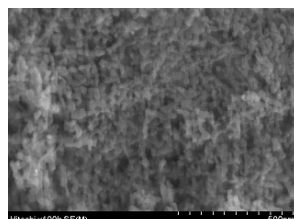
Heat treatment also affects the microstructure and phase structure of the nanotube products. The TiO₂ nanotubes derived from in-house TiO₂ powder after annealing at 500°C and hydrothermal treatment at 150°C for 20h were heat treated at each temperature for 1h. The FESEM images observed from figure 6 and 8 indicate that with an increase in annealing temperature, the tubes were cracked, shrank and became particles. XRD results (figure 9) demonstrate that the crystallinity of the resultant nanotubes increases with the increase of heat treatment temperature with one anatase phase.



(a) heat- treated at 400°C



(b) heat-treated at 500°C



(c) heat- treated at 600°C

Fig. 8. FESEM image of TiO₂ nanotubes derived from in-house TiO₂ after calcination at 500°C hydrothermal treatment at 150°C for 20h and heat- treated for 1h at various temperature

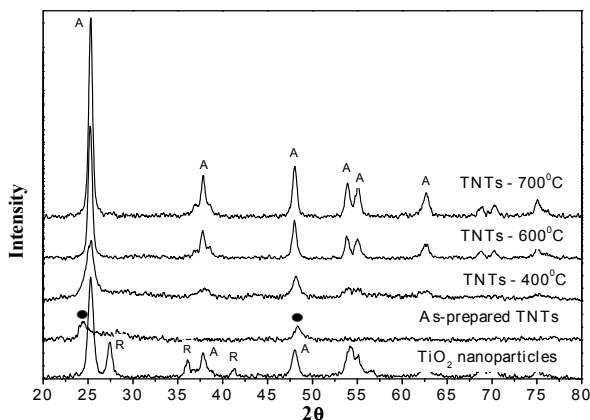


Fig. 9. XRD patterns of the starting materials TiO₂ and nanotubes products without heat treatment and those heat-treated at 400°C, 600°C and 800°C, respectively

3.3 Measurement of Photocatalytic Activity

Methylene blue (MB) has been used widely in researching the ability of the photocatalytic activity of TiO₂. The kinetics of the photocatalytic degradation of MB in an aqueous solution was investigated by Kwon et al. [11]. The photocatalytic activities of the TiO₂ nanoparticles powder, as-prepared titanate nanotubes and heat-treated TiO₂ nanotubes for 1h were evaluated by photocatalytic discolorization of the methylene blue aqueous solution. Photocatalytic degradation of MB on the products was studied at room temperature and pH 8. The concentration of un-decomposed MB at various time intervals during UV irradiation and the kinetics of photocatalytic degradation of MB were investigated (figures 10 and 11).

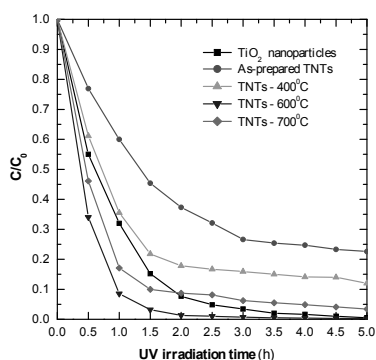


Fig. 10. Photocatalytic degradation of MB using in-house catalysts

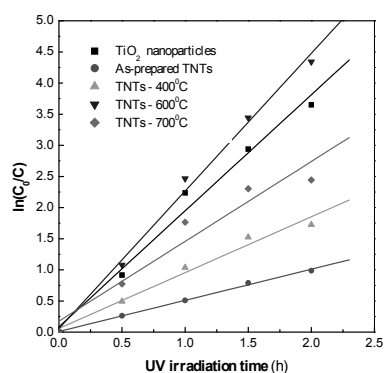


Fig. 11. Kinetics of photocatalytic degradation of methylene blue

The apparent first-order rate constant was calculated from the slopes of straight lines corresponding with the plot of $\log C_0/C$ versus time. The results show that the photocatalytic activity of TiO₂ nanotubes increases with the increase of heat treated temperature until 600°C. In comparison, the photocatalytic activity of titanate nanotubes after heat treatment at 600°C was the highest in our experiments. This is due to the fact that the TiO₂ nanotubes show better crystallization in anatase phase. With further increase in the annealing temperature, the photocatalytic activity of the sample decreases owing to the fact that the tubes were shrank and became particles, so the specific surface area of the product decreases.

4. Conclusions

In conclusion, titanium oxide nanoparticles and nanotubes were successfully prepared from titanium chloride as a starting material. TiO₂ nanotubes have been synthesized by a hydrothermally treatment method. The effects of starting material and post treatment temperature of the powders after the hydrothermal treatment on the structure and morphology of the products were also investigated. The morphology and the structure of the nanotubes are thermally unstable. The photocatalytic activities of titanium oxide powders were discussed.

Acknowledgements

This work was supported by the National Fundamental Research Programme on Natural Science (project code B2006-58-1 and B405006).

References

1. Z.Y. Yuan, B.L. Su, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 241, 173, 2004.
2. Y. Ma, Y. Lin, X. Xiao, X. Zhou, X. Li, *Mater. Res. Bulletin*, 41, 237, 2006.
3. O. Carp, C. L. Huisman, A. Reller, *Prog. in Solid State Chem.*, 32, 33, 2004.
4. P. Billik and G. Plesch, *Scripta Materialia*, 56, 979, 2007.
5. S. Mahshid, M. Askari, M. S. Ghamsari, *J. Mat. Proc. Tech.*, 189, 296, 2007.
6. W. Li, T. Fu, F. Xie, S. Yu, S. He, *Materials Letters* 61, 730, 2007.
7. P. Hoyer, *Langmuir*, 12, 141, 1996.
8. H. Imai, Y. Takei, K. Shimizu, M. Matsuda, H. Hirashima, *J. Mater. Chem.*, 9, 2971, 1999.
9. T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, *Langmuir*, 14, 3160, 1998.
10. T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, *Adv. Mater.* 11, 1307, 1999.
11. C.H. Kwon, H. Shin, J.H. Kim, W. S. Choi, K.H. Yoon, *J. Mater. Chem.*, 86, 78, 2004.

UHV Studies on CO and Methanol Adsorption and Decomposition on Pristine and Oxidized Alumina-Supported Co Nanoparticles

T. Nowitzki, V. Zielasek, and M. Bäumer

Institut für Angewandte und Physikalische Chemie, Universität Bremen,
Postfach 330440, 28334 Bremen, Germany

Abstract. Although cobalt is an important Fischer-Tropsch catalyst, there is only limited fundamental knowledge about the factors determining the elementary steps, such as the dissociation of CO, the influence of adsorbed oxygen and the formation of oxygenates as by-products. To contribute to a deeper understanding in that respect, a well-defined model consisting of Co nanoparticles supported on an epitaxial alumina film has been studied under UHV conditions. The adsorption properties of these particles have been characterized by temperature-programmed desorption (TPD) spectroscopy and photoelectron spectroscopy. The results show that a significant part of adsorbed CO dissociates on the particles and that oxygen has a drastic influence on the CO adsorption by weakening the adsorbate-particle interaction. In case of large oxygen amounts, CoO forms which could not be reduced in our experiments, neither by CO nor by hydrogen. Additionally, the decomposition of methanol (as a possible by-product in the Fischer-Tropsch reaction) has been studied. Here, complete dehydrogenation to carbon monoxide and hydrogen was observed. Therefore, according to the principle of microscopic reversibility, there must be a possible pathway of methanol formation on Co, i.e., a CO hydrogenation route without C-O bond scission.

1. Introduction

Due to the foreseeable exhaustion of the reserves of fossil energy carriers, like natural gas and petroleum, routes for their regeneration are under active discussion today. In this context, the synthesis of synthetic fuels and methanol from synthesis gas are highly interesting technologies. Note that a large potential in solving future energy problems is ascribed to methanol in particular [1]. Therefore, the underlying Fischer-Tropsch (FT) chemistry which was already discovered in the 1920s [2] currently attracts considerable attention as it allows the controlled conversion of carbon monoxide and hydrogen into hydrocarbons and oxygenates in presence of a suitable catalyst. In general, two reaction pathways are discussed in the literature for FT-processes (see [3] and references therein). The first pathway consists of the direct hydrogenation of adsorbed carbon monoxide molecules to oxygen containing species on the catalyst surface (surface carbonate mechanism) leading to alcohols or after removal of oxygen to hydrocarbons. In the second reaction route, molecular carbon monoxide is dissociated on the catalyst first and the resulting carbon species is then hydrogenated (surface carbide mechanism). Which factors govern the various pathways is still not fully understood.

One catalytically active material broadly used in the FT process is Co [2, 4–5]. To find out under which conditions carbon monoxide adsorbs only molecularly or dissociatively on Co is of considerable interest because of the above mentioned reaction pathways. Under ultrahigh vacuum conditions, only molecular adsorption was found on densely packed surfaces, such as Co(0001) and Co(1-10) [6–8]. Interestingly, such surfaces could be activated for carbon monoxide dissociation by co-deposition of magnesia [9] or by sputtering with argon ions [10]. For higher-index surfaces, such as Co(11-20) [6] and Co(10-12) [11,12] evidence for dissociation was found after heating to ~ 360 K and to ~ 470 K, respectively. These findings suggest a high importance of low-coordinated surface atoms for the dissociation of carbon monoxide.

Furthermore, the influence of oxygen on the adsorption of carbon monoxide on Co is worth being studied because oxidation of the catalyst can cause deactivation [13, 14]. The interaction of oxygen with Co was studied under UHV conditions mainly on single-crystalline surfaces [15–19]. The results show that oxidation takes place easily. For Co(0001) oxidation to Co oxide was reported even at room temperature [15, 16].

Important by-products of the FT process are alcohols [3] (for Co catalysts see ref. [20]). Methanol has a special role as it is the direct hydrogenation product of CO ($\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$). Unfortunately, synthesis reactions are difficult to investigate under ultrahigh vacuum conditions due to thermodynamic reasons, in contrast to the reverse reaction [21]. Because of the principle of microscopic reversibility, studying the decomposition of methanol can provide mechanistic information about the synthesis. With respect to Co, however, there is only limited fundamental knowledge about the interaction with methanol. Regarding its adsorption and decomposition, only a few results can be found in the literature: only singly crystal surfaces have been investigated so far [22].

Recently, we started work on supported Co particles under UHV conditions in order to contribute to a microscopic understanding of these various issues relevant for the FT process on Co. In this context, the morphology [23] and thermal stability [24, 25] of Co nanoparticles on thin alumina films was studied as well as the oxidation behavior [26] and the interaction with carbon monoxide and methanol [27, 28].

In this report, we will summarize data obtained by temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) for Co nanoparticles on thin alumina films shedding light on the *dissociation of carbon monoxide*, the *influence of oxygen* on the adsorption and the *decomposition of methanol*.

2. Experimental

All results presented in this articles were obtained for Co nanoparticles prepared under ultrahigh vacuum conditions by physical vapor deposition on a thin alumina film grown on a NiAl(110) single-crystal. Details of the experimental apparatus [29], the film and particle preparation [23, 30] and the experimental parameters

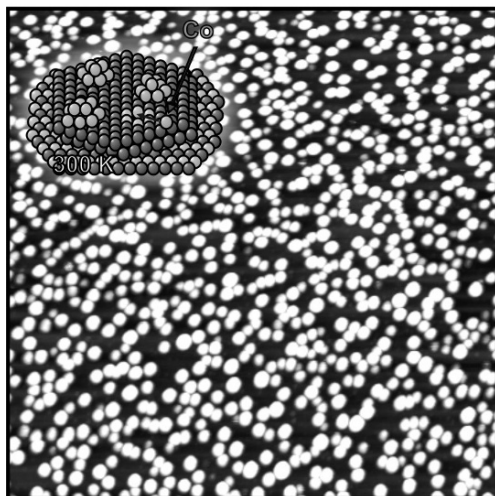


Fig. 1. STM micrograph of 0.2 nm Co deposited on a thin alumina film grown on NiAl(110) (taken from [32])

[26, 28] can be found in the literature. The amount of Co deposited onto the surface is given as a nominal film thickness as measured with a quartz microbalance. The experiments described in the following have been performed with either 0.2 nm or 0.4 nm Co. The 0.2 nm deposit corresponds to an ensemble of non-crystalline particles with a mean diameter of ~ 2.4 nm as determined with scanning tunneling microscopy [31]. Assuming a constant island density and hemispherical particles, a mean diameter of 3.0 nm is estimated for the 0.4 nm deposit. Figure 1 shows a STM micrograph of a 0.2 nm Co deposit taken from ref. [32].

3. Results and Discussion

3.1 Carbon Monoxide Dissociation

The interaction of the Co deposits (0.4 nm) with carbon monoxide was studied by TPD after saturating the surface with 10 L ($L = \text{Langmuir} = 10^{-6} \text{ Torr}\cdot\text{s}$) CO at 115 K. The obtained spectrum is plotted in figure 2 (a), trace (1). (Note that the alumina film has no adsorption above 100 K). Two desorption peaks are clearly visible at ~ 390 K and ~ 270 K, which have previously been assigned to terminally bonded CO and a multi-linear carbonyl species of the type $\text{Co}(\text{CO})_n$ ($n = 3, 4$), respectively [27]. Afterwards, the sample was exposed to 1000 L of oxygen at 300 K and again heated (*without* any carbon monoxide exposure). The corresponding spectrum is also presented in figure 2 (a), trace (2). A desorption peak is detectable above 500 K where no signal was found for pristine particles. Moreover, no such signal is found for the CO adsorption of oxygen pretreated

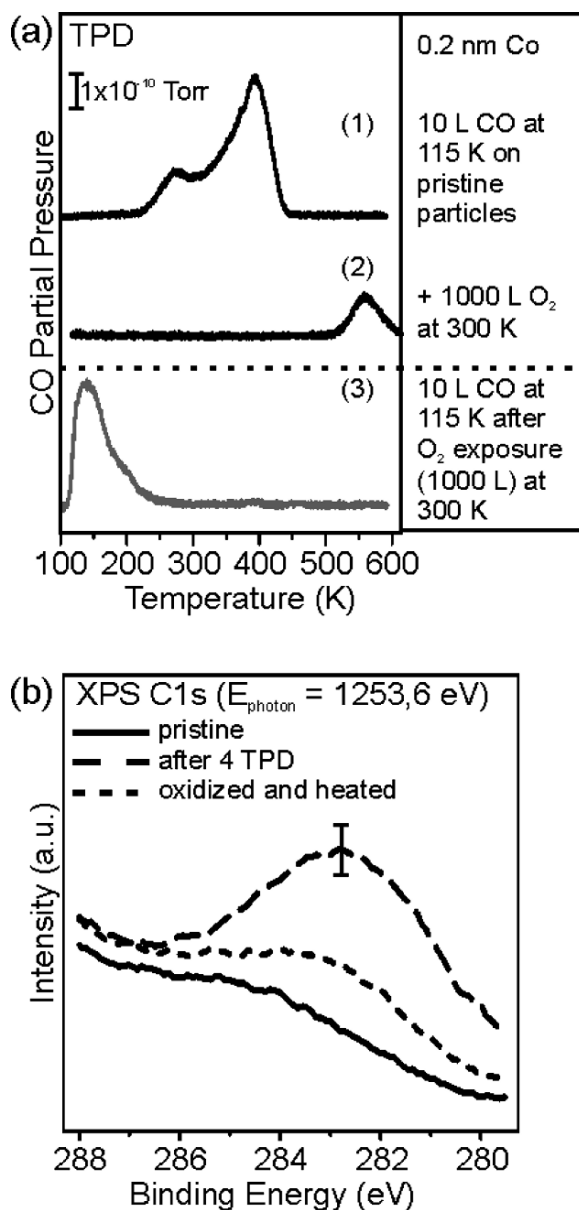


Fig. 2. (a) TPD spectra recorded after exposure of Co particles to 10 L CO at 115 K: (1) spectrum for pristine particles (2) spectrum for particles subjected to a first CO TPD and *subsequently* oxidized by exposing them to 1000 L oxygen at 300 K; (3) spectrum for particles oxidized *before* CO adsorption. (b) C1s XP spectra for pristine particles, particles subjected to several CO TPD as well as for particles finally treated with oxygen and heated

particles, which can be seen in the gray spectrum (3) showing only desorption below 250 K.

To elucidate the origin of the high temperature peak, XP spectroscopy was employed. Figure 2 (b) shows XP spectra of the C 1s binding energy region after excitation with radiation from a Mg K α anode. For the pristine particles only a very small signal is detected in that region (solid line). After recording a series of CO TPD runs, a peak has become clearly discernable at $\sim$ 282-283 eV suggesting that carbon is generated and accumulated on the surface by CO dissociation during the TPD runs. In the literature, carbon signals with a comparable binding energy on Co were assigned to carbidic carbon [10] which is thought to be the relevant species for the surface carbide mechanism in the FT process. After exposing the sample to oxygen at 300 K and heating to 600 K the intensity is mostly reduced, indicating that carbon has left the surface. Therefore, the high temperature peak observed in the corresponding TPD spectrum can be assigned to recombination of the carbon generated by carbon monoxide dissociation with the oxygen exposed to the sample.

Our results prove that CO can dissociate on small Co particles, the ratio between molecular adsorption and dissociation being approximately 6: 1. In agreement with the findings on rough single crystal surfaces, this suggests that a high number of low-coordinated sites is important for significant carbon generation.

3.2 Influence of Oxygen Pre-Treatment on the Carbon Monoxide Adsorption

In order to examine the effect of oxygen on the carbon monoxide adsorption, the Co deposits (0.4 nm) were exposed to oxygen at 300 K and afterwards probed with CO TPD as described above.

If the particles are treated with a high oxygen dosage of 1000 L the CO adsorption is drastically shifted to temperatures below 250 K as shown in figure 3. Such low desorption temperatures indicate a comparatively weak interaction of the adsorbate with the substrate which is typical for oxides [33, 34]. In agreement with that, XP spectra for the Co 2p binding energy region indeed revealed formation of CoO [26]. A second CO TPD run measured directly after this first one indicates slight reduction of the particles (see spectrum (2)), as some intensity is regained above 250 K, but the dominant peak still suggests a mostly oxidic surface. Even exposing the particles to very large amounts of carbon monoxide (1200 L) at 550 K do not lead to significant changes in the spectrum, as can be seen in trace (3). This indicates that the in-situ reduction by CO is impossible at this temperature. The same result was obtained with hydrogen (spectrum (4)). Accordingly, neither CO nor H₂, i.e., both educts in the Fischer-Tropsch process, can reduce the particles to metallic Co at temperatures below 600 K, if complete oxidation to CoO occurred. This is in line with results of temperature-programmed reduction experiments performed under ambient conditions [35].

Yet, in the Fischer-Tropsch-process only small amounts of oxygen should be present on the catalyst due to CO dissociation or a possible contamination of the gas feed. To study the effect of small oxygen dosages, Co particles were exposed to 50 L at 300 K. Interestingly, the TPD spectrum obtained from these particles

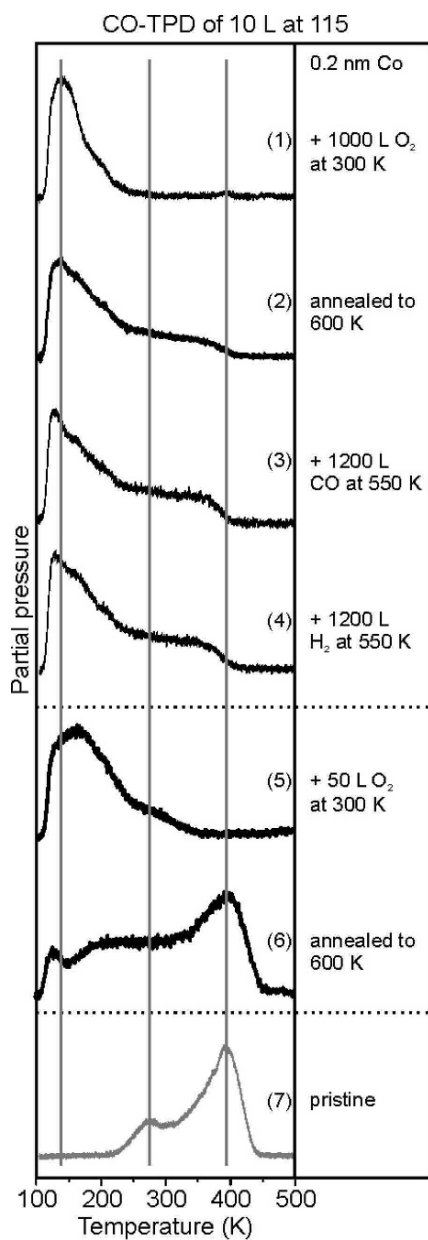


Fig. 3. TPD spectra of 10 L carbon monoxide adsorbed at 115 K on: (1) particles oxidized by an exposure to 1000 L oxygen at 300 K; (2) oxidized particles after annealing to 600 K; (3) oxidized particles after an additional exposure to 1200 L carbon monoxide at 550 K; (4) oxidized particles after an additional exposure to 1200 L hydrogen at 550 K; (5) particles exposed to 50 L oxygen at 115; (6) particles exposed to 50 L oxygen after annealing to 600 K; (7) pristine Co particles (for comparison)

(spectrum (5)) is very similar to spectrum (1) after 1000 L of oxygen. Desorption takes place below 250 K, again suggesting a mostly oxidic surface. As discussed in more detail elsewhere [26], XPS provided no evidence for oxide formation in this case, leading to the conclusion that a surface and/or subsurface oxygen species must be formed which, already in small concentrations, weakens the interaction with CO drastically.

This species is also less persistent. The second TPD spectrum measured after the small oxygen dosage looks quite different (spectrum (6)) because a dominant peak at ~390 K is detected, corresponding to the desorption of terminally bonded carbon monoxide from metallic Co. Additionally, there still is significant intensity below 250 K, indicating that the surface is in a kind of mixed state between metallic and oxidic Co.

So, oxygen exposures always result in a significant reduction of the CO adsorption energy. This effect turns out to be quite independent of the oxygen dosage. But the stability of the formed species strongly depends on the oxygen amount: small dosages are removed more easily by CO itself, whereas large dosages have a very persistent influence in line with the formation of Co oxide.

3.3 Methanol Decomposition on Co

The stability of adsorbed methanol on the Co particles (0.2 nm deposit) was investigated by saturating the particles at 120 K with 20 L of methanol and subsequent heating to 530 K during a TPD experiment. Molecular methanol, carbon monoxide and hydrogen turned out to be the only gas phase products of the decomposition. Therefore, no partial dehydrogenation of methanol occurs on Co, in agreement with data obtained for Co(0001) [22].

The upper panel of figure 4 shows the spectra for the detected products. Molecular methanol desorption exhibits a peak at ~150 K with a shoulder at ~180 K. The low temperature feature can be assigned to multilayer adsorption of methanol, whereas the shoulder at high temperature belongs to methoxide formed on the surface. Due to cracking of methanol in the mass spectrometer, the signals recorded for methanol are reflected in the traces for hydrogen and carbon monoxide in the low temperature regime. Additional features appear at higher temperatures which are due to dehydrogenation on the particles. For CO, a desorption peak is detected at ~390 K which corresponds quite well to the desorption temperature of terminally bonded species on Co (see above), indicating that the formation of CO is desorption limited on such particles. Hydrogen evolution, on the other hand, can be observed between 300 K and 450 K with a maximum at ~370 K. These temperatures are comparable to values reported for the adsorption of molecular deuterium [36] and for the methanol decomposition on Co(0001) [22] which suggests desorption limitation for the generation of hydrogen as well. Therefore, the dehydrogenation of methanol is likely to take place *below* 300 K.

Further experiments revealed that the decomposition of methanol does not only lead to CO and hydrogen as final volatile products, but also to carbon species remaining on the surface. The lower panel of figure 4 shows TPD data obtained

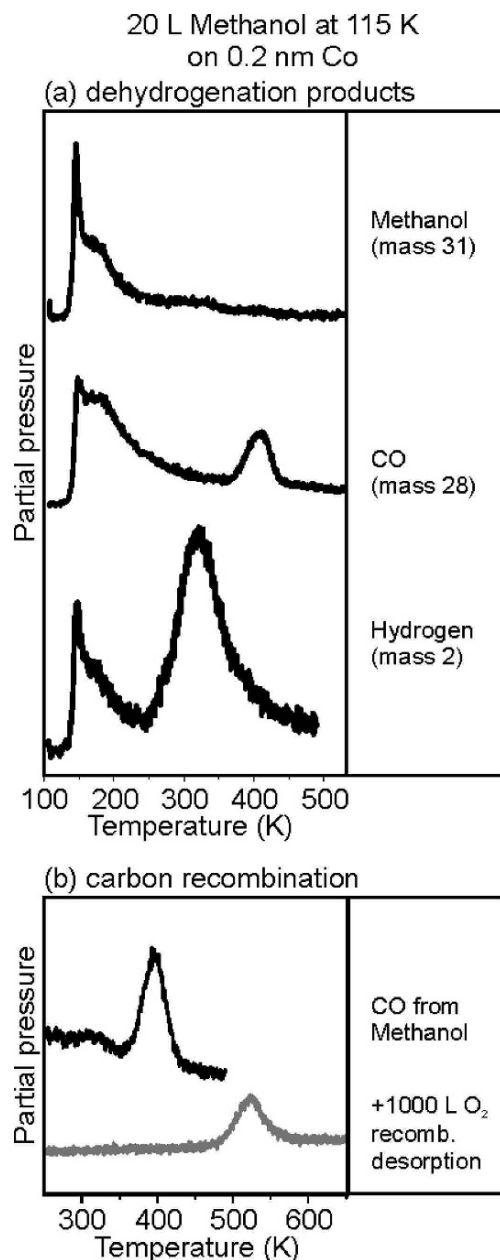


Fig. 4. (a) TPD spectra of CO and hydrogen as product molecules from methanol decomposition. The features below 250 K visible in all spectra are due to cracking in the mass spectrometer. (b) Series of two CO TPD spectra subsequently recorded after methanol adsorption at 115 K (first TPD: top, second TPD: bottom). Between the first and second TPD the particles were exposed to 1000 L oxygen at 300 K

after a first TPD with methanol and subsequent exposure to oxygen at 300 K. The peak at 520 K is again evidence of recombinative desorption of surface carbon species formed as a by-product of methanol decomposition and the oxygen. A quantitative analysis yields 40% as the amount of decomposed methanol which ends as atomic carbon on the surface. These species can either result from the scission of the C-O bond in the methanol molecule itself during the decomposition process or from the dissociation of the CO formed on the particles. This is in contrast to Co(0001) where only complete dehydrogenation was detected [22]. A similar behavior for the decomposition was also reported for Pd crystallites supported on alumina thin films [37-39]

Taking into account the principle of microscopic reversibility, the fact that no products of a partial dehydrogenation are found in the experiments suggests that formation of methanol from syngas should *in principle* be possible on metallic Co particles. Under ambient conditions, however, methanol formation was only reported for *promoted* Co catalysts [20].

4. Conclusions

In this report, results regarding the interaction of CO and methanol with pristine and oxidized Co nanoparticles have been presented. TPD and XP spectroscopic data indicate that carbon monoxide molecules can dissociate on particles in the nanometer regime, which is an important prerequisite for one possible reaction pathway in the FT process. Oxygen pre-adsorption leads to a drastic shift of the carbon monoxide desorption peaks to temperatures below 250 K indicating a weakening of the CO adsorption energy. In case of large amounts of oxygen resulting in CoO formation, we find in our UHV experiments that reduction is neither possible by heating nor by CO or hydrogen exposure. Oxidic species formed after small exposures can be mostly removed again. For the decomposition of methanol, only desorption of carbon monoxide and hydrogen as products of complete dehydrogenation is observed suggesting that methanol can form on CO particles as the direct hydrogenation product of CO. Additionally, the formation of carbon is detected on the surface as a result of C-O-bond scission occurring during the decomposition process or in the carbon monoxide finally formed.

References

1. G. A. Olah, A. Goepfert, G. K. S. Prakash, *Beyond Oil and Gas: The Methanol, Economy*, Wiley-VCH, Weinheim, 2006.
2. F. Fischer, H. Tropsch, *Brennstoff-Chem.* 7 (1926) 97.
3. V. Ponc, in *Handbook of heterogeneous Catalysis*; edited by G. Ertl; H. Knörzinger; J. Weitkamp, Wiley-VCH, Weinheim, 1997, 1876-1894.
4. H. Schulz, *Appl. Catal.*, A 186 (1999) 3-17.
5. B. H. Davis, *Fuel Process. Technol.* 71 (2001) 157-166.
6. H. Papp, *Surf. Sci.* 129 (1983) 205-218.
7. X. Gong, R. Raval, P. Hu, *Surf. Sci.* 562 (2004) 247-256.

8. R. L. Toomes, D. A. King, *Surf. Sci.* 349 (1996) 1-18.
9. J. Vaari, J. Lahtinen, A. Talo, P. Hautojärvi, *Surf. Sci.* 251/252 (1991) 1096-1099.
10. G. A. Beitel, A. Laskov, H. Oosterbeek, E. W. Kuipers, *J. Phys. Chem.* 100 (1996) 12494-12502.
11. J. J. C. Geerlings, M. C. Zonneville, C. P. M. de Groot, *Surf. Sci.* 241 (1991) 315-324.
12. K. A. Prior, K. Schwaha, R. M. Lambert, *Surf. Sci.* 77 (1978) 193-208.
13. G. Jacobs, P. M. Patterson, Yongqing Zhang, Tapan Das, Jinlin Li, B. H. Davis, *Appl. Catal.*, A 233 (2002) 215-226.
14. A. M. Hilmen, D. Schanke, K. F. Hanssen, A. Holmen, *Appl. Catal.*, A 186 (1999) 169-188.
15. G. R. Castro, J. Küppers, *Surf. Sci.* 123 (1982) 456-470.
16. M. E. Bridge, R. M. Lambert, *Surf. Sci.* 82 (1979) 413-424.
17. B. Klingenberg, F. Grellner, D. Borgmann, G. Wedler, *Surf. Sci.* 296 (1993) 374-382.
18. B. Klingenberg, F. Grellner, D. Borgmann, G. Wedler, *Surf. Sci.* 383 (1997) 13-24.
19. M. Gierer, H. Over, P. Rech, E. Schwarz, K. Christmann, *Surf. Sci. Lett.* 370 (1997) L201-L206.
20. D. Gall, E. J. Gibbson, C. C. Hall, *J. Appl. Chem.* 2 (1952) 371-380.
21. D. R. Stull, E. F. Westrum Jr., G. F. Sinke, *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York, (1969).
22. K. Habermehl-Cwirzen, J. Lahtinen, P. Hautojärvi, *Surf. Sci.* 598 (2005) 128-135.
23. M. Bäumer, M. Frank, M. Heemeier, R. Kühnemuth, S. Stempel, H. -J. Freund, *Surf. Sci.* 454-456 (2000) 957-962.
24. M. Heemeier, S. Stempel, S. K. Shaikhutdinov, J. Libuda, M. Bäumer, R. J. Oldman, S. D. Jackson, H. -J. Freund, *Surf. Sci.* 523 (2003) 103-110.
25. T. Hill, T. Risse, H. -J. Freund, *J. Chem. Phys.* 122 (2005) 164704.
26. T. Nowitzki, A. F. Carlsson, O. Martyanov, M. Naschitzki, V. Zielasek, T. Risse, M. Schmal, H. -J. Freund, M. Bäumer, *J. Phys. Chem. C* 111 (2007) 8566-8572.
27. T. Risse, A. F. Carlsson, M. Bäumer, T. Klüner, H. -J. Freund, *Surf. Sci. Lett.* 546 (2003) L829-L835.
28. T. Nowitzki, H. Borchert, B. Jürgens, T. Risse, V. Zielasek, M. Bäumer, in preparation (2007).
29. S. Stempel, PhD Thesis, Freie Universität Berlin, (1998).
30. M. Bäumer, H. -J. Freund, *Prog. Surf. Sci.* 61 (1999) 127-198.
31. M. Heemeier, PhD Thesis, Freie Universität Berlin, (2005).
32. M. Heemeier, A. F. Carlsson, M. Naschitzki, M. Schmal, M. Bäumer, H. -J. Freund, *Angew. Chem., Int. Ed.* 41 (2002) 4073.
33. H. -J. Freund, *Faraday Discuss.* 114 (1999) 1-31.
34. A. F. Carlsson, M. Naschitzki, M. Bäumer, H. -J. Freund, *Surf. Sci.* 545 (2003) 143-153.
35. N. Bahlawane, E. Fischer Rivera, K. Kohse-Höinghaus, A. Brechling, U. Kleineberg, *Appl. Catal. B*, 53 (2004) 245-255.
36. K. Habermehl-Cwirzen, K. Kauraala, J. Lahtinen, *Phys. Scr. T* 108 (2004) 28-32.
37. S. Schauermaun, J. Hoffmann, V. Jahánek, J. Hartmann, J. Libuda, H. -J. Freund, *Angew. Chem., Int. Ed.* 41 (2002) 2532.
38. S. Schauermaun, J. Hoffmann, V. Johánek, J. Hartmann, J. Libuda, H. -J. Freund, *Catal. Lett.* 84 (2002) 209.
39. S. Schauermaun, J. Hoffmann, V. Johánek, J. Hartmann, J. Libuda, *Phys. Chem. Chem. Phys.* 4 (2002) 3909.

Surface confined electrochemical compound formation: Incipient sulfidation of Au(1 1 1)

C. Schlaup ^{*a}, D. Friebe [#], P. Broekmann ^{*}, K. Wandelt ^{*}

^{*} Institut für Physikalische und Theoretische Chemie, Universität Bonn,
Wegelerstr. 12, D-53115 Bonn, Germany

[#] Stanford Synchrotron Radiation Laboratory, 2575 Sand Hill Rd,
Menlo Park, CA 94025, USA

^a tel: +49 228 73 2572; fax: +49 228 73 2551; e-mail: schlaup@pc.uni-bonn.de

Abstract. The incipient electrochemical interaction between sulfur and a Au(1 1 1) surface is investigated by keeping the sulfur coverage constant. To this end the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase of sulfur on Au(1 1 1), $\Theta_S = 0.33$ ML, is subjected to potential increases in a *S-free* NaOH solution. At anodic potentials the reversible formation of a rhombic phase is observed. The *local S coverage increase* which is required for the formation of the rhombic phase results from a coverage *decrease* within the $(\sqrt{3} \times \sqrt{3})R30^\circ$ regions, where single-S-atom-defects and, in later stages, S vacancy islands are formed. Furthermore, the growth of the rhombic phase is accompanied by a Au mass transport which clearly calls for a reinterpretation of its chemical nature.

1. Introduction

Generally gold is regarded as being largely chemically inert and corrosion resistant. However, its chemical inertness does not imply a general disability to form stable nonmetallic bonds, but is rather a consequence of high reaction barriers [1]. For example gold is widely used as a substrate for alkanethiol based self assembled monolayers (SAM) [2,4,3].

In the present work, we focus on the S-induced ring-like features on a Au(1 1 1) surface which have been observed both under electrochemical [5,6,7] as well as UHV conditions [8]. This structure motif has previously been attributed to the formation of molecular S_n species [5,9,7] in particular S_8 rings, based on its square-like appearance in STM images [5,7], as well as XPS [9,7] electron binding energies typical for elemental sulfur. A more critical view, however, reveals some inconsistencies: Calculation of the S-S bond length of the assumed S_8 structure gives an elongation of about 50%, as compared to bulk sulfur [10,11], which has been explained by a strong adsorbate - substrate interaction [5,7]. Moreover, XPS studies of both, gold sulfide nanoparticles as well as commercially available bulk Au_2S , do not show a shift in electron binding energies with respect to the elemental species due to the distinctive covalent Au-S bonding character [12]. Recently, the ring-like structure was reinvestigated with UHV-STM [8,13], and a new interpretation of this structure as a 2-dimensional

Au_xS phase was put forward, based on the observation that its formation is accompanied by a Au mass transport perpendicular to the surface [8].

Under *electrochemical* conditions, however, this Au mass transport could not be observed yet, due to the immediate formation of bulky overlayers at anodic potentials in S-containing solutions. In the electrochemical experiments presented here, we circumvent this problem by exchanging the electrolyte for a *blank* NaOH, i.e. S-free, solution after the deposition of 0.33 ML of sulfur on the Au(1 1 1) electrode. Thereby the available amount of S is kept constant, which enables us to study the potential dependent behavior of the S adlayer over a wide potential range without the formation of bulky overlayers. Instead, at anodic potentials we observed the formation of the ring-like structure together with a Au mass transport perpendicular to the surface, which clearly indicates the formation of a 2-dimensional Au_xS phase. In addition, we were able to give a more detailed description of its structural relationship to the Au(1 1 1) surface.

2. Experimental

All measurements were performed in a home built EC-STM setup [14] under an inert Argon atmosphere. STM- as well as CV-measurements were carried out in the same electrochemical cell containing a typical electrolyte volume of 1 cm^3 . Two platinum wires served as counter electrode and pseudo-reference electrode (due to the formation of stable PtO and PtS layers), respectively. All potentials for the blank 0.01 M NaOH solution in this paper are reported with respect to the standard hydrogen electrode (SHE), using the conversion $E_{\text{SHE}} = E_{\text{Pt}} + 100\text{ mV}$, unless stated otherwise.

The tunneling tips were prepared by electrochemical etching from 0.25 mm diameter Pt/Ir (90/10) wire [15] and coated with an organic polymer (commercial hot glue) to minimize faradaic currents. All STM images were recorded in the constant current mode.

The electrolyte solutions were prepared using ultrapure water (Millipore[®]), NaOH (Merck, suprapur[®]) and Na_2S (Aldrich ReagentPlus[®], 99,99+%). Before usage all electrolytes were deaerated with Argon 5.0 for at least 30 minutes.

A commercial Au(1 1 1) single crystal (MaTeck GmbH, Jülich) was prepared prior to each experiment by a flame annealing procedure [15].

3. Results and Discussion

Deposition and stabilisation of 0.33 ML S on Au(1 1 1)

In a first step the electroadsorption of S on Au(1 1 1) from a 0.01 M NaOH + 0.5 mM Na_2S solution was carried out. Our characterization with cyclic voltammetry (Fig. 1) and STM is in good agreement with previous results [7].

At a potential of -300 mV (vs. Pt/PtS) the typical $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure of a S adlayer with $\theta_S = 0.33$ ML was observed like in Refs. Gao1992, Lay2003, Vericat2004.

Subsequent to the S adsorption, the electrolyte was exchanged for *blank* 0.01 M NaOH solution at a constant potential (-300 mV with respect to the pseudo-reference electrode). After the electrolyte exchange, we confirmed with STM that the S layer had remained on the Au(1 1 1) surface, the characteristic $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure was still imaged (Fig. 2).

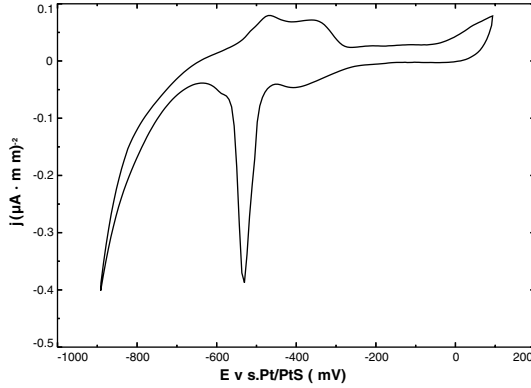


Fig. 1. Cyclic voltammogram of the Au(1 1 1) surface in the *deposition* electrolyte (0.01 M NaOH + 0.5 mM Na₂S), $dE/dt = 10$ mV/s.

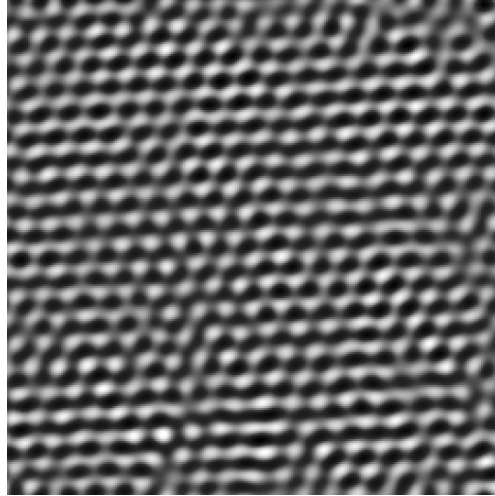


Fig. 2. $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure of the S adlayer in the *blank* 0.01 M NaOH solution, 8.7×8.7 nm², $E = -148$ mV, $U_B = 80$ mV, $I_T = 10$ nA, (band-pass filtered).

Electrooxidation of S-modified Au(1 1 1)

Subsequently the electrochemical potential was increased stepwise using a sweep rate of 10 mV/s. STM images do not show any structural changes after potential increases up to +300 mV, i.e. the characteristic $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure of the S adlayer remains unchanged. Only a further potential increase to +400 mV leads to a drastic change of both the S adlayer structure as well as the surface morphology. Islands with a rhombic structure are formed. The same structure has also been observed under UHV conditions at a higher S coverage of ca. 0.5 ML [8]. Thus, we may assume that also in the electrochemical system, the S coverage *locally* increases. This requires, due to the given amount of adsorbed sulfur, the formation of vacancies in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure, which, in fact, can be seen in Fig. 3. Simultaneously, also Au vacancies on formerly smooth terraces are formed. This clearly indicates that the growth of the rhombic phase corresponds to a Au mass transport perpendicular to the surface, and thus, to the growth of a Au_xS phase rather than to an elemental sulfur layer (Fig. 3). The observation of such a Au mass transport and the formation of the rhombic phase is in agreement with the UHV-results of *Biener et. al.* [8]. The possibility of imaging the well-known $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure simultaneously with the rhombic phase, enabled us to apply an internal calibration and drift elimination to yield highest possible accuracy of the structure determination. Drift elimination was also applied to the STM images presented in Figures 3, 4, 5, 8.

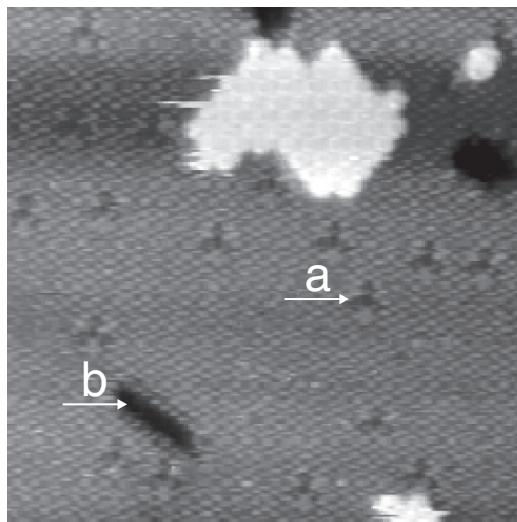


Fig. 3. Coexistence of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ S adlayer and the rhombic phase, (a) S- and (b) Au-vacancies, $23.1 \times 23.1 \text{ nm}^2$, $E = 399 \text{ mV}$, $U_B = 77 \text{ mV}$, $I_T = 10 \text{ nA}$.

The new islands of the rhombic phase contain the known ring-like structure units. They arrange in a well ordered lattice with a rhombic unit cell with $a = (0.83 \pm 0.01)$ nm and $\alpha = (83 \pm 2.0)^\circ$ (Fig. 4). These lattice parameters are in good agreement with those found under UHV conditions [8], they differ only slightly in the length of the lattice vectors (for comparison: $(0.88 \pm 0.04) \times (0.82 \pm 0.04)$ nm² [8]), yielding, in our case, a more symmetric unit cell. In addition, due to the possibility to perform an internal calibration and drift elimination here, we consider our lattice parameter more accurate. According to its lower symmetry with respect to the substrate, the rhombic phase must occur in three rotational versions with two mirror related domains each, i.e. six different orientations. An angle of $(30 \pm 2)^\circ$ between different mirror domains reveals a rotation of $(15 \pm 1)^\circ$ between the lattices of the rhombic phase and the Au(1 1 1) substrate underneath. Thus we propose an incommensurate relationship of the rhombic Au_xS phase with the substrate (Fig. 5).

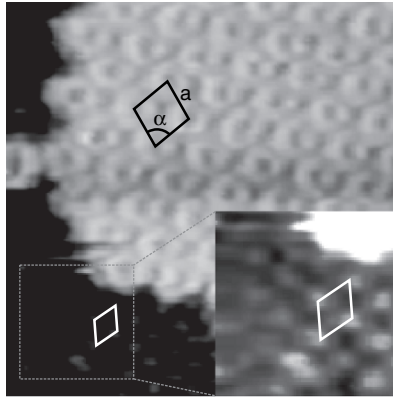


Fig. 4. High resolution STM image of the rhombic Au_xS phase and the surrounding $(\sqrt{3} \times \sqrt{3})R30^\circ$ S layer, 7.7×7.7 nm², $E = 399$ mV, $U_B = 77$ mV, $I_T = 10$ nA.

The potential induced formation of the rhombic Au_xS phase is a rather slow process under the given conditions. The STM image in Fig. 6b was taken 15 minutes after that in Fig. 6a. These images show, how the formation of the Au_xS phase coincides with the growth of Au vacancy islands on formerly smooth Au(1 1 1) terraces. Within these vacancy islands, the rhombic Au_xS phase is formed, too (Fig. 7). Adding the apparent thickness of the Au_xS islands (0.114 ± 0.003) nm and the depth of the vacancy islands (0.121 ± 0.003) nm, both measured with respect to terraces which are still covered with the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure, results in a height equal to a monoatomic step height of the Au(1 1 1)

surface (0.235 nm). Hence, the growth of these vacancy islands originates from a continuous Au mass transport out of the topmost Au layer, perpendicular to the surface, which occurs simultaneously with the formation of the rhombic Au_xS phase [8].

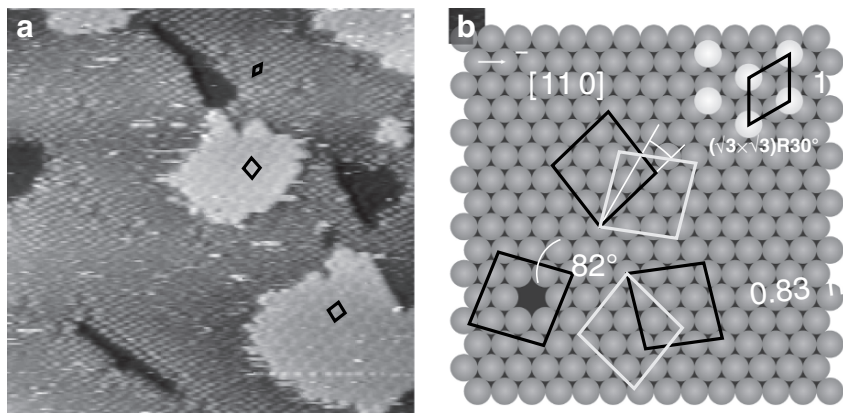


Fig. 5. Mirror domains of the rhombic phase, (a) STM image, $20.0 \times 20.0 \text{ nm}^2$, $E = 399 \text{ mV}$, $U_B = 77 \text{ mV}$, $I_T = 10 \text{ nA}$, (b) Structure model: S/Au(1 1 1) and unit cells of three rotational of two mirror domains of the rhombic Au_xS phase.

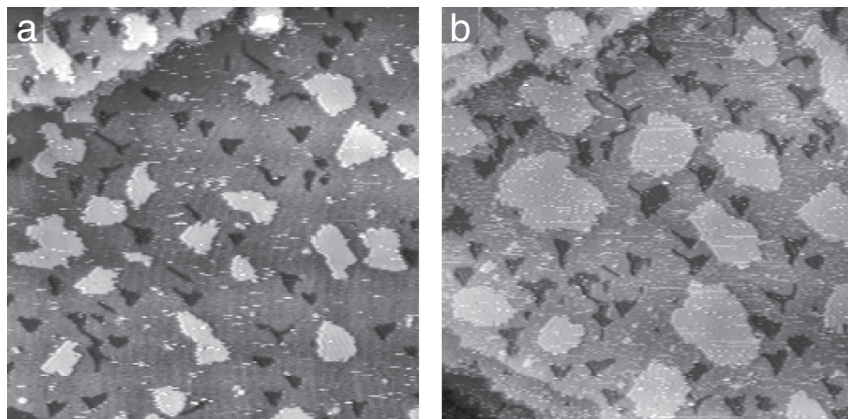


Fig. 6. Morphological changes during a time period of 15 minutes, $113.7 \times 113.7 \text{ nm}^2$, $E = 399 \text{ mV}$, $U_B = 77 \text{ mV}$, $I_T = 10 \text{ nA}$.

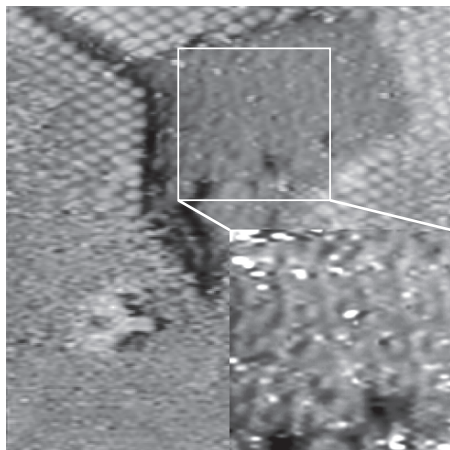


Fig. 7. Appearance of the rhombic phase within Au vacancies $14.2 \times 14.2 \text{ nm}^2$, $E = 399 \text{ mV}$, $U_B = 77 \text{ mV}$, $I_T = 10 \text{ nA}$.

The interpretation of the rhombic phase as a gold sulfide has already been proposed by Biener et al. [8] and is in strong contrast with the hitherto existing model that with increasing S coverage on Au(1 1 1), Au–S interactions would decrease in favour of increasing S–S interactions, finally leading to adsorbed S_8 molecules [9]. Likewise under electrochemical conditions, an oxidation of HS^- to S_8 on top of a rather inert Au substrate has been assumed [5,6,7]. By contrast, our results clearly indicate a relative increase of the Au–S interaction with increasing potential. This can already be seen in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ S layer, which near the formation of the rhombic phase starts to show star-like features (Fig. 3). Smaller scaled STM images (Fig. 8) show that these features represents point defects within the $(\sqrt{3} \times \sqrt{3})R30^\circ$ S layer. Despite these vacancies it is notable that atoms next to such a defect remain fixed on their initial lattice site, as verified by the superimposed unit cell in Fig. 8. This underlines the strong Au–S interaction.

Due to the continuous consumption of S atoms during the formation of the rhombic Au_xS phase, the number of defects in the S layer increases. But due to the high electrode potential, the remaining S atoms are rather immobile. This enables us, for the first time, to image S-covered $(\sqrt{3} \times \sqrt{3})R30^\circ$ islands along with uncovered Au (1×1) regions simultaneously (Fig. 7). This would neither be the case at lower potentials where a decrease of the S coverage below 0.33 ML leads to an instantaneous order-disorder transition, nor under UHV conditions where STM images of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure could not be obtained due to the high mobility of adsorbed S atoms [8].

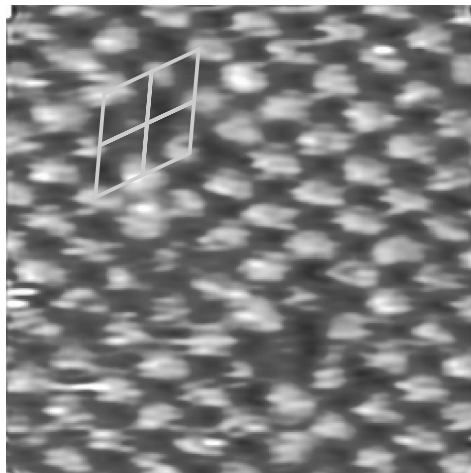


Fig. 8. Point defects within the $(\sqrt{3} \times \sqrt{3})R30^\circ$ S layer, white: unit cell of $(\sqrt{3} \times \sqrt{3})R30^\circ$ S adalyer, $4.5 \times 4.5 \text{ nm}^2$, $E = 399 \text{ mV}$, $U_B = 77 \text{ mV}$, $I_T = 10 \text{ nA}$.

Upon further progress in time, the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure is completely displaced by a mixture of uncovered (1×1) -Au(1 1 1) terraces and relatively large islands of the rhombic Au_xS phase, which is also formed within Au vacancy islands. In between islands of the rhombic Au_xS phase on top of Au(1 1 1) terraces, a continuous diffusion of probably Au_xS takes place, indicated by a permanent change of the island shape and typical noise in the STM images (horizontal stripes in Fig. 5, 6). Hence, we assume relatively weak interactions between the Au_xS layer and the substrate. Accordingly, the phase transition between the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure and the rhombic Au_xS phase can be completely reversed by decreasing the potential below -100 mV vs. SHE again. Simultaneously with the reappearance of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure and the decomposition of the rhombic phase, Au vacancies heal out in most instances, yielding smooth S covered Au(1 1 1) terraces again. A further potential decrease below -600 mV leads to the irreversible desorption of sulfide into the *blank* electrolyte.

Concluding the observations mentioned above, which are in good agreement with Ref. Biener2005, they strongly suggest the interpretation of the rhombic phase as an Au_xS phase. Assuming an alternative interpretation of the rhombic phase as being a kind of elemental sulfur, e.g. S_8 [5,9,7], this could explain the disappearance of the $(\sqrt{3} \times \sqrt{3})R30^\circ$, but not a Au mass transport out of the surface, resulting in Au vacancies on formerly smooth Au(1 1 1) terraces. A conceivable alternative interpretation of the morphological changes as being due

to gold oxide or hydroxide formation can be ruled out, because at the given pH, the oxidation of Au(1 1 1) in pure 0.01 M NaOH starts only at potentials above +600 mV [16]. Furthermore, an interpretation of the ring-like structural unit of the rhombic phase as consisting of S_8 would result in a next neighbor S–S distance (d) of $d \approx 0.3$ nm, which is much longer than the typical next neighbor distance of S_x oligomers ($d \approx 0.2$ nm) [10]. The assumption of a strong substrate influence on the molecular geometry, which may expand the S–S bond length [7], conflicts with the observed high mobility of the rhombic phase as well as the incommensurate lattice relationship between the rhombic phase and the Au(1 1 1) surface.

4. Summary

We have reinvestigated the electrochemical potential dependence of the S–Au(1 1 1) interaction. In order to prevent the formation of amorphous and bulky overlayers at higher potentials, we exchanged the solution for a *S-free* electrolyte after deposition of 0.33 ML sulfur. Hence, we were able to study the structural and morphological changes of the S-covered Au(1 1 1) surface at higher potentials with STM at constant S-coverage.

1. The Au–S interaction in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure of 0.33 ML S on Au(1 1 1) becomes stronger with increasing potential, resulting in a decreased mobility of adsorbed S atoms, which can thus be imaged with STM even in the presence of vacancies which would usually - at lower potentials - be too mobile.
2. The electrooxidation of S-covered Au(1 1 1) does not lead to the formation of adsorbed S_8 , but rather to a 2-dimensional $Au_x S$ layer.
3. The structure of the $Au_x S$ layer has been determined with high accuracy, using the known $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure for internal calibration.

Acknowledgment

D. FriebeI thanks the Alexander von Humboldt Foundation for a Feodor Lynen Fellowship.

References

1. Hammer, B.; Norskov, J. *Nature* **1995**, 376, 238–239.
2. Poirier, G. *Chem. Rev.* **1997**, 97, 1117–1128.
3. Ulman, A. *Chem. Rev.* **1996**, 96, 1533–1554.
4. Poirier, G.; Pylat, E. *Science* **1996**, 272, 1145–1148.
5. Gao, X.; Zhang, Y.; Weaver, M. J. *Phys. Chem.* **1992**, 96, 4156–4159.

6. Lay, M.; Varazo, K.; Stickney, J. *Langmuir* **2003**, *19*, 8416–8427.
7. Vericat, C.; Vela, M.; Gago, J.; Salvarezza, R. *Electrochim. Acta* **2004**, *49*, 3643–3649.
8. Biener, M.; Biener, J.; Friend, C. *Langmuir* **2005**, *21*, 1668–1671.
9. Rodriguez, J.; Dvorak, J.; Jirsak, T.; Liu, G.; Hrbek, J.; Aray, Y.; González, C. *J. Am. Chem. Soc.* **2003**, *125*, 276–285.
10. Meyer, B. *Chem. Rev.* **1976**, *76*, 367–388.
11. Rettig, S.; Trotter, J. *Acta Cryst.* **1987**, *C43*, 2260–2262.
12. Morris, T.; Copeland, H.; Szulcowski, *Langmuir* **2002**, *18*, 535–539.
13. Queck, S.; Biener, M.; Biener, J.; Bhattacharjee, J.; Friend, C.; Waghmare, U.; Kaxiras, E. *J. Phys. Chem. B* **2006**, *110*, 15663–15665.
14. Wilms, M.; Kruft, M.; Bermes, G.; Wandelt, K. *Rev. Sci. Instr.* **1999**, *70*, 3641–3650.
15. Friebe, D.; Schlaup, C.; Broekmann, P.; Wandelt, K. *Surf. Sci.* **2006**, *600*, 2800–2809.
16. Štrabac, S.; Hamelin, A.; Adžić, R. *J. Electroanal. Chem.* **1993**, *362*, 47–53.

Giant Spin-Polarization and Magnetic Anisotropy of Nanostructures at Surfaces

H. Brune

Institute of the Physics of Nanostructures (IPN),
Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne

We present spin-polarized scanning tunneling microscopy measurements demonstrating spin-polarizations of up to 80 % for Co islands on a Pt(111) surface and a tunnel magneto resistance of 850~\% between the islands and an anti-ferromagnetic Cr-coated W-tip. These values remain constant up to ± 0.7 V bias. We report on the magnetic moments and anisotropy energies of two-dimensional Co islands on Pt(111) comprising only a few atoms. Our results show the correlation between orbital moments and magneto-crystalline anisotropies and reveal that both properties strongly depend on the lateral atomic coordination. The anisotropy of single adatoms is found to be 200 times the Co hcp bulk value. We also present well ordered superlattices of Co islands self-assembled on Au(788). The particles have uniaxial out-of-plane magnetization and no dipolar interactions. They present a model system for ultra-high density storage media since they have the most uniform anisotropy energies and the highest density of non-interacting particles so far realized.

Spin-polarization in STM-Junctions

Magnetic random access memories (MRAMs) will possibly replace our current dynamic random access memories (DRAMs) due to their shorter access times and to the fact that they are non-volatile. Depending on cost, they may even replace hard-drives and flash-memories. The MRAM cell consists of a planar tunnel junction between two ferromagnets with its tunnel-magneto-resistance (TMR) being used for readout. The TMR is defined in recent papers as $(R_a - R_p)/R_p$, with R_p and R_a being the junction resistance for parallel and anti-parallel magnetization of the ferromagnets. One finds $\Delta R/R_p =$ with $P = (g^+ - g^-)/(g^+ + g^-)$ being the ferromagnets spin polarizations and g^+ and g^- denoting the density of states for spin up, respectively, spin down electrons at E_F . For comparison with TMR values mentioned in early papers we note that $\Delta R/\bar{R} = 2\Delta R/(R_p + R_a) = 2P_1P_2$ [1] and $\Delta R/R_a = 2P_1P_2/(1 + P_1P_2)$ [2]. Note also that appreciable differences between the three definitions occur only at high P .

Theory predicts that coherent and state selective tunneling in fully epitaxial junctions may give rise to TMRs of the order of 1000 % [3,4]. Experimental junctions have rapidly improved their TMR over recent years ; today they come indeed close to the theoretical maximum. A breakthrough was achieved in 1995 when the TMRs went from former values of a few percent up to 18 % in Fe/Al₂O₃/Fe [1] and 12 % in CoFe/Al₂O₃/Co tunnel junctions [2] (we refer to

values at 300 K). Another order of magnitude was achieved in 2004, where 188 % were reported for fully epitaxial Fe/MgO(100)/Fe junctions [5], 220 % for polycrystalline FeCo/MgO/FeCoB junctions with (001) texture [6]. Subsequently, 230 % were reported for CoFeB/MgO(100)/CeFeB junctions with polycrystalline ferromagnets facilitating fabrication of many junctions with uniform properties [7]. The highest room-temperature TMR-value to date observed for epitaxial junctions is 410 % and has been measured on Co(100)/MgO(100)/Co(100) junctions [8].

However, these TMR values are restricted to very small bias. They steeply decrease as the voltage is increased to technical useful values [5, 6]. A second important characteristic for applications is therefore the voltage $V_{1/2}$ at which the TMR drops to half of its close to zero bias value. This voltage defines the memory output voltage, $V_{\text{out}} = V_{1/2}(R_a - R_p)/R_a$, which is one of the parameters defining the MRAM density limit. In planar junctions, $V_{1/2}$ has been increased from 0.2 [2] to 0.6 V [7]. Compared to the achieved TMR increase this is moderate improvement and prompts the question how much of the bias dependence is being intrinsic. An intrinsic effect is the variation of the g 's with energy. However, this is expected to show up only beyond 0.5 V and to give rise to a relatively small decrease up to 1 V. Other effects are interfacial spin-scattering, magnon creation in the oxide, or tunneling via trap states formed by oxide defects [9]. Perfect interfaces and perfect oxides would avoid some of these effects. Which one of them is dominant, and what are the ultimate values of $V_{1/2}$ and V_{out} of a perfect junction, are at present open questions. We briefly note that the so-called zero-bias anomaly usually refers to a TMR-peak observed at low T and at a view milli-volts [10]. This peak is related to Kondo and/or inelastic spin-excitations [11] and has to be discerned from the above discussed TMR decrease at large bias values, which currently affects the operation of planar junctions in MRAMs.

The junction of a spin-polarized STM has controlled interfaces and a clean vacuum barrier. Therefore it promises TMR values closer to the theoretical upper limit and higher stability of these values with increasing bias. Most importantly, however, one of the junction interfaces can be "seen" on the atomic scale, enabling to investigate the causes of performance limits of planar junctions in a systematic way. We present spin polarization and TMR measurements on single planar monodomain islands. TMR values reach up to 850 % for vacuum STM tunnel junctions formed by out-of-plane magnetized ferromagnetic bilayer Co islands on Pt(111) (140 K) and anti-ferromagnetic Cr-coated W-tips (280 K). These values are observed up to biases of ± 0.7 V, shifting $V_{1/2}$ far beyond 1.0 V [12].

The Co islands shown in Fig. 1a) were created by atomic vapor deposition of 0.40 monolayers (ML, 1 ML being one Co atom per Pt surface atom) on a Pt(111) substrate held at 130 K and subsequent annealing to 340 K [13]. The -9.4 % misfit between Co and Pt leads to partial dislocations in first layer islands [14]. In the double layer islands imaged here the stress is partly relieved by a moiré structure [15, 16]. The moiré implies smooth transitions of the Co adsorption sites between three-fold hollow and on-top sites leading to a long-period vertical modulation of the atomic positions reflected in their apparent heights in constant current STM

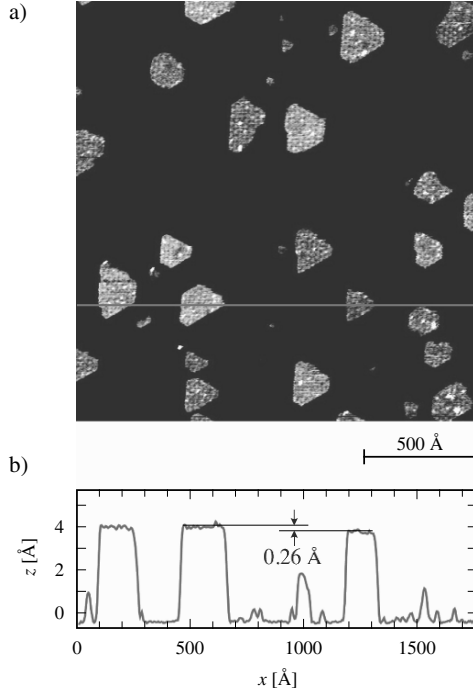


Fig. 1. a) Constant current STM image of double-layer Co islands on Pt(111) recorded with a Cr-coated W tip. Islands with opposite magnetization appear with two different heights ($T_{\text{sample}} = 140$ K, $T_{\text{tip}} \approx 280$ K, $V_t = -0.08$ V, $I_t = 0.3$ nA). **b)** Averaged line-profile (± 5 lines) at the indicated position in figure **a)** showing a difference of 0.26 ± 0.05 Å in the apparent height of islands with opposite magnetization.

images. Part of this modulation is still visible in the averaged line scans, and looks as if it was noise (Fig. 1b)).

In addition to the corrugation of the moiré, one clearly discerns two island species by an apparent height difference. This contrast is magnetic since it is only obtained with magnetic tips (either Cr-coated W-tips, or FeMn bulk-tips), and it vanishes above the island blocking temperature of $T_b = 180$ K, which we independently determined by means of magneto-optical Kerr effect (MOKE) [13]. The MOKE measurements also reveal out-of-plane magnetization in agreement with the fact that spin contrast is only observed with a Cr coating thickness of 20 – 40 ML reported to give out-of-plane polarization of the tip [17].

The magnetic contrast amounts to $\Delta z = 0.26 \pm 0.05$ Å and can be analyzed in terms of the junction polarization and the TMR that would be observed at constant gap width of the junction. With the above definitions, one finds:

$$P_t P_s = \frac{I_p - I_a}{I_p + I_a} = \frac{\exp(A\sqrt{\phi}\Delta z) - 1}{\exp(A\sqrt{\phi}\Delta z) + 1}, \quad (0.1)$$

where ϕ is the average over the work-functions of tip and sample and $A = 2\sqrt{2m_e/\hbar^2} = 1.025 \text{ eV}^{-1/2} \text{ \AA}^{-1}$. With a typical value of $\phi = 4 \text{ eV}$ we find $P_t P_s = 0.26 \pm 0.06$ from the difference in apparent height of Fig. 1. This is significantly higher than $P_t P_s$ values reported between Co(0001) surfaces and amorphous Co-based alloy tips [9]. Evidently, the spin contrast depends on the orientation of the magnetic moment of the atoms at the apex. These strongly vary for each newly prepared tip, as we conclude from different Δz values from day to day, $0.2 \text{ \AA}$ being a typical value. In a single case we observed a difference of $\Delta z = 1.1 \pm 0.1 \text{ \AA}$, corresponding to $P_t P_s = 0.80 \pm 0.04$ [12]. This value implies a polarization of the Co islands of at least 80 %, about two times larger than the Co bulk value determined by Andreev reflection [18, 19]. This can be rationalized by the low dimensionality of the islands increasing the density of states at E_F , or by state selective tunneling leading to a higher polarization than the state averaged value.

The TMR for a tunnel junction formed by the tip kept at constant height above an island which magnetization switches between up and down evaluates to:

$$\Delta R / R_p = \frac{2P_t P_s}{1 - P_t P_s} = \exp\left(A\sqrt{\phi}\Delta z\right) - 1 \quad (0.2)$$

For our typical Δz values Eq. 0.2 gives $\Delta R/R_p = 70 \pm 15 \%$, and the largest observed magnetic contrast corresponds to $\Delta R/R_p = 850 \pm 200 \%$. The latter value largely overcomes the highest TMR value yet reported and can be considered as bench mark for ideal planar junctions. From density functional theory calculations it is found that adsorbates at the STM-tip apex may cause magnetic contrast in the range of the reported values [20]. We observe stable TMR values up to biases of $\pm 0.7 \text{ V}$ [20], which is in agreement with former SP-STM junctions [9, 21]. Our results suggest that SP-STM experiments are well suited to investigate the effect of structural and chemical defects on the TMR bias dependence.

Magnetic Anisotropy of Single Adatoms

The energy barrier associated with magnetization reversal by coherent rotation of all spins in a uniaxial system is the magnetic anisotropy energy K_2 , which we call here K for brevity. This energy causes magnetic memories to be non-volatile since it preserves the magnetization from reversing its orientation by thermal excitation. K also defines together with the particle moment M the switching field $H(T)$. The anisotropy energy has several origins, such as shape, magneto-crystalline, surface and interface. In 3D particles several of these causes are present and it is difficult to disentangle them unambiguously. In 2D nanostructures at single crystal surfaces this is facilitated when morphology and magnetism are investigated *in-situ* on the same sample. This has led to the discovery that the low coordinated step atoms contribute 20 times more to the anisotropy of islands than the laterally 6-fold coordinated atoms sitting inside [13].

In Fig. 2 we present the most spectacular example of this coordination effect in showing magnetization curves recorded for single Co atoms adsorbed on a Pt(111) surface with X-ray magnetic circular dichroism (XMCD) along the easy axis (out-of-plane) and at 70° to it [22]. Isolated Co adatoms have been created by atomic vapor deposition onto a substrate held at low enough temperature to entirely freeze thermally activated tracer diffusion of the deposited species. When atoms adsorb onto a surface, there is the possibility that part of their adsorption energy is transferred into motion along the surface. However, this transient mobility has been found to be absent in all metal/metal systems studied so far [23]. The atoms therefore come to rest at their site of impact. Size distributions for this case called statistical growth can be inferred at low coverage from mathematics [24], and at higher coverages, where deposition onto filled sites comes into play, from kinetic Monte-Carlo or rate theory models [25]. The mean “island” sizes for the coverages used here go from 1.02 (coverage $\theta = 0.007$ ML) to 1.11 atoms ($\theta = 0.030$ ML), therefore at the surface are almost exclusively monomers, in agreement with the uniform apparent height for most of the islands in STM images.

Application of the XMCD sum rules [26] to the spectra measured for the sample shown in Fig. 2a) at saturation and along its easy axis yields $m_L = 1.1 \pm 0.1 \mu_B/\text{atom}$ (the number of core holes needed for this evaluation was calculated

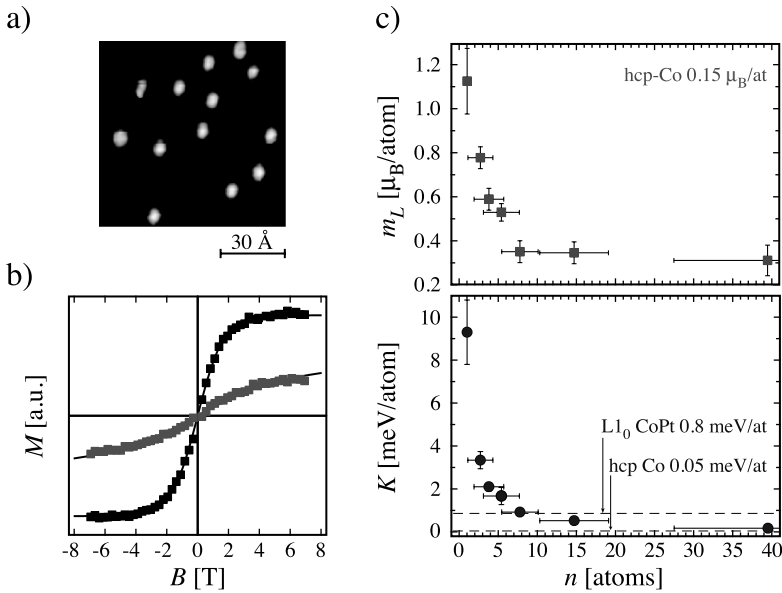


Fig. 2. **a)** STM image of isolated Co adatoms created by statistical growth on Pt(111) ($\theta = 0.010$ ML, deposition temperature $T_{\text{dep}} = 5.5$ K). **b)** XMCD magnetization curves at 0° (black squares) and 70° (red squares) with respect to the surface normal measured at $T = 5.5$ K. The solid lines are fits to the data considering the Zeeman energy resulting from the applied field and the magnetic moments of the atoms and assuming uniaxial out-of-plane anisotropy energy K per atom. **c)** Atomic orbital moments m_L and anisotropy energies K deduced from XMCD measurements taken out on island ensembles of varying mean size n .

within the local spin density approximation to be 2.4). This value is smaller than $3 \mu_B$ of Co atoms in the gas phase, but much higher than orbital moments in the bulk, where the hybridization of the d -states reduces m_L to $0.1 - 0.2 \mu_B$. The high m_L value comes from the reduced coordination of the adatoms favoring d -electron localization and thus the survival of atomic-like character in the $3d$ orbitals. In a band picture, the d -bands are narrowed increasing the local density of states near the Fermi level. This is expected to augment the spin-orbit energy and thereby also the magneto-crystalline anisotropy energy.

Figure 2b) shows the magnetization along the field applied once parallel to the easy axis (out-of-plane) and once at 70° to it. The data points represent the peak of the L_3 XMCD intensity at 778.6 eV divided by the pre-edge intensity at 775 eV as a function of B . The difference between the 0° and 70° curves was checked for consistency with the XAS-normalized XMCD spectra. The fits yield $K = 9.3 \pm 1.6$ meV/atom, which is 200 times the Co hcp bulk value. It is also much higher than the anisotropies of hard magnets, such as SmCo_5 or CoPt L1_0 ($K = 1.8$, and 0.8 meV/Co atom, respectively [27]), and higher than the values formerly reported for atomic Co chains attached to Pt-steps ($K = 2.0$ meV/Co atom [28]). The CoPt alloys, the Co chains, as well as the present system, benefit from strong spin-orbit coupling of the Pt $5d$ -states resulting in additional anisotropy energy of the induced magnetization [29]. The fact that the value reported here is much higher than formerly reported ones suggests that coordination has a stronger effect than polarization and spin-orbit coupling of a second element. In line with the dominant role of coordination we observe in Figure 2c) a rapid decrease of m_L and K when going from monomers to dimers, trimers, tetramers and so forth [22]. XMCD yields $K = 1.0 \pm 0.1$ meV/atom for Co heptamers, which are almost entirely composed of step atoms. This is in very good agreement with our MOKE-results on much larger Co islands on Pt(111), where we found $K_p = 0.9 \pm 0.1$ meV/step-atom [13].

It remains an open issue whether at low T Co monomers on Pt(111) behave as classical magnetic moments with a remanent magnetization, or whether their ground state is a superposition of at least two eigenstates of quantum number $+m$ and $-m$. Strong coupling to the surface can favor the first situation, however, experimental evidence for it is currently not available. Single atom experiments exist on systems where the coupling of the magnetic atom to the metal surface has been reduced by an oxide or nitride spacer [30]. In the case of Fe atoms on $\text{CuN/Cu(100)-(2 \times 2)}$ the magnetic state of the atoms is a wavefunction with weight in $m = -2, 2$ and 0 , and field dependent spin-excitation spectroscopy measurements with the STM reveal the Hamiltonian containing the anisotropy energies [31]. At which size the transition from quantum mechanical spins to classical magnetic moments with remanent magnetization takes place remains to be investigated. This question is particularly interesting for strongly coupled adsorbate/substrate systems. From our present data, the smallest unit to store information magnetically at room temperature is a ring of 400 2-fold coordinated atoms, each having an anisotropy of 3.3 meV.

Self-assembly of Model Systems for Ultra-high Density Magnetic Storage Media

Magnetic hard disk media are believed to reach very soon a bit density where the magnetic grains used to store one bit become super-paramagnetic, *i.e.*, their magnetization reverses due to thermal excitation on a time scale shorter than the desired memory retention time of typically 10 years. Since then the memory gets volatile, there is considerable interest in further shifting this limit, and in knowing its ultimate value.

Here we present a way to create model systems suited to explore the ultimate density limit of magnetic information storage. Our example are Co islands self-assembled on a Au(788) surface. The islands are monodomain particles and have a density of 26 Tbits/in². They are characterized by uni-axial out-of-plane magnetization, by the absence of dipolar interactions, and by unprecedentedly narrow magnetic anisotropy energy and moment distributions [32].

Figure 3a) shows an STM image of a Au(788) surface onto which 0.35 ML of Co have been deposited at 130 K with subsequent annealing to 300 K. The Au(788) surface is stable against faceting [33] due to the following reasons. The steps repel each other due to elastic substrate mediated interactions [34]. The sample is cut in such a way that the steps form dense {111}-facets, which are energetically favored

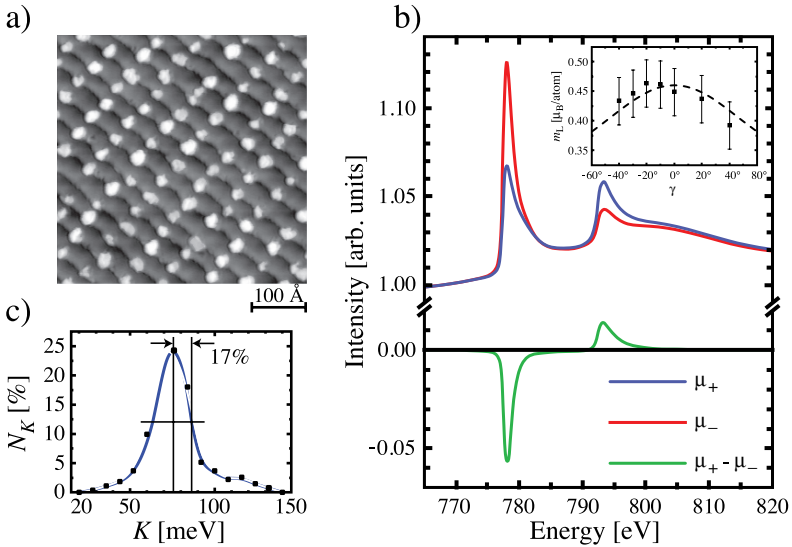


Fig. 3. a) STM image showing Co bilayer islands self-assembled on Au(788) into a long-range ordered superlattice with a unit-cell of 3.5×7.0 nm, corresponding to a density of 26 Tera-islands/in² ($\theta = 0.35$ ML, $T_{\text{dep}} = 130$ K, $T_{\text{ann}} = 300$ K). **b)** XAS spectra and the resulting XMCD taken at normal incidence ($\gamma = 0^\circ$) on a sample with 0.35 ML Co ($T = 10$ K, $B = 5$ T, $B_{\text{sat}} = 2.5$ T). **c)** The K -distribution inferred from MOKE is with HWHM = 17 % roughly two times more narrow than the size-distribution having HWHM = 32 % ($\theta = 0.75$ ML deposited in several steps, each time followed by annealing with temperatures as in a)).

with respect to the more open $\{100\}$ -facets, which would be present on a pristine Au(877) surface. The $\{111\}$ -faceted steps can be crossed perpendicularly [35] by the partial surface dislocations of the $(\sqrt{3} \times 22)$ -reconstructed terraces [36]. Finally, elastic interactions align the reconstruction pattern from one terrace to the next. Altogether, this leads to a long range ordered lattice formed by the intersections of steps and reconstruction lines. These intersections are the nucleation sites for Co [33, 37], leading to a regular lattice of double layer high Co islands extending phase-coherently over the entire crystal, since on this surface steps do not destroy the coherence from terrace to terrace.

The XMCD-measurements of the angular dependence of the orbital moment m_L shown in figure 3b) reveal a common easy magnetization axis close to out-of-plane, tilted by 15° towards the ascending steps. Zero-field susceptibility measurements with MOKE as a function of temperature, $\chi(T)$, show the transition from the blocked to the superparamagnetic state to take place in a narrow temperature window with a width of 15 K. Comparison of STM-derived island size and perimeter length distributions with the $\chi(T)$ -curve leads to an anisotropy energy per perimeter atom of $K_p = 0.8 \pm 0.1$ meV and yields the distribution of island anisotropy energies K shown in Fig. 3c). The K -distribution has a HWHM_K of 17 %. This value is almost a factor of two smaller than the one of the size of 32 %. In fact, this is expected since the anisotropy is largely given by the perimeter length, which in 2D has a distribution half as wide as the one of the size. The value of 17 % is also less than half of the best result so far achieved for colloid particles [38]. The fact that our islands have a more narrow distribution of magnetic properties than the much more mono-disperse looking colloid particles can be rationalized by the fact that the magnetic moments of 2D lattices of colloid particles are not yet uni-axial, implying dipolar interactions. In addition, the competition between several causes of anisotropy, such as faceting, strain or shape anisotropy, may give rise to several easy axes per particle [39].

The value for the anisotropy energy per perimeter atom is in agreement with 0.9 ± 0.1 meV obtained for Co/Pt(111) [13], and with the estimate of 1.0 ± 0.3 meV derived from Ref [40] for Co islands with comparable size on Au(111). We can compare the anisotropy of the orbital moment, $m_{L,\parallel} - m_{L,\perp}$, derived from XMCD, with the magneto-crystalline anisotropy K_{MC} per atom, independently derived from MOKE. Both quantities are predicted to be linked to each other by the relation [41]

$$K_{MC} = -\alpha \frac{\xi}{4\mu_B} (m_{L,\parallel} - m_{L,\perp}), \quad (0.3)$$

with the spin-orbit coupling constant $\xi = 70$ meV for Co [42]. Since MOKE determines the total anisotropy per atom, $K = K_{MC} + K_{\text{shape}}$, we subtract the shape anisotropy $K_{\text{shape}} = -0.08$ meV/atom, obtained assuming circular islands, and obtain $K_{MC} = 0.45 \pm 0.04$ meV/atom. With $m_{L,\parallel} - m_{L,\perp} = 0.11 \pm 0.01 \mu_B$ we find $\alpha = 0.23 \pm 0.02$, confirming previously reported estimates of 0.2 [43]. This result

points out the direct connection between increased orbital moments of low coordinated atoms and their increased anisotropy energy.

Dipolar interactions between monodomain particles manifest themselves by a flatter than $1/T$ -decrease of the $\chi(T)$ -curve above T_b [44]. For the present system, we find the slightly steeper than $1/T$ -decrease, characterizing ensembles of non-interacting particles. The absence of dipolar interactions is further corroborated by a double peak in $\chi(T)$ for a bimodal size distribution, showing that small islands can become superparamagnetic at their blocking temperature, independent of the larger ones which are still blocked and sit next by.

The Co particle superlattices created by self-assembly on a Au(788) surface have an unprecedented narrow anisotropy distribution, a common out-of-plane easy magnetization axis, and the absence of mutual magnetic interactions at a density record of 26 Tbits/in². Admittedly, one has to work on the blocking temperature, which is with 50 K too low. This can be done by adding more Co, for example by growing pillars in the third direction [45], which, according to our data, would still be non-interacting, or by using CoFe or CoPt alloys, which we currently investigate.

The author acknowledges the contributions of his collaborators P. Gambardella, S. Rusponi, T. Cren, N. Weiss, M. Eppele, P. Bulushek, and L. Claude to this work, as well as fruitful collaborations with S. Rousset and C. Carbone.

References

1. T. Miyazaki and N. Tezuka, *J. Magn. Magn. Mater.* 139, L231 (1995).
2. J.S. Moodera, L. R. Kinder, T. M. Wong, and R. Meservey, *Phys. Rev. Lett.* 74, 3273 (1995).
3. J. Mathon and A. Umerski, *Phys. Rev. B* 63, 220403 (2001).
4. X.G. Zhang and W.H. Butler, *Phys. Rev. B* 70, 172407 (2004).
5. S. Yuasa, T. Nagahama, A. Fukushima, Y. Suzuki, and K. Ando, *Nat. Mater.* 3, 868 (2004).
6. S.S.P. Parkin, C. Kaiser, A. Panchula, P.M. Rice, B. Hughes, M. Samant, and S.H. Yang, *Nat. Mater.* 3, 862 (2004).
7. D.D. Djayaprawira, K. Tsunekawa, M. Nagai, H. Maehara, S. Yamagata, N. Watanabe, S. Yuasa, Y. Suzuki, and K. Ando, *Appl. Phys. Lett.* 86, 092502 (2005).
8. S. Yuasa, A. Fukushima, H. Kubota, Y. Suzuki, and K. Ando, *Appl. Phys. Lett.* 89, 042505 (2006).
9. W. Wulfschel, H. F. Ding, and J. Kirschner, *J. Magn. Magn. Mater.* 242, 47 (2002).
10. M. Jullière, *Phys. Lett. A* 54, 225 (1975).
11. R. Meservey and P.M. Tedrow, *Phys. Rep.* 238, 173 (1994).
12. S. Rusponi, N. Weiss, T. Cren, M. Eppele, and H. Brune, *Appl. Phys. Lett.* 87, 162514 (2005).
13. S. Rusponi, T. Cren, N. Weiss, M. Eppele, P. Bulushek, L. Claude, and H. Brune, *Nat. Mater.* 2, 546, 551 (2003).
14. T. Cren, S. Rusponi, N. Weiss, M. Eppele, and H. Brune, *J. Phys. Chem. B* 108, 14685 (2004).
15. P. Grütter and U.T. Dürig, *Phys. Rev. B* 49, 2021 (1994).
16. E. Lundgren, B. Stanka, M. Schmid, and P. Varga, *Phys. Rev. B* 62, 2843 (2000).
17. A. Kubetzka, M. Bode, O. Pietzsch, and R. Wiesendanger, *Phys. Rev. Lett.* 88, 057201 (2002).

18. R.J. Soulen, J.M. Byers, M.S. Osofsky, B. Nadgorny, T. Ambrose, C.F. Cheng, P.R. Broussard, C.T. Tanaka, J. Nowak, J.S. Moodera, et al., *Science* 282, 85 (1998).
19. S.K. Upadhyay, A. Palanisami, R.N. Louie, and R.A. Buhrman, *Phys. Rev. Lett.* 81, 3247 (1998).
20. W.A. Hofer, K. Palotás, S. Rusponi, T. Cren, and H. Brune, *Phys. Rev. Lett.* 100, 026806 (2008).
21. H.F. Ding, W. Wulfhchel, J. Henk, P. Bruno, and J. Kirschner, *Phys. Rev. Lett.* 90, 116603 (2003).
22. P. Gambardella, S. Rusponi, M. Veronese, S.S. Dhesi, C. Grazioli, A. Dallmeyer, I. Cabria, R. Zeller, P.H. Dederichs, K. Kern, et al., *Science* 300, 1130 (2003).
23. H. Brune, in *Physics of Covered Solid Surfaces*, edited by H.P. Bonzel (Springer, Berlin, 2001), vol. 42 Subvolume A, Part 1 of Landolt Börnstein New Series, Group III: Condensed Matter, pp. 217–258.
24. M.F. Sykes and M. Glen, *J. Phys. A: Math. Gen.* 9, 87 (1976).
25. H. Brune, *Surf. Sci. Rep.* 31, 121 (1998).
26. B.T. Thole, P. Carra, F. Sette, and G.v.d. Laan, *Phys. Rev. Lett.* 68, 1943–1946 (1992).
27. D. Weller and A. Moser, *IEEE Trans. Mag.* 35, 4423 (1999).
28. P. Gambardella, A. Dallmeyer, K. Maiti, M.C. Malagoli, W. Eberhardt, K. Kern, and C. Carbone, *Nature* 416, 301 (2002).
29. I.V. Solovyev, P.H. Dederichs, and I. Mertig, *Phys. Rev. B* 52, 13419 (1995).
30. A.J. Heinrich, J.A. Gupta, C.P. Lutz, and D.M. Eigler, *Science* 306, 466 (2004).
31. C.F. Hirjibehedin, C.Y. Lin, A.F. Otte, M. Ternes, C.P. Lutz, B.A. Jones, and A.J. Heinrich, *Science* 317, 1199 (2007).
32. N. Weiss, T. Cren, M. Epplé, S. Rusponi, G. Baudot, V. Repain, A. Tejada, V. Repain, S. Rousset, P. Ohresser, et al., *Phys. Rev. Lett.* 95, 157204 (2005).
33. V. Repain, G. Baudot, H. Ellmer, and S. Rousset, *Mat. Sci. Eng. B* 96, 178 (2002).
34. G. Prévot and B. Croset, *Phys. Rev. Lett.* 92, 256104 (2004).
35. V. Repain, J.M. Berroir, S. Rousset, and J. Lecoeur, *Europhys. Lett.* 47, 435 (1999).
36. J.V. Barth, H. Brune, G. Ertl, and R.J. Behm, *Phys. Rev. B* 42, 9307 (1990).
37. S. Rohart, G. Baudot, V. Repain, Y. Girard, S. Rousset, H. Bulou, C. Goyhenex, and L. Provaille, *Surf. Sci.* 559, 47 (2004).
38. S.I. Woods, J.R. Kirtley, S. Sun, and R.H. Koch, *Phys. Rev. Lett.* 87, 137205 (2001).
39. G.A. Held, G. Grinstein, H. Doyle, S. Sun, and C.B. Murray, *Phys. Rev. B* 64, 012408 (2001).
40. H.A. Dürr, S.S. Dhesi, E. Dudzik, D. Knabben, G.v.d. Laan, J.B. Goedkoop, and F.U. Hillebrecht, *Phys. Rev. B* 59, R701 (1999).
41. P. Bruno, *Phys. Rev. B* 39, 865 (1989).
42. T. Koide, H. Miyauchi, J. Okamoto, T. Shidara, A. Fujimori, H. Fukutani, K. Amemiya, H. Takeshita, S. Yuasa, T. Katayama, et al., *Phys. Rev. Lett.* 87, 257201 (2001).
43. D. Weller, J. Stöhr, R. Nakajima, A. Carl, M.G. Samant, C. Chappert, R. Mégy, P. Beauvillain, P. Veillet, and G. A. Held, *Phys. Rev. Lett.* 75, 3752 (1995).
44. R.W. Chantrell, N. Walmsley, J. Gore, and M. Maylin, *Phys. Rev. B* 63, 024410 (2001).
45. O. Fruchart, M. Klaua, J. Barthel, and J. Kirschner, *Phys. Rev. Lett.* 83, 2769 (1999).

The Role of Spin-Polarized Tunneling on Transport Properties of $(1-x)\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 + x\text{Al}_2\text{O}_3$ Nanocomposites ($x = 0 \div 5\text{wt}\%$)

Pham Thanh Phong^{1,2}, Nguyen Van Khiem³, Nguyen Xuan Phuc², and Le Van Hong²

¹ Ninhhoa Department of Education, Khanhhoa, Vietnam

E-mail: khnguyen1995@yahoo.com

² Institute of Material Science, Vietnamese Academy of Science and Technology Hanoi, Vietnam

³ Hongduc University, Thanhhoa, Vietnam

Abstract. We have investigated the effect of artificial grain boundaries on the electro-magnetic properties of $(1-x)\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 + x\text{Al}_2\text{O}_3$ nanocomposites ($x = 0 \div 5\text{wt}\%$). Based upon a spin-polarized tunneling mechanism we have proposed a phenomenological model to explain the observed electrical transport behavior over the whole temperature range (70 ÷ 300K), especially the gradual drop of metal-insulator transition temperature (T_p) as a function of increasing Al_2O_3 content, while the ferromagnetic-paramagnetic transition temperature (T_C) remains almost constant ($T_C = 250\text{K}$). A large low-field magnetoresistance was observed for all the composite samples and the largest magnetoresistance ratio was recorded for a composition with $x = 0.01$.

1. Introduction

The colossal magnetoresistance (CMR) manganites of the type $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ (where $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{etc.}$ and A is a bivalent doping cation) with perovskite structure have been studied extensively in recent years. So far, two CMR effects have been found in these manganites, that is, the intrinsic CMR and the extrinsic CMR. For most $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ manganites, the CMR effect is maximum near the metal – insulator (M-I) transition temperature (T_p) accompanied by a simultaneous paramagnetic to ferromagnetic (PM-FM) transition at the Curie temperature (T_C). This is the so called intrinsic CMR [1]. The intrinsic CMR, caused by the double exchange (DE) mechanism proposed by Zener in 1951 [2], is useful to explain CMR phenomena mostly observed near T_C at a relatively high magnetic field. However the extrinsic CMR, which is absent in a single crystal, is related to natural and artificial grain boundaries [1,3,4] and atomic size defects at the film – substrate interface [5]. Spin polarized tunneling [1] or spin dependent scattering [3] among neighbouring grains seems to be responsible for this kind of CMR effects. This extrinsic effect may enhance low field magnetoresistance (LFMR) in a wide temperature range and can be more useful for practical application to magnetic switching of recording devices.

In order to enhance the CMR effects, many groups have attempted to synthesize CMR-insulators composites, such as LSMO/CeO₂ [6], LSMO/glass [7],

LSMO/NiO [8], LBMO/YSZ [9] and bilayers of LCMO with Fe_3O_4 [10], LBSMO/PMMA [11].

There are many reported papers dealing with CMR composites [12,13], but studies related to the electrical transport behavior of the $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3/\text{Al}_2\text{O}_3$ composite in a lower magnetic field are rare. In this study, we mainly analyzed the effects of structure and grain boundaries of the LCMO on the electrical transport properties. So we synthesized the LCMO- Al_2O_3 composites by a solid-state reaction method combined with a high energy milling method. Al_2O_3 was mainly dispersed at grain boundaries. Using this method, the enhanced LFMR was observed in the composites

2. Experiment

The $(1-x)\text{LCMO} + x\text{Al}_2\text{O}_3$ ($x = 0; 0,01; 0,02; 0,03; 0,04; 0,05$) composites were prepared by three step. First, the LCMO powder was synthesized by a conventional solid state reaction method combine with a high energy milling method. High purity (99,99%) La_2O_3 , CaCO_3 and MnO powders were mixed in the appropriate stoichiometric ratio and ground. The well-mixed powders were preheated at a temperature of 1250°C for 15h. Subsequently, it was heated at 1300°C for 10h. Next the LCMO and Al_2O_3 powders were ground by a high energy milling machine for 2h. Finally, the appropriate amounts of LCMO nano powder and Al_2O_3 nano powder were mixed and a homogenous powder was pressed in pellets at pressure of $10\text{MPa}/\text{cm}^2$ and sintered at 900°C for 3h.

The structural characterization was done by employing the X-ray diffraction (XRD) technique at room temperature in the 2θ range of $(20^\circ - 75^\circ)$ with a step size of 0.03° using $\text{CuK}\alpha$ ($\lambda = 1.5406\text{\AA}$) radiation and the surface morphology was observed by scanning electron microscopy (SEM). The temperature dependence of the resistivity, $R(T)$, and the magnetoresistance of the samples were measured by a standard four-probe technique in the temperature range of $(70 \div 300\text{K})$ in a magnetic field range of $0 \div 3\text{kOe}$. The magnetization of the samples was measured by a Vibrating Sample Magnetometer (VSM) in the temperature range of $(100 \div 300\text{k})$.

3. Results and Discussion

The XRD patterns of the composites ($x = 0; 0,01; 0,02; 0,03; 0,04$ and $0,05$) are shown in Fig. 1. It is found that the reflection peaks of LCMO do not shift. It suggests that Al_2O_3 and LCMO coexist in the composites. Besides, the addition of the Al_2O_3 did almost not change position of the peaks of LCMO phase, which implies that Al_2O_3 is probably distributed at the grain boundaries of the LCMO grains.

The average crystallite size of the samples has been estimated from the X-ray line width by using the Scherrer formula $k\lambda/\beta\cos\theta$, where $k = 0,9$ is the shape factor, λ is the wavelength ($\lambda = 1,5406\text{\AA}$), β is the difference of the half width of the X-ray peaks between the samples and the standard silicon that is used as an

internal calibrate of the equipment, and θ is the diffraction angle. The average crystallite size of the samples is calculated to be about 48 nm, but the particle sizes obtained from SEM (Fig. 2) are much larger, 75 nm. This difference is probably due to the fact that an LCMO particle consists of several crystallites, and/or the internal stress, defects in the structure [14].

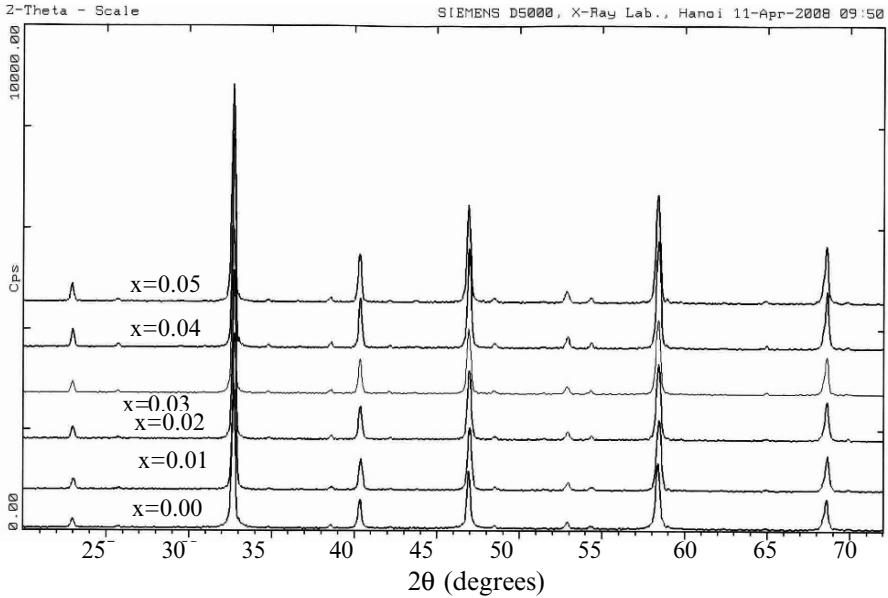


Fig. 1. XRD patterns of $(1-x)\text{LCMO} + x\text{Al}_2\text{O}_3$ composites

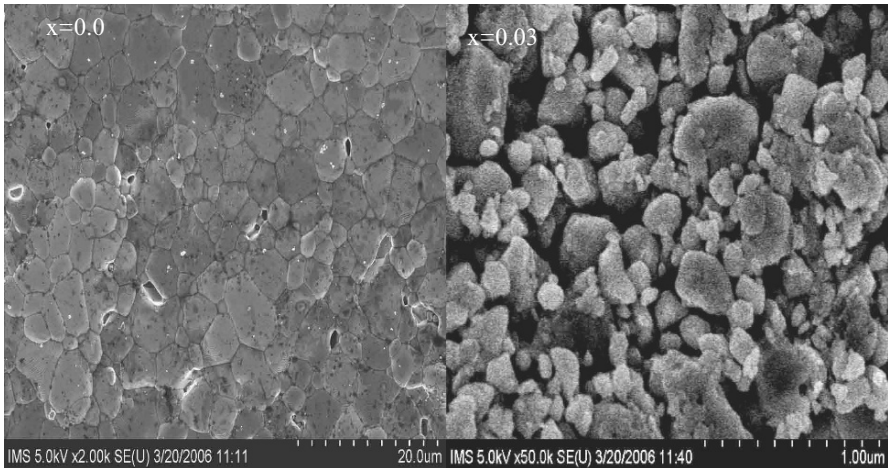


Fig. 2. SEM photograph of $\text{LCMO}/\text{Al}_2\text{O}_3$ samples with $x = 0.0$ and $x = 0.03$. The bright spots in the figure correspond to Al rich boundaries until the Al_2O_3 content increases up to 0.05

Figure 3 presents the magnetization (M) as a function of temperature at 100 Oe for pure LCMO and LCMO/ Al_2O_3 samples. All these samples undergo a sharp ferro-paramagnetic (FM-PM) transition at the same temperature. The Curie temperature T_C is about 250 K. The addition of Al_2O_3 does not change the magnetic transition of LCMO. This indicates that Al_2O_3 mainly exists outside the grains. The reason for this heterogeneous distribution can be understood in terms of two aspects as follows: One is related to the lattice strain. As known the radius of Al^{3+} ion (0,675 Å) is larger than that of Mn^{3+} (0,53 Å), and as reported by [15] the larger ion difficultly enters into the lattice and probably is being pushed out towards the grain boundary in order to release the local strain. The other reason for this distribution is attributed to the synthesis method. Al_2O_3 in the mixture composite may wrap the LCMO grain during the preparation process. As reported by [16] the active Al_2O_3 may attach to the surface of the LCMO grain to reduce its surface energy. Sintering temperature and time affect the entering of the Al_2O_3 into the LCMO lattice. It means that the diffusion of Al_2O_3 into the lattice of LCMO could be optimized by controlling the sintering temperature and time.

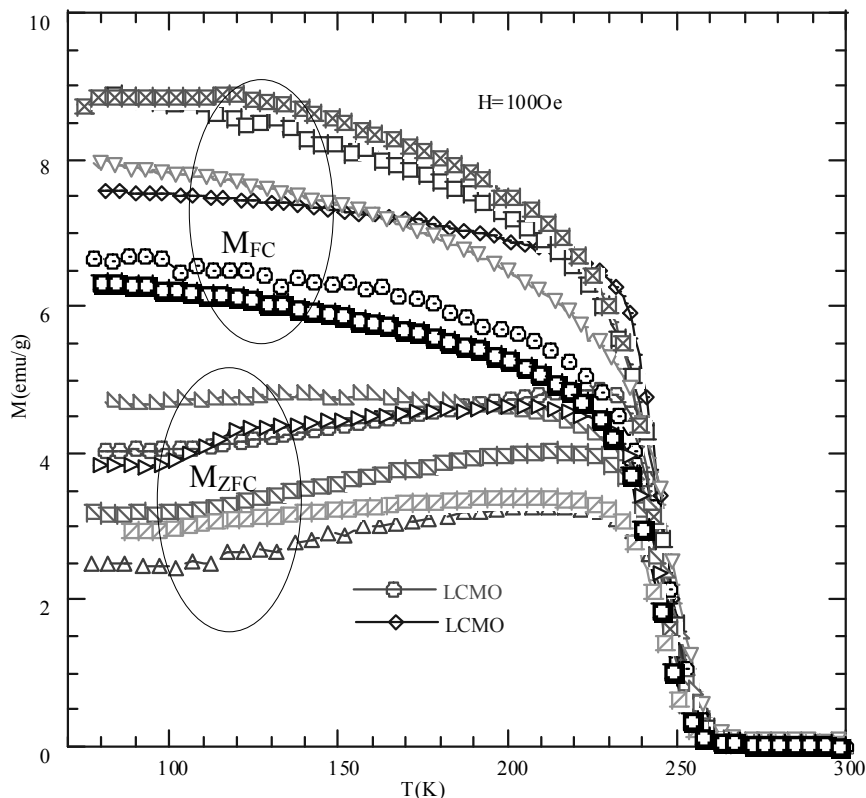


Fig. 3. Magnetization (M) as a function of temperature under an applied field of 100 Oe for $(1-x)\text{LCMO} + x\text{Al}_2\text{O}_3$

Figure 4 shows the temperature dependence of the resistivity for the LCMO/ Al_2O_3 composites with different Al_2O_3 content, measured within a temperature range of 70–300K without magnetic field and a field of 3 kOe. All the composites show a distinct metal – insulator transition. It is clear that the resistivity of all the composites increases in comparison with the pure LCMO and their T_p shifts down to lower temperature. The strong depression of the T_p could be caused by the induced lattice disorder and also by the increase in the non-magnetic

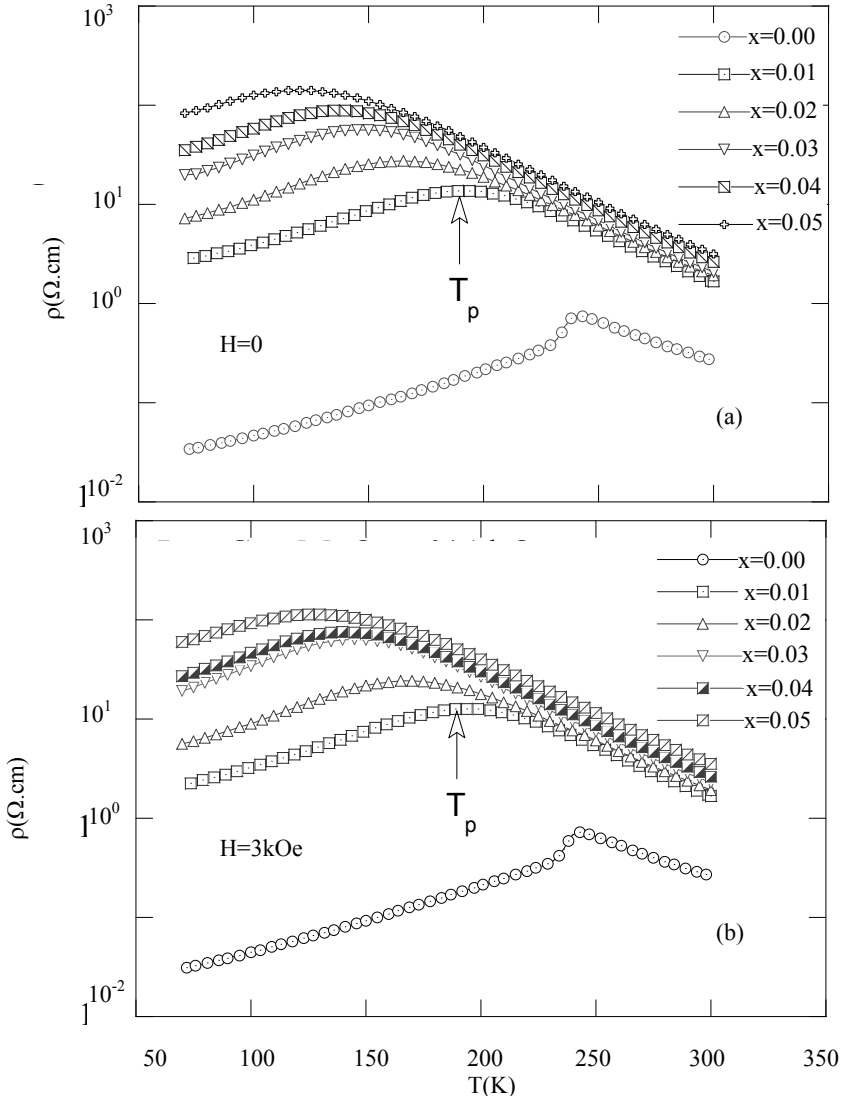


Fig. 4. Temperature dependence of resistivity for $(1-x)\text{LCMO} + x\text{Al}_2\text{O}_3$. (a) $H = 0$ Oe, (b) $H = 3$ k Oe

Al_2O_3 phase fraction. This also causes an increase in the carrier scattering leading to a corresponding enhancement in the resistivity. Thus, increasing Al_2O_3 content reduces the metallic transition temperature and, hence, implies a concomitant increase in resistivity. When a magnetic field is applied, the FM clusters increase in size and the interfacial Mn spin disorder is suppressed, and therefore induces an improvement in connectivity, and consequently the resistivity of the samples decreases as observed in Fig. 4b. It is well known that the resistivity of the composites decreases with increasing grain size [17]. However, in the present composites, the resistivity of the samples does not change regularly with the grain size. Hence, it is reasonable to assume that the distribution and the connectivity of the grains play a more important role in the conduction. In order to clearly explain the electrical transport, a modified model proposed by de Andres *et al.* [18], Rubinstein *et al.* [19], D. Das *et al.* [20] is accepted and the most adopted one. They proposed the concept of a conduction channel mechanism based upon the nature of connectivity between grains. Moreover, due to the disordered nature of the grain boundaries, grain boundary resistivity is higher than the resistivity inside the grains. Al_2O_3 behaves differently at different concentrations. In the pure LCMO samples the electrical transport is realized through a direct contact between the LCMO grains, the electrical channel homogeneous between the intergrains of LCMO. This direct contact is diluted/disturbed as a result of the introduction of an Al_2O_3 insulator. The Al_2O_3 , mostly located at the grain boundaries, acts as a barrier. In case of the LCMO/ Al_2O_3 composites two kinds of conduction channel coexist in parallel. One is related to the LCMO grains, which determines the transport properties of the system. The second is related to Al_2O_3 grains, mostly distributed at the grain boundaries of LCMO.

Since the resistivity of Al_2O_3 is larger than that of LCMO, the second channel can be regarded as an energy barrier that inhibits the direct conduction between the LCMO grains. Therefore, with the increase of Al_2O_3 grains at the grain boundaries, the effective electrical channel of the composites can be reduced, leading to the increase of the resistivity.

Figure 5 shows the curves of the magnetoresistance ratio $\text{MR} = [(\rho_0 - \rho_H)/\rho_0] \times 100\%$ versus the applied H field obtained at 30K for all the composites, where ρ_0 and ρ_H are the resistivity in zero and H field, respectively. The results show that all the samples exhibit LFMR at low temperature. LFMR is largest for the composites with $x = 0.01$ and become weaker when x increase. The reason for this may be related to the structure of the composite. Al_2O_3 is distributed mostly at the grain boundaries of LCMO in the composites with relative low Al_2O_3 content, which can be viewed as diluting the ferromagnetic metallic grains in an insulating matrix. So, the conduction carrier's spin-scattering distance become large and the corresponding MR effect increases. When the content of Al_2O_3 is above 0.01, some Al_2O_3 grains may aggregate and segregate as the second grain phase. This leads to the increase of the resistivity at zero magnetic field, and the resistivity in a magnetic field, resulting in MR, decreases. On the other hand, for the composites with high concentration of Al_2O_3 , the thickness of the grain boundaries may exceed the spin memory length resulting in the decrease of the LFMR effect [16]. Usually grain size and grain boundaries play an important role in the spin dependent tunneling and scattering of the conducting electrons [1,6]. It originates

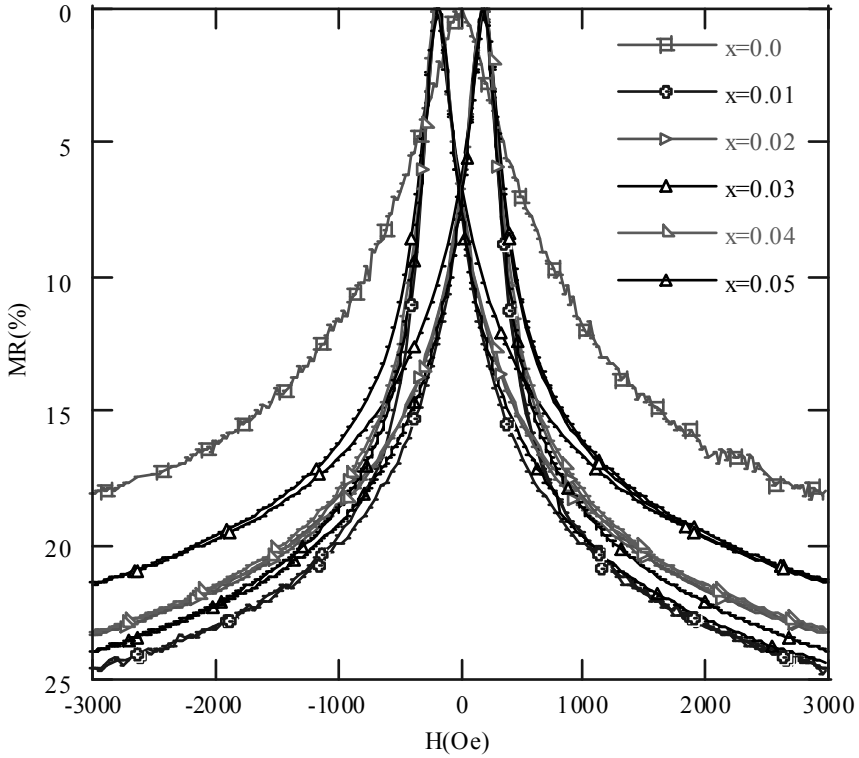


Fig. 5. Field dependence of MR for $(1-x)\text{LCMO} + x\text{Al}_2\text{O}_3$ composites at 30K

from the spin dependent tunneling and scattering process at the interfaces of the grains. Hwang *et al.* [1] were the first to introduce a spin-polarized tunneling mechanism (proposed first by Helman and Abeles [21] in granular nickel films) in the case of manganites on the basis of a feature noted for these materials, namely the high degree of spin polarization of the charge carriers, caused by the half metallic nature of these materials [22]. Later, Yuan *et al.* [23] discussed the transport phenomena for polycrystalline manganites in the light of the spin-polarized tunneling model with a major consideration of grain size, which is essentially larger than 100 nm (i.e., micron size particle) in their case. With LCMO/ Al_2O_3 composites, the enhancement of the LFMR in the samples is closely related to the improvement of the disordered state at the grain boundaries.

4. Conclusions

$(1-x)\text{LCMO} + x\text{Al}_2\text{O}_3$ composites were prepared by a conventional solid state reaction method combined with a high energy milling method. The XRD and SEM results show that no reaction between Al_2O_3 and LCMO takes place, and most Al_2O_3 is distributed at the grain boundaries. The resistivity of the composites is larger than that of the pure LCMO. Further, we have explained the gradual drop of the metal-insulator transition temperature T_p with increasing Al_2O_3 content, while the Curie temperature T_C remains almost constant. An enhanced LFMR is

observed for the composites. Large low field magnetoresistance (LFMR) was achieved for the composites and the largest LFMR appeared when $x = 0.01$. The obtained result may be attributed to the structure and spin polarized tunneling at intergrains.

Acknowledgments

This work has been sponsored by the Institute of Materials Science (IMS-VAST, Vietnam), Hongduc University (HDU, Vietnam) and National Program on basic Research of Vietnam. The authors would like to thank Dr. Dao Nguyen Hoai Nam for her keen interest in this work.

References

1. H.Y. Hwang, S.W. Cheong, N.P. Ong, B. Batlogg, Phys. Rev. Lett. 77 (1996) 2041
2. C. Zener, Phys. Rev. 82 (1951) 403
3. Gupta, J.Z. Sun, J. Magn. Magn. Mater. 200 (1999) 24
4. S.P. Issac, N.D. Mathur, J.E. Events, M.G. Blamire, Appl. Phys. Lett. 72 (1998) 2038
5. S. Jin, T.H. Tiefel, M. McCormack, H.M. O'Bryan, L.H. Chen, R. Ramesh, D. Schurig, Appl. Phys. Lett. 67 (1995) 557
6. L.I. Balcells, A.E. Carrilo, B. Martinez, J. Fontcuberta, Appl. Phys. Lett. 74 (1999) 4014
7. S. Gupta, R. Ranjit, C. Mitra, P. Raychaudhury, R. Pinto, Appl. Phys. Lett. 78 (2001) 362
8. Gaur, G.D. Varma, Solid State Commun. 139 (2006) 310
9. Z.C. Zia, S.L. Yuan, W. Feng, L.J. Zhang, G.H. Zhang, J. Tang, L. Liu, S. Liu, G. Peng, D.W. Niu, L. Chen, Q.H. Zheng, Z.H. Fang, C.Q. Tang, Solid State Commun. 128 (2003) 291
10. S.N. Sadakale, R.J. Choudhary, M.S. Sahasrabhdhe, A.G. Banpurkar, K.P. Adhi, S.I. Patil, S.K. Date, J. Magn. Magn. Matter 286 (2005) 450
11. Jitendra Kumar, Rajiv K. Singh, P.K. Siwach, H.K. Singh, Ramadhar Singh, O.N. Srivastava, J. Magn. Magn. Matter 299 (2006) 155
12. R. Bath, S.R. Shide, K.M. Gapchup, K.P. Adhi, S.I. Patil, J. Magn. Magn. Matter 256 (2003) 425
13. J. Blasco, J. Garci, J.M. Teresa, M.R. Ibarra, J. Perez, D.A. Algarabel, C Marquina, Phys. Rev. B 55 (1997) 8905
14. Vazquez, M.C. Blanco, M.A. Lopez-Quintela, R.D. Sanchez, J. Rivas and S.B. Oseroff, J. Mater. Chem. 8(4) (1998), 991
15. S.L. Yuan, Y.P. Yang, Z.C. Xin, G. Peng, G.H. Zhang, J. Tang, Solid State Commun. 123 (2002) 55
16. L.W. Lei, Z.Y. Fu, J.Y. Zhang, H. Wang, Solid State Commun. 140 (2006) 261
17. L.W. Lei, Z.Y. Fu, J.Y. Zhang, H. Wang, Matee. Sci. Eng. B (2006) 128, 70
18. A.de Andres, M. Garcia-Hernandez, J.L. Martinez, Phys. Rev. B 60 (1999) 7328
19. J.M. Rubinstein, J. Appl. Phys. 87 (2000) 5019.
20. D.D. Srivastava, D. Bahadur, A.K. Nigam. and S.K. Malik, J. Phys.: Condens Matter 16(2004)4089
21. J.S. Helman and B. Abeles, Phys. Rev. Lett. 37 (1976) 1429
22. M. Viret, M. Drouet, J. Nassar, J.P. Contour, C. Fermon and A. Fert, Europhys. Lett. 39 (1997) 545
23. S.L. Yuan, J. Tang, L. Liu, W. Chen, W. Chen, L.F. Zhao, Y. Tian, H. Cao, G.H. Zhang, L.J. Zhang, W. Feng, S. Liu and Z.C. Xia, Europhys. Lett. 63 (2003) 433

Advanced Metallic Magnetic Materials Prepared by Electro-Chemical Deposition, Vapor Deposition and Rapid Quenching

Nguyen Hoang Nghi¹, Mai Thanh Tung², Hoang Nhat Hieu³, Nguyen Van Dung¹,
Nguyen Huu Tinh⁴, Le Cao Cuong¹, and Trinh Thi Thanh Nga¹

¹ Institute of Engineering Physics, Hanoi University of Technology, Hanoi, Vietnam
E-mail: nghi10000@yahoo.com

² Faculty of Chemical Technology, Hanoi University of Technology, Hanoi, Vietnam

³ University of Qui Nhon, Qui Nhon City, Vietnam

⁴ Hanoi Teacher's College N° 2, Xuan Hoa town, Vietnam

Abstract. By use of Electro-Chemical, Vapor Deposition and Rapid Quenching (RQ) techniques several magnetic materials in the form of thin layers are manufactured and investigated. These, generally, nano sized and multiphase, 3d-based materials exhibit a series of properties and effects such as Giant-Magneto Resistance (GMR) and Giant-Magneto Impedance (GMI) effects depending on their composition. The results of long-standing research in the Hanoi University of Technology on preparation technology, structure, properties and application of this kind of materials are shown and discussed in terms of their practical use.

1. Introduction

Traditionally metallurgy processes are carried out at higher melting-points, and subsequently cooled with low speed, so, generally the structure and the phases obtained in this way are in equilibrium and determined by well-known phase diagrams. By contrast, in the chemical plating, vapor deposition and rapid quenching process, the metallic layers probably show a non-crystalline structure due to the rapid deposition of atoms in chemical and vapor deposition and rapid solidification from the melt in RQ. The metallic solids manufactured by these techniques, generally, are distinguished by super-saturation of elements and disordered structure that creates the unstable states. The subsequent heat treatment causes their crystallization. Because the crystallization process happens in the solid state at low temperature, it can be easily controlled to get the nano sized and multi-phase structures, i.e. the desired structures with the given properties. For obtaining the magnetic properties, all studied materials are based on 3d metals (Fe, Co, Ni). The GMI effect is observed in thin layers with ultra-soft magnetic properties. Thin CoP-layers chemically plated on Cu-wires, thin Co-based amorphous and nanocrystalline ribbons are materials with high GMI ratio because they exhibit high soft magnetic properties and on the other hand, they naturally have a small thickness. The Me-3d alloys (Me: Cu, Ag; 3d: Co, Fe) after annealing consist of ferromagnetic Co particles embedded in the Cu matrix leading to a so-called granular structure. The granular structure of Co-Cu alloy is easily to be made and this structure exhibits the GMR effect, although the GMR ratio is not so

large compared to those of the multilayered structure. All above-mentioned magnetic materials are not far from practical application as new magnetic sensors. The various materials with GMI and GMR effects prepared by different techniques were widely reported [1–9].

2. Experiments and Results

2.1. GMI Effect in Amorphous Alloys

The GMI effect is a classical electromagnetic phenomenon where the high frequency impedance of a magnetic conductor is changing strongly under the application of a magnetic field. The effect is related to the combination of skin effect and field dependence of the circumferential magnetic permeability associated with the circular motion of magnetic moment and the dimension of the conductor. So the GMI effect is based on both intrinsic magnetic properties and geometry of the samples. The nano GMI effect is described by the Magneto-Impedance Ratio (MIR). MIR is written as $MIR(\%) = \Delta Z/Z(0) = [Z(H) - Z(0)]/Z(0)$, where ΔZ is the change of impedance of the magnetic conductor $\Delta Z = Z(H) - Z(0)$, with $Z(H)$: impedance with applied magnetic field, $Z(0)$: impedance without the field.

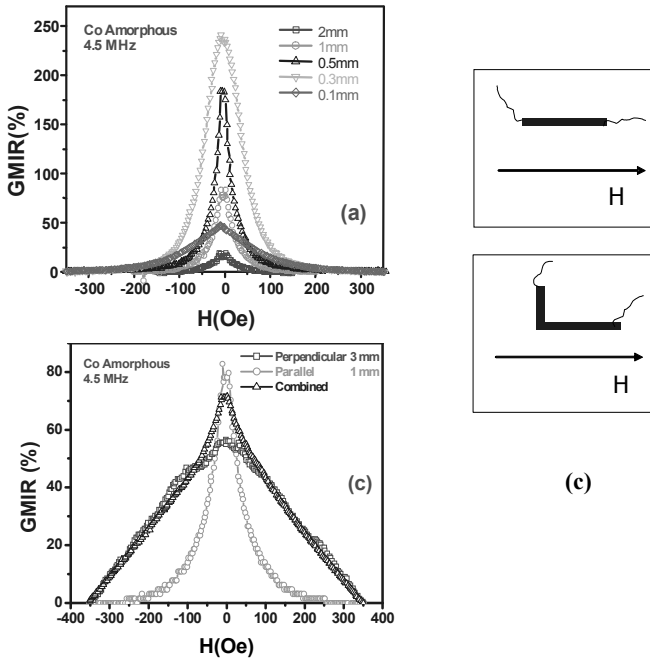


Fig. 1. (a) GMI profiles of amorphous Co samples with different width (the length is fixed), (b) GMI profiles of the combined samples consisting of parallel and perpendicular parts to the direction of the field H, (c) The shape of the samples

The amorphous soft materials in the form of ribbon are produced by RQ and subsequent heat treatment for the mechanical stress removal and crystallization. They exhibit high soft magnetic properties and naturally have small thickness of about 20 μm . The GMI profile (MIR-H dependence) is measured at 4.5 MHz to be 200–350% in the field of about 300 Oe. The MIR strongly depends not only on intrinsic properties but also on the dimension of the sample (thickness, width, length and form) due to a high frequency skin effect. Series of Co-Fe-B-Si ribbons were studied. The studied samples (GMI sensors) were made in the shape of a thin sheet of rectangular form of 10–15 μm in thickness, 0.1–0.5 mm in width and 1–7 mm in length. Besides, combined sensors consisting of parallel and perpendicular parts have been made. The GMI profiles of the amorphous Co samples with different width (the length is fixed) and GMI profiles of the combined samples consisting of parallel and perpendicular parts to the direction of the field H are shown in Fig. 1(a and b). The shape of the samples is shown in Fig. 1(c). From the same material, quite different forms of MIR-H dependence could be obtained by varying the shape and dimension of the sensor, in which the MIR, the linearity and the saturation field strongly changed. The works of this topic are listed in [10, 11] in which besides amorphous ribbons, the GMI effect in the Fe-based nanocrystalline soft magnetic ribbons was investigated.

2.2. Cu/CoP Plated Wires with GMI Effects

Two layer Cu/CoP wires were prepared as follows: By electroplating, a layer of CoP alloy was deposited on the Cu core (wire). The thickness of the CoP layer depends on the electro-chemical conditions (potential, current, time, temperature and the composition of the electrolyte). The electrolyte was a mixture of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, H_3PO_4 and H_3PO_3 . The composition of the CoP layer is controlled by changing the concentration of the phosphorous acid H_3PO_3 which was changed from 0 over 20 g/l, 30 g/l, and 40 g/l to 50 g/l. The electroplating conditions are: current density $\sim 750 \text{ mA/cm}^2$, plating time $\sim 3\text{--}15$ mins., temperature $\sim 60^\circ\text{C}$. An SEM image of a Cu/CoP wire is shown in Fig. 2 in which two layers (Cu core, CoP cover) are clearly seen. The thickness of the deposited layer varies from about 5 micrometers to 50 micrometers depending on the deposition time and current density. X-ray patterns confirm the non-crystalline structure of all samples plated by different conditions. It is supposed that the amorphous state of the CoP layer provides magnetic softness needed for the GMI effect. The composition of the CoP layers is analyzed by an Energy Dispersion Spectrum. The phosphor concentration (%P) in the CoP layer depends on the content of phosphorous (H_3PO_3) acid in the electroplating electrolyte. The maximum P concentration is measured to be 15 wt% for the CoP layer obtained by use of an electrolyte of 30 g/l of H_3PO_3 . The P concentration is controlled by both the pH and the concentration of phosphorous acid in the electrolyte. The GMI effect of the Cu/CoP wires prepared by different technological conditions is investigated. The GMI profiles and the dependence of the GMI ratio (%) measured at 4.5 MHz and 10.7 MHz on electrolyte composition is shown in Fig. 3. It is noted that, the content

of H_3PO_3 in the electrolyte has great influence on the P content in the CoP layer, it determines the soft magnetic property of the layer. The maximum of MIR ($\sim 220\%$) is obtained for the sample containing 15wt% of P. It was obtained in an electrolyte of 30 g/l of H_3PO_3 and corresponds to the minimum coercivity (1.65 Oe).

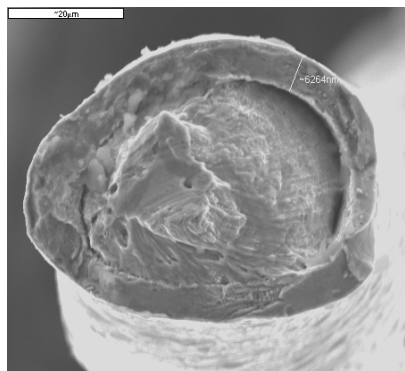


Fig. 2. SEM images of the cross section of Cu/CoP wire. The CoP plated cover is about 5–50 μm thick dependent on the plating conditions

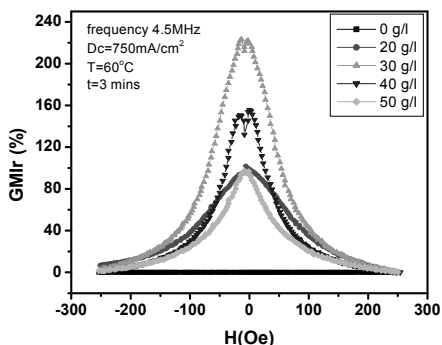


Fig. 3. The GMI profile measured at 4.5 MHz for the samples prepared in electrolyte with different content of H_3PO_3

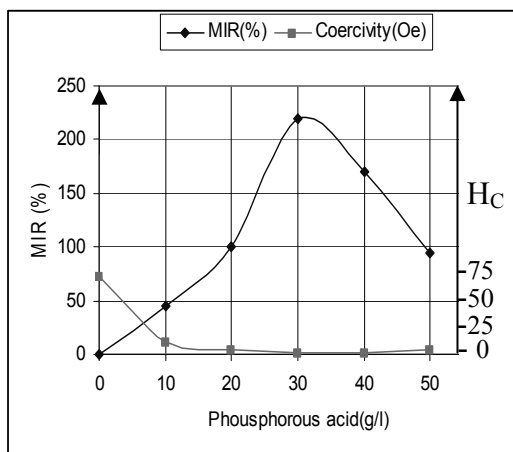
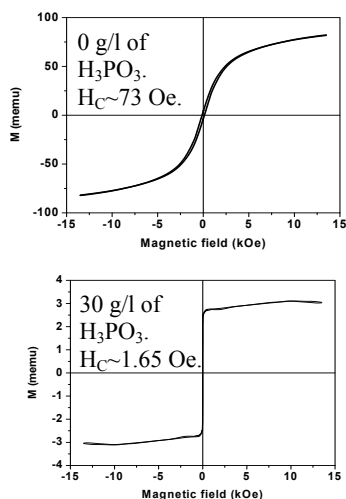


Fig. 4. MIR and Coercivity H_C of CoP layers prepared in an electrolyte with different content of H_3PO_3 , (750 mA/cm^2 for 3 mins.). The values of H_C were deduced from hysteresis loops (left)

Figure 4 shows hysteresis loops of these samples and the dependence of coercivity and MIR on the H_3PO_3 concentration in the electrolyte. The coercivity H_C decreases with increasing of the phosphor content in the CoP layer which depends on the concentration of phosphorous acid. The minimum value of H_C (1.65 Oe) is observed in the CoP sample containing 15wt% phosphor obtained in the 30 g/l H_3PO_3 electrolyte. Generally, the coercivity H_C dramatically decreases with the existence of P in the layer (from ~ 70 Oe to less than 5 Oe) and changes not so much when P varies between 8–15 w% by increasing the content of H_3PO_3 from zero to 20–40 g/l [12, 13].

2.3. GMR Effect in Rapidly Quenched Co-Cu Ribbon

The GMR effect based on the spin dependent conduction of electrons was firstly discovered in multi-layer magnetically heterogeneous structures. Later this effect was also observed in granular structures consisting of ferromagnetic and non-ferromagnetic particles of nano size. This granular structure is easily prepared by precipitation of super saturated rapidly quenched Me-3d materials (Me: non-ferromagnetic metals, 3d: Fe, Ni, Co) alloys.

The samples in the shape of thin ribbons are prepared by rapid quenching in air. The obtained samples are of 2–20 mm in width and 20–25 micrometer in thickness. The studied samples were $\text{Co}_x\text{Cu}_{(100-x)}$, ($x = 6, 8, 10, 14, 20, 25, 30$). A fully amorphous (glassy) state is not seen in the rapid quenching process. A crystalline structure is observed in all samples before and after annealing. The co-existence of two phases of Cu and Co was confirmed by chemical, X-ray and AES analysis. The distribution of particles in the Co-Cu samples was investigated by use of Auger Electron Spectroscopy (AES) (compositional mapping). The effect of annealing on the particle size is different for Cu and Co: Cu particles in the as-spun and annealed sample are homogenously distributed and their particle size is nearly identical and unchanged during heat treatment (Fig. 5, right). For Co particles, Auger mapping shows that there are two sizes for Co particles: a small and a larger one (Fig. 5, left). It is supposed that, the small particles of nano size, which are homogenously distributed in the samples, play the main role for the GMR effect. It is noted that before annealing, the Co size is identical. Magnetization curves of the samples change significantly depending on the composition (Fig. 6). The ferromagnetic behavior of the Co-rich samples (50–90 at%) does not correspond to a high GMR ratio, on the contrary, the samples with 8–12 at% Co exhibiting super paramagnetic (SPM) behavior, show a GMR ratio up to 5.5% (for $\text{Co}_{10}\text{Cu}_{90}$ sample, at room temperature) and over 20% at 177 K. The total experimental magnetization of the samples can thus be written as:

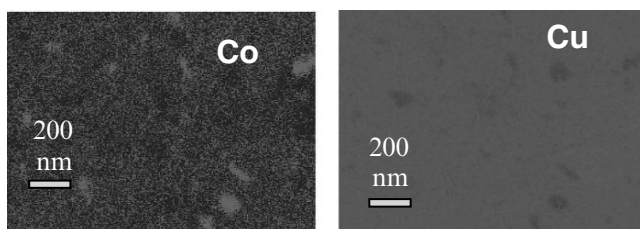


Fig. 5. SEM image and elements mapping of $\text{Co}_{10}\text{Cu}_{90}$ sample annealed at 450°C for 60 mins

$$M(H) = M^{FM}(H) + M^{SPM}(H)$$

where the term $M^{FM}(H)$ gives the ferromagnetic fraction of the Co particles. The term $M^{SPM}(H)$ presents the SPM fraction of the Co particles. By separating the ferromagnetic part from the experimental magnetization curve $M(H)$, using the Langevin theory of paramagnetism, it is possible to write:

$$M^{SPM}(H) = pM_sL\left(\frac{mH}{k_B T}\right) = pM_s\left[\coth\left(\frac{mH}{k_B T}\right) - \frac{k_B T}{mH}\right]$$

where p is the volume fraction of the magnetic particles, $m = M_s V$ is the magnetic moment of a single particle with volume V , H is the external field, M_s is the saturation magnetization of a Co particle. Assuming that the Co particles are spherical with a diameter of D , $V = \frac{\pi D^3}{6}$, the size of the Co particle is nearly 5 nm [8,14,15].

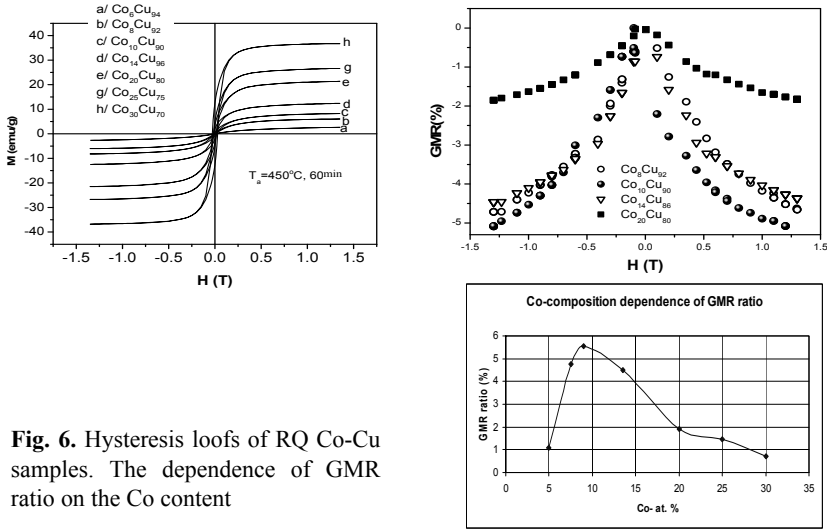


Fig. 6. Hysteresis loops of RQ Co-Cu samples. The dependence of GMR ratio on the Co content

2.4. GMR Effect in Vapor Deposited Co-Ag Thin Films

Thin films of Co-Ag were evaporated in high vacuum by use of a vibrating mechanism in which, the mixture of Co-Ag powder drops by small portion onto the W heating element. This technique (flash vapor) provides high speed of evaporation. The substrate was a Si-plate (monocrystal) (Fig. 7).

Hysteresis loops (Fig. 8) show super paramagnetic behavior for the low (20–40 at%) Co-content samples and

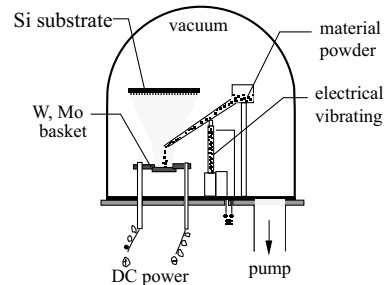


Fig. 7. Scheme of “flash” vacuum vapor deposition

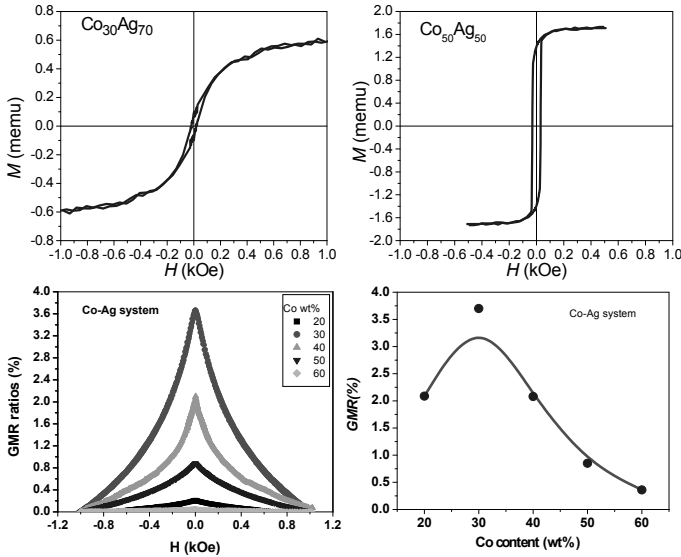


Fig. 8. Hysteresis loops and GMR profiles of the vapor deposited Co-Ag thin films. The composition dependence of the GMR ratio.

ferromagnetic behavior for high Co-content. High GMR ratios were observed for the super paramagnetic samples with 20–40 at% of Co (highest GMR ratio is 3.6% for 30 at% Co sample). The composition dependence of GMR ratio is shown in the Fig. 8 [16].

2.5. Potential Application

The high magnitude of MIR, the multiform of GMI profiles and the simplicity in preparation technology create a possibility for the application of both Cu/CoP wires and Co-based ribbons as highly sensitive magnetic sensors. An ampere meter using a GMI sensor has been designed and assembled (Fig. 9). The measuring range of currents is easily changed (up to thousands of amperes) due to easy changes of the MIR profile. Furthermore, GMI ampere meter can be used to measure simultaneously both DC and AC currents. The graph in Fig. 9 show the coincidence of two U-I curves for AC and DC in the range from 0 to 30 A.

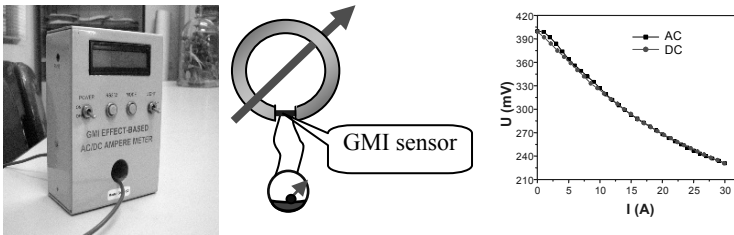


Fig. 9. Current sensor using GMI effect. The U-I characteristic for AC & DC currents.

3. Conclusive remark

1. Various magnetic materials in the form of thin layers and wires showing GMI and GMR effects are produced by use of electrochemical deposition, vapor deposition and rapid quenching. The high quality of the manufactured materials and the simplicity of their preparation are the main features of the above mentioned techniques.
2. The Co-based amorphous ribbons and chemical deposited Cu/CoP wires show a high GMI ratio of about 200–350%. The GMI profile is easily and strongly variable by changing the form of the samples.
3. The GMR effect was observed in both vapor deposited thin films and rapidly quenched ribbons. Granular GMR materials do not show a high GMR ratio, but the effect does not depend on the measuring direction.

Acknowledgement

This work was financially supported by: The Program of Basic Science, MOST (Vietnam), 2004–2006 and Korean Research Fund (Korea), 2006. The authors express their thanks to Prof. O.S. Song (UOS) and Dr. N.A. Tuan (HUT) for discussion, to Masters of Science, Mr B.X. Chien, Miss N.T.H. Tam, Miss B.T. K. Nhung and student, Mr N.H. Hoang for sample preparation and measurements.

References

1. M.N. Baibich, J.M. Broto, A. Fert, Nguyen Van Dau, R.F. Petroff, P. Eitenne, G. Creuzet, A. Freiderich and J. Chazelas, “Giant Magnetoresistance of (001)Fe(001)Cr Magnetic Superlattices”, *Phys. Rev. Lett.*, 61, (1988) 2472.
2. A.E. Berkowitz, J.R. Mitchell, R.S. Beach, D. Rao, F.T. Parker and F.E. Spada, “Giant Magnetoresistance in Heterogeneous Alloy Films”, *IEEE Trans. Magn.*, 30, (2), (1994) 353-357.
3. L.V. Panina and K. Mohri, *J. Appl. Phys.*, 65 (1994), 1189.
4. M. Knobel, K.R. Pirota and C.G. Polo, The Fifth Latin American Workshop on Magnetism, Magnetic Materials and their Applications, September 3 - 7, 2001.
5. A.F. Cobeno, A. Zhukov, J.M. Blanco and J. Gonzalez, *J.M.M.M.*, 234 (2001), L359-L365.
6. K.R. Pirota, L. Kraus, H. Chiriac and M. Knobel, *J.M.M.M.*, 221 (2000), L 243-L247.
7. Nguyen Hoang Nghi, Nguyen Van Dung, et al., “GMI effect in Amorphous and Nanocrystalline Materials”, *Physica B*, vol. 327 (2003), p. 253.
8. Nguyen Hoang Nghi, “The combined properties of the amorphous alloys and nanosized multiphase structures”, *Adv.in Tech. of Mat. And Mat, Proc. J. (ATM)*, (Japan), Vol. 6 [1] (2004) 11-16.
9. Nguyen Hoang Nghi , Nguyen Van Dung , Nguyen Huu Tinh , Trinh Thi Thanh Nga, Nguyen Thi Hong Tam, Bui Thi Khanh Nhung, Mai Thanh Tung and Hoang Nhat Hieu, “Advanced magnetic materials produced by rapid quenching technology”, 1st IWOFM and 3rd IWONN, Ha long 9/2006, p. 784.

10. Nguyen Hoang Nghi, Nguyen Van Dung and Phi Hoa Binh, "Giant magnetoimpedance effect in ultra-soft magnetic materials", Proceeding of the 9th Asia Pacific Physics Conference, Hanoi, October 25-31, 2004.
11. Nguyen Hoang Nghi, Nguyen Van Dung, Nguyen Huu Hoang, Tran Anh Phong, Phi Hoa Binh, "Dependence of giant magnetoimpedance effect of Co-based and Fe based nanocrystalline ribbons on measuring configuration", The ninth Asia Pacific physics Conference, Hanoi, October 25-31, 2004.
12. N.V. Dung, B.T.K. Nhung, N.T.H. Tam, M.T. Tung, N.H. Nghi, Ohsung Song, "Magnetoimpedance effect of CoP/Cu electrodeposited wires", Proceeding of the International Conference on Engineering Physics, Hanoi, Vietnam, 2006, p. 159.
13. Mai Thanh Tung et al. "Electrodeposition of the Permalloy film (80Ni20Fe) with Giant Magnetoimpedance (GMI) Effect onto Insulating substrates", Journal of Chemistry (Vietnam), vol. 52, 2006.
14. N.H. Nghi, B.X. Chien, N.V. Dung, T.A. Phong, N.A. Tuan, N.H. Duc and V.N. Thuc, "The influence of heat treatment on magnetoresistance effect in granular Cu-Co alloys prepared by rapid quenching", Adv. in Tech. of Mat. And Mat, Proc. J. (ATM), (Japan), Vol. 6 [1], (2004) 83-86.
15. Nguyen Hoang Nghi, Tran Anh Phong, Vu Nguyen Thuc, Bui Xuan Chien, Nguyen Van Dung, M. Inoue, Hoang Ngoc Thanh, "Magnetization process in granular Cu₉₀Co₁₀ alloys", 7th VGS, Halong 4/2004.
16. Hoang Nhat Hieu, Nguyen Van Dung, Trinh Thi Thanh Nga, Nguyen Anh Tuan, Oshung Song and Nguyen Hoang Nghi, "The giant magneto resistance effects of Co-Me (Me=Cu,Ag) thin films fabricated by flash vapor deposition", 1st IWOFM and 3rd IWONN, Ha long 9/2006, p781.

Magnetic Interaction Between Polycrystalline Ultrathin Antiferromagnetic and Ferromagnetic Films

Roland Mattheis and Klaus Steenbeck

Institut für Photonische Technologien e.V.,
Albert-Einstein-Straße 9, 07745 Jena, Germany

Abstract. The interaction of a soft ferromagnetic film (F) with an antiferromagnetic film (AF) is governed by the exchange interaction at the interface causing the well known shift of the hysteresis loop (the so called exchange bias) and a large rotational loss. We analysed the AF thickness dependence of this behaviour in terms of a Stoner-Wohlfarth model and compared it to experimental results obtained on polycrystalline $\langle 111 \rangle$ textured NiFe/IrMn film systems. Within the model we can explain all observed effects, the exchange bias, the unidirectional anisotropy, the rotatable anisotropy, the rotational loss and the enlarged coercivity. The temperature dependent torqueometry was used to determine the magnetic anisotropy of the IrMn and to estimate the distribution of the F/AF coupling energy density.

1. Introduction

The interaction at the interface between thin films of an antiferromagnet (AF) and a ferromagnet (F) establishes interesting magnetic effects: a unidirectional magnetic anisotropy which causes a shifted hysteresis loop of the ferromagnet, rotatable anisotropy, hysteresis loss and an enlarged coercivity of the ferromagnetic film. The shifted hysteresis loop, causing a fixed direction of the ferromagnet at zero magnetic field, is very useful for the definition of a reference direction necessary in any magnetoelectronic devices. This so called exchange bias (EB) effect was discovered long time ago by Meiklejohn and Bean [1] and has found wide application for the last 10 years. Rotatable anisotropy and rotational loss are of minor importance and therefore not in the focus of the most investigations. Whereas a phenomenological description of a variety of effects is given in [2–6] and references herein, a knowledge of the crucial parameters like coupling energy $J_{F/AF}$ or the anisotropy K_{AF} of the antiferromagnetic layer and their thickness and temperature dependences is still missing. This problem is caused by the fact that these properties can be investigated only by studying the (global) interaction of an AF with an F layer whereas the exchange interaction between F and AF itself is of local nature. At least for polycrystalline film systems

- the exchange stiffness of the AF magnetization is drastically reduced at the grain boundaries of the AF, which are randomly oriented and
- the interaction is determined by the local net moments at the F/AF interface which can strongly vary from grain to grain [2].

To give more insight in the F/AF interaction we analyse the properties of polycrystalline F/AF sandwiches at very low AF thicknesses. In that thickness region we can surly neglect the interaction between the AF grains. As a result the AF layer behaves like an ensemble of individual noninteracting AF grains coupled to a homogeneous F layer. Assuming a homogeneous magnetisation within every AF grain we can describe the whole system as a system of individual AF grains with the same intrinsic properties (anisotropy) and, due to their individual interface structure, with different F/AF coupling strength j and a coupling strength distribution function $P(j)$.

The paper is organised in the following: in chap. 1 we analyse the interaction of individual AF grains with the F and derive the importance of the knowledge of the local coupling and the AF anisotropy, which both are connected to the observed effects namely the uniaxial anisotropy, the rotational loss and the rotatable anisotropy of films. In chap. 2 we describe our way to derive reliable data for K_{AF} . Chapter 3 deals with the coupling energy density distribution and with quantitative analysis of the thickness dependence of the rotational loss of NiFe/IrMn films.

2. Analysis of the F/AF Interaction

Three properties govern the F/AF interaction: the anisotropy of the antiferromagnet, the interface coupling strength and the AF grain to grain interaction.

Until now there are no direct methods for characterisation of at least one of these properties. All our knowledge is derived from interpretation of the action of the outer field H with a ferromagnetic layer which interacts itself with the AF layer with respect of a model. Most experiments use loop racer measurements and deal with the enlarged coercivity H_c and the exchange bias field H_{EB} . Both are connected in a complex way with the unidirectional anisotropy, rotatable anisotropy and hysteresis loss of the F/AF system. We concentrate on the description of the torque in a magnetic field of a F/AF sandwich. As it is shown below this method is sensitive to all of the interactions we have to characterise in a more direct way. Additionally, the investigation of torque losses is insensitive to the conditions of the freezing-in process because it senses the interaction over a full circle.

Therefore we start our analysis in terms of a Stoner-Wohlfarth model. We describe the interaction of a single AF grain with a homogeneously magnetised soft ferromagnetic layer. We assume that the lateral size of the grain is small enough to avoid splitting of AF magnetisation in AF domains within the grain itself (typical lateral grain size of the AF is in the order of 12–15 nm). The thickness of the AF under investigation is $t_{AF} < 3$ nm, well below the thickness of an AF domain wall. Therefore we can assume a homogeneous magnetisation within the AF grain at least in the vertical direction. The interaction between AF and F is governed by a net magnetisation μ of the AF at the interface which we assume to be rigidly coupled to the AF. From experiments we know that this

effective moment is in the order of 0.03 [7] of the moment of a ferromagnetic monolayer. For real polycrystalline systems the growth of the AF needs a preferred orientation to get large effects. We concentrate on application related systems like IrMn and PtMn. IrMn grows preferentially in a strong (111) texture (typical $\Theta_{50} < 5^\circ$). That means we have three $\langle 110 \rangle$ directions lying in the F/AF interface, $[1\bar{1}0]$, $[\bar{1}01]$ and $[01\bar{1}]$, resulting in a three axial anisotropy in that plane.

Low index directions for the (111) texture are $\langle 110 \rangle$ and $\langle 112 \rangle$, which represent the directions with the highest and lowest anisotropy energy. Assuming that one of these directions, e.g., the $\langle 110 \rangle$ direction, has a lower energy density ε . The rotation in that plane is therefore governed by the difference of the energy in these both directions. Therefore, we consider the in-plane anisotropy K_{AF} responsible for the interaction under investigation.

$$K_{AF} = \frac{\varepsilon_{\langle 112 \rangle} - \varepsilon_{\langle 110 \rangle}}{t_{AF}} \quad (1)$$

Then we have three easy axes (ea) within the plane $[1\bar{1}0]$, $[\bar{1}01]$ and $[01\bar{1}]$ as shown in Fig. 1 because we have three possible $\langle 110 \rangle$ axes in the plane: all forming a 60° angle with each other. This leads to the number $q = 3$ of ea in the plane of (111) oriented IrMn.

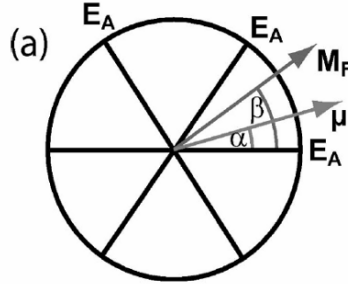


Fig. 1. Top view on F/AF interface for an AF with $q = 3$

The energy density per area ε of the F/AF system in a magnetic field rotating parallel to the IF plane is:

$$\varepsilon = K_{AF} * t_{AF} * \sin^2(q\alpha) - j * \cos(\beta - \alpha) - K_F * t_F * \sin^2(\beta_F) \quad (2)$$

where $q = 3$ is the number of easy axes of the AF within the plane, β is the direction of the magnetisation of the F layer (equal to the direction of the magnetic field H for large H), β_F is the direction of the F magnetisation M_F with respect to the ea of the F layer (assumed to be uniaxial), t_F is its thickness, and α is the direction of the net moment with respect to one of the easy axes of the AF. Contributions of the anisotropy of the F are neglected in the following because of the softness of the F layer and the used large H ($H \gg H_K^F < 4$ Oe, $K_F < 200$ J/m³).

Therefore, the orientation α of the net moment μ , which is assumed to coincide to the direction of one of the magnetic sublattices of the AF magnetisation, is only determined by the ratio $r = j/K_{AF}t_{AF}$ and the value of q .

By analysing the equation (1) we get different types of the energy landscape (Fig. 2, 3 und 6) and three classes of solutions:

1. continuous change of α with β for strong coupling $j > K_{AF}t_{AF}2q^2 = j_2$
2. jump-like change of α with β for intermediate coupling $j_1 < j < j_2$
3. only small α oscillations with β around the ea of the AF for weak coupling $j < K_{AF}t_{AF}q = j_1$.

Let's start with the analysis of case 1. In the ideal case of an atomic flat F surface and an uncompensated AF interface one can expect $j/K_{AF}t_{AF} \gg 20$ as long as $K_{AF} < 10^6 \text{ J/m}^3$. Such parameters result in an energy landscape shown in Fig. 2. Here we get a nearly sinusoidal potential, its minimum moves with the angle β of the F magnetisation (and therefore the magnetic field). This corresponds to the case of a rigid F/AF coupling. Because $\alpha \approx \beta$, the quasistatic F/AF behaviour can be described by a total anisotropy K_{F-tot} as a superposition of K_F and K_{AF} normalized by the factor t_{AF}/t_F . This system does not show any of the AF/F features like exchange bias, hysteresis loss, and rotational anisotropy. Only the effective anisotropy is changed.

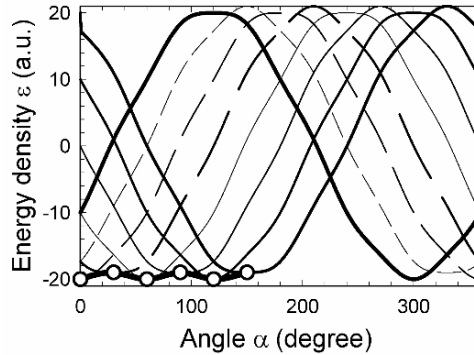


Fig. 2. Energy landscape for the strong coupling case: $j/Kt = 20$, $q = 3$ for field angles $\beta = 60^\circ; 90^\circ; 120^\circ; 150^\circ; 180^\circ; 210^\circ; 240^\circ$ and 270°

Now let's reduce the coupling strength to the intermediate case, this means a value for r between 3 and 18 for $q = 3$ or between 1 and 2 for $q = 1$. Figure 3 shows the case for a three axis AF grain and $r = 4$. The different curves visualise the energy landscape for a magnetic field at $\beta = 60^\circ, 80^\circ, 100^\circ, 110^\circ, 120^\circ$ and 180° , respectively. For this case the angle α of the local energy minimum changes only slightly from $\alpha = 60^\circ$ to $\alpha = 75^\circ$ during rotation of H from 60 to 120° . At angles slightly larger than 120° a jump of the direction of the net moment and therefore also the AF magnetisation occurs. After that jump we have, with respect to the energy landscape, the same situation as we had at 60° . The jump is

connected with energy loss. Therefore, we observe rotational loss and rotational anisotropy.

The third case is visualised in Fig. 4. With a full rotation of the F magnetisation the angle α of the net moment (position of the energy minimum) only hardly changes. The energy of AF increases to its maximum after field rotation by 180° , causing the unidirectional anisotropy and the exchange bias field. Therefore, only the weakly coupled grains are responsible for the shift of the hysteresis curve and the definition of a preferred direction in F/AF systems.

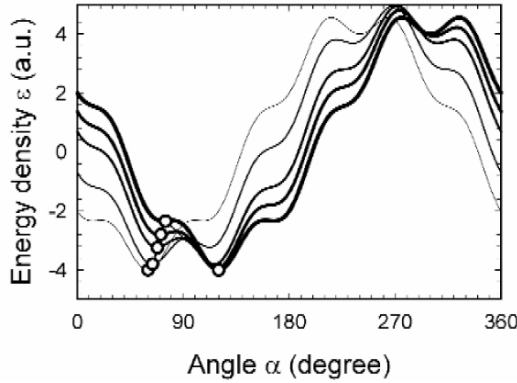


Fig. 3. Energy landscape for an intermediate coupling ratio: $j/Kt = 4$ and $q = 3$. The black circles illustrate the movement of the grain net moment in the energy minimum by a step-like field rotation of $\Delta\beta = 20^\circ$. A jump occurs from $\alpha = 75^\circ$ to $\alpha = 120^\circ$

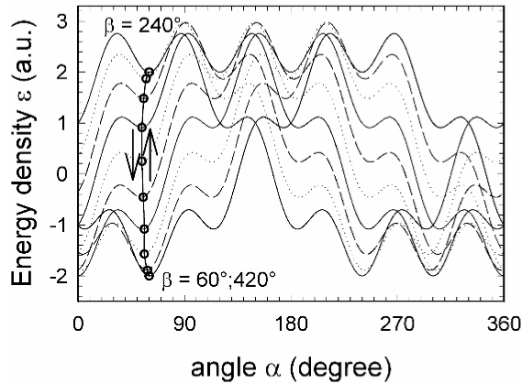


Fig. 4. Energy landscape for low coupling ratio: $j/Kt = 2$ and $q = 3$. The circles show the movement of the grain net moment in the energy minimum by field rotation from $\beta = 60^\circ$ to 420° , every step $+20^\circ$

Figure 5a and b summarize our findings For $q = 1$ and $q = 3$ for strong and intermediate coupling. Jumps of the direction α of μ occur for intermediate coupling. They cause hysteresis loss $\Delta\varepsilon$. As shown in Fig. 6a and ba transition of the behaviour of the AF occurs at $r = q$. For $r < q$ the AF net moment does not follow the rotation of the F layer magnetisation. This is the only case where exchange bias occurs!

Summarising we have:

1. Only modified effective anisotropy of F/AF for strong coupling.
2. Hysteresis loss(causing an enlarged coercivity) and rotatable anisotropy for intermediate coupling.
3. Unidirectional anisotropy and exchange bias field for weak coupling.

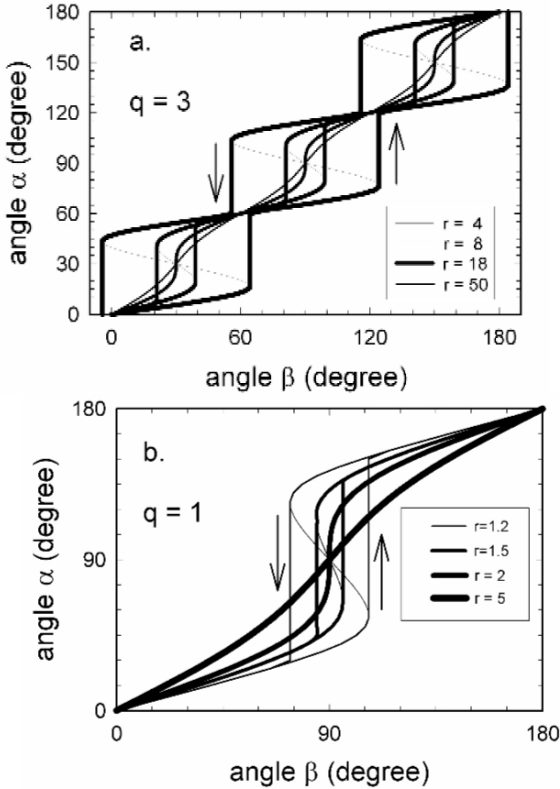


Fig. 5a, b. Dependence of the AF net moment angle α on the field angle β for strong coupling ($r = 18; 50$ for $q = 3$, $r = 2; 5$ for $q = 1$) and for intermediate coupling ($r = 4; 8$ for $q = 3$ and $r = 1.2; 1.5$ for $q = 1$). The latter causes jumps as shown by vertical lines causing rotational loss

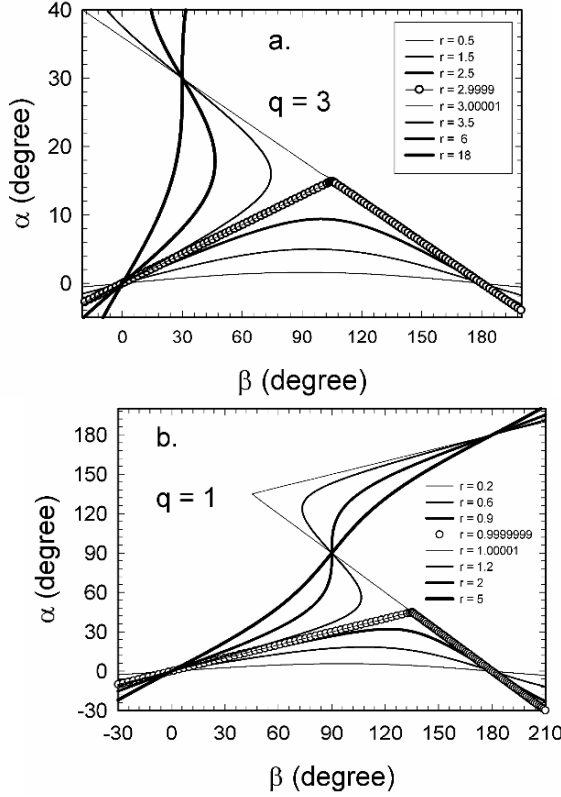


Fig. 6a, b. Dependence of the AF net moment angle α on the field angle β for weak coupling ($r = 0.5; 1.5; 2.5; 2.999$ for $q = 3$, and $r = 0.2; 0.6; 0.9; 0.999$ for $q = 1$) and for intermediate coupling

3. Determination of the AF Anisotropy K_{AF}

Up to this point we only considered the behaviour at $T = 0$. Figure 7 shows the energy landscape for $r = 4$ and $q = 3$ around the angle $\beta = 123^\circ$. Only at $T = 0$ the switching occurs exactly at $\beta = 124^\circ$. At field angles $\beta < 124^\circ$ an energy barrier E_B exists, but such a barrier can be overcome by a thermal activation. Our polycrystalline films have a typical grain size of about 15 nm. Without AF grain-to-grain interaction the thermal energy $k_B T$ is not negligible as compared to the anisotropy energy of a single grain at least for low thickness t_{AF} . Therefore, the switching processes itself is modified at $T > 0$. The field angles where the switching occurs, the critical coupling strengths j_1 and j_2 and the amount of energy density losses $\Delta\epsilon$ are reduced with increasing temperature as shown in Fig. 8. The calculations are done with a relaxation time $\tau \sim 1$ s, adapted to our experimental situation and discussed in detail in [8]. The vanishing of the rotational loss at a critical temperature T_B is directly related to the K_{AF} by:

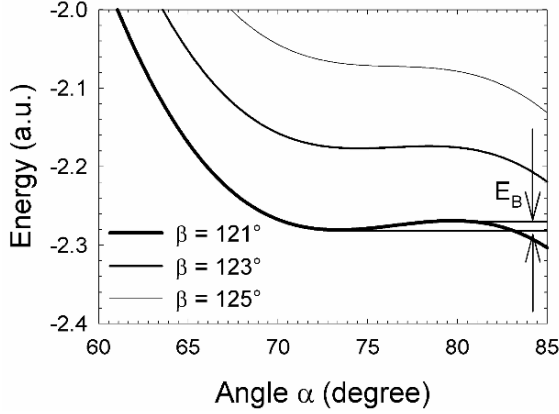


Fig. 7. Energy landscape for inter-mediate coupling: $j/Kt = 4$ and $q = 3$ around the angle β where the jump of α occurs

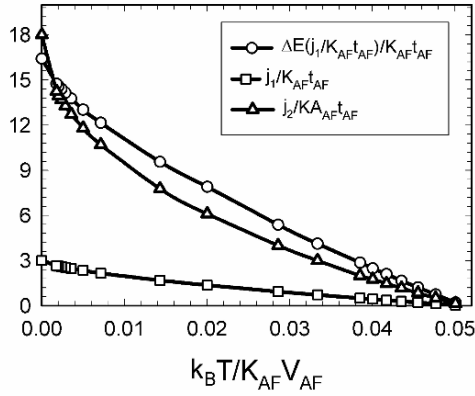


Fig. 8. Dependence of $j_1/K_{AF}t_{AF}$, $j_2/K_{AF}t_{AF}$ and $\Delta E(j_1/K_{AF}t_{AF})/K_{AF}t_{AF}$ on the activation parameter $k_B T / K_{AF} V_{AF}$ for $q=3$

$$K_{AF} = \frac{k_B T_B}{0.052 V_{AF}} \quad (3)$$

with the volume V_{AF} of a single AF grain. Figure 9 shows, as an example, a measured torque curve $L(\beta)$ for cw and ccw field rotation for a NiFe(16nm)/IrMn (1.9 nm) film system at $T = 200\text{K}$ with an energy loss density $\epsilon_{\text{loss}} = 317 \mu\text{J}/\text{m}^2$ determined from the area of the hysteresis curve. Such loss disappears at T_B . By determining the blocking temperature of the hysteresis loss T_B for different thicknesses t_{AF} (Fig. 10) we have derived a value for $K_{AF} = (3 \pm 1)10^5 \text{ J}/\text{m}^3$ for (111) textured IrMn films of $t_{AF} < 2.5 \text{ nm}$.

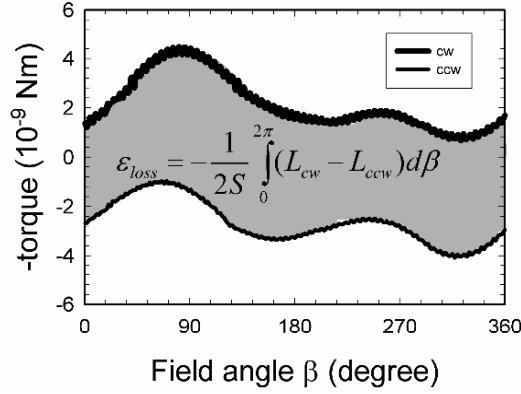


Fig. 9. Measured torque curve of a NiFe/IrMn film system for cw and ccw field rotation. S = film area, $\epsilon_{\text{loss}} = 317 \mu\text{J}/\text{m}^2$.

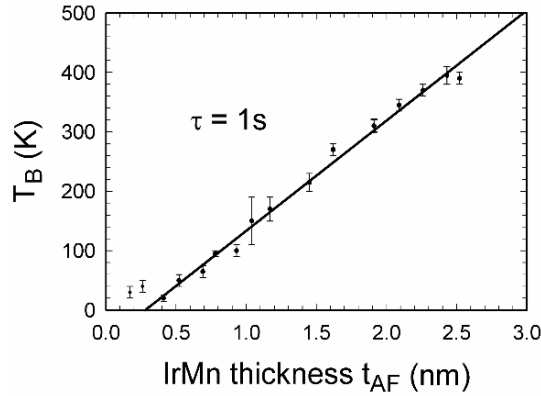


Fig. 10. Dependence of the blocking temperature T_B (vanishing rotational loss) determined by torqueometry on the IrMn thickness t_{AF} .

4. AF Coupling Strength Distribution $P(j)$

In a real polycrystalline film the individual coupling j of the grains is distributed and can be characterized by a distribution function $P(j)$. To our knowledge, the distribution $P(j)$ was not measurable until recently [9], but has merely been adapted from a theoretical understanding with statistical assumptions [3, 10, 12, 13]. $P(j)$ is linked with the coupling energy J and the exchange bias field $H_{\text{EB}} = J/M_F t_F$ of the whole film and with its energy loss density ϵ_{loss} which is proportional to the coercivity enhancement ΔH_C .

$$J = c \int_0^{j_1} j * P(j) dj \quad (4)$$

(The factor $c < 1$ depends among others on the field cooling procedure).

$$\varepsilon_{loss} = \int_{j_1}^{j_2} \Delta \varepsilon(j) P(j) dj \quad (5)$$

Different models have been applied to explain J , j , and $P(j)$ considering the AF net moment, F magnetization, exchange constant, grain size, grain size distribution, interface roughness etc. Comprehensive explanations about the mechanisms in polycrystalline F/AF systems are given in Ref. [3, 5-10]. An important model [12] reflecting the statistical nature of the F/AF interface by a Gaussian distribution of non compensated interface spins results in the distribution function $P(j)$ shown in Fig. 11.

$$P(j) = \sqrt{2/\pi} \sqrt{n/\gamma} * \exp(-j^2 n / 2 \gamma^2) \quad (6)$$

Herein n is the number of interface spins, $\gamma = J_{INT}/a^2$ is the ratio of the interface exchange constant J_{INT} and the area a^2 for one magnetic atom in the AF. Figure 11 also pictures J and ε_{loss} as the marked areas under the corresponding functions. With this distribution the principal thickness dependencies of ε_{loss} and of J can be explained. The thickness dependencies are involved in equ. (5) and (6) because j_1 , j_2 , and $\Delta \varepsilon$ are functions of $K_{AFt_{AF}}$. Figure. 12 shows two calculated function $\varepsilon_{loss}(t_{AF})$ for $T = 0$ applying equ. (5) and the distribution (6). We used $K = 3.5 * 10^5 \text{ J/m}^3$ with $J_{INT} = 47 * 10^{-22} \text{ J}$ and $K = 4 * 10^5 \text{ J/m}^3$ with $J_{INT} = 55 * 10^{-22} \text{ J}$, and $n = 2300$, $a^2 = 8.2 * 10^{-20} \text{ m}^2$ which correspond to our experiments with NiFe/IrMn film systems. K_{AF} and J_{INT} were chosen to fit our experimental results [9] which are also shown in Fig. 12.

The results show that equ. (6) is an acceptable approximation of the distribution function. The fitted K_{AF} agrees well with the results derived in chapter 2, and the fitted interface exchange constant J_{INT} is in the right order. J_{INT} is only roughly known and depends among others on the interface quality. As discussed in Ref. [13] J_{INT} can be compared with the exchange constant in AF (typical $J_{AF} = 30 * 10^{-22} \text{ J}$) or in FM Ni and Fe alloys (typical $J_{FM} = (15-80) * 10^{-22} \text{ J}$).

Another way to get information on the coupling strength distribution is to do torque measurements just after a field rotation reversal [9]. Their analysis showed, that for increased temperatures the centre of $P(j)$ is shifted to lower coupling strengths j .

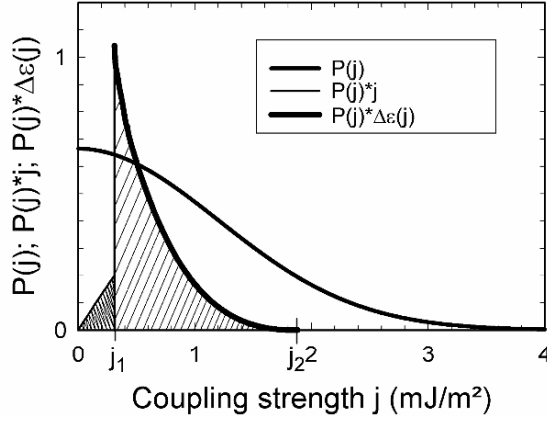


Fig. 11. Distribution function $P(j)$ for $\gamma/\sqrt{n} = 1.2$ mJ/m² and the functions $P(j)*j$ for $0 < j < j_1$ and $P(j)*\Delta\epsilon(j)$ for $j_1 < j < j_2$. j_1, j_2 , and $\Delta\epsilon$ are taken for $K_{AF} = 3.5 \cdot 10^5$ J/m³, $t_{AF} = 0.3$ nm, and $T = 0$. The hatched areas correspond to J and to ϵ_{loss} , respectively.

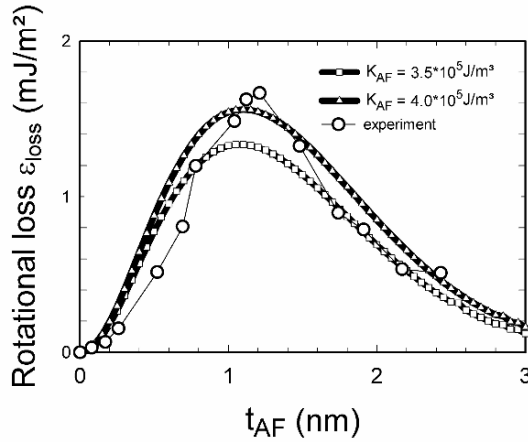


Fig. 12. Rotational loss (open circles) measured at 10K in comparison to the calculated values for the parameters of $K_{AF} = 3.5 \cdot 10^5$ J/m³ with $\gamma/\sqrt{n} = 1.2$ mJ/m² and $K_{AF} = 4 \cdot 10^5$ J/m³ with $\gamma/\sqrt{n} = 1.4$ mJ/m².

5. Summary

The magnetic interaction in polycrystalline textured F/AF film systems has been investigated theoretically and experimentally for ultrathin AF films allowing the use of a Stoner-Wohlfarth model. Within this model the typical properties of these film systems (exchange bias, unidirectional anisotropy, rotatable anisotropy,

rotational loss, enlarged coercivity) are explained and pictured. Measurements done by torquemetry with NiFe/IrMn film systems at 10 K to 450 K allow us the quantitative determination of rotational loss and thus also of the AF anisotropy and give information about the value and distribution of the F/AF coupling energy density.

References

1. W.H. Meiklejohn and C.P. Bean, Phys. Rev. 102, 1413 (1956); Phys. Rev. 105, 904 (1957)
2. E. Fulcomer and S.H. Charap, J. Appl. Phys. 43, 4190 (1972)
3. H. Fujiwara, J. Magn. Soc. Jpn. 26₁₂, 1151 (2002)
4. M. Takahashi and M. Tsunoda, J. Phys. D 35, 2365 (2002)
5. J. Nogués and I.K. Schuller, J. Magn. Magn. Mater. 192, 203 (1999)
6. E. Berkowitz and K. Takano, J. Magn. Magn. Mater. 200, 552 (1999)
7. H. Ohldag, A. Scholl, F. Nolting, E. Arenholz, S. Maat, A.T. Young, M. Carey, and J. Stöhr, Phys. Rev. Lett 91, 017203 (2003)
8. K. Steenbeck, R. Mattheis, and M. Diegel, J. Appl. Phys. 101, 09E517 (2007)
9. K. Steenbeck and R. Mattheis, Phys. Rev. B 75, 134419 (2007)
10. K. Takano, R.H. Kodama, A.E. Berkowitz, W. Cao, and G. Thomas, J. Appl. Phys. 83, 6888 (1998)
11. K. Steenbeck, R. Mattheis, and M. Diegel, J. Magn. Magn. Mater. 279, 317 (2004)
12. M.D. Stiles and R.D. McMichael, Phys. Rev. B 60, 12950 (1999)
13. M.D. Stiles and R.D. McMichael, Phys. Rev. B 59, 3722 (1999)

The (100) → (111) Transition in Epitaxial Manganese Oxide Nanolayers

F. Allegretti, M. Leitner, G. Parteder, B. Xu, A. Fleming, M.G. Ramsey, S. Surnev, and F.P. Netzer

Institute of Physics, Surface and Interface Physics,
Karl-Franzens University Graz, A-8010 Graz, Austria

Abstract. The growth and structure of epitaxial MnO(100) and MnO(111) nanolayers on Pd(100) surfaces have been investigated. We found that despite the large lattice mismatch to the Pd(100) substrate MnO(100) layers can be kinetically stabilised at low temperatures ($\leq 350^\circ\text{C}$) and at oxygen pressures between 2×10^{-7} mbar and 5×10^{-7} mbar. Annealing in ultra-high vacuum to 650°C or, alternatively, deposition of manganese metal in oxygen pressure $< 1 \times 10^{-7}$ mbar causes the transformation of the MnO(100) to a polar MnO(111) surface. It is suggested that the growth of MnO(111) layers is energetically preferred over MnO(100) due to the epitaxial stabilisation at the metal-oxide interface.

1. Introduction

The problem with the stability of polar ionic crystal surfaces has long been recognised [1-3] and has been the subject of intensive experimental and theoretical investigations that are discussed in recent books [4] and review articles [5,6]. The issue arises from the divergent surface potential and non-zero dipole moment perpendicular to the surface that a bulk-terminated polar surface would possess [1]. As such, understanding the stabilisation mechanism of polar surfaces, even for the structurally most simple (111) surface of rock-salt metal oxides, still remains a challenge. Experimentally, bulk oxide single crystals cannot be cleaved in this direction and it is often problematic to prepare stoichiometric and structurally well-ordered oxide surfaces with low defect densities, whether by oxidation of a single crystal metal surface or by deposition of a dissimilar metal in oxygen atmosphere. From a theoretical point of view, it has been shown that the compensation of polarity occurs through an interplay of different mechanisms, such as changes of the surface electronic structure, structural reconstructions accompanied by changes in the surface stoichiometry and interaction with the residual atmosphere (adsorption, hydroxylation etc.) [7-10].

In this work we study the formation of MnO(100) and MnO(111) surfaces on a 20 to 30 layers thick MnO film, which has been reactively evaporated on a single crystal Pd(100) surface. We find that, despite of the large lattice mismatch ($\sim 14\%$) to the Pd(100) substrate, a well-ordered MnO(100) surface can be kinetically stabilised at low temperatures ($\leq 350^\circ\text{C}$) and at oxygen pressures between 2×10^{-7} mbar and 5×10^{-7} mbar. Annealing at elevated temperatures ($> 600^\circ\text{C}$) in *vacuo* or

reactive evaporation at lower oxygen pressures ($\sim 1 \times 10^{-7}$ mbar) induces a transformation of the MnO(100) into a MnO(111) surface, which is covered by three-sided pyramids with (100) facets. It is suggested that the driving force for this transformation is the epitaxial stabilisation of the MnO(111) layers at the metal-oxide interface, due to a row matching relation to Pd(100).

2. Experimental

Manganese monoxide (MnO) films with a thickness of 10-30 monolayers (ML) (~ 50 -75 Å) have been grown on a clean Pd(100) surface by reactive evaporation of Mn metal in an oxygen atmosphere. The geometric structure and morphology of the MnO layers have been characterised by spot profile analysis low-energy electron diffraction (SPA-LEED) and dynamic atomic force microscopy, operated in a frequency modulation mode (FM-AFM). High-resolution electron energy loss spectroscopy (HREELS), high-resolution x-ray photoemission spectroscopy (HR-XPS), and near-edge X-ray absorption spectroscopy (NEXAFS) experiments have been performed to elucidate the phonon and electronic structure of the MnO films. The HR-XPS and NEXAFS spectra were measured at beamline I311 at the Swedish synchrotron radiation facility MAX II in Lund.

3. Results and Discussion

The reactive deposition of 20-30 ML manganese in 5×10^{-7} mbar oxygen atmosphere on the Pd(100) surface at 250°C, followed by a brief post-annealing step in UHV up to 600°C, results in the growth of a well-ordered MnO(100) layer. This is evident from the SPA-LEED image presented in Fig. 1(a), which displays sharp reflexes arranged in a square pattern on a very low background. The surface lattice constant determined from the separation of the LEED spots measures 3.14 ± 0.03 Å, which is identical with the (100) in-plane lattice parameter of bulk MnO crystals. The FM-AFM image (Fig. 1b) shows that the MnO(100) surface is atomically flat and consists of terraces with lateral dimensions of up to 500 Å, which are separated by monatomic steps running predominantly along the main azimuthal substrate crystallographic directions.

The MnO stoichiometry of the Mn-oxide film has been confirmed by photoemission spectra taken in the Mn 2p core level region (Fig. 1c). In the Mn 2p spectrum the main lines display the well resolved doublet structure caused by local and non-local screening effects and both lines show ~ 6 eV charge transfer satellites (S), typical for MnO [11]. Thus, the characteristic Mn 2p profile of MnO, as observed in [12,13] for bulk crystals, is reproduced. The Mn L-edge (2p) NEXAFS spectrum of Fig. 1(d) is in close correspondence with the spectrum of Gilbert et al. [14] for MnO and thus gives further evidence for the monoxide MnO stoichiometry of our films.

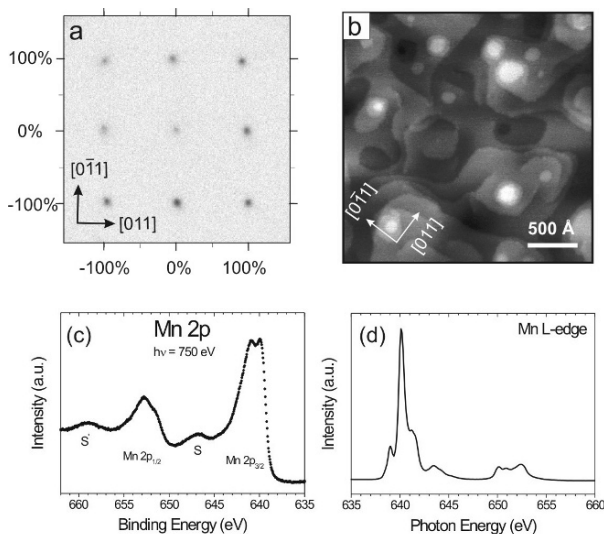


Fig. 1. 30 ML MnO(100) layers on Pd(100): (a) SPA-LEED pattern, recorded with an electron energy of 90 eV. The scan range is given in % of the surface Brillouin zone of the MnO(100) surface; (b) FM-AFM image of the MnO(100) surface (size: 2500Åx2500Å); (c) Mn 2p core level spectra excited by a photon energy of 750 eV. The peaks indicated S correspond to charge transfer satellites; (d) Mn 2p NEXAFS spectrum.

The experimental characterisation of the MnO(100) surface is completed with the measurement of its phonon spectrum by HREELS, as shown in Fig. 2(a). It contains a main phonon loss peak at ~ 65 meV and a weak structure at ~ 48 meV (the peaks at 130 meV and 195 meV are double and triple loss structures of the 65 meV peak, respectively). Our HREELS spectrum agrees well with previously published data for a MnO(100) single crystal surface, where a single Fuchs-Kliwer phonon loss peak has been observed at ~ 71 meV [15].

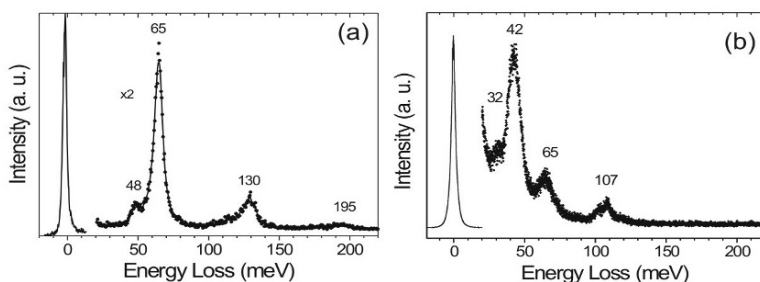


Fig. 2. HREELS spectra of the MnO(100) (a) and MnO(111) (b) surface.

Annealing to above 650°C in UHV causes significant structural changes in the MnO(100) overlayer, as evident from the SPA-LEED and FM-AFM images reported in Fig. 3. In the SPA-LEED pattern (Fig. 3a) extra spots (indicated by arrows) appear and the AFM image (Fig. 3b) shows that three-dimensional (3D) islands of triangular shape form near the step edges of the MnO(100) terraces. The 3D islands are flat on the top and have an average size of 1000 Å and a height of ~ 150 Å. The LEED pattern in Fig. 3a can be interpreted as a superposition of diffraction spots from the MnO(100) surface lattice and a hexagonal structure with the same lattice constant. This suggests a MnO(111) lattice, which is aligned with one of the unit cell vectors along the substrate <011> direction. The corresponding reciprocal-space pattern (including the diffraction contribution of two rotational MnO(111) domains, as small black and grey circles, and of the MnO(100) lattice, as large empty circles) is shown schematically in Fig. 3(c). It reproduces correctly the experimental one in Fig. 3(a), suggesting that the 3D triangular islands are built up of MnO(111) layers lying parallel to the Pd(100) surface. This is an interesting and unexpected result, having in mind the intrinsic thermodynamic stability of the neutral MnO(100) surface, which appears to be replaced by a polar MnO(111) surface. Prolonged annealing at 650°C or higher temperatures increases the portion of the MnO(111) islands, but a complete conversion of the MnO(100) into a MnO(111) phase is hindered by a significant reduction of the oxide film thickness, as evidenced by LEED (Pd spots become visible, encircled in Fig. 3a) and XPS. This is presumably the result of oxide decomposition at the oxide-metal interface and of the migration of Mn into the Pd bulk. In order to prepare a homogeneous MnO(111) surface a different route has been followed, which involves the reactive evaporation of Mn at lower oxygen pressures and higher substrate temperatures.

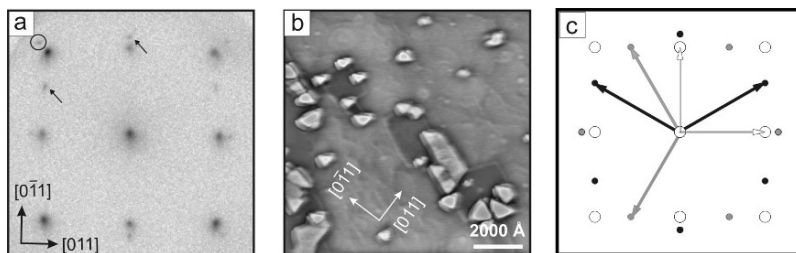


Fig. 3. The MnO(100) surface after annealing to 650°C in UHV: (a) SPA-LEED pattern, recorded with an electron energy of 90 eV. The arrows indicate the extra MnO(111) spots and the encircled spot is due to the Pd(100) substrate; (b) FM-AFM image (size: 10000Åx10000Å). The triangular-shaped islands correspond to the MnO(111) structure; (c) Reciprocal-space model of the superposition of MnO(100) and MnO(111) lattices: small black and grey circles correspond to diffraction from two 90° rotated domains of MnO(111) and the large empty circles is due to the MnO(100) lattice.

Figure 4(a) shows a conventional LEED pattern from a ~ 10 ML thick Mn-oxide film deposited at $p(\text{O}_2) = 1 \times 10^{-7}$ mbar at 400°C and post-annealed in UHV at 500°C . The LEED reflexes exhibit now a pure hexagonal arrangement due to the MnO(111) layer. The corresponding Mn 2p NEXAFS spectrum (not shown) is virtually identical to that of the MnO(100) surface (Fig. 1d), thus confirming the MnO stoichiometry of the (111) overlayer. The LEED picture in Fig. 4(a) exhibits also a faint streakiness, which is indicative of the presence of some faceting. The latter becomes more pronounced at the higher oxide coverage of ~ 30 ML, as demonstrated by the SPA-LEED images taken at electron energies of 54 eV (Fig. 4b) and 70 eV (Fig. 4c). The presence of a triangularly shaped diffuse intensity around the (00) spot is notable: it expands on going from 54 eV to 70 eV, indicating that it is due to satellites moving in the k-space as a function of the electron energy. This is the characteristics of faceting, which will be described in more detail below. The FM-AFM image of Fig. 4(d) shows that the whole surface is now covered by flat triangular MnO(111) islands with lateral dimensions extending up to several thousand Å.

The HREELS spectrum of an MnO surface displaying a LEED pattern as shown in Fig. 4(a) is presented in Fig. 2(b). This spectrum is significantly different from the one of the MnO(100) surface (Fig. 2a), with the most intense loss peak at 42 meV, a weaker structure at 65 meV and some loss intensity around 32 meV. The peak at 107 meV loss energy is most likely associated with a

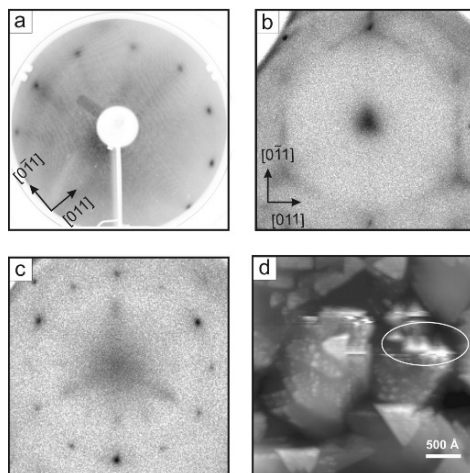


Fig. 4. (a) Conventional LEED (electron energy = 76 eV) of ~ 10 ML MnO(111) layers on Pd(100) evaporated at 400°C in $p(\text{O}_2) = 1 \times 10^{-7}$ mbar and annealed in UHV to 500°C ; (b) and (c) SPA-LEED patterns of a 30 ML MnO(111) layers on Pd(100) evaporated at 400°C in $p(\text{O}_2) = 1 \times 10^{-7}$ mbar and annealed in UHV to 550°C , recorded with electron energies of 54 eV and 70 eV, respectively; (d) FM-AFM image of the MnO(111) surface (size: $2500\text{Å} \times 2500\text{Å}$). The encircled area contains three-sided pyramids, supported on the MnO(111).

combination double loss. Since the identity of the MnO(111) layer has been established beyond any doubt, we associate the loss spectrum of Fig. 2(b) with the characteristic phonon fingerprint of the MnO(111) surface. Interestingly, the measured phonon frequencies on the MnO(111) surface agree somewhat better with the DFT calculated phonon modes of bulk MnO [16] than those of the (100) surface.

The faceting phenomena on the MnO(111) surface have been examined in detail by SPA-LEED [16]: LEED line profiles taken along the [011] direction in k -space at different electron energies for the MnO(111) surface annealed to 650°C have shown that some spots move towards higher scattering vectors with the increase of the electron energy while others do not – the former behaviour is a clear indication of faceting. In order to determine the orientation of the facets with respect to the MnO(111) surface the positions of the moving spots have been plotted in the reciprocal space (k perpendicular vs. k parallel), as done in Fig. 5(a). The facet rods are inclined with respect to the (00) rod of the MnO(111) surface by an angle of $53^\circ \pm 3^\circ$, which is very close to the angle of 54.7° , expected between bulk (111) and (100) planes, suggesting that the facets are of (100) type. The distance between two facet rods, recorded at in-phase conditions (scattering phases $S = 3$ and 4 in Fig. 6a), is $k = 2.03 \text{ \AA}^{-1}$, which corresponds to a surface lattice constant $a = 2\pi/k = 3.10 \text{ \AA}$ in the real space, a value which is compatible with both MnO(100) and MnO(111) surfaces. However, note that this simple conversion formula is only valid for lattice rods of the (100) plane, and this confirms the assignment of the facets to (100). Since three such facets are possible

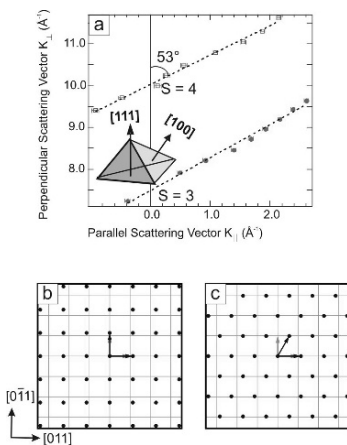


Fig. 5. (a) Determination of the facets angle in an Ewald (k perpendicular vs. k parallel) plot. The two facet rods, taken at in-phase conditions (scattering phase $S = 3$ and 4), are inclined by an angle of $\sim 53^\circ$ with respect to the MnO(111) surface rod. The insert shows a sketch of a three-sided pyramid exposing (100) side facets; (b) and (c) Real-space models of the MnO(100)- and MnO(111)-Pd(100) interfaces. Note the row-matching condition along the $[011]$ rows at the MnO(111)-Pd(100) interface.

on each side of the (111) plane, this should result in the formation of three-sided pyramids, as sketched in the insert of Fig. 5(a). The FM-AFM image (Fig. 4d) demonstrates that such pyramids are indeed present on the MnO(111) surface (see encircled area in Fig. 4d), which have a side length of up to 200 Å and a height of up to 150 Å, and coexist with the flat MnO(111) areas.

4. Conclusions

The experimental results presented above demonstrate that well-ordered epitaxial MnO(100) films can be grown on a Pd(100) surface under suitable preparation conditions. This is in line with the high thermodynamic stability of the neutral (100) rock-salt oxide surface. Epitaxial growth of MnO(100) layers has been also reported on a Ag(100) substrate, as characterised by LEED measurements [17,18]. How can we then rationalise the replacement of the MnO(100) surface by the polar MnO(111) upon annealing to high temperatures in UHV? The MnO(111) surface is covered by MnO pyramids, which expose neutral (100) facets with the lowest surface energy. However, the faceting argument alone cannot explain the shift of the energetic balance in favour of the MnO(111) surface. To understand this result we need to take into account the strain energy at the metal-oxide interface, which is determined by the lattice matching conditions. The MnO(100)-Pd(100) interface is characterised by a large lattice mismatch of ~ 14% along the [011] rows (Fig. 5b), whereas for the MnO(111)-Pd(100) interface in one direction the lattice mismatch is only ~ 1%, which results in an almost perfect row matching along the [011] rows, as illustrated in Fig. 5(c). This lowers the energy of the MnO(111)-Pd(100) interface and stabilises the formation of the MnO(111) overlayer. We therefore argue that the MnO(100) layers observed at low temperatures are only kinetically stabilised on Pd(100) by the low energy of the (100) surface.

The phenomenon of epitaxial stabilisation of thin films is quite common and is also well documented for oxide materials [19]. The results obtained here show that when considering the stabilisation mechanism of polar surfaces of oxide films the metal-oxide interface can play an important role. With increasing oxide layer thickness the formation of the (100) faceted pyramids on top of the MnO(111) surface provides an additional channel for minimising the total energy: the MnO(100) surface is energetically the most favourable one, but for the MnO(100) facets on MnO(111) no lattice mismatch exists. Similar (100)-faceted pyramids have been recently observed with AFM by Mocuta et al. [20] on NiO(111) films supported on an α -Al₂O₃(0001) surface.

Acknowledgements

This work has been supported by the Austrian Science Funds through the National Research Network “Nanoscience on Surfaces” and by the 6th Framework Programme of the European Community (GSOMEN). The support of the staff at MAX-Lab; Lund, Sweden, is gratefully acknowledged.

References

1. F. Betaut, *Compt. Rend.* 246, 3447 (1958).
2. R. Lacman, *Colloq. Int. C.N.R.S.* 152, 195 (1965).
3. P.W. Tasker, *J. Phys. C: Solid State Phys.* 12, 4977 (1979).
4. C. Noguera, *Physics and Chemistry at Oxide Surfaces* (Cambridge University Press, Cambridge 1996).
5. C. Noguera, *J. Phys.:Condens. Matter* 12, R367 (2000).
6. M. Gajdardziska-Josifovska, R. Plass, M.A. Schofield, D.R. Giese, R. Sharma, *J. Electron Microsc.* 51, S13 (2002).
7. O. Dulub, U. Diebold, and G. Kresse, *Phys. Rev. Lett.* 90, 016102 (2003).
8. G. Kresse, O. Dulub, U. Diebold, *Phys. Rev. B* 68, 245409 (2003).
9. V. K. Lazarov, R. Plass, H.C. Poon, D. K. Saldin, M. Weinert, S. A. Chambers, and M. M. Gajdardziska-Josifovska, *Phys. Rev. B* 71, 115434 (2005).
10. F. Bottin, F. Finocchi, C. Noguera, *Phys. Rev. B* 68, 035418 (2003).
11. J. van Elp, R.H. Potze, H. Eskes, R. Berger, G.A. Sawatzky, *Phys. Rev. B* 44, 1530 (1991).
12. J. Park, S. Ryu, M. Han, S.-J. Oh, *Phys. Rev. B* 37, 10867 (1988).
13. M. Oku, K. Hirokawa, S. Ikeda, *J. Electron Spectr.* 7, 465 (1977).
14. B. Gilbert, B.H. Frazer, A. Belz, P.G. Conrad, K.H. Nealson, D. Haskel, J.C. Lang, G. Srajer, G. De Stasio, *J. Phys. Chem. A* 107, 2839 (2003).
15. M.A. Langell, C. W. Hutchings, G.A. Carson, M.H. Nassir, *J. Vac. Sci. Technol. A* 14, 1656 (1996).
16. F. Allegretti, C. Franchini, V. Bayer, M. Leitner, G. Parteder, B. Xu, A. Fleming, M.G. Ramsey, R. Podloucky, S. Surnev, F.P. Netzer, *Phys. Rev. B*, 2007 in press
17. F. Müller, R. de Masi, D. Reinicke, P. Steiner, S. Hüfner, K. Stöwe, *Surf. Sci.* 520, 158 (2002).
18. E.A. Soares, R. Paniago, V.E. de Carvahlo, E.L. Lopes, G.J. P. Abreu, H.D. Pfannes, *Phys. Rev. B* 73, 035419 (2005).
19. O. Yu. Gorbenko, S.V. Samoilenov, I.E. Graboy, A.R. Kaul, *Chem. Mater.* 14, 4026 (2002).
20. C. Mocuta, A. Barbier, G. Renaud, Y. Samson, M. Noblet, *J. Magn. Magn. Mater.* 211, 283 (2000).

Growth and Structure of Zinc Oxide Nanostructured Layer Obtained by Spray Pyrolysis

Son Vo Thach¹, Michel Jouan², Sang Nguyen Xuan¹, Thoan Nguyen Hoang¹, and Hung Pham Phi¹

¹ Institute of Engineering Physics, Hanoi University of Technology, No.1 Dai Co Viet Road, Hanoi, Vietnam
E-mail: sonvt@mail.hut.edu.vn

² Laboratoire SPMS - UMR 8580 du CNRS, Ecole Centrale Paris (ECP) Grande Voie des Vignes, F92295 Châtenay-Malabry Cedex, France
E-mail: michel.jouan@ecp.fr

Abstract. Undoped zinc oxide nanostructured layers were prepared on glass substrates by the spray pyrolysis technique using 0.1–0.2 mol/l aqueous solution of $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ in the temperature range 350–570°C. The nanostructured layers were characterized by SEM, XRD and UV-VIS spectrophotometry. A nanostructured layer evolved into the form of single crystalline hexagonal prisms with the formation of nanorods at different deposition temperatures. The increase of the deposition temperature and of the solution concentration had a significant influence on the nanorod dimensions. We found that the formation of flower-like deposits occurred at 550°C. X-ray diffraction revealed that the ZnO nanostructured layers growing from 0.1 and 0.2 mol/l in the temperature range 450–570°C were c-axis-oriented with the (002) orientation in most of the samples. UV-VIS investigation showed the dependence of refractive indices and thickness on the deposition temperature.

1. Introduction

One-dimensional semiconductor nanostructures are of great interest for future nanoscale electronic and optoelectronic devices and zinc oxide is one of the most promising materials for this research. The potential applications of zinc oxide include solar cells, gas sensors, short-wavelength light-emitting and field-effect devices, Schottky diodes, etc...[1, 2, 3, 4].

There are many ways to deposit thin films of zinc oxide, including techniques such as sputtering, vapor-liquid-solid, chemical vapor deposition and spray pyrolysis [8, 9, 10, 11].

Among the aforementioned techniques, spray pyrolysis is preferred due to its simplicity, low cost and greater versatility than the other techniques [1, 2, 3, 4, 5, 6, 7]. It allows the coating of large surfaces and is easy to implement in an industrial production line.

In this paper, ZnO nanostructured layers were deposited by the spray pyrolysis technique on glass substrates. Deposition temperatures and solution concentrations were then varied to determine their influence on the formation of the nanostructured layers. Optical properties of the thin films were investigated by UV-VIS spectrophotometry. The resulting films thicknesses and refractive indices are indicated.

2. Experimental

ZnO nanostructure layers were deposited on glass substrates using a spray pyrolysis system as illustrated in Fig. 1. The spray solution used is zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) (Merck) dissolved in de-ionized water mixed with methanol (Merck) in a 1:3 ratio. The concentration of zinc acetate was varied from 0.1 to 0.2 mol/l. The deposition temperature (temperature at the substrate surface, T_s) was varied from 350°C to 570°C with an accuracy of $\pm 1^\circ\text{C}$ using a temperature controller.

We used glass with low absorption in the ultraviolet region (wavelength of above 320 nm) as substrates. Nitrogen was used as the carrier gas and the spray rate was maintained at approximately 5 ml/min. X-ray diffraction (XRD) patterns were recorded with a PANalytical Diffractometer using the $\text{Cu-K}\alpha$ radiation. The surface morphology of the deposited layers was examined using a scanning electron microscope (SEM- Jeol model 60 PA). The optical transmittance spectra of the films were measured using a Carry 100 UV-VIS Spectrophotometer in the wavelength region of 350–900 nm. The thicknesses of the films were calculated by the Spektrum software.

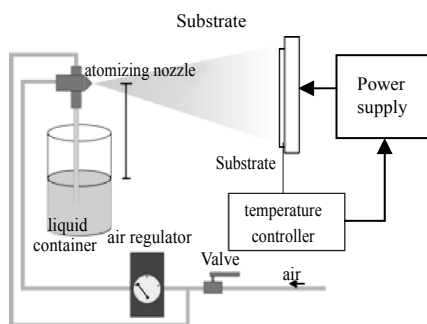


Fig. 1. Schematic diagram of the spray system

Nitrogen was used as the carrier gas and the spray rate was maintained at approximately 5 ml/min. X-ray diffraction (XRD) patterns were recorded with a PANalytical Diffractometer using the $\text{Cu-K}\alpha$ radiation. The surface morphology of the deposited layers was examined using a scanning electron microscope (SEM- Jeol model 60 PA). The optical transmittance spectra of the films were measured using a Carry 100 UV-VIS Spectrophotometer in the wavelength region of 350–900 nm. The thicknesses of the films were calculated by the Spektrum software.

3. Results and Discussion

3.1 Effect of the Substrate Temperature

To study the effect of the deposition temperature, we used zinc acetate solution with a concentration of 0.2 mol/l. According to the optical transmittance spectra (Fig. 2), the deposition at substrate temperatures around 350°C resulted in thin films with an optical transparency in the visible region of about 85% while at 450°C and 550°C the optical transparencies in the visible region of the spectrum are about 78% and 65%, respectively. Thus, an increase of the deposition temperature leads a significant decrease of the optical transparency of the films.

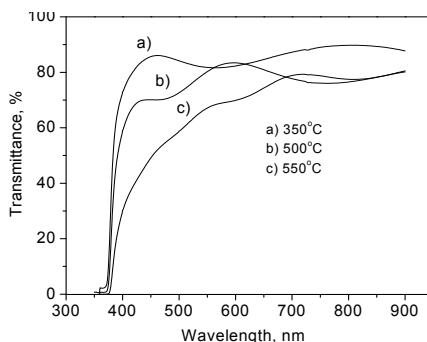


Fig. 2. Optical transmittance spectra of the films at different deposition temperatures 350°C (a), 500°C (b) and 550°C (c)

The SEM images of the morphology of these films are presented in Fig. 3. We can see that at the deposition temperature of 350°C, the film consists of densely packed grains with sizes between about 10 nm and 15 nm, and exhibits no clear sign of formation of nanorods. As the temperature increases, the film then consists of nanorods with a diameter varying from about 10 nm to 30 nm (Fig. 3b, c). A further temperature increase to 550°C results in films consisting of sharp elongated hexagonal prisms with diameters of 20 to 40 nm. It is interesting to note that the diameters of the nanorods obtained in our experiments are much smaller than in the previously published results [1]. In addition, at the temperature of 550°C, we have discovered a special flower-like structure which had never been published before. SEM images of this structure are shown in Fig. 4. We can see that the nanorods have grown into flower-like structures with diameters of about 10–20 nm.

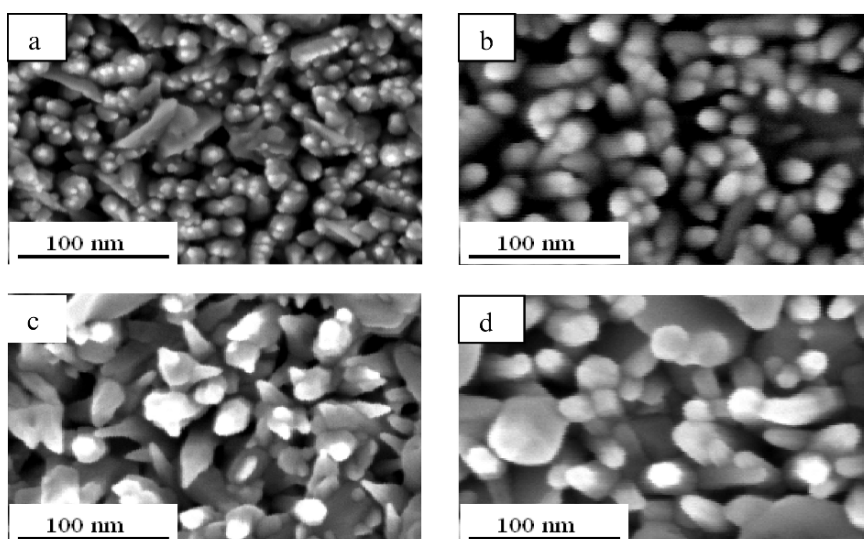


Fig. 3. SEM images of ZnO surface at substrate temperatures of (a) 350°C; (b) 450°C; (c) 500°C and (d) 550°C

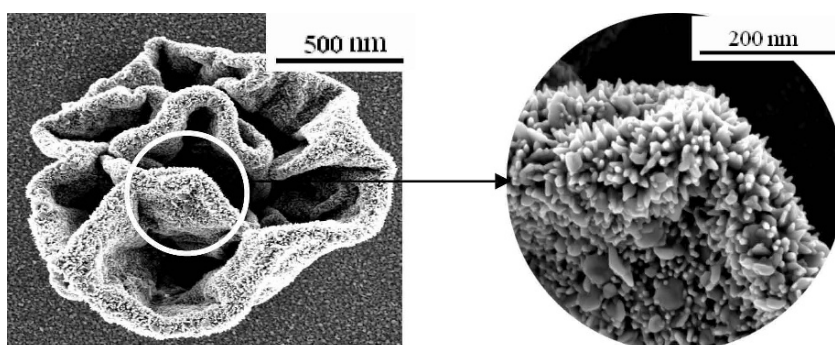


Fig. 4. SEM image of ZnO with flower-like structure

Figure 5 shows the XRD pattern of the ZnO films at substrate temperatures varying from 450°C to 550°C. The calculated ratios of the intensities of (002) and (101) planes (I_{002}/I_{101}) vary from 1.42 to 10.44 and are presented in Table 1. The results affirm that the characteristics of the ZnO films are well-shaped c-axis-oriented hexagonal columns.

Deposition temperature also affects the thickness of the ZnO nanolayers. The results show a decrease of the film thickness with increasing deposition temperature (Fig. 6). This decrease can be attributed to an increase in the evaporation rate at higher temperatures. Our results are similar to those of earlier reports [4, 7].

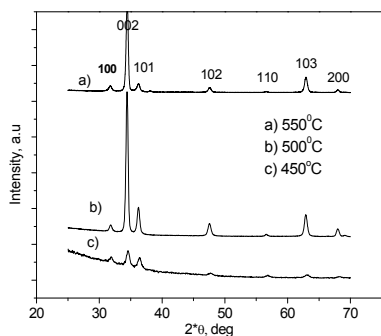


Fig. 5. XRD patterns of ZnO films deposited at different temperatures 450°C(a), 500°C (b) and 550°C (c)

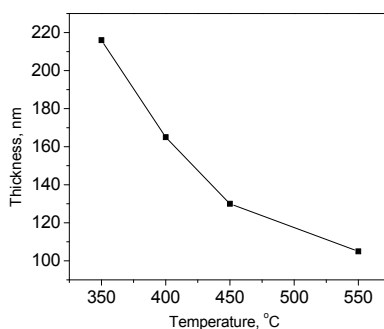


Fig. 6. The dependence of thickness of ZnO films on deposition temperature

Table 1. The ratio of the (002) and (101) reflections (I_{002}/I_{101}) in the X-ray pattern and the diameter (D) of the nanorods as a function of the deposition temperature and the solution concentration

	C, mol/l	T_s , °C	I_{002}/I_{101}	D, nm
Effect of T_s	0.2	350	2.15	10–15
	0.2	450	1.42	10–20
	0.2	500	4.75	20–30
	0.2	550	10.44	20–40
Effect of concentration	0.1	550	1.68	10–30
	0.2	550	3.76	20–40

3.2 Effect of the Solution Concentration

The deposition temperature was fixed at 550°C to study the effect of the zinc acetate solution concentration on the ZnO nanorods formation. In this case the zinc acetate concentration was varied from 0.1 mol/l to 0.2 mol/l. An increase in

the solution concentration from 0.1 mol/l to 0.2 mol/l resulted in an increase of the nanorods diameters from 10–30 nm to 20–40 nm. SEM images of this observation are shown in Fig. 7. The images also suggest that the increase in concentration also affects the alignment of the nanorods.

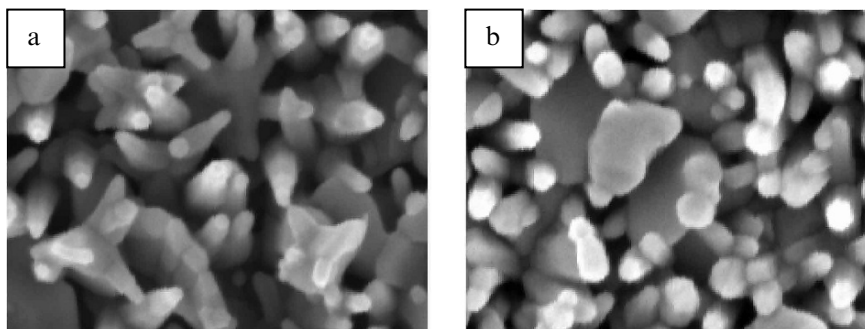


Fig. 7. SEM image of ZnO surfaces obtained from solutions of 0.1 mol/l (a), 0.2 mol/l (b)

Figure 8 presents the XRD patterns of the layers deposited with solutions of different concentrations. According to XRD, a concentration of 0.1 mol/l resulted in c-axis-oriented layers with the I_{002}/I_{101} ratio of 1.68. With an increase of the concentration of the solution to 0.2 mol/l the intensity ratio increases to 3.76. Thus, XRD and SEM both indicate that increasing the concentration of the solution results in an increase of the c-axis-orientation of the columns on the glass substrates.

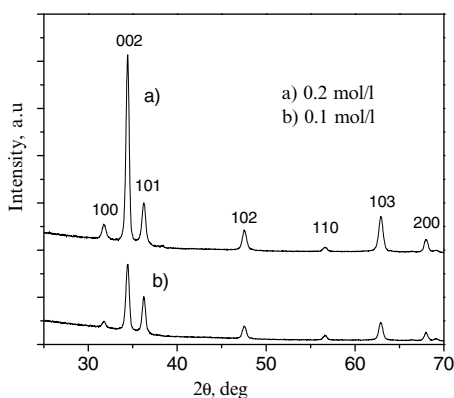


Fig. 8. XRD patterns of ZnO layers deposited onto glass substrate at 550°C from zinc acetate solutions with concentration of 0.1 mol/l (a) and 0.2 mol/l (b)

4. Conclusion

Nanostructured ZnO layers comprising single crystal nanorods can be prepared by the spray pyrolysis deposition of aqueous Zinc acetate solutions at a temperature of about 450°C. An increase in the deposition temperature leads to an increase in the diameter of the ZnO nanorods deposited on the glass substrate as well as a decrease of the optical transparency in the visible region and of the thickness of

the films. XRD patterns show that the characteristics of the ZnO films are well-shaped hexagonal columns and c-axis-oriented. A variation of the solution concentration from 0.1 to 0.2 mol/l resulted in an increase of the nanorod diameters from 10–30 nm to 30–50 nm. The diameter of the nanorods obtained at the deposition temperature of 550°C and for a solution concentration of 0.2 mol/l is about 20–50 nm, which is smaller than the results that had been previously published.

Acknowledgements

We thank the Laboratoire Structures, Propriétés, Modélisation des Solides (SPMS), Ecole Centrale Paris (ECP), France for its hospitality and excellent working conditions. We also thank Mrs F. Garnier (Laboratoire MSS-MAT) for SEM measurements.

References

1. M. Krunk, T. Dedova, I. Oja Acik, *Thin Solid Films*, Vol. 515, 1157, 2006.
2. F. Paragoay, D.W. Estrada, L.D.R. Acosta, N.E. Andrade, M. Miki –Yoshida, *Thin Solid Films*, Vol. 350, 192, 2006.
3. J.L. van Heerden, R. Swanepoel, *Thin Solid Films*, Vol. 299, 72, 1997.
4. M. Krunk, E. Mellikov, *Thin Solid Films*, 270 (1995) 33
5. Ashour, M.A. Kaid, N.Z. El-Sayed, A.A. Ibrahim, *Applied Surface Science*, Vol. 252, 7844, 2006.
6. S. Tirado-Guerra, M. de la L. Olvera, A. Maldonado, L. Castaneda, *Solar Energy Materials & Solar Cells*, Vol. 90, 2346, 2006.
7. C. Gumus, O.M. Ozkendir, Y. Ufuktefe, *Journal of optoelectronics and advanced materials*, Vol. 8, No.1, p. 299, Feb 2006.
8. B. Joseph, P. K. Monoj and Vaidyan, *Bull. Materials Science*, Vol. 28, No. 5, p. 487, August 2005.
9. M. Andres-Verges, M. Martinez-Gallego, A. Lozano-Vila, and J. Diaz-Alvares, *Current Issues on Multidisciplinary Microscopy Research and education*.
10. P.S. Patil, *Materials chemistry and physics*, Vol. 59, 185, 1999.
11. P. Nunes, E. Fortunato, R. Martins, *Thin solid film*, Vol. 383, 277, 2001.

Influence of Different Post-treatments on the Physical Properties of Sprayed Zinc Oxide Thin Films

Thoan Nguyen Hoang¹, Son Vo Thach¹, Michel Jouan², Sang Nguyen Xuan¹, and Hung Pham Phi¹

¹ Institute of Engineering Physics, Hanoi University of Technology N°1 Dai Co Viet Road, Hanoi, Vietnam

E-mail: hoangthoan-iep@mail.hut.edu.vn

² Laboratoire SPMS - UMR 8580 du CNRS, Ecole Centrale Paris (ECP)

Grande Voie des Vignes, F92295 Châtenay-Malabry Cedex, France

E-mail: michel.jouan@ecp.fr

Abstract. Polycrystalline ZnO thin films have been prepared on glass substrates by spray pyrolysis technique. The deposition temperature was varied between 350°C and 570°C. The effects due to post-thermal annealing on the structure and optical properties of thin films have been studied depending on the annealing temperature in the range of 200 ÷ 550°C. The crystal structure and surface characteristics were investigated by mean of X-ray diffraction (XRD) and scanning electron microscopy (SEM). The optical properties were studied by optical transmission spectrometry using a UV-VIS spectrophotometer. The optical measurements reveal that thin films have a maximum transmittance of about 86% and a direct band gap of 2.29 eV. XRD and SEM both indicate that increasing the annealing temperature results in an increase of the c-axis-oriented columns on the glass substrates.

1. Introduction

The increased interest on transparent conductive thin films for optoelectronic devices, such as solar cells, liquid crystal displays, heat mirrors and multilayer photo-thermal conversion systems leads to an optimization of the electro-optical properties of these films. Zinc oxide ZnO has emerged as one of the most used transparent conductive oxides due to its electro-optical properties, high electro-chemical stability, large band gap, abundance in nature and absence of toxicity [1, 2, 3].

Several techniques have been used to produce many distinct zinc oxide films, such as radio frequency magnetron sputtering [4], pulsed laser deposition [5], spray pyrolysis [2,3,6–15]. Nevertheless, the spray pyrolysis technique is cheaper, simpler and more versatile than the others and permits to obtain films with required properties for optoelectronic applications. So, in our study, we used this method to fabricate ZnO thin films.

The properties exhibited by the ZnO thin films depend on the non-stoichiometry of the films resulting from the presence of oxygen vacancies and interstitial zinc. The electro-optical properties are generally dependent on the deposition and post-deposition conditions, because these properties change significantly with the absorption and desorption of oxygen that occurs during these

processes [11]. In our study, ZnO nanostructured layers were deposited by the spray pyrolysis technique on glass substrates. We will present the effect of the annealing temperature on the optical and structural properties of ZnO thin films, with the purpose of improving the film properties.

2. Experimental

The ZnO films were grown on glass, using a typical spray pyrolysis apparatus. The solutions used were 0.2 M zinc acetate (Merck) diluted in de-ionized water mixed with methanol (Merck) in a 1:3 ratio. Nitrogen was used as the carrier gas. The nozzle to substrate distance was about 40 cm. The solution was sprayed onto a glass substrate at a temperature in the range of 350–550°C using as carrier gas nitrogen at a flow rate of 12 l/min. After deposition, the films were annealed at temperatures between 200 and 550°C for 2 hours in N₂ gas atmosphere. Before annealing and after each annealing cycle, the structural and optical characteristics of the samples were measured. The crystal structure of the ZnO films was analyzed by X-ray diffraction (XRD) using X-Pert Pro (PANalytical) with Cu K α radiation ($\lambda = 0.154056$ nm) and by scanning electron microscopy (SEM- Jeol model 60 PA). The optical transmittance spectra of the films were measured using a Cary 100 UV-VIS Spectrophotometer in the wavelength region of 300–900 nm. The film thickness was estimated through transmittance spectra using the Spektrum software.

3. Results and Discussion

3.1. Optical Properties

Figure 1 shows the transmittance spectra of the ZnO films deposited at 350°C without and with further annealing in nitrogen at different temperatures in the range of 200–500°C. The transmittance spectra show that all films exhibit high transmittance in the range of 400 ÷ 900 nm. Transmission, however, falls very sharply in the ultra-violet (UV) region due to the onset of fundamental absorption.

We observed a shift in the absorption edge towards shorter wavelengths and an increase in the average transmission with the increase of the annealing temperature. For the film deposited at 350°C and annealed at 450°C for 2 hr in nitrogen, the absorption edge of transmittance shifts to the shortest wavelength compared to other films. When annealed at 500°C, the transmittance of the films decreases slightly. The larger transmittance in the film annealed at 450°C may be due to its structural homogeneity and crystallinity as shown by the SEM images (shown below).

Figure 2 shows the transmittance spectra of the ZnO films deposited at different temperatures in the range of 200–550°C and annealed under the same conditions, at 450°C for 2 hr in N₂. For the film deposited at 350°C, the average transmittance is largest and the absorption edge of transmittance shifts to the shortest wavelength compared to the other films. When deposited at 350°C and annealed at

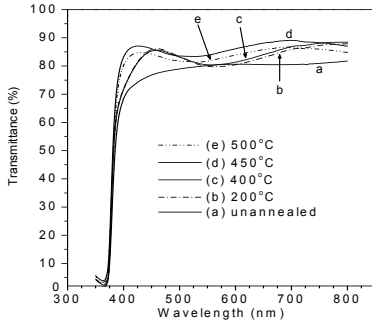


Fig. 1. Optical transmittance spectra of the films deposited at 350°C without or with further annealing at different temperature for 2h in nitrogen: (a) unannealed; (b) 200°C; (c) 300°C; (d) 450°C and (e) 500°C

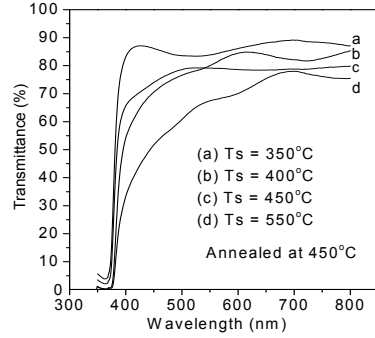


Fig. 2. Optical transmittance spectra of the films deposited at different temperature with further annealing at $T_a = 450^\circ\text{C}$ for 2h in nitrogen: (a) 350°C; (b) 450°C; (c) 500°C and (d) 550°C

450°C, the obtained films have high transparency in the visible region (about 85%), while deposited at higher temperature, the films have smaller transmittance of about 60 ÷ 70%. Thus, an increase of the deposition temperature leads to a significant decrease of the optical transparency of the films.

We can further demonstrate the phenomenon of absorption edge shifts from the plots of $(\alpha h\nu)^2$ versus photon energy. Figure 3 shows the $(\alpha h\nu)^2$ versus photon energy curves of an as-sprayed film and a film annealed at 450°C in nitrogen.

The absorption edge for direct inter-band transition is given by [6]:

$$\alpha h\nu = C \sqrt{h\nu - E_g} \quad (1)$$

where C is a constant for a direct transition, and α the optical absorption coefficient, which is given from dividing absorbance by film thickness. The optical energy gap E_g can then be obtained from the intercept of $(\alpha h\nu)^2$ versus $h\nu$ for direct allowed transitions.

The as-sprayed as well as ZnO films annealed at different temperatures have optical band-gap energies in the range of 3.26–3.29 eV (as shown in Table 1). We can see that post-deposition annealing in N_2 influences the optical properties of ZnO films inducing a band-gap increase.

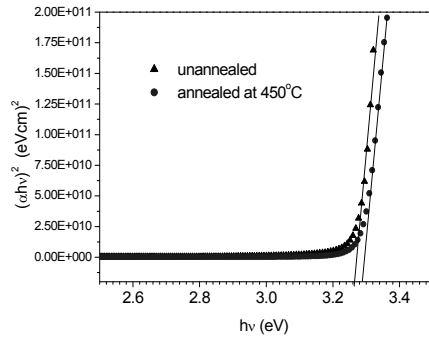


Fig. 3. $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of ZnO films deposited at 350°C without or with further annealing at 450°C for 2 h in nitrogen

Table 1. Average transmission and bandgap energy of ZnO thin films

Annealing temperature T_a (°C)	Films deposited at $T_s = 350^\circ\text{C}$		Films deposited at $T_s = 450^\circ\text{C}$	
	Average transmission (%)	E_g (eV)	Average transmission (%)	E_g (eV)
Unannealed	79.39	3.26	66.59	3.25
200	83.41	3.28	68.84	3.26
400	83.89	3.28	66.97	2.26
450	86.45	3.29	69.28	3.27
500	84.25	3.27	63.45	3.28

3.2. Structural Properties

Structural studies can be helpful for explaining the optical properties of the zinc oxide films. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to investigate the structural properties of the ZnO thin films in order to explain the influence of post-treatment on optical properties.

Figure 4 shows SEM images of as-sprayed ZnO films being deposited at different substrate temperatures and after being further annealed at 450°C . We can see that, at the deposition temperature of 350°C , the unannealed film consists of densely packed grains with a size ranging between 10 nm and 15 nm. After being annealed at 450°C , the thin ZnO film becomes denser and consists of packed grains and nanorods with a size of 20–40 nm. The films annealed at 450°C show higher UV transparency (as shown in Figure 1) possibly due to their higher density and very small size porosity.

The SEM images in Figures 4c and 4d indicate that the aligned hexagonal ZnO nanorods grow uniformly in large scale. With as-sprayed ZnO films deposited at substrate temperature of 450°C without annealing, the film consists of nanorods with a diameter varying from 20 nm to 50 nm (Fig. 4c). However, after annealing at 450°C for 2h, the film consists of denser nanorods, with larger diameter of about 30–60 nm (Fig. 4d). In addition, the diameter of the nanorods obtained in our experiments is much smaller than those previously published [8,15].

Figure 5 shows the typical X-ray diffraction patterns, and reveals that the films are polycrystalline with preferred (002) orientations together with (100), (101), (102), (110), (103) and (112) peaks. These patterns also show an increase in the film crystallinity as the annealing temperature increases. This behavior was observed in all annealed films. According to other reports [6,10,17] this enhancement in the crystallinity of the film may lead to an increase in the carrier mobility.

Table 2 shows the atomic distances d_{100} , d_{002} and d_{101} , calculated from the X-ray diffraction patterns for ZnO films annealed at different temperatures. The values compare well with the ASTM cards, showing a hexagonal unit cell having the wurtzite structure [16]. When the annealing temperature rises, the (002) peak intensity increases, the FWHM decreases and its position shifts slightly to lower angles. The observed d_{100} value is 2.816 Å, which is in good agreement with the standard d value (2.815 Å) taken from the ASTM card number 36–1451 [16]. The slight decrease in cell volume indicates disorder, which may be due to residual compressive stresses in the films.

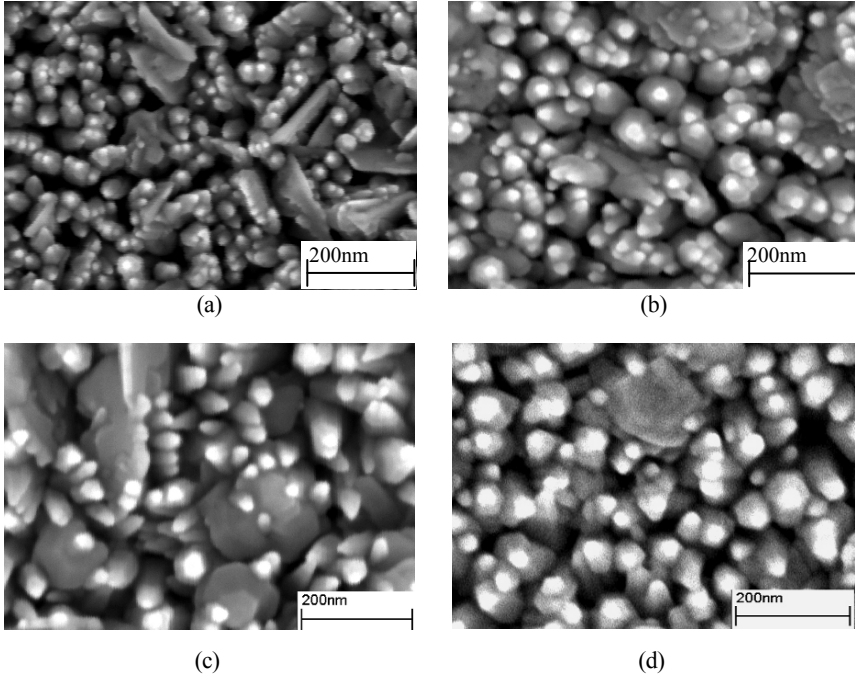


Fig. 4. SEM images of as-sprayed ZnO films deposited at different substrate temperature and films post-annealed at 450°C: (a) As-sprayed film deposited at $T_s = 350^\circ\text{C}$; (b) Film deposited at $T_s = 350^\circ\text{C}$ and annealed at 450°C; (c) As-sprayed film deposited at $T_s = 450^\circ\text{C}$; (d) Film deposited at $T_s = 450^\circ\text{C}$ and annealed at 450°C

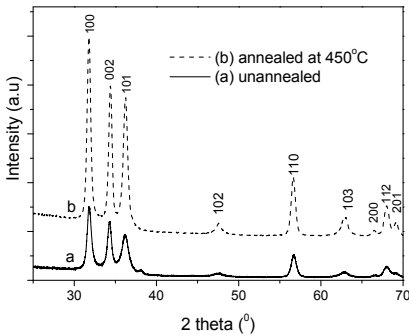


Fig. 5. XRD patterns of an as-sprayed ZnO film deposited at 350°C without (a), and with further annealing at 450°C (b)

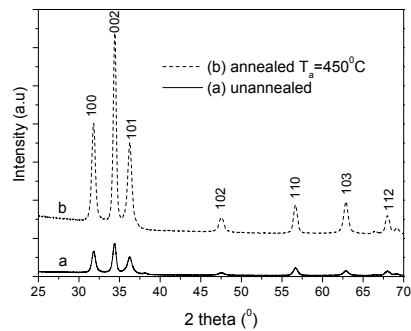


Fig. 6. XRD patterns of an as-sprayed ZnO film deposited at 450°C without (a), and with further annealing at 450°C (b)

Table 2. X-ray investigation of ZnO films prepared at substrate temperature of $T_s = 350^\circ\text{C}$ or 450°C

T _s (°C)	T _a (°C)	2θ (°)	FWHM (°)	hkl	d _{hkl} (Å)	a (Å)	c (Å)	I ₀₀₂ /I ₁₀₁
350	Un-annealed	31.812	0.615	100	2.811	5.230	3.246	1.27
		34.265	0.628	002	2.615			
		36.165	1.076	101	2.482			
350	450	31.753	0.479	100	2.816	5.214	3.250	1.29
		34.372	0.440	002	2.607			
		36.208	0.677	101	2.479			
350	500	31.794	0.413	100	2.815	5.210	3.250	1.34
		34.431	0.413	002	2.605			
		36.249	0.472	101	2.478			
450	Un-annealed	31.795	0.536	100	2.812	5.218	3.248	1.89
		34.347	0.478	002	2.609			
		36.215	0.817	101	2.478			
450	450	31.772	0.482	100	2.814	5.212	3.249	2.35
		34.381	0.388	002	2.606			
		36.226	0.572	101	2.478			
ZnO		31.770	—	100	2.814	5.207	3.250	0.44
ASTM card		34.422	—	002	2.603			
36-1451		36.253	—	101	2.476			

The ratio of the intensities of the (002) and the (101) plane (I_{002}/I_{101}) were calculated and presented in Table 2. The results affirm that the characteristics of the ZnO films are well-shaped hexagonal columns and c-axis-orientation.

With films deposited at a substrate temperature smaller than 450°C , there are significant changes after annealing at 450°C as shown by X-ray patterns and SEM images. This influences the transmittance of thin films.

4. Conclusion

The optical measurements reveal that thin films have a maximum transmittance of about 86% and a direct band gap of 2.29 eV. An increase in annealing temperature leads to an increase in the diameter of ZnO nanorods as well as an increase of the optical transparency in the visible region. The band-gap energies also increase with an increase of the annealing temperature. XRD and SEM both indicate that increasing the annealing temperature results in an increased c-axis-orientation of the columns on the glass substrates.

Acknowledgements

We thank the Laboratoire Structures, Propriétés et Modélisation des Solides (SPMS), Ecole Centrale Paris (ECP), France for its hospitality and excellent working conditions.

We thank Mr. Jacques Chevreul for setting up the spray pyrolysis apparatus and Mrs. Françoise Garnier for recording the SEM photographs.

References

1. S.J. Pearton, D.P. Norton, K. Ip, Y.W. Heo, T. Steiner, *Progress in Materials Science*, Vol. 50, 293, 2005.
2. M.H. Aslan, A.Y. Oral, E. Mensur, A. Gul, E. Basaran, *Solar Energy Materials & Solar Cells*, Vol. 82, 543, 2004.
3. B.J. Lokhande, P.S. Patil, M.D. Uplane, *Materials Letter*, Vol. 57, 573, 2002.
4. R. Hong, J. Huang, H. He, Z. Fan and J. Shao, *Applied Surface Science*, Vol. 242, 346, 2005.
5. X. Chen, W. Guan, G. Fang, X.Z. Zhao, *Applied Surface Science*, Vol. 252, 1561, 2005.
6. C. Gumus, O.M. Ozkendir, Y. Ufuktefe, *Journal of Optoelectronics & Advanced Materials*, Vol. 8.1, 299, 2006.
7. M.N. Islam, T.B. Ghosh, K.L. Chopra, H.N. Acharya, *Thin Solid Films*, Vol. 280, 20, 1996.
8. M. Krunk, T. Dedova, I. Oja Acik, *Thin Solid Films*, Vol. 515, 1157, 2006.
9. M. Krunk, E. Mellikov, *Thin Solid Films*, Vol. 270, 33, 1995.
10. J.L. van Heerden, R. Swanepoel, *Thin Solid Films*, Vol. 299, 72, 1997.
11. P. Nunes, E. Fortunato, R. Martins, *Thin Solid Films*, Vol. 383, 277, 2001.
12. Osvaldo Vigil, Francisco Cruz, Guillermo Santana, Lidice Vaillant, Arturo Morales-Acevedo, Gerardo Contreras-Puente, *Applied Surface Science*, Vol. 161, 27, 2000.
13. A. Pan, R. Yu, S. Xie, Z. Zhang, C. Jin, B. Zou, *Journal of Crystal Growth*, Vol. 282, 165, 2005.
14. L.L. Chen, H.P. He, Z.Z. Ye, Y.J. Zeng, J.G. Lu, B.H. Zhao, L.P. Zhu, *Chemistry Physics Letters*, Vol. 420, 358, 2006.
15. F. Paragoay, D.W. Estrada, L.D.R. Acosta, N.E. Andrade and M. Miki-Yoshida, *Thin Solid Films*, Vol. 350, 192, 1999.
16. Powder Diffraction File, *Joint Committee on Powder Diffraction Standards, ASTM*, Philadelphia, PA, Card 36-1451, 1967.
17. M.T. Mohammad, A.A. Hashimb, M.H. Al-Maamory, *Materials Chemistry and Physics*, Vol. 99, 382, 2006.

The Effect of SiO₂ Addition in Hydrophilic Property of TiO₂ Films

Tran Thi Duc¹, Nguyen Thi Mai Huong¹, Vu Thi Bich², Nguyen Dinh Dung¹, Nguyen Trong Tinh¹, and Tran Xuan Hoai¹

¹ Institute of Applied Physics and Scientific Instruments, VAST, 18 Hoang Quoc Viet, Hanoi – Vietnam

Email : ttduc@capsi.ncst.ac.vn

² Institute of Physics and Electronics, VAST, 18 Hoang Quoc Viet, Hanoi – Vietnam

Abstract: In this research, TiO₂ - SiO₂ composite films are prepared by sol-gel method. The relationship between the effect and amount of SiO₂ addition on properties of TiO₂ films is investigated. X-ray diffraction, SEM observation of the microstructure and infra-red spectroscopy is used to determine the film's property. It was found that the SiO₂ addition less than 40 mol% has a suppressive effect on the transformation of anatase to rutile and on the crystal growth of anatase in calcinations and thus the large specific surface area is maintained. With the consequence that the photocatalytic activity of TiO₂ and capability of holding absorbed water are increased during UV irradiation. Thus the self-cleaning effect is improved.

1. Introduction

Recently, it has been found that TiO₂ presents hydrophylic properties. Super-hydrophylic property of the surface allows water to spread completely across the surface rather than remaining as droplets. The result is TiO₂ coated glass which is antifogging and self-cleaning. Self-cleaning TiO₂ films on glass substrates have a high potential for practical applications such as mirrors, windows glasses, windshields of automobiles, etc. [1, 2].

In the case of a film which consists of only TiO₂, the contact angle of water becomes almost zero during UV irradiation. However, the contact angle goes up and is restored quickly in the dark. For actual use, it is desirable that the contact angle rises slowly in the dark and stays low for a long time. It was found that by adding SiO₂, not only the hydrophylic but also the photocatalytic properties of the composite films are improved [3]. However, a little attention has been paid to the physical and chemical characteristics of TiO₂/SiO₂ composite films.

In this paper, we report the effect of SiO₂ addition on the properties of TiO₂ films prepared by sol-gel method. The mechanism of enhanced hydrophylicity of the TiO₂/SiO₂ composite films are discussed and explained by measurement of X-ray diffraction, SEM observation and Infra-red spectroscopy.

2. Experimental Methods

TiO₂/SiO₂ composite films were prepared by the sol-gel method. The TiO₂ colloidal sol (solid content 5 wt %) was prepared by hydrolysis of titanium isopropoxide (TPOT - Merck) as described in a previous paper [4, 5]. One mol tetraethoxyorthosilicate (TEOS - Merck) in 20 mol ethanol containing 0.2 mol HNO₃ is hydrolyzed for 3 h and used as TEOS precursor solution. Then TiO₂ sol and various amounts of TEOS precursor solution are mixed together. The content (mol %) of SiO₂ is varied from 0,10,20,30 and 40 to 60%, respectively. Glass and silicon plates are used as the support substrates. The coatings are prepared on the supports by spin – coating methods. Powder samples were prepared apart from the above – described film samples. Gel coatings were then dried and heat-treated in air at 500 – 600°C for 1 h. Titanium dioxide sol and mixed – solutions of TiO₂-SiO₂ sol which has the same composition as film's samples were dried at 50°C and calcined at 800°C for 1 hour by furnace. X-ray diffraction (XDR) patterns of these powder samples were measured with a diffractometer (D-5000 Siemens). The samples are characterized using SEM observation (Field Emission Scanning Electron Microscope, S-4800, Hitachi), and Fourier Transform Infrared Spectroscopy (FTIR) Nicolet (Germany) in the range of 400–4000 cm⁻¹ by the KBr pellet technique.

3. Results and Discussion

3.1. X-ray Diffraction

X-ray diffraction pattern which was obtained from powder of the same composition as the thin film on the glass samples are show in Figs. 1 and 2.

Fig. 1 shows the partterns of pure TiO₂ powder after drying at 50°C and calcining at 500°C and 800°C for 1 hour. As shown in Fig.1, the anatase peaks

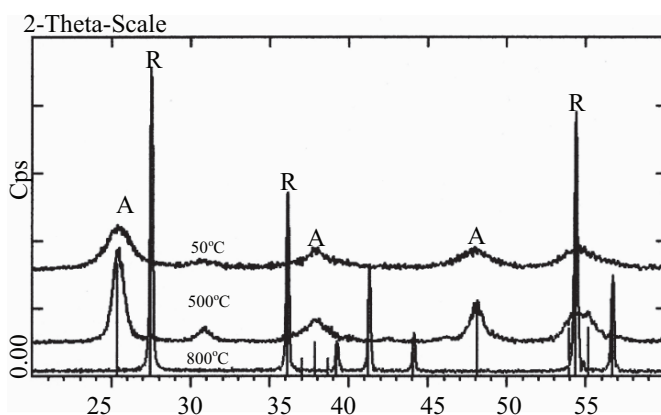


Fig. 1. XRD patterns of pure TiO₂ powder heat treated at 50, 500 and 800°C

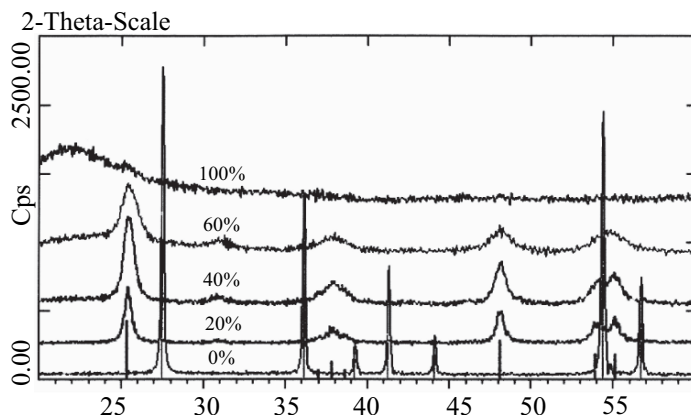


Fig. 2. XRD patterns of TiO₂/SiO₂ powder heated at 800°C; SiO₂ content: 0%; 20%; 40%; 60% and 100 mol% (from bottom)

“A” are seen in the samples dried at 50°C and calcined at 500°C, the rutile peaks “R” (transition from crystalline anatase) are seen after calcining at 800°C. The heat treatment gives higher crystallinity and the particle size increase from 10 nm at 50°C to about 20 nm at 500°C (from FWHM of XDR peaks).

XRD patterns obtained from TiO₂/SiO₂ composite samples after calcining at 800°C for 1 h are shown in Fig. 2. XDR measurements show that all the samples are anatase crystal structure. The rutile peak is not seen in all TiO₂/SiO₂ composite samples. The smaller is the crystal cells, the broader the diffraction peak. With the increasing of SiO₂ content, the peak gradually becomes broad. That means that the particle size of TiO₂ becomes smaller with the addition of SiO₂.

As for the SiO₂ containing sample, contact between TiO₂ particles is barred by SiO₂ or Ti-O-Si bonds during the growth progress. The grain growth of TiO₂ crystallinity is suppressed and particle size is maintained as in the original state.

3.2. Microstructures

The colloidal solution was prepared through the controlled hydrolysis of titanium tetraisopropoxide in water. A stable TiO₂ colloidal sol resulted from this procedure. Using transmission electron microscopy (TEM 125K Russia – Japan) it has been demonstrated that the size of the colloidal particles was ca. 10 nm (Fig. 3a). Figure 3 b, c, d show SEM photographs of the surface of TiO₂/SiO₂ thin films calcined at 800°C for 1 hour (a) 0 mol% SiO₂, (b) 20 mol% SiO₂, (c) 40 mol% SiO₂. It is observed that the particles size of TiO₂ is considerably different in the presence of different amount of SiO₂. That is, in the case of the thin film which consists only TiO₂ (Fig. 3b), after calcining at 800°C, the rutile TiO₂ crystal structure is formed and the particle size is increased from about 10 nm to 20–30 nm. On the other hand, the thin film with 20 mol% SiO₂ (Fig. 3c) has particle size of TiO₂ as small

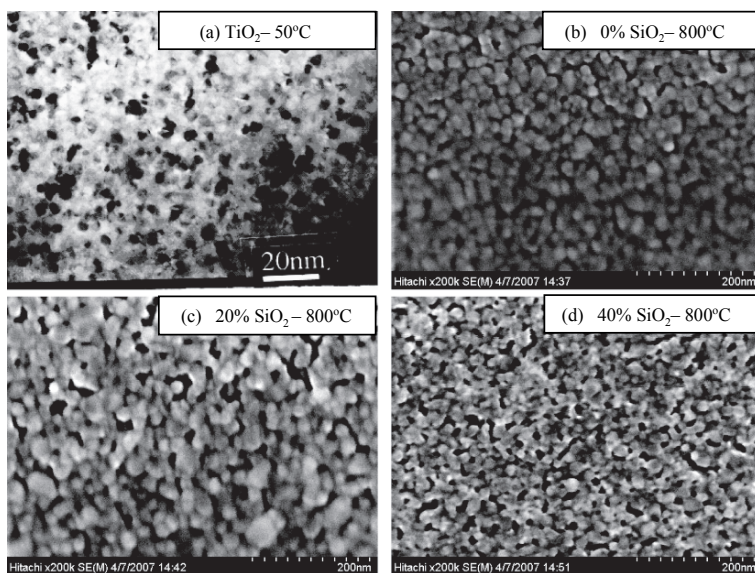


Fig. 3. TEM image (a) and SEM photographs (b, c, d) of $\text{TiO}_2/\text{SiO}_2$ composite with SiO_2 content: 0 mol% (a, b), 20 mol% (b), 40 mol% (d)

as about 15–20 nm, and it has a little angular form as compared with Fig. 3b. As for the thin film with 40 mol% SiO_2 (Fig. 3d), the particle size became as smaller as about 10–15 nm.

If the film consists of only TiO_2 , many large rounded particles are observed, because of sintering and grain growth. As for the sample with SiO_2 addition, contact between TiO_2 particles is barred by SiO_2 . In spite of the temperature at which sintering happens, grain growth of TiO_2 crystal is suppressed. It was also recognized in X-ray diffraction, that the suppressive effect of grain growth is higher when SiO_2 content is higher.

The results of x-ray diffraction and SEM observation mentioned above consist with the result of specific surface area measurements. Figure 4 shows the result of measured specific surface area by BET method using the powder of the same composition of commercial TiO_2 and SiO_2 sol [7]. It can be seen that, in the case of pure TiO_2 , the specific surface area of powder dried at 110°C is the smallest. Crystal growth has taken place by heating at 800°C and the surface area decreased. SiO_2 addition in the range of 10 to 50 mol%, the grain growth at 800°C sintering is suppressed. Due to the contact of TiO_2 particles is barred by SiO_2 , the small size of TiO_2 particles is persisted and the decrease of surface area is suppressed. If the amount of SiO_2 addition is more than 50 mol%, contact of SiO_2 particles will increase and sintering of SiO_2 at 800°C decreases the surface area.

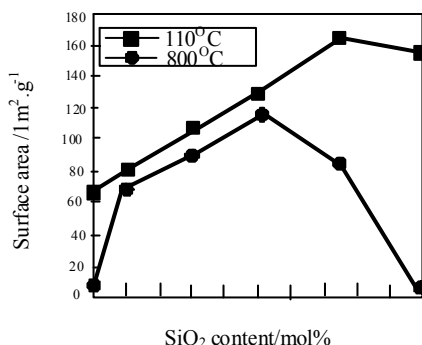


Fig. 4. BET surface area of TiO₂/SiO₂ powder [7]

3.3. Infra-Red Spectroscopy

Figure 5.1 shows the FTIR spectra of TiO₂/SiO₂ containing (a) 0%; (b) 20%; (c) 40% SiO₂, respectively. Characteristic absorption peaks of silica were observed in spectra of all samples with 20% and 40 mol% SiO₂ heat treated at 100°C, 600°C, and 800°C. A broad absorption peak is seen at 3000–3800 cm⁻¹, which is assigned to the stretching modes of O-H bands and related to surface adsorbed water. The peak at about 1600 cm⁻¹ is attributed to the bending vibration of H-O-H bond, which is assigned to chemisorbed water. The peak at approximately 440 cm⁻¹ is due to the stretching vibration of Ti-O-Ti and Ti-O bonds. In Fig. 5.1 b and c, two new absorption peaks are seen at about 950 and 1050 cm⁻¹ which are ascribed to the asymmetric stretching vibrations of the Ti-O-Si and Si-O-Si bands, respectively. As can be seen in Fig. 5.1, the intensities of the peaks at 950 and 1050 cm⁻¹ increase with increasing content SiO₂. It can be deduced that TiO₂ and SiO₂ form not only separate oxide particles but also complex oxide ones. The peak at 3000–3800 cm⁻¹ related to the physically and chemically adsorbed water is also increased with increasing SiO₂ content. It is assigned to the fact that the addition of SiO₂ has the capability of absorbing water in air [7]. In the obtained spectrum for a sample with 40% mol SiO₂ heat treated at 100, 600 and 800°C (Fig. 5.2) there are no differences in band position. The band at about 950 cm⁻¹ is observed in all TiO₂/SiO₂ samples, which is often used as evidence for the vibration of Ti-O-Si bond [6]. The band at 3000–3800 cm⁻¹ related to surface adsorbed water decreases in intensity with increasing temperature to 800°C. Significant changes in FTIR spectra due to SiO₂ addition occur in the region of 3000–3800 cm⁻¹ and around 1600 cm⁻¹, which are assigned to OH groups having strong hydrogen bonds such as in liquid water. These bands can be attributed to water adsorbed on SiOH group.

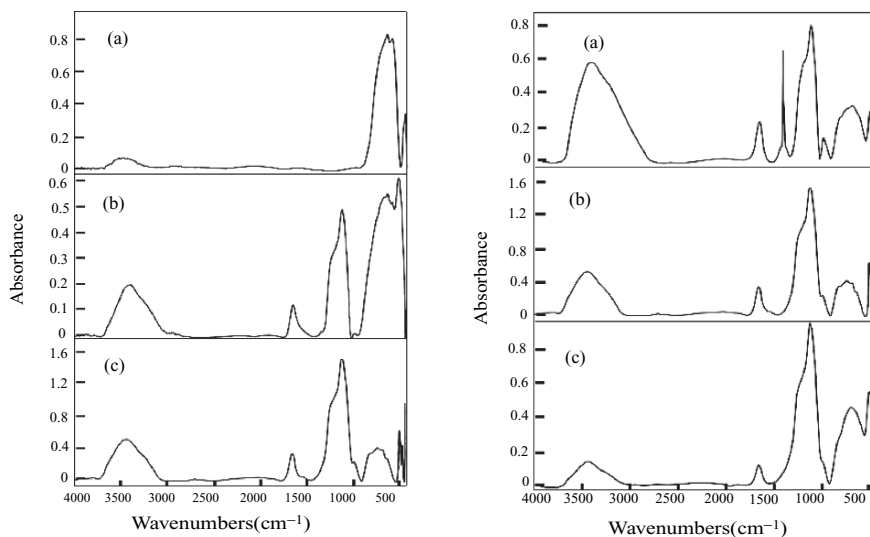


Fig. 5. FTIR spectra of $\text{TiO}_2/\text{SiO}_2$ containing SiO_2 : (a) 0 mol%; (b) 20 mol%; (c) 40 mol%; calcined at 600°C (5.1); 40 mol% heat treated at (a) 100°C , (b) 600°C , (c) 800°C (5.2)

3.4 Mechanism of Addition of SiO_2 in TiO_2 to Improve the super-Hydrophilic Property and Self-Cleaning Effect

When the surface of TiO_2 film is exposed to UV light, the contact angle of the TiO_2 film with water is reduced gradually. After enough exposure to light, the surface becomes super-hydrophilic (0° water contact angle). In this case, electrons and holes are still produced, but they react in a different way. The electrons tend to reduce the Ti (IV) cations to the Ti(III) state, and the holes oxidize the O_2^- anions. In this process, oxygen atoms are ejected, creating oxygen vacancies. Water can then occupy these oxygen vacancies, producing adsorbed OH groups, which tend to make the surface hydrophilic [2].

Guan et al. [6] have reported that the addition of SiO_2 in TiO_2 film can enhance the acidity of the composite oxide $\text{TiO}_2/\text{SiO}_2$. The increase in acidity has been explained by a model, which assumes that the dopant silicon cation enters the lattice of TiO_2 and retain its original coordination number. A charge imbalance is created because the silicon cation is still bonded to the same number of oxygen even though the oxygen atoms are now of a new coordination. Due to the positive charge in the binary oxide $\text{TiO}_2/\text{SiO}_2$, Lewis sites are formed. The enhanced acidity of the film is considered as the main reason to improve the photocatalysis and hydrophilicity. The surface improved acidity of the composite can adsorb more OH radicals than pure TiO_2 surface. Because, silicon cations, exactly Ti-Si ligand, can capture the OH^- of adsorbed H_2O molecules and O^{2-} can bind with H^+ of adsorbed water molecules.

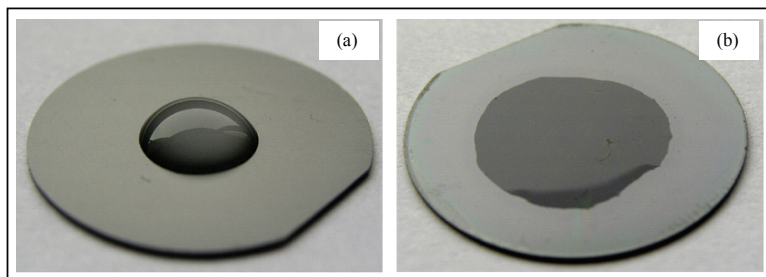


Fig. 6. Water drop on a silicon surface (a) and a thin water sheet formed on a TiO₂/SiO₂ coated silicon surface after UV irradiation

There is a competitive adsorption process for contaminating compounds and water on the surface coated by the composite TiO₂/SiO₂. Because of the enhanced acidity on the surface, the water (OH groups) is preferentially adsorbed and contamination is decreased on the surface. This may be the reason why the addition of SiO₂ in TiO₂ film decreases the extent of contamination more than the film of pure TiO₂. Applying TiO₂ or TiO₂/SiO₂ film on the surface of glass or tiles, the surface of the material will be hydrophilic and exhibit a self-cleaning effect under UV irradiation [1]. Hydrophilic action makes the water to penetrate under the stains on the surface. The water lies flat on the surface in sheets instead of forming drops (Fig. 6). Dust and other contaminants are easily wiped away with water. Therefore, there are no dirty marks on the surface even after it is dry.

4. Conclusions

In this research, TiO₂ films to which SiO₂ is added, are prepared by sol-gel method, and their characteristics are investigated. The following results are obtained:

1. In the case of pure TiO₂, after heating at 800°C crystal growth has taken place, the anatase structure is changed to the rutile one and the specific surface area decreased. But TiO₂/SiO₂ composite samples have a suppressive effect on the transformation of anatase to rutile and on the crystal growth of anatase during calcinations, so that they retain a large specific surface area. As a consequence the photocatalytic activity of TiO₂ during UV irradiation is improved.
2. Significant changes in FTIR spectra due to SiO₂ addition occur in the region which is assigned to the physically and chemically absorbed water. Its amount increases with increasing SiO₂ content. This is assigned to the fact that the addition of SiO₂ has the capability of holding absorbed water.
3. SiO₂ and TiO₂ form single mixed oxide particles in the film, which also contain Ti-O-Si bonds. The composite oxides have an enhanced surface acidity, which results in an increase of the OH content in the composite films, with the consequence that the hydrophilicity and the capability to hold absorbed water are increased and can be maintained for a long time in the dark.

Acknowledgement

This work is financially supported by The National Fundamental Research Program on Physics, N. 4 102 06 and N. 4 030 06.

References

1. A. Fujishima et al., TiO_2 Photocatalysis, Published by BKC, Inc. Japan (1999)
2. R.Wang,K.Hashimoto, A. Fujishima, et al., Nature 388 (31) (1997) 431
3. Sakai, J. Phys. Chem. B 105 (2001) 3023
4. T.T. Duc, P. Binh, N.T. Tinh and T.X. Hoai: Proceedings IWOMS'99 p. 617-620
5. T.T. Duc, N.T. Tinh, T.X. Hoai: Proceedings of 9 th APPC; pp. 308 (2004)
6. K. Guan, Surface and Coatings Technology 191 (2005) 155
7. M. Machida, et al., Journal of Materials science 34 (1999) 2569

Investigation of the Transformation of a Modified Iron Oxide Structure During Redox Reaction

Luu Thi Lan Anh¹, Nguyen Ngoc Trung², and Van Dinh Son Tho³

¹ International Training Institute for Materials Science – Hanoi University of Technology

² Institute of Engineering Physics – Hanoi University of Technology

E-mail: nntrung-iep@mail.hut.edu.vn

³ Faculty of Chemical Technology – Hanoi University of Technology

No1 - Dai Co Viet Street – Ha Noi – Viet Nam

E-mail: thovds-petrochem@mail.hut.edu.vn

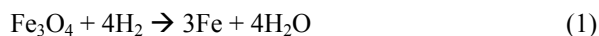
Abstract: Iron oxides can be used for the storage of hydrogen based on their redox reaction. Iron oxides were synthesized by the sol-gel method was a structure transformation of maghemite $\gamma\text{-Fe}_2\text{O}_3$ into hematite $\alpha\text{-Fe}_2\text{O}_3$ during calcinations process could be observed. The addition of a Mo^{6+} cation by the preparation method results in the substitution of Mo^{6+} into the Fe_2O_3 structure and formation of $\text{Fe}_2(\text{MoO}_4)_3$. There was a formation of two crystalline phases Fe_2O_3 and ZrO_2 separately incase of the addition of Zr^{4+} cation into Fe_2O_3 . During redox reaction, the structure of Fe_2O_3 was converted into Fe and regenerated Fe_3O_4 . There was a transformation of $\text{Fe}_2(\text{MoO}_4)_3$ into $\text{Fe}_2\text{Mo}_3\text{O}_8$ phases after reduction. However ZrO_2 was did not change its structure during redox reaction. The $\text{Zr-Fe}_2\text{O}_3$ very easy to be reduced into Fe and convenience formed hydrogen in the oxidation.

Keywords: Hydrogen • transformation • redox reaction of iron oxides • Iron oxides added with Zr and Mo cation.

1. Introduction

Iron oxides are of technological importance as catalytic materials, sorbents, pigment, flocculents, coatings, gas sensor. It is accepted that iron oxide catalysts are well studied for Fischer-Tropsch synthesis and currently many applications of iron oxide catalyst have been mentioned such as a catalyst for the oxidation of various organic contaminants and for the removal of carbon monoxide in a burning cigarette [1].

As a multiple valence metal, iron forms three kinds of oxide: FeO , Fe_2O_3 and Fe_3O_4 . The valence of iron in FeO is +2, in Fe_2O_3 is +3 but in Fe_3O_4 two-thirds of the iron is +3 and of the rest +2, with the “nominal” valence +8/3. Therefore, there is a difference between the electronic structures of iron in the three oxides, so they should have different catalytic effects. Based on the redox activity of Fe_2O_3 and Fe_3O_4 , the hydrogen storage had been proposed [2,3,4] and the technology is based on the redox reaction of magnetite in equation (1,2)





Fe_3O_4 is reduced with H_2 to Fe metal. The Fe metal is packed in cassettes, which will be mounted on means of transportation. The recovery and the supply of H_2 can be done by the equation (2), i.e. the re-oxidation of Fe metal with H_2O , which correspond to 4.8 wt% of Fe metal (theoretical value). Iron and iron oxides are quite cheap and environment-friendly materials. These materials are stable under atmosphere pressure at room temperature, thus easy to be handled. Furthermore, since the fuel is just water, there is no risk of explosion when vehicles collide.

Iron oxides containing Mo^{+6} and Zr^{+4} cations could form hydrogen over several cycles through the redox reaction, while iron oxide without any promoters was deactivated quickly for the redox reaction. The addition of Zr^{+4} into iron oxides enhanced the hydrogen formation through the oxidation of iron metal with water vapor at low temperatures. However, the role of these promoters by the formation of iron oxides is still unclear. In the present study, the structures of iron oxide during the redox reaction and the addition of Mo and Zr cations were investigated.

2. Experimental

Samples were synthesis by sol-gel method. Iron (III) nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were used as metal sources. Aqueous solutions of iron (III) nitrate 0.05M was mixed with the salt of the metals M (M = Zr, Mo) or purely magnetically stirred. A 1M solution of citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) is added with radio ΣM^{n+} : Ac = 0.85. The mixture was heated to 70°C . Ammonium hydroxide was added to the solution to adjust the pH x-value between 6.5 and 7 and the solution was then continuously stirred until a gel was formed. The gel was dried at 70°C for 24 hours. The sample was heated to 300°C for 60 minutes and then sintered at 500°C for 3 h in air. The amount of Zr or Mo species added into iron oxides ($\text{Zr-Fe}_2\text{O}_3$ or $\text{Mo-Fe}_2\text{O}_3$) was adjusted to be 5 mol% of all metal cations.

The reduction of iron oxides with hydrogen and the subsequent oxidation of the reduced-sample with water vapor were performed with a conventional gas flow system with a fixed bed. The iron oxide sample was packed in a tubular reactor made out of quartz glass. The amount of iron oxide samples packed in the reactor was 2.0 mg. For the reduction, hydrogen (10% H_2/Ar) was introduced into the reactor. The reduction of iron oxide with hydrogen was kept until the consumption of hydrogen could not be detected anymore. After using argon to purge out the remaining hydrogen in the reactor, the oxidation of the reduced-sample was started by contact with water vapor. The oxidation was continued until H_2 was not observed any longer. During the reaction, a part of the effluent gases was analyzed by gas chromatography (GC).

X-ray diffraction (XRD) measurement for the samples was performed with a PANalytical XPERT-PRO diffractionmeter using $\text{Cu-K}\alpha$ radiation at room temperature in air. SEM images of the samples were recorded on EDS + SEM-Quanta 200. The thermal analysis was investigated by a Nertzsh STA 409PC. The flow rate of air was adjusted to 40 ml/mins and the temperature of the oven was increased continuously up to 700°C by the rate of $5^\circ\text{C}/\text{mins}$.

3. Result and Discussion

Figure 1 shows a typical Differential Scanning Calorimetry- Thermogravimetry (DSC-TG) of iron oxides. This analysis gives us the information of calcinations process of the sample. At the lower temperature range ($<100^{\circ}\text{C}$), the temperature program of the instrument is not linear with time, therefore the signal of DSC and TG during this temperature range should be neglected. However, in this range there is only the loss of absorbed water. There is one exothermic peak at 193.43°C this is a results of the combustion of organic substances in the range 150°C – 250°C . At above 250°C , there is no observation of weight loss of the sample and there is no thermal effect in the DSC curve. It suggests that the thermal decomposition of the sample is completely occurred during calcinations process so the sample has stable structure at the range of 400 – 600°C .

In order to investigate the crystalline structure of the sample during calcinations process, the XRD pattern of iron oxide samples after heating at 300°C and calcinations at 500°C and the results are shown in Figure 2.

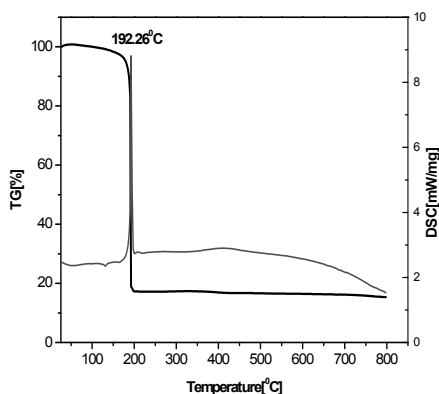


Fig 1. DSC diagrams of xerogel

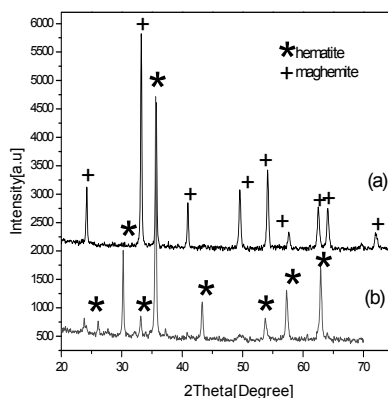


Fig 2. XRD patterns of iron oxides (a) before calcine; (b) after

Figure 2 shows the diffraction peaks of iron oxide samples after heating at 300°C (a) and calcinations at 500°C (b). The diffraction peaks at 300°C are consistent with maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and the intensity of diffraction lines suggest that $\gamma\text{-Fe}_2\text{O}_3$ structure is well crystallized. During drying, there is an exothermic process, which results in the combustion of an organic substance. This reaction supplies heat for the crystallizations of the samples. After calcinations at 500°C , it can be seen that there are diffraction lines, which are assigned to $\alpha\text{-Fe}_2\text{O}_3$. There was a transformation of maghemite $\gamma\text{-Fe}_2\text{O}_3$ into hematite $\alpha\text{-Fe}_2\text{O}_3$ during the calcinations process. The same phenomenon is also observed with $\text{Zr-Fe}_2\text{O}_3$ and the corresponding diffraction pattern is shown in Figure 3. It means that after drying at 300°C , there was a formation of a good crystalline structure of $\gamma\text{-Fe}_2\text{O}_3$ and it transformed into $\alpha\text{-Fe}_2\text{O}_3$ after calcinations at 500°C . It is also observed that there are peaks at

$2\theta = 30.28^\circ$ and 43.52° . This is consistent with of ZrO_2 crystalline structure. This result suggests that there was no substitution of ZrO_2 into the $\alpha\text{-Fe}_2\text{O}_3$ structure.

Figure 4 is a X-ray diffraction (XRD) pattern of $\text{Mo-Fe}_2\text{O}_3$ after drying at 300°C and after calcinations at 500°C . A low intensity of diffraction lines can be seen in pattern (a). It means that there is an amorphous structure at low temperature. However, after calcinations the diffraction lines of $\alpha\text{-Fe}_2\text{O}_3$ at $2\theta = 23.84^\circ$, 33.92° and 53.1° are observed. Nevertheless, there is another structure phase that complies with the structure of $\text{Fe}_2(\text{MoO}_4)_3$ ($2\theta = 23.16^\circ$; 25.2° ; 26.38°). The intensity of this phase is not high enough due to the poor crystalline structure of $\text{Fe}_2(\text{MoO}_4)_3$. It can be said that, the addition of Mo^{+6} into Fe_2O_3 forms two crystalline phases: $\alpha\text{-Fe}_2\text{O}_3$ and $\text{Fe}_2(\text{MoO}_4)_3$.

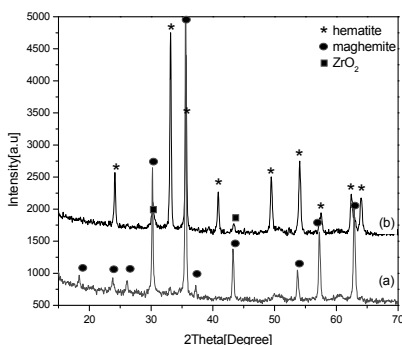


Fig. 3. XRD patterns $\text{Zr-Fe}_2\text{O}_3$ before (a) and after (b) calcinations

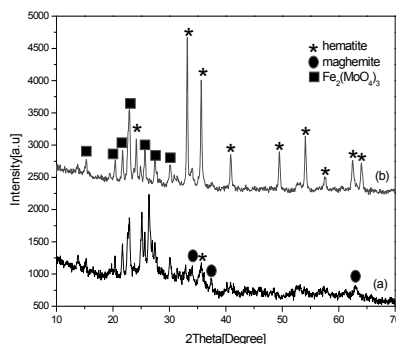
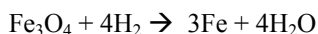
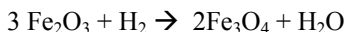


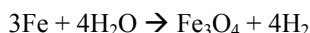
Fig. 4. XRD patterns $\text{Mo-Fe}_2\text{O}_3$ before (a) and after (b) calcinations

Figure 5 is a Temperature programmed reduction (TPR) profile of iron oxide (a) and modified iron oxide samples (b, c). The left horizontal is a TCD signal and the right one is a function of temperature with time. The peaks of the TCD curve represent the reduction stage of iron oxide. It is well accepted that the first one is a reduction of Fe_2O_3 into Fe_3O_4 and the second one is a transformation of Fe_3O_4 into Fe [12].



In case of Fe_2O_3 and $\text{Zr-Fe}_2\text{O}_3$, the first step appears around 350°C , however the first peak of $\text{Mo-Fe}_2\text{O}_3$ is at 500°C (150°C higher than other peaks). The second one appears at 600°C but the TCD intensity signal of $\text{Mo-Fe}_2\text{O}_3$ is lower than of Fe_2O_3 and $\text{Zr-Fe}_2\text{O}_3$. Base on the reduction line and the hydrogen consumption for the reduction, it suggests that both Fe_2O_3 and $\text{Zr-Fe}_2\text{O}_3$ samples have a good activity for the reduction and iron oxides were reduced into iron metal. For $\text{Mo-Fe}_2\text{O}_3$, in combination with XRD patterns, there is a coexistence of a Fe_2O_3 and a $\text{Fe}_2(\text{MoO}_4)_3$ phase and just only Fe_2O_3 is reduced during the reduction therefore a smaller amount of hydrogen is consumed in the reduction.

The oxidation equation of the reduced-sample by water vapor is



The temperature of the hydrogen formation by oxidation is shown in figure 6. It is clearly that the hydrogen formation is proportional to the temperature. The maximum amount of hydrogen is formed within the 400–600°C range. Based on a kinetic hydrogen evolution, it can be said that the amount of the H_2 formation of Fe_2O_3 and $\text{Zr-Fe}_2\text{O}_3$ is larger than of $\text{Mo-Fe}_2\text{O}_3$. These results are well correlated with the reduction behaviour. A small amount of Fe_2O_3 was reduced into Fe oxidation as well. For Fe_2O_3 and $\text{Zr-Fe}_2\text{O}_3$, a larger amount of iron oxides were transformed into iron by the reduction, and so a larger amount of H_2 is formed by oxidation.

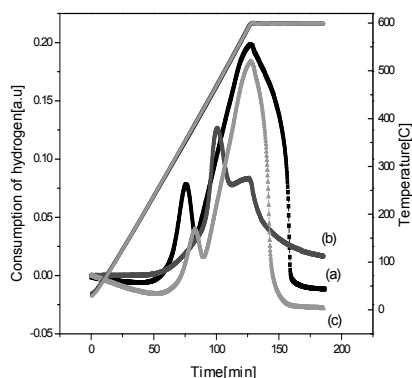


Fig. 5. Temperature programmed reduction profiles of (a) Fe_2O_3 ; (b) $\text{Mo-Fe}_2\text{O}_3$; (c) $\text{Zr-Fe}_2\text{O}_3$.

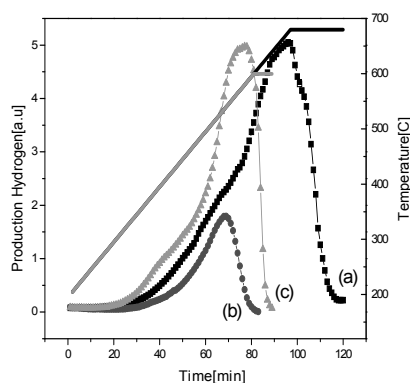


Fig. 6. Temperature programmed oxidation profiles of (a) Fe_2O_3 ; (b) $\text{Mo-Fe}_2\text{O}_3$; (c) $\text{Zr-Fe}_2\text{O}_3$.

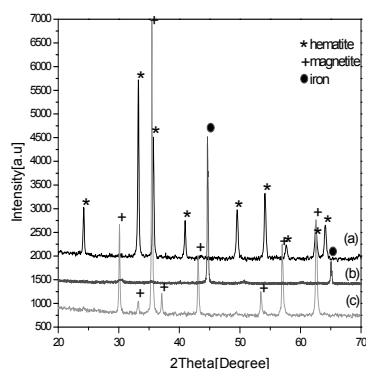


Fig. 7. XRD patterns of Fe_2O_3 : (a) fresh Fe_2O_3 ; (b) after reduction; (c) after oxidation

The structure of fresh iron oxide, after reduction and oxidation of the samples are analyzed by XRD. The pattern is given in Figure 8.

The upper line is a XRD of a fresh sample and it shows a $\alpha\text{-Fe}_2\text{O}_3$ structure. There is just one phase of Fe metal after reduction reaction (middle line). It means

that all iron oxides were completely reduced into Fe metal at the experiment condition. The last line is a XRD of sample after oxidation and it consists with Fe_3O_4 structure. It means that iron oxide was regenerated after oxidation step. There is a change of the iron oxides structure samples during redox cycles as follow: $\alpha\text{-Fe}_2\text{O}_3 \rightarrow \text{Fe} \rightarrow \text{Fe}_3\text{O}_4$.

The transformation of the $\text{Zr-Fe}_2\text{O}_3$ structure during the redox cycle is shown in figure 8. We observe the transformation of $\alpha\text{-Fe}_2\text{O}_3$ into the Fe structure after reduction and continuous change into Fe_3O_4 after oxidation with water vapor. It means that all iron oxides were reduced completely in the reduction and all the Fe is totally oxidized with water vapor. The ZrO_2 phase of fresh sample is clearly observed (as mentioned before) and there is a low diffraction peak of ZrO_2 at 30.28° and 50.74° . The line (c) is a XRD of the sample after oxidation. There is an overlap of the ZrO_2 structure with Fe_3O_4 at $2\theta = 30.28^\circ$ and fortunately the intensity at 50.74° is remained. These results suggest that the structure of ZrO_2 did not change after reduction and oxidation.

Figure 9 is a XRD pattern of $\text{Mo-Fe}_2\text{O}_3$ during redox reaction. Before the reduction (spectrum a), there was a coexistence of Fe_2O_3 and $\text{Fe}_2(\text{MoO}_4)_3$ phase. We also observe the formation of Fe metal after reduction with the lower diffraction line (spectrum b) and the regeneration of Fe_3O_4 after oxidation (spectrum c).

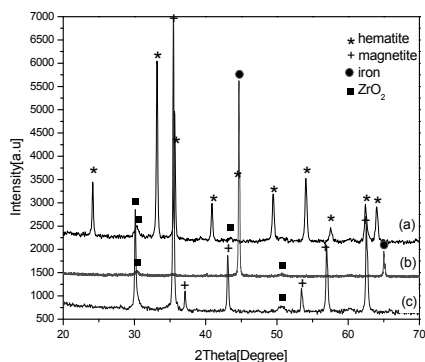


Fig. 8. XRD patterns of $\text{Zr-Fe}_2\text{O}_3$: (a) fresh $\text{Zr-Fe}_2\text{O}_3$; (b) after reduction (c) after oxidation

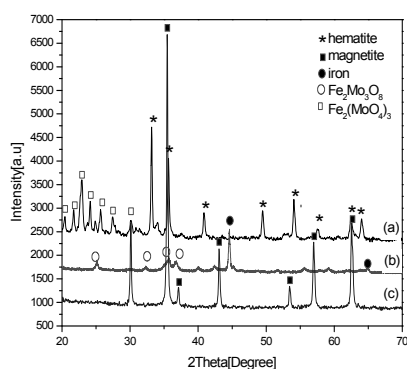


Fig. 9. XRD patterns of $\text{Mo-Fe}_2\text{O}_3$ (a) fresh $\text{Mo-Fe}_2\text{O}_3$; (b) after reduction; (c) after oxidation

It can be explained by TPR analysis that $\text{Fe}_2(\text{MoO}_4)_3$ was not be reduced in the reduction. However, its structure is changed into $\text{Fe}_2\text{Mo}_3\text{O}_8$ ($2\theta = 25.46, 32.36, 35.64$ and 36.68) after reduction. So in the reduction environment, two oxygen atoms of $\text{Fe}_2(\text{MoO}_4)_3$ are reduced by hydrogen and formation of $\text{Fe}_2\text{Mo}_3\text{O}_8$. The diffraction lines of this phase could not be seen in XRD pattern of sample after oxidation, cause of high intensity of diffraction line of Fe_3O_4 sample. Therefore the intensity, which assign for $\text{Fe}_2\text{Mo}_3\text{O}_8$, is overlapped by the base line of XRD. Therefore the structure of Mo^{+6} addition cation into iron oxide is not discovered.

4. Conclusion

The Fe_2O_3 and $\text{Zr-Fe}_2\text{O}_3$ samples were synthesized by sol-gel method and after elimination of citric acid by drying at 300°C , the good crystalline structure of $\gamma\text{-Fe}_2\text{O}_3$ was formed and it continuously changed into $\alpha\text{-Fe}_2\text{O}_3$ after calcinations at 500°C . For $\text{Mo-Fe}_2\text{O}_3$, an amorphous sample was originated after heating to 500°C and its structure was not completely crystallized under the synthesis conditions.

The addition of Mo^{+6} into iron oxide formed the substitution of MoOx into the structure of Fe_2O_3 and formation of spinel phase. In case of the addition of Zr^{+4} into Fe_2O_3 , there was not substitution of Zr^{+4} into the iron oxide structure and there was co-existence of two separated crystalline phase: ZrO_2 and $\gamma\text{-Fe}_2\text{O}_3$. The structure of Fe_2O_3 was changed into Fe by the reduction and then regenerated to Fe_3O_4 in the oxidation with water vapor. The ZrO_2 did not change its structure during redox reaction, however there was a transformation of $\text{Fe}_2(\text{MoO}_4)_3$ into $\text{Fe}_2\text{Mo}_3\text{O}_8$ after reduction.

The Fe_2O_3 and $\text{Zr-Fe}_2\text{O}_3$ are easier reduced by hydrogen and the formation of hydrogen by the oxidation is easier compared to a $\text{Mo-Fe}_2\text{O}_3$ sample.

Acknowledgement

The authors gratefully acknowledge the receipt of a grant from Flemish Interuniversity Council for University Development cooperation (VLIR UOS), which enable them to carry out this work. This work was also supported by the Vietnamese Ministry of Education and Training under the project B2007-01-132.

References

1. Bao-Lian Su et al., *Catalysis Today*, (2004) 743–750
2. K. Otsuka et al., *Journal of Power Sources* 122 (2003) 111–121
3. Stakemaka et al., *Journal of Catalysis* 228 (2004) 66–74.
4. S. Poulston et al., *Journal of Catalyst* 178 (1998) 658.
5. G. Barkhordarian et al., *Scripta Mater*, 49 (2003) 213–217.
6. S. Golunski et al., *Catalysis Today* 72 (2002) 107.
7. M. Y. Song et al., *International Journal of Hydrogen Energy* 30 (2005), 1107–1111.
8. S. Takeaka et al., *Applied Catalysis A: General* 282 (2005) 333–341.
9. W. Oelerich et al., *J. Alloys Compound*. 315 (2001) 237–242.
10. S. Takenaka et al., *Journal of Catalysis*, Vol 228, p. 405–416, 2004.
11. S. Takenaka et al., *International Journal of Hydrogen Energy* 31 (2006) 1732–1746.
12. Werner Smykatz-loss ‘Differential thermal analysis’. Springer-Verlag Berli Heidelberg New York 1974

Structural Modification of Near-Surface Region of Strontium Titanate Single Crystal Under the Influence of a Static Electric Field Enhanced by X-ray Irradiation

Alexandr A. Levin* and Dirk C. Meyer

Institut für Strukturphysik, Technische Universität Dresden, Zellescher Weg 16, 01069 Dresden, Germany

*E-mail: levin@physik.phy.dresden.de

Abstract. A single-crystalline SrTiO₃ (STO) (001) wafer with as-cut unpolished surface was investigated by means of Wide Angle X-ray Diffraction (WAXRD) *in-situ* under applying a d.c. electric field. The changes of WAXRD patterns measured in vicinity of 00/*l* (*l* = 2 and 4) STO reflections give evidences of a tunable and reversible formation of domains with a distorted crystalline structure. Different time-voltage procedures were used. An enhancement of the structural distortions by the influence of X-ray irradiation is established. A diffusion nature of the phenomenon is discussed.

1. Introduction

Single-crystalline SrTiO₃ (STO) wafers are widely used for deposition of thin films interest for technical applications. Due to deviations from the stoichiometric chemical composition and to defects, strains and other lattice distortions, the near-surface regions of the single-crystalline STO wafers can change significantly in comparison to the bulk materials. As a result, appearance of new structural and physical properties of the near-surface regions different from the properties of the bulk material can be observed [1, 2].

The bulk STO is characterized by a cubic perovskite-type of structure (space group $Pm\bar{3}m$, $a = 3.905 \text{ \AA}$ [3]) at room temperature (RT). Oxygen vacancies give rise to an expansion of the cubic lattice parameters [4] or a stabilisation of distorted perovskite-type of structure with lower (tetragonal) symmetry at RT ($a = 3.917 \text{ \AA}$, $c = 3.889 \text{ \AA}$, space group $P4/mmm$ [5]). Incorporation of additional SrO layers in between the perovskite STO structure-blocks accompanied by shear motions can lead to the formation of Ruddlesden-Popper phases (STO-RP) (SrO)_{*n*}SrTiO₃ with perovskite-related tetragonal structure (space group $I4/mmm$, $a \approx 3.9 \text{ \AA}$, $c \approx (2n + 1)a$). The members with low $n \leq 3$ were obtained in polycrystalline powder samples [6–8]. In thin films, the STO-RP members with $n \leq 11$ were found [9]. A coherent intergrowth of STO-RP and STO was observed [9]. The formation of STO-RP ($n = 1, 2, 3$) phases in the near-surface region of a single-crystalline STO plate was observed after annealing in an oxygen atmosphere [10–12]. Similarly, the electric field demonstrates a big influence on the state of the surface of STO single-crystalline plates. A characteristic electrocoloration of reduced material near cathode and oxidized material at anode has

been observed under application of an external d.c. electric field at temperatures of 100°C–325°C to a STO single-crystalline plate doped with transition metals [13]. A drift of oxygen vacancies is proposed to be the reason for the phenomenon. In an external electric field, the formation of STO-RP phases after ambient air annealing can be enhanced near the surface, acting as an anode due to an electro-migration of Sr-O-complexes to the anode [10].

Recently [14], we have reported on the observation of reversible structural changes in a STO (001) single-crystalline plate by means of Wide-Angle X-ray Diffraction (WAXRD) *in-situ* under the influence of an external static (d.c.) electric field at RT. The influence of the electric field was reflected by the development of a shoulder in the WAXRD reflection profile of the STO 00 l reflections ($l = 1 \dots 4$). The phenomenon was observed exclusively for the surfaces of the samples acting as anode and exhibiting an initially asymmetrical shape of the WAXRD profiles of the reflections (usually for as-cut unpolished sample surfaces) which can be interpreted properly by assuming a combined contribution of the ideal STO and a phase with a similar lattice parameter in the direction perpendicular to the sample surface [14–15]. Thus, a necessary condition for the appearance of extended electric field-induced distortions is the existence of a certain amount of regions with a structure differing from that of ideal cubic STO or at least lattice defects as precipitates in the STO sample anode region [15]. The electric-field induced structure modification can be interpreted as a result of development of nanoscale intergrowth-domains of STO-RP and matrix STO in the near-anode sample region [16]. A model of growth of monolayer SrO precipitates by dislocation climb is proposed in [17] assuming the field-driven diffusional transport of O and Sr ions along dislocation cores to the near-surface region.

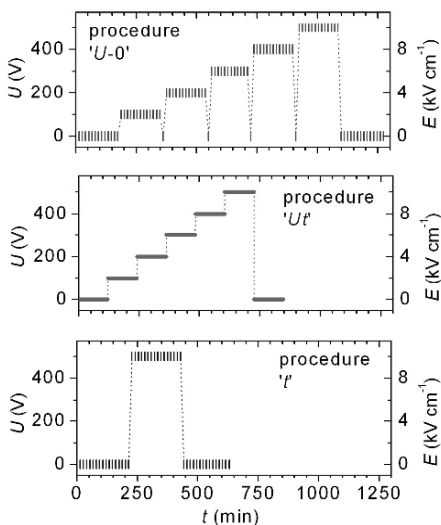


Fig. 1. Scheme of procedures of electric field switching during the WAXRD measurements. Line bares (procedures ‘U-0’ and ‘t’) represent individual scans carried out. In case of ‘Ut’ procedure individual scans are shown by large solid horizontal lines. The duration of one scan was of about 11.8 min (STO 002 reflection in procedure ‘t’), 13.4 min (004 reflection in procedures ‘U-0’ and ‘t’), 90 min (002 reflection in procedure ‘Ut’) and 120 min (004 reflection in procedure ‘Ut’). The scheme is shown for WAXRD measurement of STO 004 reflection as an example. Ordinate shows the voltage U (left) and corresponding electric field strength E (right) applied. The time scale is the same for all diagrams

In the current paper we are presenting the results of *in situ* X-ray diffraction characterization of an STO (001) single-crystal plate under the influence of an external d.c. electric field at RT using different time-voltage (t - U) procedures (procedures ' U -0', ' U t ' and ' t ' in Figure 1). The influence of X-ray irradiation on the phenomenon observed is outlined additionally.

2. Experimental Methods

One-side-polished single-crystalline STO (001) wafers with dimensions of about $5.5 \times 0.5 \text{ mm}^3$ (delivered by Crystec GmbH, Germany) were used for investigations. On both coplanar sides of the wafers, electrodes (70 nm metallic Mo/30 nm dielectric B_4C films) were deposited by means of DC magnetron sputtering. WAXRD structural characterization of the samples at ambient conditions and *in situ* under the influence of an external static electric field were carried out using an X-ray diffractometer URD-6 (Seifert FPM GmbH, Germany; Bragg-Brentano geometry; monochromatized Cu-K_α radiation). The 00 l reflection profiles were recorded in a symmetrical coupled θ - 2θ scan mode allowing for detection of the Bragg reflections from the lattice planes oriented parallel to the sample surface. During the measurements using different t - U procedures, the X-ray irradiation of the sample surface was switched off between the scans for a duration of not more than 1 min. Between the different procedures as well as between the ' t '-procedures of different voltage, the samples were maintained for about 8 hours at ambient conditions in zero electric field and without X-ray irradiation. A more detailed description of the experimental techniques is published elsewhere [14, 16].

3. Results and Discussion

As an example, Figure 2 presents characteristic WAXRD patterns of 00 l reflections ($l = 2$ and 4) recorded from the unpolished as-cut side of the STO wafer

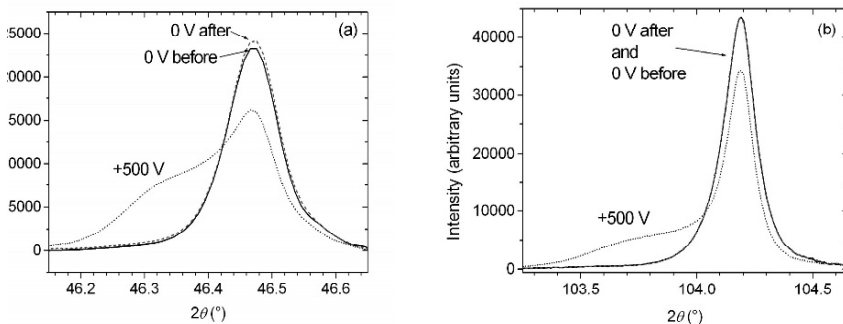


Fig. 2. WAXRD patterns recorded in vicinity of 002 (a) and 004 (b) STO reflections in zero electric field before and after applying a voltage and under application of the field (voltage $U = +500 \text{ V}$). The WAXRD patterns shown were taken after stabilization of the reflection profiles. Contribution of $\text{Cu-K}_{\alpha 2}$ radiation is corrected

using a t - U procedure ' t ' (Figure 1) and demonstrating the formation of a shoulder of the reflection profiles under application of the electric field. The reversibility of the WAXRD profile changes is illustrated by a good coincidence of the WAXRD reflection profiles recorded in zero electric field before and after application of a positive voltage (Figure 2). On the contrary, negative voltage applied to the sample surface did not show any effect on the reflection profiles recorded (see an example in [17]).

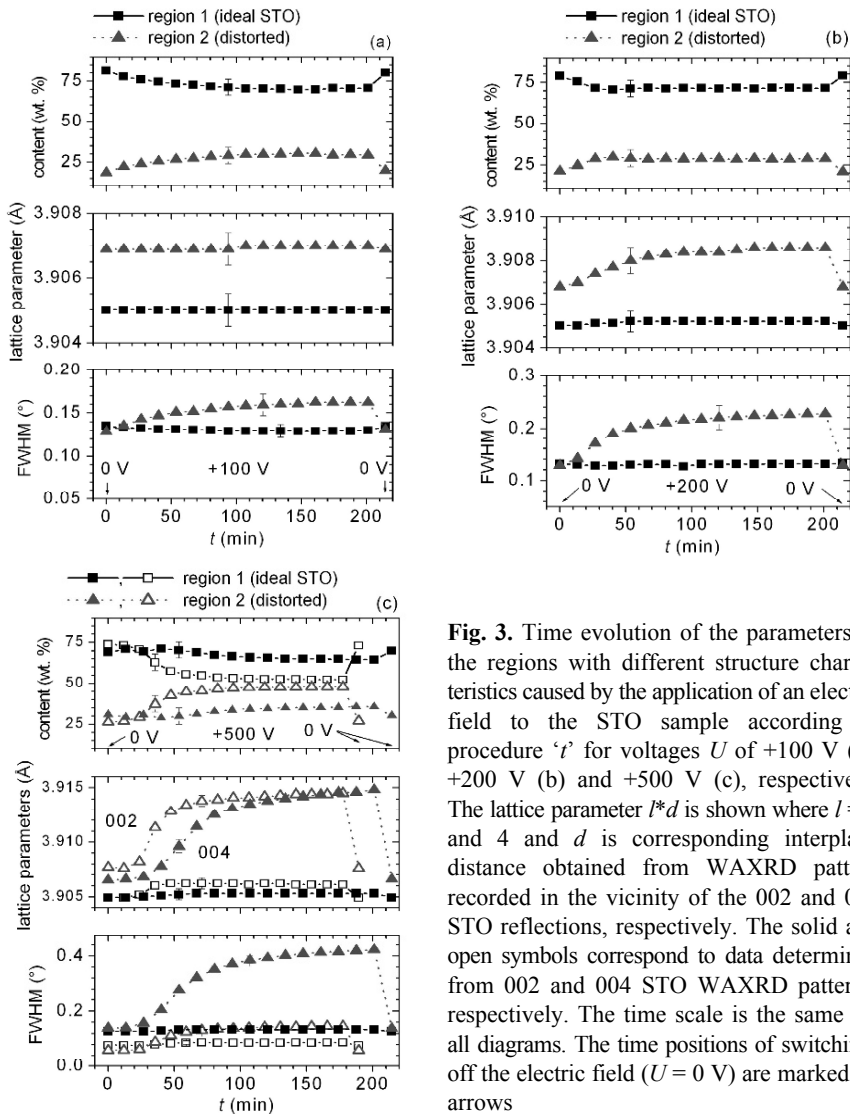


Fig. 3. Time evolution of the parameters of the regions with different structure characteristics caused by the application of an electric field to the STO sample according to procedure ' t ' for voltages U of +100 V (a), +200 V (b) and +500 V (c), respectively. The lattice parameter l^*d is shown where $l = 2$ and 4 and d is corresponding interplane distance obtained from WAXRD pattern recorded in the vicinity of the 002 and 004 STO reflections, respectively. The solid and open symbols correspond to data determined from 002 and 004 STO WAXRD patterns, respectively. The time scale is the same for all diagrams. The time positions of switching-off the electric field ($U = 0$ V) are marked by arrows

Figures 3–5. show results of fitting the experimental WAXRD patterns (lattice constants, full width at half maximum (FWHM) of the contributing reflection profiles and relative contents (scattering volumes) of the main STO phase and of the minor distorted regions) recorded in vicinity of the STO 00 l reflections *in-situ* using different t - U procedures. The technique of fitting the reflection profiles is described elsewhere in detail [14].

Time dependence of the structural changes. The time-evolution of the phase parameters for the ' t '-procedures recorded for 002 and 004 reflections is presented in Figure 3. For the ' U -0' procedure, we refer to [14, 15]. Application of the positive E to a relaxed sample (i.e. procedure ' t ') results in an increase of the relative content (i.e. scattering volume) of the distorted region accompanied by an expansion of corresponding lattice and an increase of the FWHM of the reflections forming the shoulder of 00 l profiles. These structural modifications develop significantly in a limited time followed by a stabilization (or, more precisely, followed by a moderate change of the same sign for the time of about 200 min). For the 004 STO reflection profile, the "stabilization" time was of about 40 min, 65 min and 80 min for the voltages of +100 V, +200 V and +500 V, respectively. For the 002 STO reflection profile, stabilization was observed after about 50 min of application of the voltage of +500 V (Figure 3c).

The time dependence of the structural modification of the STO plate gives evidence for a diffusion-driven nature of the electric-field phenomenon found. The electric-field induced diffusion of oxygen ions to anode leading to the further diffusion of strontium–oxygen complexes can be considered [17]. A faster development of the structural changes observed for WAXRD patterns recorded in the vicinity of the STO 002 reflection under the influence of the electric field could be explained by a layer-like concentration of the distorted regions enriched by O and Sr-O complexes near the anode. As the diffusion of the Sr and O atoms arises in direction to the sample surface acting as an anode, the saturation will occur at first in layers near the surface. According to linear absorption coefficient of STO and the values of incident and exit angles of the incoming and diffracted X-rays [18], the penetration depth reached $\sim 7\text{ }\mu\text{m}$ and $\sim 14\text{ }\mu\text{m}$ for 002 and 004 STO reflections, respectively. As a result, the 002 reflection profile stabilized faster. Additionally, for the higher- 2θ -angle STO 004 reflection, the contribution of the ideal STO matrix from the deeper layers is more significant and can mask the structural changes in near-surface regions.

At first stage of voltage processing of +100 V, the ' U -0' procedure applied to a relaxed sample exhibited a similar time-evolution development like ' t '-procedure (see Figure 3 and [15] for comparison). However, for the next stages of the voltage a memory effect was observed resulting in a faster saturation of the 004 STO reflection profile (for a stabilization time of ~ 27 min).

Electric-field strength dependence of the structural changes. Similarly to the faster development of the profile changes for the smaller- 2θ -angle 002 STO reflection in comparison to higher- 2θ -angle 004 STO, a higher relative content and larger lattice parameter for the non-ideal regions obtained from WAXRD patterns recorded in the vicinity of 002 STO under the influence of the electric

field of different strength in comparison to 004 STO (Figure 4 for '*Ut*' *t*-*U* procedure as an example) can be explained by diffusion of O atoms to anode as it was discussed above.

Figure 5 shows a comparison of the electric-field strength dependencies of the phase parameters contributing to the WAXRD pattern in vicinity of STO 004 for '*U*-0', '*Ut*' and '*t*' time-voltage procedures. All data were obtained after analysis of the last scan at every voltage applied, i.e. after stabilization of the reflection profiles. As it is seen, the different *t*-*U* procedures result in a different final state of the sample.

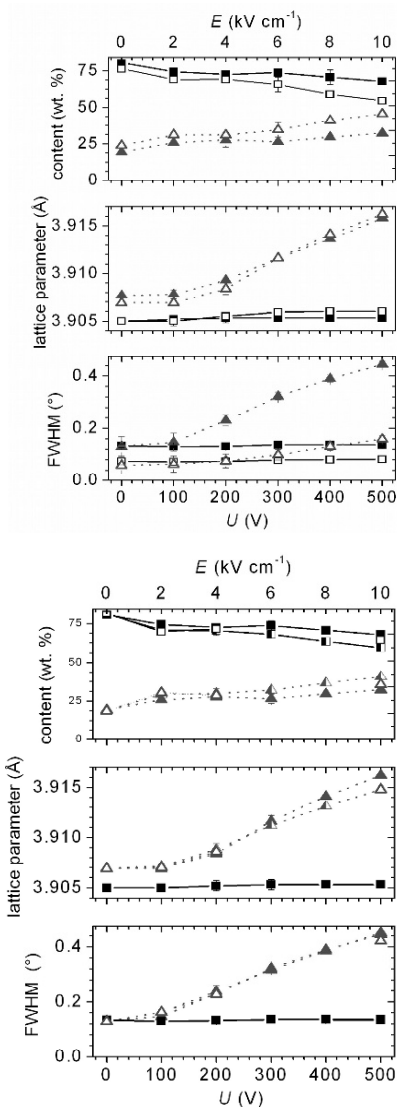


Fig. 4. Voltage-dependent changes of the parameters of the regions with different structure characteristics due to application of an electric field to the STO sample according to procedure '*Ut*'. The parameters are obtained by fitting the WAXRD patterns recorded in vicinity of STO 002 (open symbols) and 004 (solid symbols) reflections after profile stabilization. The data corresponding to ideal STO structure are represented by squares whereas triangles correspond to data for distorted regions

Fig. 5. Comparable to Figure 4 for '*Ut*' (solid symbols), '*U*-0' (half-solid symbols) and '*t*' (open symbols) time-voltage procedures. The parameters are obtained by fitting the WAXRD patterns recorded in vicinity of 004 STO reflections after profile stabilization

The larger lattice parameter of the distorted regions is obtained for procedure '*Ut*' where the duration of switching-off the X-ray irradiation during the procedure was minimum. However, the relative content of the distorted regions developed in this '*Ut*' experiment (~32 wt.%) was lower than in '*t*'- (~36 wt.%) and '*U*-0'- (~41 wt.%) procedures, probably due to lower duration of the electric-field processing of the sample at

every stage of the voltage (~ 120 min for ' Ut ' whereas ~ 214 min for ' t ' and ~ 174 min for ' $U-0$ ' procedure). The highest relative content of the distorted regions was found for ' $U-0$ ' procedure demonstrating the influence of the electric-field processing of the sample by a sequential increase of the voltage in comparison to ' t '-procedure where only one voltage level was used.

Influence of X-ray irradiation on the structural changes. The comparison of results of different t - U procedures shown above gives rise to a supposition that the X-ray irradiation acts on the distortion of the near-anode regions of the STO wafer under application of the d.c. electric field [18]. By use of a new virgin sample, a new kind of experiments was performed. The intensity was measured at the diffraction angle-position 2θ (and the incidence angle $\omega = 2\theta/2$) of the shoulder formed in the vicinity of STO 002 reflection under application of the electric field. The duration of the intensity measurement was of 10 s. In the first 4 cycles of the measurements, the X-ray window was closed for the time of a few minutes between the intensity measurements. In the 5th measurement cycle, after about 300 min repetition of the intensity measurements according to the scheme described above (with closing the X-ray window between the measurements), the sample surface was irradiated the whole time without interruption. The 1st cycle performed for the virgin sample exhibited a delayed increase of the shoulder intensity in comparison to next cycles showing (probably due to a memory effect discussed above) a behavior similar to the 5th cycle without X-ray irradiation between the intensity measurements (see Figure 6). A continuous X-ray irradiation resulted immediately in a significant increase of the shoulder intensity. Thus, the process of the structural modifications was really enhanced under X-ray irradiation (Figure 6). Apparently, the X-ray radiation generates further ionic species to be moved by electric field gradient.

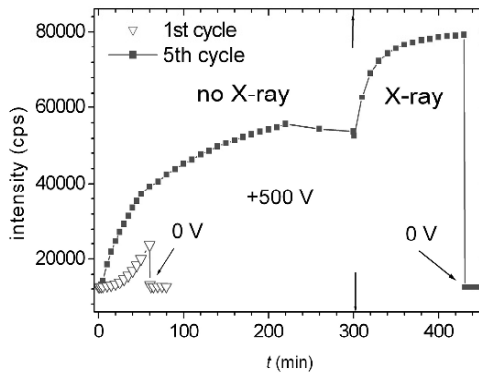


Fig. 6. Intensity at the angle-position of the shoulder ($2\theta = 46.27^\circ$) formed near the STO 002 reflection ($2\theta_{002} = 46.47^\circ$) after switching-on the voltage $U = +500$ V for a virgin sample (1th cycle of measurements) and for the sample after the 5th cycle of measurements. For other explanations see the text

4. Conclusions

The reversible and tunable structural modifications of a near-surface region of an STO (001) single-crystal wafer in an external static electric field were investigated using different time-voltage procedures with increasing the electric field strength up to $+10 \text{ kV}\cdot\text{cm}^{-1}$. Evidences of diffusion nature of the phenomenon are found to be caused probably by electro-migration of O atoms and Sr-O-complexes to the anode. X-ray irradiation of the anode-surface of the sample results in an enhancement of the structural distortions.

Acknowledgements

The authors are indebted to DFG FOR 520 for financial support. The team of S. Braun (Institut für Werkstoff- und Strahltechnik Dresden) is gratefully acknowledged for electrode deposition.

References

1. K. Szot, W. Speier, G. Bihlmayer, and R. Waser, *Nature Mat.* **5**, 312, 2006.
2. A.A. Levin, P. Paufler, and D.C. Meyer, *Phys. B* **394**, 373, 2007.
3. H.E. Swanson and R.K. Fuyat, *Natl. Bur. Std. Circ.* **539**(3), 44, 1954; PDF2, card 35-0734.
4. R. Perez-Casero, J. Perrière, A. Gutierrez-Llorente, D. Defourneau, E. Millon, W. Seiler, and L. Soriano, *Phys. Rev. B* **75**, 165317 (2007).
5. W. Gong, H. Yun, Y.B. Ning, J.E. Greedan, W.R. Datars, and C.V. Stager, *J. Solid State Chem.* **90**, 320, 1991.
6. E.M. Levin, C. R. Robbins, and H. F. McMurdie, in *Phase Diagrams for Ceramicists*, Amer. Ceram. Soc., Columbus, 1964.
7. S.N. Ruddlesden, and P. Popper, *Acta Cryst.* **10**, 538, 1957.
8. S.N. Ruddlesden, and P. Popper, *Acta Cryst.* **11**, 54, 1958.
9. R.J.D. Tilley, *J. Solid State Chem.* **21**, 293, 1977.
10. K. Szot, M. Pawelczyk, J. Herion, C. Freiburg, J. Albers, R. Waser, J. Hulliger, J. Kwapulinski, and J. Dec, *Appl. Phys. A* **62**, 335, 1996.
11. K. Szot and W. Speier, *Phys. Rev. B* **60**, 5909, 1999.
12. K. Szot, W. Speier, J. Herion, and C. Freiburg, *Appl. Phys. A* **64**, 55, 1997.
13. J. Blanc and D.L. Staebler, *Phys. Rev. B* **4**, 3548, 1971.
14. D.C. Meyer, A.A. Levin, S. Bayer, A. Gorbunov, W. Pompe, and P. Paufler, *Appl. Phys. A* **80**, 515, 2005.
15. D.C. Meyer, A.A. Levin, T. Leisegang, E. Gutmann, M. Reibold, P. Paufler, and W. Pompe, *Mater. Res. Soc. Symp. Proc.* **928E**, 0928-GG14-21, 2006.
16. D.C. Meyer, A.A. Levin, T. Leisegang, E. Gutmann, P. Paufler, M. Reibold, and W. Pompe, *Appl. Phys. A* **84**, 31, 2006.
17. M. Bobeth, N. Farag, A.A. Levin, D.C. Meyer, W. Pompe, and A.E. Romanov, *J.J. Ceram. Soc. Jpn.* **114**, 1029, 2006.
18. A. Kumar, U. Welzel, and E.J. Mittemejer, *J. Appl. Cryst.* **39**, 633, 2006.
19. D.C. Meyer, A.A. Levin, and P. Paufler, in *10th German-Vietnamese Seminar on Physics and Engineering*, Universität Bonn, 36, 2007.

Thermoelectric Properties of Heavily Doped Polycrystalline SrTiO₃

Nguyen Trong Tinh¹ and Toshihide Tsuji²

¹ Institute of Applied Physics & Scientific Instruments, Vietnam Academy of Science and technology, 18 Hoang Quoc Viet st., Cau Giay, Hanoi, Vietnam
E-mail: nttinh@capsi.vast.ac.vn

² School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Ishikawa, Nomi city, Japan
E-mail: tsuji@jaist.ac.jp

Abstract. The thermoelectric properties of the n-type Sr deficient polycrystalline SrTiO₃ singly or co-doped with Dy and Nb were systematically investigated. The Nb doped samples prepared in forming gas have a solubility limit at about 20 at% against 8 at% of Dy. All prepared samples have metallic behavior of the electrical conductivity above 300°C. The Nb doped samples can reach a high value of electrical conductivity comparable to early reported [5] La-doped ones, however Dy doped samples have a lower thermal conductivity. The behavior of the Seebeck coefficient of Nb and Dy singly doped samples as a function of doping concentration is the same. The containing 4 at% Dy sample heavily co-doped with Nb has a lower thermal conductivity while keeping a high value of electrical conductivity. The highest value of the dimension less figure of merit is about 0.24 at 1273K for the co-doped sample with 4 at% Dy and 20 at% Nb.

1. Introduction

Thermoelectric oxide materials have attracted much interest recently as a promising candidate for thermoelectric power generators in the high-temperature region. The efficiency of the thermoelectric materials is expressed by the figure of merit Z :

$$Z = \frac{S^2 \sigma}{k} \quad (1)$$

Where S is Seebeck coefficient, σ and k are the electrical and thermal conductivities respectively.

The Cobalt based oxides with layered structure such as Na_xCoO₂, Ca₃Co₄O₉ and their derivatives [1–3] are known to be good p-type thermoelectric materials with a high figure of merit, but n-type oxide materials comparable with Co-based oxides have not been found yet. One of the most promising candidates for n-type thermoelectric material is doped SrTiO₃. Heavy doping of La on Sr sites or Nb on Ti sites of SrTiO₃ gave high electrical conductivity [4, 5], but high thermal conductivity [6, 7]. Consequently, the figure of merit does not improve so much. In contrast, doping of rare earth elements on Sr site of SrTiO₃ gave reasonably low thermal conductivity [6]. The co-doping on both sites Sr and Ti of SrTiO₃ is the way to improve the figure of merit.

From a defect chemistry point of view, two different approaches have been realized in the preparation of n-type doped SrTiO_3 . The first approach involves formulation of the composition according to the electronic compensation regime $\text{Sr}_{1-x}\text{M}_x\text{TiO}_{3-d}$ (M is the dopant, for example La [4] or rare earth elements [6,8]) and sintering in reducing gas [4], in Ar gas at very high temperature ($\sim 1600^\circ\text{C}$) [6] or using the hot pressing technique [8]. The second approach involves the vacancy-compensated compounds such as $\text{Sr}_{1-3x/2}\text{M}_x\text{TiO}_3$ (M is a three-valent dopant) with sintering at lower temperatures ($1400\text{--}1450^\circ\text{C}$) in forming gas [5, 9]. In our work, according to the later approach, we have realized the Sr deficient composition with formulas $\text{Sr}_{1-3x/2-y/2}\text{Dy}_x\text{Ti}_{1-y}\text{Nb}_y\text{O}_3$.

In this report, we have investigated systematically the singly Dy doped, singly Nb doped and co-doped 4 at% Dy with Nb from 0 to 30 at% samples. The effects of doping concentration, preparation condition on the thermoelectric properties and phase structure are discussed.

2. Experimental Methods

The Sr deficient polycrystalline samples with chemical formula $\text{Sr}_{(1-1.5x-0.5y)}\text{Dy}_x\text{Ti}_{1-y}\text{Nb}_y\text{O}_3$ were prepared by solid-state reaction. The sintering process was carried out at 1450°C in the forming gas (95%Ar + 5%H₂) for 4 hrs. Some samples were sintered at 1400°C in air for studying the influence of sintering atmosphere on the phase structure and thermoelectric properties. The crystal structure of the prepared samples was examined by powder X-ray diffraction using a Cu-K α radiation (RINT 1500). The oxygen deficiency was determined from TG-DTA data in air. The samples for electrical and Seebeck coefficient measurements were prepared in the form of cylinders with a diameter of about 4.5 mm and 17 mm long. For voltage contact, on the sintered cylinder, grooves about 0.2 mm deep were cut with a distance of 4–5 mm. Pt wire (0.2 mm) was wounded tightly into the grooves to form the potential probes. Two Pt-Pt13%Rh thermocouples were attached to both ends of the cylinder by Pt paste as electrical contacts and for measuring the temperature difference. The contacts were cured in situ under forming gas for 30 minutes at 1000°C . The electrical conductivity was measured in various atmospheres over the temperature range of $20\text{--}1000^\circ\text{C}$. The values of electrical resistance were calculated from the linearized slope of the voltage drop against current over the range -100 to 100 mA. The Seebeck coefficient measurement was carried out simultaneously with the electrical conductivity measurement. The values of thermoelectric power were calculated from the linearized slope of the thermo electromotive force against the temperature difference over the range $1\text{--}10\text{K}$.

The samples for thermal conductivity measurements were prepared in the form of pellet with about 1.5 mm thickness and 8.5 mm diameter. The thermal conductivity was evaluated by the following expression:

$$K = D \times C_p \times d \quad (2)$$

where K , D , C_p and d are the thermal conductivity, the thermal diffusivity, the heat capacity and the experimental measured density of the sample respectively.

The thermal diffusivity can be measured by ULVAC TC-7000 laser flash equipment in vacuum. The heat capacity was calculated from the constituent oxides using Thermodynamics Database of The Japan Society of Calorimetry and Thermal Analysis (MALT2).

3. Results and Discussion

3.1. Preparation and Solubility limitation of Dy and Nb doping in SrTiO₃

We have prepared the Nb singly doped samples with a chemical formula Sr_(1-0.5y)Ti_(1-y)Nb_yO₃ ($y = 0, 0.1, 0.13, 0.17, 0.2, 0.24, 0.3$) in forming gas and air. As determined by XRD, all Nb singly doped samples prepared in air have a single phase and the lattice parameter changes linear with the doping concentration (Fig. 1). This means solubility limit of Nb is higher than 24 at% for the samples prepared in air. However, the samples prepared in forming gas have a small impure Nb rich second phase for a doping concentration higher than 20 at%. This impure second phase has been identified earlier [5] by EDX chemical analysis. The lattice parameter of the samples prepared in forming gas changes linear with Nb doping concentration up to 20 at% as seen in Figure 1. The lattice parameter of the sample with 24 at% Nb doping exhibits a change in slope. This is possibly due to a solubility limitation of Nb doping at about 20 at%.

The Dy singly doped samples with a chemical formula Sr_(1-1.5x)Dy_xTiO₃ have another behavior. The samples prepared in air have an impure second phase Dy₂Ti₂O₇ above a Dy dopant concentration of 4 at% while other ones, prepared in forming gas, have a single phase with a Dy concentration up to 8 at%. The analysis from XRD measurements (Fig. 1) shows the linear dependence of the

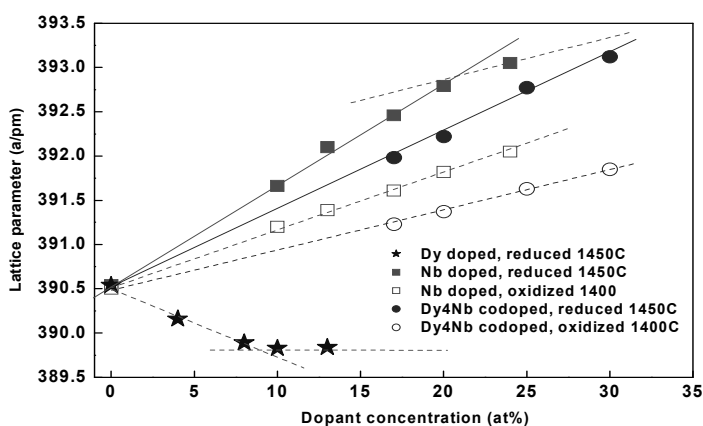


Fig. 1. Lattice parameter vs. doping concentration. The singly Dy doped, singly Nb doped and 4 at% Dy on the Sr site co-doped with Nb on the Ti site samples have been marked as Dy doped, Nb doped and Dy4Nb codoped in the picture respectively. A drop of linearity determines the solubility limitation

lattice parameter against Dy doping concentration up to 8 at%. From these facts, we can suggest that, the solubility limit of Dy doping in the samples prepared in forming gas is about 8 at%. The solubility limit of Dy doping can be increased up to 10 at% by very high sintered temperature or pressure [6]. Another way to get more heavily doped samples is co-doping Dy and Nb with optimized concentrations. We applied the doping of 4 at% of Dy for the Sr site with co-doping of Nb for the Ti site. Our result shows that samples can be prepared in forming gas with a solubility limit of Nb higher than 20 at%.

3.2. The Electrical Conductivity

The electrical conductivity of various singly Dy doped samples are shown in figure 2. For Dy doping, the electrical conductivity increase with dopant content up to 10 at%. The highest value of the electrical conductivity is about $400 \text{ Ohm}^{-1}.\text{cm}^{-1}$ at 500K. For higher Dy doping, it decreased due to the impure second phase $\text{Dy}_2\text{Ti}_2\text{O}_7$. This result is a little bit different compared with the solubility limitation of Dy doped samples (about 8 at%) as obtained by the XRD analysis above. The reason is maybe due to the influence of the impure phase $\text{Dy}_2\text{Ti}_2\text{O}_7$ which is present to some extent.

In the high temperature region (above 500K) Dy doped samples have a temperature dependent behavior, that obeys the phonon scattering mechanism. The comparison of the $T^{-1.5}$ temperature dependence line and the temperature dependence of the electrical conductivity are shown in Figure 2.

Unlike Dy doped samples, Nb singly doped ones have a higher solubility limitation. The electrical conductivity of the singly Nb doped samples increases with dopant content up to 20 at% and decreases after that. It is about $700 \text{ Ohm}^{-1}.\text{cm}^{-1}$ for 20 at% singly Nb doped samples (that is the solubility limitation of singly Nb

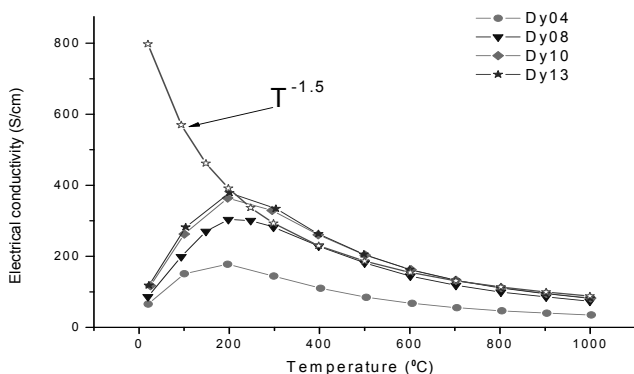


Fig. 2. Temperature dependence of the electrical conductivity for the singly Dy doped samples. The at% of doping are given as a number

doped samples). We applied the co-doping of Dy on Sr site in heavily Nb doped samples to reach a higher solubility limitation. As a result, we can get the best one for 4 at% Dy co-doping. The solubility limitation of Nb in the co-doped 4 at% Dy samples is higher than 20 at% as shown in the result of the XRD analysis. However, the electrical conductivity has the highest value at 20 at% Nb doping only and decreases for higher doping concentration (Fig. 3).

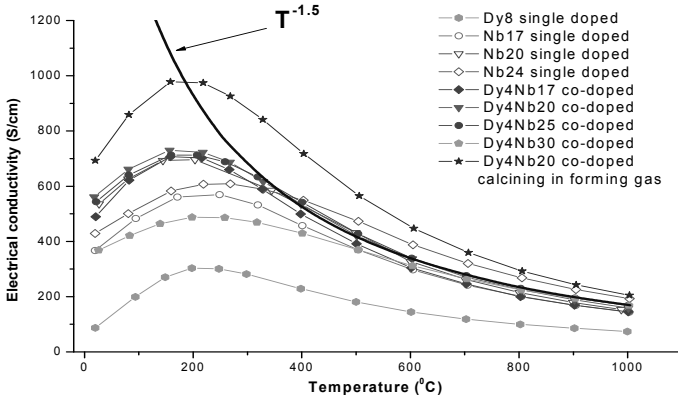


Fig. 3. The temperature dependence of the electrical conductivity for various doping concentrations and preparation conditions. The singly doped Dy, Nb and co-doped 4 at% Dy samples have been marked as **Dy**, **Nb** and **Dy4Nb** respectively

In the high temperature region, the influence of the doping concentration is more clear: the electrical conductivity increases with the total doping concentration. The sample, that has been calcined at 1200°C and sintered at 1450°C in the forming gas, has the highest electrical conductivity. It was comparable with heavily La doped samples reported earlier [5]. The complicated behavior of the electrical conductivity in the low temperature region may be explained by the influence of grain boundaries on the electrical conductivity.

The temperature dependence of the electrical conductivity of all samples shows a behavior ($\sim T^{-1.5}$), which is following phonon scattering mechanism in the high temperature region above 300°C.

3.3. Thermoelectric Power

Following the Ioffe theory of the thermoelectric semiconductor, the thermopower of a non-degenerate broad band semiconductor can be written as:

$$\eta = -\frac{k}{e} \cdot \left(\ln \frac{N_c(T)}{n} + A e \right) \quad (3)$$

$N_c(T)$, n are the convenient effective density of states and the electron concentration of a doped semiconductor. Ae is the transport factor that describes possible

interaction between electrons in the conduction band and the crystal lattice. It cannot be calculated without the knowledge of the scattering mechanism.

All Dy and Nb doped samples, prepared in forming gas, are n-type thermoelectric semiconductor. The electrical conductivity of our doped samples can be compared with La doped samples that was report earlier [5]. Consequently, we can suggest that, the electron concentration in formula 3 can be determined by the concentration of the total ionized dopant. The temperature dependence of the Seebeck coefficient for various doped samples is shown Figure 4. It is clear that the absolute value of the Seebeck coefficient decreases with increasing doping concentration. This result is qualitatively coincided with the Ioffe theory of thermoelectric semiconductor (formula 3). Our detailed calculation of the thermoelectric power for various doping concentration shows a good agreement with earlier reported calculations for heavily La doped samples [10].

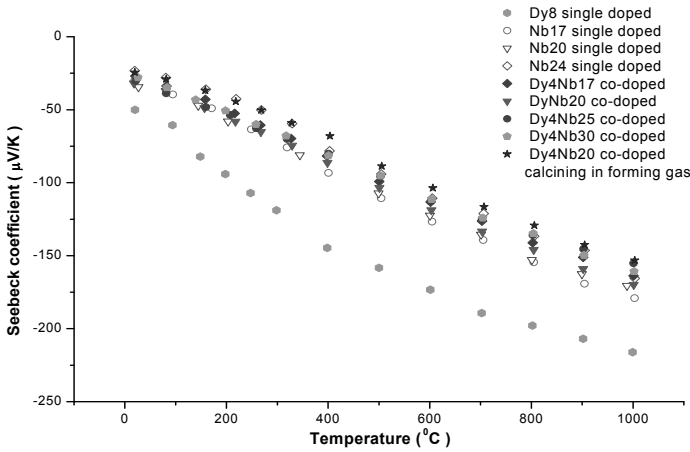


Fig. 4. Seebeck coefficient of samples with various doping concentrations. The singly Dy, Nb doped and co-doped 4 at% Dy samples have been marked as **Dy**, **Nb** and **Dy4Nb** respectively

The power factor F of a thermoelectric material is determined as follows:

$$F = S^2 \cdot \sigma \quad (4)$$

where S and σ are the Seebeck coefficient and the electrical conductivity respectively.

The heavy Nb doping for our samples results in a good electrical conductivity, but the absolute value of the Seebeck coefficient decreases with increasing doping concentration. The decreasing of the absolute value of the Seebeck coefficient with increasing doping concentration goes along with a compensation of the increasing electrical conductivity. Consequently, the power factor does not increase so much as expected. The way to improve the figure of merit is a decreasing thermal conductivity, while keeping the high power factor.

3.4. The Thermal Conductivity

An early report [1] has shown that the doping of SrTiO₃ by rare earth elements could decrease the thermal conductivity. This is a good way to improve the figure of merit by decreasing the thermal conductivity, while keeping a high power factor. We have realized the doping of 4 at% Dy for Sr sites to the heavily Nb doped samples. Dy has a heavy atom mass, so we hope that Dy doping can affect the phonon scattering. Consequently, the thermal conductivity can be reduced. Figure 5 shows the lattice thermal conductivity of samples with various doping concentrations. The lattice thermal conductivity can be obtained after subtracting the electron thermal conductivity calculated by the Wiedermann-Franz law.

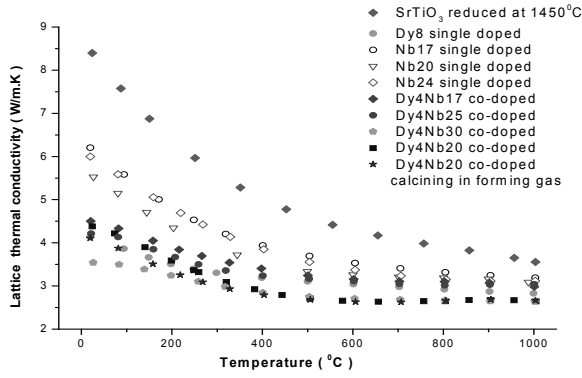


Fig. 5. Lattice thermal conductivity of samples with various doping concentrations. The singly doped Dy, Nb and co-doped 4 at% Dy samples have been marked as **Dy**, **Nb** and **Dy4Nb** respectively

Heavy singly Nb doping can reduce the thermal conductivity from $9 \text{ W.m}^{-1}.\text{K}^{-1}$ for pure SrTiO₃ prepared in forming gas, to about $6.5 \text{ W.m}^{-1}.\text{K}^{-1}$ for a 24 at% Nb singly doped sample. However, the Dy co-doping has more influence on the thermal conductivity. The lattice thermal conductivity of the Nb co-doped with 4 at% Dy sample decreases from $6.5 \text{ W.m}^{-1}.\text{K}^{-1}$ to $4 \text{ W.m}^{-1}.\text{K}^{-1}$. The sample with very heavy Nb doping (30 at%) has a lower thermal conductivity. However, we suggest that, this low thermal conductivity is possibly due to phonon scattering on the impure second phase in the samples. This suggestion is coincided with the XRD and electrical conductivity investigations that give evidence for the presence of the impure second phase in the 30 at% Nb doped sample.

The Dy doped samples have a lower thermal conductivity compared with Nb doped ones, but the electrical conductivity is lower as shown above. We apply the co-doping of Dy to Sr sites for heavily Nb doped sample to get a lower thermal conductivity while keeping a high electrical conductivity. As a result, we can reduce the thermal conductivity of the heavily Nb doped samples almost 3 time lower than pure SrTiO₃, while keeping a high value of power factor.

3.5. The Figure of Merit

Figure 6 shows the figure of merit Z of the various doped samples. It is clear that the figure of merit of the heavily Nb doped samples is almost unchanged in the high temperature region. The highest value is $1.2 \times 10^{-4} \text{ K}^{-1}$ (at temperature 800°C) for a 20 at% Nb doped sample. The more heavily doped sample has a lower figure of merit. This behavior is maybe due to the presence of the impure second phase in the sample, which reduces the sample electrical conductivity. By co-doping Dy to a heavily doped Nb sample, we can increase the value of the figure of merit (for 4 at% Dy and 20 at% Nb doped sample) to $1.9 \times 10^{-1} \text{ K}^{-1}$ at a temperature of about 800°C . The dimensionless figure of merit ZT has the highest value for the co-doped 4 at% Dy and 20 at% Nb sample. The best result can give ZT as high as 0.24 at a temperature of 1000°C .

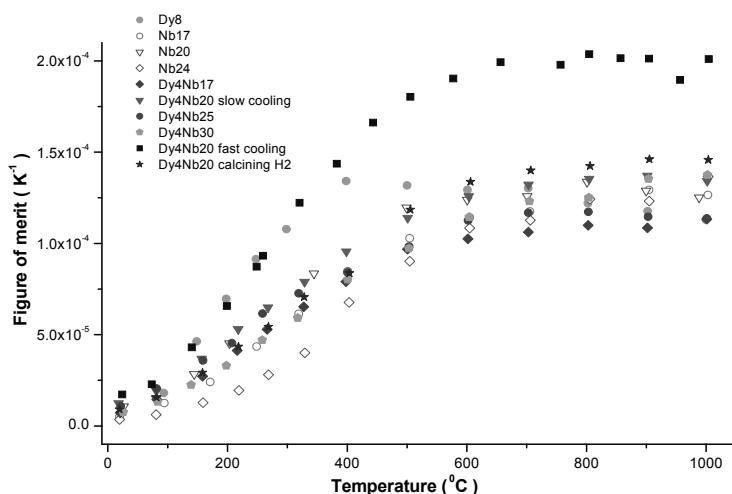


Fig. 6. Figure of merit of various samples as a function of doping concentration and preparation conditions. The singly doped Dy, Nb and co-doped 4 at% Dy samples have been marked as **Dy**, **Nb** and **Dy4Nb** respectively

4. Conclusions

SrTiO_3 samples heavily doped by Dy for the Sr and Nb for the Ti sites have been systematically investigated. The solubility limitation of the singly Dy doped samples is about 8 at% while that of singly Nb doped is about 20 at%. The co-doped samples have a higher solubility limitation. The electrical conductivity, the Seebeck coefficient and the thermal conductivity have been measured in the temperature range from room temperature to 1000°C . The electrical conductivity and the Seebeck coefficient show a temperature dependence, which obeys a phonon scattering mechanism. The heavily doped samples show a reduction of the lattice thermal conductivity from $9 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for pure SrTiO_3 to $3.5 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for

Dy 4 at% and Nb 20 at% co-doped sample at room temperature. By the co-doping approach, we can reduce the thermal conductivity while keeping a high power factor of the material, consequently, the figure of merit can be increased. As a result, the sample co-doped with 4 at% Dy and 20 at% Nb can give the highest value of the figure of merit Z that is about $1.9 \times 10^{-4} \text{ K}^{-1}$ at 800°C, and a dimensionless figure of merit ZT as high as 0.24 at 1000°C.

Acknowledgements

We would like to thank the Japan Advanced Institute of Science and Technology for supporting the experimental facility to conduct this work.

References

- 1 I. Terasaki, Y. Sasago and K. Uchinokura, Phys. Rev. B **56**, 12685(1997)
- 2 R. Funahashi and M. Shikano, Appl. Phys. Lett. **81**, 1459 (2002)
- 3 M. Mikami, R. Funahashi, M. Yoshimura, Y. Mori and T. Sasaki, J. Appl. Phys. **94**, 6579 (2003)
- 4 R. Moos and K. H. Hardtl, J. Appl. Phys. **80**(1), 393-400 (1996)
- 5 T. Kolodiazhnyi and A. Petric, J. Electroceram. **15**, 5-11 (2005)
- 6 T. Kolodiazhnyi and A. Petric, J. Electroceram. **15**, 5-11 (2005)
- 7 S. Ohta, T. Nomura, H. Ohta and K. Koumoto, J. Appl. Phys. **97**, 034106 (2005)
- 8 H. Obara, A. Yamamoto, C. H. Lee, K. Kobayashi, A. Matsumoto and R. Funahashi, Jpn. J. Appl. Phys. **43**(4B), L540-542 (2004).
- 9 S. Hui and A. Petric, J. Electrochem. Soc. **149**, (2002) J1.
- 10 R. Moos, A. Gnudi and K.H. Hardtl, J. Appl. Phys. **78**(8), 5042-5047 (1995).

Optimization Study of TiO₂ Film Deposited by IAD Process

Pham Hong Tuan¹

¹ Thin Film Technology Laboratory, National Center for Technology Progress,
C6 Thanh xuan Bac, Hanoi, Vietnam
E-mail: phtuan@hn.vnn.vn

Abstract. Ion assisted deposition (IAD) is a well established method to enhance the quality of optical thin film such as: higher packing density, lower spectrum shift due to moisture, higher reproducibility, more controllable film stress. TiO₂ is one of the favorable thin film materials, which gains benefits from the IAD. But the searching of an optimum parameter set for the IAD process is not a simple task. Most publications only describe optical thin film properties obtained in particular parameter set of the IAD process. This study deals with the refractive index of TiO₂ film as a main target for optimization. By application of Design of Experiment methodology (DOE), a relation between the TiO₂ film refractive index and the parameters of IAD process was functioned. On the basis of an established function, the effect of each IAD parameter to the film's refractive index was demonstrated and an optimum parameter set was pointed out.

1. Introduction

As we have already seen in numerous papers, Ion Assisted Deposition (IAD) has become well established as a mean of improving optical coating performance and reducing cost [1,2,3,4]. Some performance improvements include durability, optical spectrum stability with humidity and temperature, controllable stress, and better stoichiometry. Cost reduction results from low temperature deposition and increased rates for reactive processes. A lot of materials such as TiO₂, SiO₂, Al₂O₃, and Ta₂O₅ have gained benefits from IAD process. In practice, searching the optimum parameter set of the IAD process for a particular material is an important but not simple task. So far most publications describe the optical properties of a thin film (mainly film refractive index) obtained in a limited set of IAD parameters without pointing out the optimum point.

The optimization of the film deposition process can sometimes turn into a complicated problem because a lot of variables might be included: base pressure, substrate material, substrate preparation, substrate temperature, soak time, reactive gas partial pressure, gas mixture, deposition material, deposition rate, material evaporation pattern, E-gun high voltage and filament current, chamber cleaning, calotte rotation speed... In IAD with an ion source included, we can add: gas flow rate, chamber pumping speed, drive volts, drive current, filament current, and at least five degrees of freedom of source positioning and aiming and other variables.

The common practice is to attempt to hold the entire would-be variables constant except the one under investigation and find the best setting for that one variable. If we were to attempt to optimize a 10 variable process as described above by only two tests per variable with the assumption that the result would be linear, we would need to perform 2^{10} (or 1024) experiments to find the best result for one output such as refractive index or density. Obviously this is an unfeasible task that many of us have undertaken over years. However, there is an approach to reduce the number of experiments from thousands to the order of 50 or less, but still to gain better knowledge of the process. That is a methodology Design of Experiment (DOE) [5]. Experiments are then conducted at the conditions of each of the designed sample points (Fig. 1) and the results are recorded. There are a lot types of Design of Experiment and corresponding sample point schemes. Normally more than one type of result can be recorded for each data point, such as absorption, index, hardness ...Then the obtained data is analyzed by professional software, such as Design ExpertTM[6] to get the relationship between process parameter and output result.

TiO₂ is widely used in thin film technology due to its high index in visible and near infrared spectrum and relative robustness [7]. This study aims to establishing the functioned relationship between the optical properties of TiO₂ with the basic parameters of IAD process, then searching the optimum point for optical property on the basis of an established function.

2. Experimental Methods

The study was conducted in a diffusion-pumped coating chamber equipped with e-beam evaporator, quartz crystal rate/thickness controller XTC/2 from Inficon Inc, 4 kW resistance substrate heating and cold cathode ion source CC-105 from Denton Vacuum Inc [8,9]. The e-beam and the ion source is set symmetrically 10 cm off-center position. The distance between substrate and e-beam source is 40cm. The system is pumped down by diffusion pump (suction power of 3000 l/sec) to base vacuum pressure of 1×10^{-5} Torr, then oxygen is fed into the chamber through the ion source inlet controlled by the gas flow controller FC-7700CD from Advanced Energy Inc.

One of the mostly expected advantages of IAD process is enhancing the film packing density and the reduced spectrum shift [1, 2, 3, 4]. The denser film, the harder film and the lower spectrum shift due to moisture adsorption is. As reported in publications [10,11], there is a direct relation between the film packing density and its refractive index, so the film refractive index can be used as a measure to evaluate the impact of IAD to film packing density. In this work the film refractive index is evaluated through a transmission spectrum of the sample by the software "The Essential Macleod" [12]. An additional result, the spectrum shift, was evaluated through the shift of the sample's transmission spectrum recorded at a temperature of 20°C and 150°C respectively.

Mueller [13,14] showed that two fundamental parameters of IAD process, which decide the film packing density, are the ion energy and the ratio of energy per a deposited ad atom. In practice these two values depend on numerous sub parameters of the equipment and operating conditions. In this work three parameters,

which have a dominant affect to the IAD result, are chosen as a variable (or factor): Deposition rate, Gas flow, and Anode current of ion source [15]. Meanwhile the other parameters are kept constant. From the previous performed experiments the useful ranges for these 3 parameters were chosen (Table 1).

Table 1. Variables of IAD process and its operating range

Factor	Low level	High level
Gas flow [cm ³ /s]	8	15
Anode current of ion source CC-105 [A]	0.5	1.5
Deposition rate [nm/sec]	0.1	0.3
Fixed parameter: Filament current 20A, Substrate temperature 150°C, Film thickness 140 nm, distance ion source-substrate 40 cm		

Regarding the DOE method, there are two often used designs: Box-Behnken and Box-Wilson. Both permit to evaluate the linear and quadratic effect and a two factor interaction. Their advantages are very efficient in terms of the number of experiment and the provided information. In this work we chose Box-Behnken (Fig. 1), which is established to be more efficient than Box-Wilson in case of three factors at three levels [5]. The choices above (number of factor, type of design, values of high and low level, result type) were entered in the DOE software Design Expert 7 [7] to calculate the points to be sampled (Table 2) which satisfy the Box-Behnken design. 15 experiments have to be performed, then the measured results (refractive index and spectrum shift) are added into the corresponding column of the Table 2.

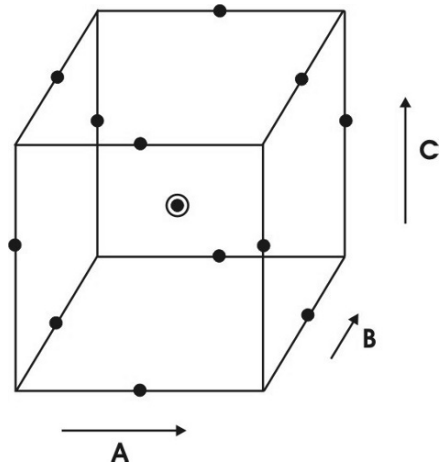


Fig. 1. Sample point schemes for Box-Behnken design with three factor of A, B, C

3. Results and Discussion

First of all, the measured data in Table 2 were analyzed by the software Design Expert 7 to choose the function model among: linear, two factor interaction, quadratic, or cubic polynomial. The linear model, which fits best to the measured data, is suggested to select by Design Expert 7 through evaluating statistical index such as: F-value, significance of the model, lack of fit test [4,5].

Table 2. Design sheet for experimental points in Box-Behnken design

Order	A:deposition rate (nm/sec)	B:Gasflow (sccm)	C: anode current (A)	Refractive index @ 550 nm	Spectrum shift (nm)
1	0.10	8.00	1.00	2.598	~1
2	0.30	8.00	1.00	2.440	2
3	0.10	15.00	1.00	2.415	9
4	0.30	15.00	1.00	2.326	18
5	0.10	11.50	0.50	2.326	18
6	0.30	11.50	0.50	2.140	24
7	0.10	11.50	1.50	2.580	~1
8	0.30	11.50	1.50	2.652	~1
9	0.20	8.00	0.50	2.430	2
10	0.20	15.00	0.50	2.245	18
11	0.20	8.00	1.50	2.560	~1
12	0.20	15.00	1.50	2.562	~1
13	0.20	11.50	1.00	2.490	2
14	0.20	11.50	1.00	2.490	2
15	0.20	11.50	1.00	2.486	2

With linear model as suggested, Design Expert 7 give the following equation:

$$n = 2.43 - 0.45*A - 0.02*B + 0.3* C \quad (1)$$

Where:

n- TiO₂ film refractive index

A-deposition rate [nm/sec]

B- gas flow to ion source [sccm]

From Eq. (1) following remarks were drawn: the coefficients of the factors have different value and sign. This means that the effect of the factors (strength and direction) to the refractive index is not the same for each factor. The positive coefficient of the anode current means that higher current causes higher refractive index. Meanwhile, the factors of deposition rate and gas flow have a negative coefficient, so refractive index decreases with the increasing of both of these factors.

The relationship between the TiO₂ film refractive index and the three factors above can be seen visually in a 3D response surface plot, Fig. 2. It is clear that the slope of the refractive index surface plot is different in the axes, it decreases from high to low in the order: anode current, gas flow, deposition rate. Anode current has the highest effect to refractive index, and the lowest one is the deposition rate.

Based on the above obtained function, Design Expert 7 can predetermine the factor set for the expected value of the refractive index (the maximum, the minimum or any value of refractive index) as shown in Table 3. The results were tabled in column “Predicted value...” and “Actual value...” From these results it can be seen that the predicting error is around 1–3%.

Design-Expert® Software

Refractive index

2.652

2.14

X1 = C: Anode current

X2 = A: Deposition rate

Actual Factor

B: Gas flow = 11.50

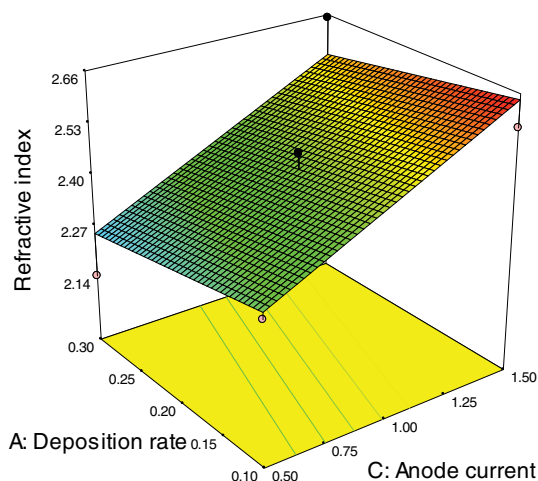


Fig. 2. Surface plot of TiO₂ film refractive index versus deposition rate and anode current

Table 3. The predetermined parameter set for a particular value of TiO₂ refractive index

Expected refractive index	Gas flow [sccm]	Anode current [A]	Deposition rate [nm/s]	Predicted value of refractive index	Actual value of refractive index
Maximum	15	1,5	0,3	2,62	2,58
2,4	8,9	0,9	0,3	2,40	2,41
Minimum	15	0,5	0,3	2,09	2,13

From Table 2 we know samples with refractive index higher than 2.45 have a spectrum shift of approximately 1–2 nm. At this level of refractive index and upward, the film packing density is high enough so the moisture adsorption in film body is very low and the induced spectrum shift is dramatically low .

4. Conclusions

In this work it was shown that by utilizing DOE method, the IAD process of TiO₂ film can be described by statistical models. The expenditure of the deposition process could be minimized by determining the suitable ranges of the deposition parameters thoroughly and documenting all other possible influential quantities. The DOE was presented as a successful way of determining the relation between thin film property and process parameters in an economic way. The high light of this study was the optimization of the refractive index of the film.

Acknowledgements

I would like to thank Dr. Dang Xuan Cu (Vice president of NACENTECH) for providing the necessary facility for my work. The supports of Dr. Harmut Kupfer (Institute of Physics, TU Chemnitz) was very highly appreciated.

References

1. Takagi T., Role of ions in ion-based film formation. *Thin Solid Films* 92, 1-17(1982)
2. Ebert J., Activated reactive evaporation. *Proc. SPIE-Int. Soc. Opt. Eng.* 325, 29 (1982).
3. Martin P.J., Ion-based methods for optical thin film deposition. *J. Mater. Sci.* 21, 1-25 (1986)
4. Morton. D.E. and Fridman V. Society of Vacuum Coaters 41st Annual Technical Conference Proceeding 1998.
5. Schmidt. S.R., Launsby R.G. Understanding Industrial Designed Experiment. Air Academy Press Colorado Springs 1994 Edition.
6. State- Estate., Inc. Software Design Expert version 7.0
7. Pulker, H.K., Refractive indices of TiO₂ films produced by reactive evaporation of various titanium oxide phases, *Appl. Opt.*, 15, pp. 2986-2991 (1976).
8. Denton Vacuum Inc., CC-105 cold cathode ion source system- User Manual.
9. Morton D.E. Characterization of a plasma ion source and of ion assisted deposited optical thin films. *Proc 41st Annual Technical conference of the SVC* p. 297.
10. Kinoshita K. and Nishibori M., Porosity of MgF₂ films- evaluation based on changes in refractive index due to adsorption of vapors, *Journal of Vacuum Science and Technology*, 6, 730-733 (1969).
11. Bragg W.L. and Pippard A.B., The form birefringence of macromolecules, *Acta Crystallographica*, 6, 865-867 (1953).
12. Thin Film Center Inc., The Essential Macleod.
13. Muller K.H., Model for ion-assisted thin-film densification, *J. Appl. Phys.* 59, 2803-2807 (1986)
14. Muller K.H., Modeling ion-assisted deposition of CeO₂ films, *J. Appl. Phys. A* 40, 209-213 (1986).
15. P.H. Tuan, Dissertation, Hanoi University of Technology, (2006).

Polymorphs in GeO₂ Liquid

P.K. Hung, N.T. Nhan, L.T. Vinh, and T.T.B. Phuong

Department of Computational Physics, Hanoi University of Technology, Vietnam

E-mail: thunhan-iep@mail.hut.edu.vn

Abstract. Local structure in liquid GeO₂ with density ranging from 3.56 to 5.89 g/cm³ has been investigated in MD model containing 1998 atoms. The simulation revealed that the germania liquid is composed of three species: GeO₄, GeO₅ and GeO₆ with fraction varying with density. The density as well as volume fraction of voids can be expressed as a linear function of the fraction of those species. Low-density liquid is mainly consisted of GeO₄ and has a large number of O- and Ge-voids (OV,GV) and very large void tube (LVT). This LVT contained most OVs and was spread over whole system. The low-density liquid differs from high-density liquid also in the oxygen linkage characteristics.

1. Introduction

In the last years, there has been growing interest in the liquid-liquid phase transition, which occurs without a change in chemical composition, but with a change in density, as pressure or temperature is varied [1-6]. Experimental evidence for such transition was found for a wide range of system, including Si [7], C [8], P [10], H₂O [9] and Al₂O₃-Y₂O₃ [6]. Liquids with tetrahedral network structure such as SiO₂ and GeO₂ exhibit pressure-induced polymorphism. GeO₂ has not so much applications such as SiO₂, however, from a experimental point of view it is attractive, because it presents many properties of silica, but for less extreme conditions. Liquid polymorphism of GeO₂ is suggested from *in situ* x-ray absorption study [4], where it was found that liquid germania at 1273 K consisting tetrahedral coordinated germanium with increasing pressure up to 2.5 GPa shows an abrupt fourfold-to sixfold-coordination change around 3 GPa. The evidence of liquid polymorphism was also given by computer simulations. Two MD studies [1,3] reproduced the liquid-liquid transition from tetrahedral to higher-density phase with highly coordinated germanium. Moreover, it was noted that such transition is accompanied with anomalous behavior of the diffusion constant for both Ge and O with pressure [3].

Closely associated with the possibility of liquid-liquid transition is the phenomenon of polyamorphism, which refers to the occurrence of distinct amorphous forms for a substance [11–14]. The change in short-range order and the existence of different polymorphs was well documented for GeO₂ glass [11, 17, 18]. It has been proposed that the polyamorphism of amorphous solids may be due to the trend towards liquid-liquid separation and recent simulations seem to confirm this hypothesis [15–16]. More detail about GeO₂ glass can be found in a recent review [19]. Models proposed to explain these phenomena are based on the assumption

that two energetic distinct states coexist in proportions that vary with pressure and temperature. However, very little detail was provided to the structural entities that constitute these states and the atomic-scale mechanism that underlie the structural transition between the states. Therefore, the present simulation has been conducted to shed new insight in local structure of these states, using both the topology and void analysis.

2. Calculation Method

Molecular dynamic simulations of liquid GeO_2 were performed in the NVE ensemble, using a model of 1998 atoms interacted via an Oeffner and Elliott potential. Detail of this potential can be found elsewhere [1, 20]. The long-range Coulomb interactions are calculated with the standard Ewald summation technique. We used the Verlet algorithm with a time step of 0.4 fs. The initial structure was molten at 5000 K in The NPT ensemble for more than 100000 MD steps. The structure was quenched down to 3000 K and held at this temperature and ambient pressure in NVE ensemble within 200000 MD steps to obtain a well-equilibrated liquid. From this liquid we prepared 13 systems with different densities by reducing simultaneously the lengths of the simulation box and rescaling the positions of all atoms. Each system was relaxed at constant temperature and pressure (NVT simulation) within 100000 MD steps and then at constant volume (NVE simulation) for another 100000 steps. After that the positional and angular characteristics were determined. In order to improve statistics, all the positional and angular characteristics were calculated by averaging over last 1000 configurations separated by 10 MD steps.

If every atom is considered as a sphere, then there is a part of system into which no atomic sphere lies. The radius of Ge and O atoms is 1.52 and 0.73 Å, respectively [21,22]. A void is defined as a sphere that can be inserted in contact with four atomic spheres without intersecting with any atom. Algorithm used for void calculation is described elsewhere [21,22]

3. Results and Discussion

3.1. Local Structure

An overview of our simulations is presented in Fig. 1 displaying the density-pressure plots. The structural characteristics are summarized in Table 1. In order to estimate the size effect we also presented the data for a large model consisting of 3000 atoms. The data shows that the Ge-O bond-length is little changed with applied pressure and there are only small discrepancies of structural characteristics between two models. The tetrahedral network structure can be seen through distribution of building blocks GeO_x (basic unit), where x is 4, 5 and 6. It is necessary to determine the coordination number (CN). To calculate CN we used a cutoff distance chosen as minimum after the first peak in the pair radial distribution functions (PRDF).

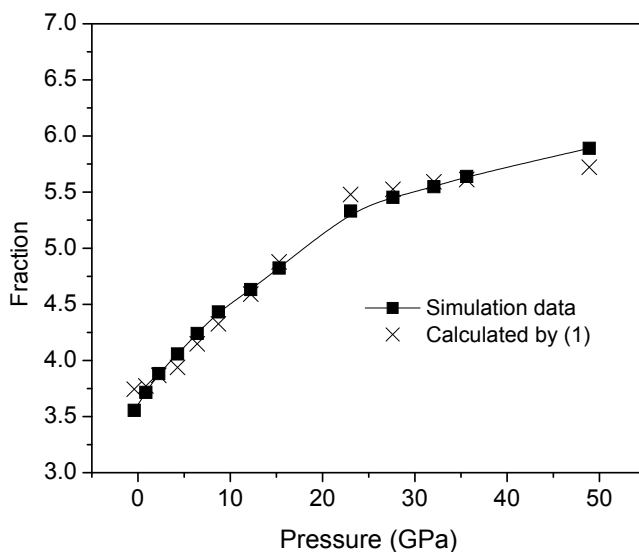


Fig. 1. The pressure dependence of density for liquid models at 300 K

Table 1. Structural characteristics of liquid germania. r_{ij} , g_{ij} -the position and height of the first peak in the PRDFs Z_{ij} - the coordination number. Here 1-1 stands for the Ge-Ge pair; 1-2 for the Ge-O pair; 2-1 for the O-Ge pair; 2-2 for the O-O pair. * - Data for models of 3000 atoms

Density, g/cm ³	$r_{ij}(\text{\AA})$			g_{ij}			Z_{ij}			
	1-1	1-2	2-2	1-1	1-2	2-2	1-1	1-2	2-1	2-2
3.56	3.36	1.74	2.84	2.29	12.23	3.00	4.33	4.05	2.02	9.5
3.56*	3.26	1.74	2.84	2.37	14.23	3.25	4.39	4.08	2.04	9.8
3.72	3.36	1.74	2.84	2.17	11.79	2.92	4.46	4.06	2.03	10.58
3.88	3.32	1.74	2.84	2.08	11.33	2.86	4.52	4.12	2.02	11.08
4.06	3.32	1.74	2.82	1.99	10.60	2.79	4.81	4.16	2.08	11.91
4.24	3.34	1.74	2.78	1.94	10.07	2.75	4.97	4.13	2.15	11.88
4.43	3.34	1.74	2.78	1.91	9.34	2.74	5.43	4.41	2.21	12.76
4.63	3.32	1.74	2.74	1.81	8.63	2.74	5.73	4.6	2.3	13.29
4.82	3.34	1.76	2.70	1.75	8.10	2.73	6.25	4.81	2.41	13.77
5.33	3.38	1.78	2.66	1.87	7.98	3.15	7.4	5.37	2.69	15.19
5.45	3.42	1.78	2.64	1.86	7.96	3.2	7.52	5.41	2.71	15.57
5.55	3.4	1.78	2.64	1.84	7.82	3.28	7.75	5.5	2.75	15.41
5.64	3.42	1.78	2.62	1.87	7.84	3.34	7.89	5.51	2.76	15.49
5.89	3.38	1.78	2.6	2.03	7.83	3.45	8.39	5.7	2.85	15.49

As shown from Table 1 the mean CN for pair Ge-O changed from 4.05 at low-density (LD) to 5.7 in high-density (HD) model indicating the transformation from tetrahedral to octahedral network structure. Figure 2 depicts the fraction of various basic units as function of density. We can see a maximum of GeO_5 fraction at pressure of 13.98 GPa. As pressure increased up to 13.98 GPa the fraction of GeO_4 decreased by three times and most of loss of GeO_4 is accompanied by an increase in GeO_5 . With further increasing pressure, GeO_6 gradually replaced GeO_5 and GeO_4 . Beyond 50 GPa the fraction of GeO_6 reached about 70% and there are also considerable amount of GeO_5 (its fraction is greater than 30%).

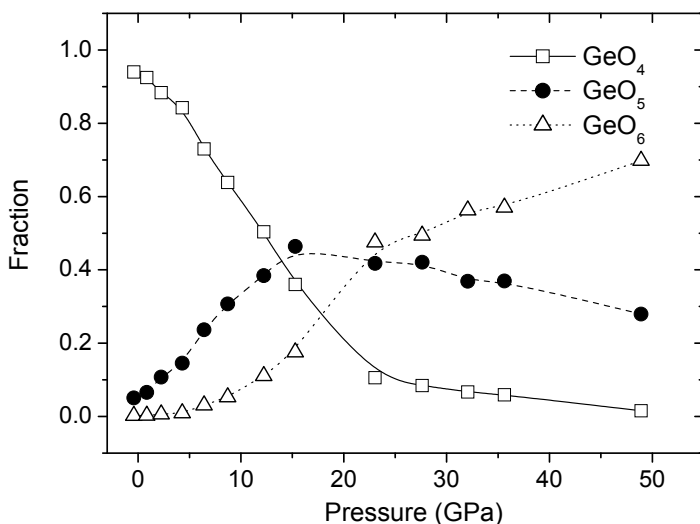


Fig. 2. The pressure dependences of GeO_4 , GeO_5 and GeO_6 fractions

The bond angle O-Ge-O characterizes the topology of basic units GeO_x and the connectivity between them can be described by angle Ge-O-Ge. The distribution of first angle for GeO_4 , GeO_5 and GeO_6 is presented in Fig. 3. For ideal tetrahedron with Ge in center and four oxygen atoms in vertices the angle O-Ge-O is 109.7° , therefore the peak located at 108° for curve GeO_4 indicated the slightly distorted tetrahedral network structure. In the case of GeO_5 and GeO_6 we observed two peaks centered at 89° and 167° respectively. It is interesting to note that the distributions of angle O-Ge-O was almost unchanged as density was varied. Combining those results with bond length Ge-O we can conclude that the characteristic feature of GeO_2 liquids is a presence of species such as GeO_4 , GeO_5 and GeO_6 . And the system prefers a mixture of those species proportion, depending on pressure. Two-state model in which the liquids are assumed to be consisted of low- and high-density species, was successfully described the polymorphism for a wide range of liquids such as SiO_2 , GeO_2 and H_2O . According to our simulation these species are GeO_4 , GeO_5 and GeO_6 ; and their relative amount vary with pressure. Furthermore, from this it follows that the structural properties of GeO_2 liquid could be presented as function of GeO_4 , GeO_5 and GeO_6 fractions. Thereby, the density of system ρ can be given as

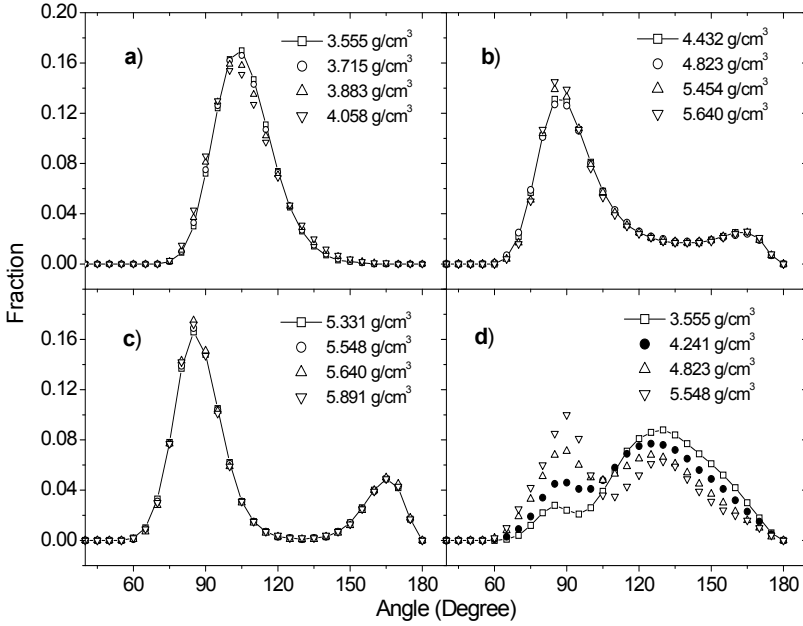


Fig. 3. The distributions for O-Ge-O bond-angles in GeO₄(a), GeO₅(b), GeO₆(c) and for Ge-O-Ge angles between two adjacent basic units(d); a typical error bar is $\pm 3.5\%$ of data.

$$\rho = aC_{GeO4} + bC_{GeO5} + cC_{GeO6} \quad (1)$$

where C_{GeO4} , C_{GeO5} , C_{GeO6} are the fraction of GeO₄, GeO₅ and GeO₆ given from Fig. 2. a, b and c are fitting parameters which are equal to 3.679, 5.413 and 5.950 g/cm³, respectively. As shown from Fig. 1, the calculated data from the simulation and by (1) are in excellent agreement.

The detailed information about linkage between two adjacent GeO_x is provided by Ge-O-Ge angle and so-called bridge oxygen distribution. As seen from Fig. 3 d, there are two peaks located at 90° and 130°, but the curves vary strongly with pressure: the height of left peak increased with pressure, whereas it decreased for the right peak. Notice that in liquid silica the angle Si-O-Si (144°) is bigger than in liquid germania. This indicated that germania has a more compacted packing of basic units, a fact that is reflected in the O-O coordination numbers, 9 for germania, compared to 6 for silica [23]

Figure 4 displays the distribution of different connectivity. Two adjacent units GeO_x ($x = 4, 5$ and 6) are linked to each other through bridge oxygen atoms. As shown in Fig. 5, most connectivity is one-oxygen and its fraction decreased with density. Meanwhile the fraction of two-oxygen connectivity increased with increasing density. Furthermore, graphs present a jump at point of 5.45 g/cm³. It means that the LD system changes from corner-sharing network to HD system in which the linkage between two adjacent units was performed by corner as well as by edges or by faces (three-oxygen connectivity). Obviously, three-oxygen connectivity is relatively unstable due to ionic charge of oxygen closed to 2.

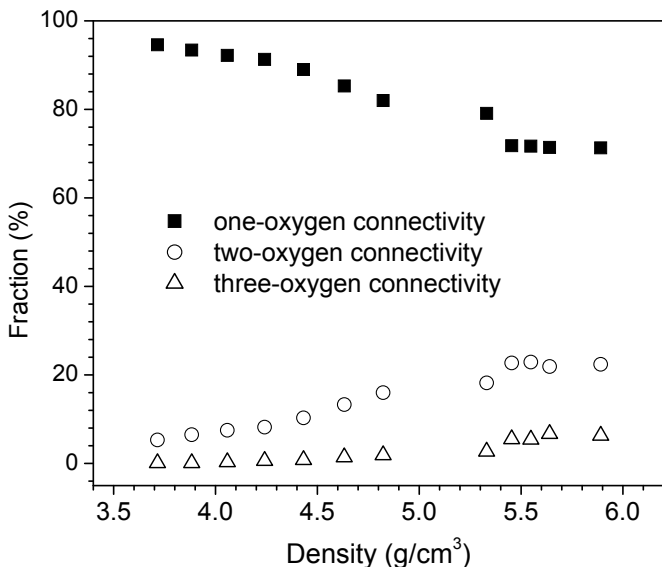


Fig. 4. The density dependence of the fraction of different connectivity

3.2. Voids and Void Aggregations

The valuable information about void distribution in disordered system can be inferred from void radii distribution (VRD), shown in Fig. 5. The major changes, observed here are the shifting of the main peak to smaller radius with density and the VRD became broader upon low density. In particular, the position of VRD peak changes from 1.05 ± 0.05 for LD to 0.75 ± 0.05 Å for HD system. Generally, the shape of VRD strongly changes with density. In the considered density range, the height of VRD increased from 0.12 to 0.20 (see Fig. 5).

Voids are not isolated in system, rather they can aggregate and form large void cluster. In the current work we examined two kinds of void aggregations: void cluster (VC) and void tube (VT). First void aggregation is a set of voids consisted of a central void and several smaller voids overlapped with central void. The second one contained a number of voids with radius bigger than radius of oxygen atom and each void in VT must overlap at least with one adjacent void by section circle with a radius also bigger than the oxygen radius. From geometric viewpoint the VT is a channel along which the oxygen can travel without intersection with any atomic sphere. Some typical VC and VT clusters detected in our models are presented in Fig. 6.

To gain more detail about VC we calculated its volume. The VC's volume was computed by generating several thousand points in a cubic cube containing VC inside. The volume of VC is calculated as: $V_{VC} = V_{cube} \cdot n_{in} / n_{total}$. Here V_{cube} is the volume of the cube; n_{total} is total number of generating points, n_{in} is number of points located within VC. The VC volume distributions are presented in Table 2.

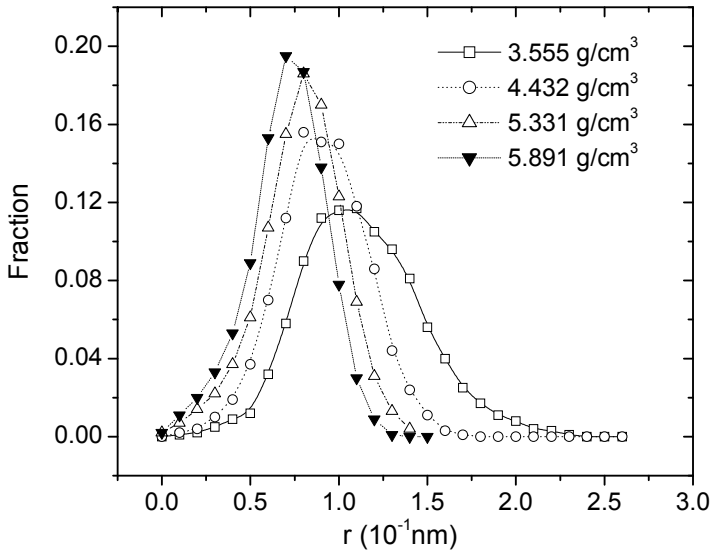


Fig. 5. The radii distribution of voids

Table 2. The volume distribution of VC. The first column indicated the volume range of mV_{Ge} to $(m+1)V_{\text{Ge}}$. Here V_{Ge} is the volume of Ge atom and $m = 0, 1, \dots, 10$. Next column showed the number of VC. For example, at 0.85 GPa there are 220 VC with volume ranging between 14.71–29.42 Å³

Volume range, Å ³	Density, g/cm ³										
	3.56	3.72	3.88	4.06	4.24	4.43	4.63	4.82	5.33	5.45	5.55
0–14.71	1485	1543	1790	2085	2243	2294	2372	2512	2570	2558	2738
14.71–29.42	196	220	228	227	196	161	118	84	84	70	34
29.42–44.13	98	101	86	46	17	18	2	3	1	1	0
44.13–58.84	43	39	16	4	3	3	0	0	0	0	0
58.84–73.55	19	14	3	1	0	1	0	0	0	0	0
73.55–88.26	9	5	3	0	0	0	0	0	0	0	0
88.26–102.97	4	4	0	0	0	0	0	0	0	0	0
102.97–117.68	6	2	0	0	0	0	0	0	0	0	0
117.68–132.39	3	1	0	0	0	0	0	0	0	0	0
132.39–147.1	3	0	0	0	0	0	0	0	0	0	0
>147.1	1	1	0	0	0	0	0	0	0	0	0

Here we can see that the number of voids with volume bigger than 29.42 Å³ (Volume of germanium is $4\pi r_{\text{Si}}^3/3 = 14.71 \text{ Å}^3$; r_{Ge} is the germanium atomic radius), decreased with density. Meanwhile, in contrast the number of VC with volume

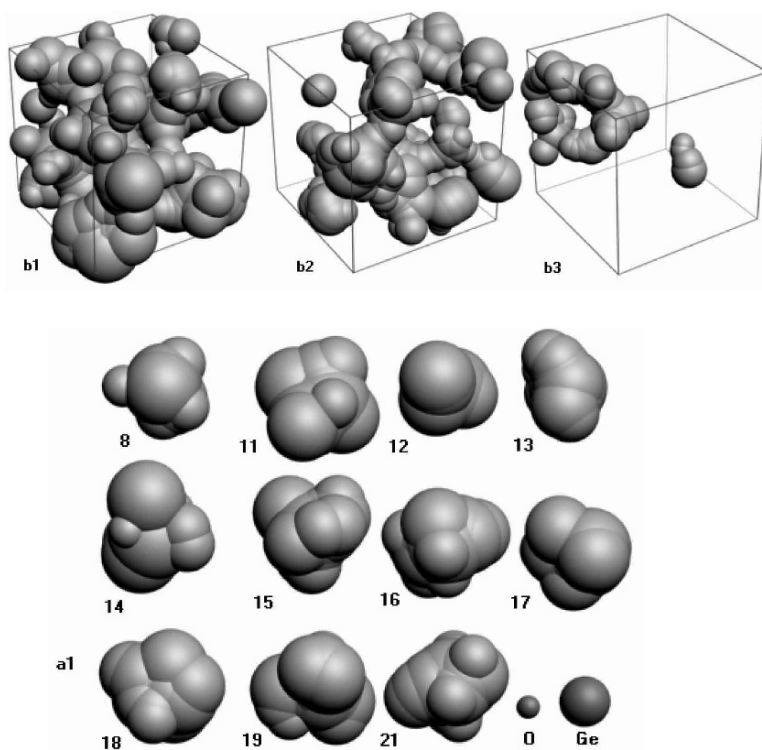


Fig. 6. The VC (a1) in simulation cell and the VT (b₁, b₂ and b₃) in cubic box with size of $10 \times 10 \times 10$ Å. Here b₁, b₂ and b₃ corresponds to the models with densities of 3.6, 4.8, and 5.49 g/cm³, respectively. The numbers under the picture indicated the number of voids in VC

smaller than Ge volume increased as density increased. At density of 3.56 g/cm³ we found 26 very big VCs with volume 5 times bigger than volume of germanium atom. Obviously, these VCs prefer the microscopic cavity.

Table 3 showed that the number of VC and VT increased by 1.5 and 3.5 times, respectively as density increased from 3.56 to 5.55 g/cm³. For each model we denoted the largest VT among ones detected in system as LVT. Upon density of 3.56 g/cm³ the LVT contains 6701 voids, which is 95% of the voids with radius bigger than the oxygen radius. Hereafter, we call this void as O-void (OV) and void with radius bigger than germanium radius as Ge-void (GV). At higher density system the number of OV in LVT rapidly decreased. Accordingly, in the system with a density of 5.55 g/cm³ the LPT has only 92 OVs (about 2% of OVs). To estimate the behavior of void and void aggregation with density we calculated the ratio between the volume occupied by different voids or void aggregations and

Table 3. The characteristics of void aggregations., N_{VC} , N_{VT} and N_{VVT} are the number of VCs, VTs and the number of voids in largest VT.

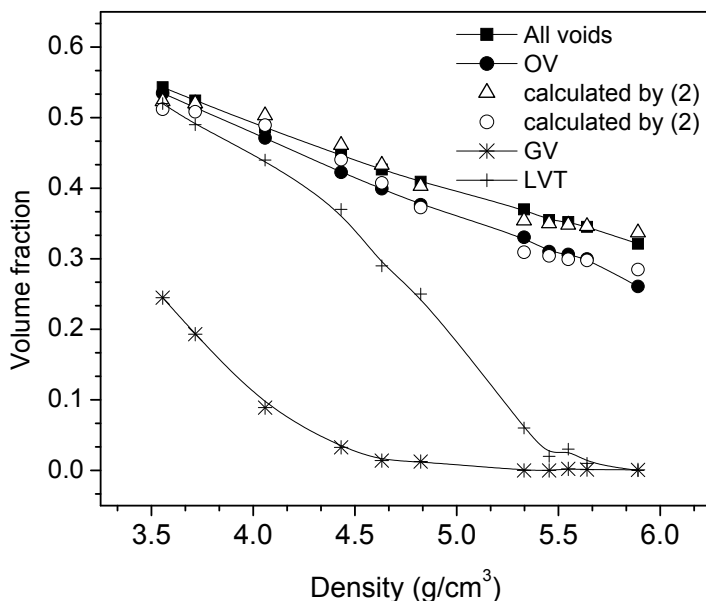
	Density, g/cm ³										
	3.56	3.72	3.88	4.06	4.24	4.43	4.63	4.82	5.33	5.45	5.55
N_{VC}	1867	1930	2126	2363	2459	2477	2492	2599	2655	2629	2772
N_{VT}	189	216	275	395	465	454	494	591	587	616	670
N_{VVT}	6701	6827	6845	6226	5060	4415	1058	346	458	212	92

the volume of simulation cell. Fig. 7 displays the volume fraction of all voids, OV, GV and LVT versus density.

We can see that for LD system the volume fraction of all voids, OV and LVT is close to each other, but upon higher-density, the volume fraction of LVT rapidly decreased to zero. The difference between volumes occupied by all voids and OVs in contrast increased. The volume fraction of all voids and OVs also can be expressed via fractions of GeO₄, GeO₅ and GeO₆ as given below

$$\nu_v = a_v C_{GeO4} + b_v C_{GeO5} + c_v C_{GeO6} \quad (2)$$

Here $a_v = 0.538$; $b_v = 0.322$; $c_v = 0.342$ for all voids and $a_v = 0.529$; $b_v = 0.286$; $c_v = 0.281$ for OVs. The data calculated by (2) is presented in Fig. 7 and we observed again a good agreement. This result supports the view that polymorph of GeO₂ liquid concerns the presence of three species of GeO₄, GeO₅ and GeO₆.

**Fig. 7.** The density dependence of volume fraction of voids and void aggregations

4. Conclusions

The simulation shows that the germania liquid is made up by mixture of three species GeO_4 , GeO_5 and GeO_6 their relative amount varying with density. This is reflected by fact that the density as well as volume fraction of voids can be expressed by a linear function of GeO_4 , GeO_5 and GeO_6 fractions. LD liquid (low pressure) is constructed mainly by GeO_4 and has a large number of OV, GV and very large LVT. This LVT contains most of the OVs and is spread over whole system. Furthermore, we also found several microscopic cavities (large VC) in the LD system. For HD liquid, the number of OV, GV as well as the volume of LVT are significantly decreased in comparison with LD liquid. Structure of LD differs from HD liquid also in the fraction of oxygen connectivity between basic units.

References

1. G. Gutierrez, J. Rogan, Phys. Rev. E 69, (2004) 031201.
2. P.F. McMillan, J. Mater. Chem., 14 (2004) 1506
3. V. Van Hoang, N.H. Tuan anh, H. Zung, Phys. B, 390(2007) 17
4. Osamu Ohtaka et al., Phys. Rev. Lett., 92 (2004) 155506
5. Ivan Saika-Voivod, Francesco Sciortino and Peter H. Poole, Phys. Rev. E, 63 (2000) 011202
6. P.F. McMillan, M. Wilson and Martin C. Wilding J. Phys.: Condens. Matter, 15 (2003) 6105
7. M.O. Thompson, G.J. Galvin, J.W. Mayer, P.S. Peercy, J.M. Poate, D.C. Jacobson, A.G. Cullis, and N.G. Chew, Phys. Rev. Lett. 52 (1984) 2360.
8. M. Togaya, Phys. Rev. Lett. 79 (1997) 2474
9. O. Mishima, Phys. Rev. Lett. 85 (2000) 334.
10. Y. Katayama, T. Mizutani, W. Utsumi, O. Shimomura, M. Yamakata, K.I. Funakoshi, Nature, 403 (2000) 170
11. K.H. Smith, E. Shero, G. Chizmeshya, H. Wolf, J. Chem. Phys., 102, 17 (1995) 6851
12. K. Trachenko, M.T. Dove, V. Brazhkin and F.S. El'kin, Phys. Rev. Lett., 93, 13 (2004) 135502.
13. M. Guthrie et al., Phys. Rev. Lett., 93, 11 (2004) 115502.
14. E. Principi, A. Di Cicco, Fr  d  ric Decremps and Alain Polian, Simone De Panfilis, Phys. Rev. B, 69 (2004) 201201
15. S. Harrington, R. Zhang, P.H. Poole, F. Sciortino, and H.E. Stanley, Phys. Rev. Lett. 78 (1997) 2409.
16. I. Saika-Voivod, F. Sciortino, and P.H. Poole, Phys. Rev. E 63 (2000) 011202.
17. J.P. Itie et al., Phys. Rev. Lett. 63 (1989) 398.
18. D.J. Durben and G.H. Wolf, Phys. Rev. B 43(1991) 2355.
19. M. Micoulaut, L. Cormier, G.S. Henderson, J. Phys. C (2006) R753.
20. R.D. Oeffner, S.R. Elliott, Phys. Rev. B 58, (1998) 14791.
21. P.K. Hung, H.V. Hue, L.T. Vinh, J. Non-cryt. Sol., 352 (2006) 3332
22. P.K. Hung, L.T. Vinh, D.M. Nghiep, P.N. Nguyen, J. Phys.: Condens. Matter., 18 (2006), 9309.
23. R. Hussin, R. Dupree, and D. Holland, J. Non-Cryst. Solids, 246, (1999) 159.

Formation of Chiral Aggregates of Tetralactam Macrocycles on the Au(111) Surface

Jordan Kossev, Thorsten Felder¹, Christoph A. Schalley^{1,2}, Fritz Vögtle¹, and Mortiz Sokolowski*

Institut für Physikalische und Theoretische Chemie der Universität Bonn, Wegelerstraße 12, 53115 Bonn, Germany

¹ Kekulé-Institut für Organische Chemie und Biochemie, Universität Bonn, GerhardDomagk-Straße 1, 53121 Bonn, Germany

² New address: Insitut für Chemie und Biochemie – Organische Chemie, Freie Universität Berlin, Takustraße 3, 14195 Berlin, Germany
E-mail: sokolowski@pc.uni-bonn.de

Abstract. Monolayers of a large tetralactam macrocycle were prepared by vacuum sublimation on the Au(111) surface and investigated by scanning tunnelling microscopy. The macrocycles form three different highly ordered monolayer structures α , β , and η . The α and β structure are stable at room temperature and can be understood as two dimensional networks which are held together by hydrogen bonds between the next neighbour molecules. These structures were described in detail before [Kossev et al., Adv. Mat. 17, 513 (2007)]. The third structure, which is described here, is only observed after heating at 400 K and rapid cooling to low temperatures. It consists of chiral aggregates, composed of three molecules. These aggregates are either left or right handed. The surface is covered by a racemic mixture of long range ordered domains with either left or right handed aggregates.

Keywords. supramolecular structures • chirality • macrocycle • scanning probe microscopy • self-organization

Prepared for the Proceedings of the 10. German Vietnamese Workshop on Physics and Engineering”, to appear in “*Springer proceedings in Physics*”

Version:

24/09/2008

1. Introduction

During the last years an increasing interest in self-organized molecular structures on microscopically well defined surfaces has evolved [1-4]. Whereas at the beginning of these investigations the adsorption of smaller organic molecules on surfaces was studied, the current trend goes in the direction of larger and larger molecules, for instance biomolecules or larger molecules which are used in the synthesis of supramolecular structures. Of particular interest are of course adsorbate/surface combinations where long range ordered, two dimensional structures form spontaneously [2]. Besides their attraction from an aesthetic viewpoint, ordered structures of large organic molecules on surfaces are of interest for building molecular architectures with well defined functionalities, e.g., for sensors, for catalytic purposes, or for surface supported molecular machines [5].

Adsorbed layers of molecules which exhibit chiral structures are of special interest. The formation of the chiral structures may have two different origins [2, 6]. Either intrinsically chiral molecules are adsorbed (including molecules which exhibit a chiral geometry only in the adsorbed state, but not in the gas phase), or the lateral arrangement on the surface of the intrinsically *non-chiral* molecules leads to chiral structures.

In this manuscript, we report on a chiral self-organised structure of large macrocycles on the Au(111) surface. These macrocycles (see Fig. 1) exhibit no intrinsic chirality and also form two other non-chiral long range ordered structures (named α and β). These have been described in detail in a previous publication [7] but for comparison we will briefly mention some of the most important aspects of the α structure at the beginning of the results section.

The macrocycle investigated here was first reported by Hunter [8] and has been used intensively in the synthesis of mechanically interlocked molecules, as catenanes and rotaxanes [9-15]. The structure of the molecule is illustrated in Fig. 1. The macrocycle contains four amide groups (see Fig. 1), which are, in particular,

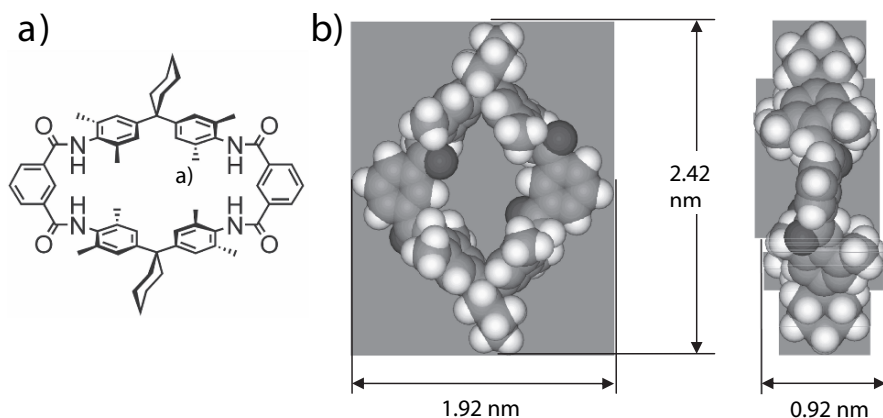


Fig. 1. Structure of the tetralactam macrocycle (TLM). (a) Chemical structure; (b) hard sphere model, view perpendicular to the molecular plane and in-plane view. The structure was obtained by DFT calculations [1]. Oxygen atoms are red, nitrogen atoms are dark blue

involved in the formation of hydrogen bonds during the threading process in the rotaxanes synthesis [16], or in the formation of the above mentioned α and β structures of the macrocycles adsorbed on surfaces. The molecule is rather flexible, since the rotational barriers for the amide groups are small [17]. Due to these rotations, the molecule itself does *not* possess a chiral structure. The projections of the two conformers with the lowest energies into the plane of the ring exhibit the symmetry D_{2h} (see Fig. 1 in ref. [17]). For these two conformers, the protons of the four amide groups are pointing inward, whilst the carbonyl groups are oriented outward. The four dimethyl phenylene groups are roughly perpendicular to the ring plane and can act as “spacers or legs” if the molecule is adsorbed on a surface. In the following, the molecule will be abbreviated as **TLM** (tetralactam macrocycle). We note that the macrocycle is non-planar and despite its rigidifying building blocks conformationally rather flexible (for details see ref. [7]).

2. Experimental

The adsorption experiments described in this paper were done exclusively under UHV. As the substrate surface we chose the close-packed Au(111) surface, since this surface is chemically rather inert and, hence, exhibits only a weak tendency to form localized bonds between Au surface atoms and specific functional groups of the **TLM** molecule. However, for the structure reported here, we will discuss below that interactions between Au surface atoms and the **TLM** molecule are important in addition to intermolecular interactions.

The structural investigations of the adsorbed layers were performed by STM (scanning tunnelling microscopy), using a beetle type STM from RHK technology at different temperatures. In order to avoid a destruction of the adsorbate structures by interaction with the STM tip, very small currents in the pA range had to be used. For the synthesis, purification and details of the deposition of the **TLM** molecules on the Au(111) surface see ref. [7]. In the experiments described here, the sample was kept at low temperature (~ 150 K) during the deposition. Subsequently, the sample was annealed at room temperature for about two hours prior to the first STM measurements, which showed large domains of the α structure. The heating of the sample was performed by radiation from a hot filament behind the sample. The STM images were recorded at room temperature or at low temperatures. We note that although **TLM** is a rather large molecule ($M = 905.05$ g/mol), vapour deposition of intact molecules onto surfaces is possible due to the high thermal stability of the substance [7].

3. Results and Discussion

3.1. The α Structure

We start with a short description of the so-called α structure. An STM picture of this structure is shown in Fig. 2. A corresponding hard sphere model of the structure is given in the lower part of the figure. This structure is stable at room temperature and is the predominating structure on the Au(111) surface at room temperature.

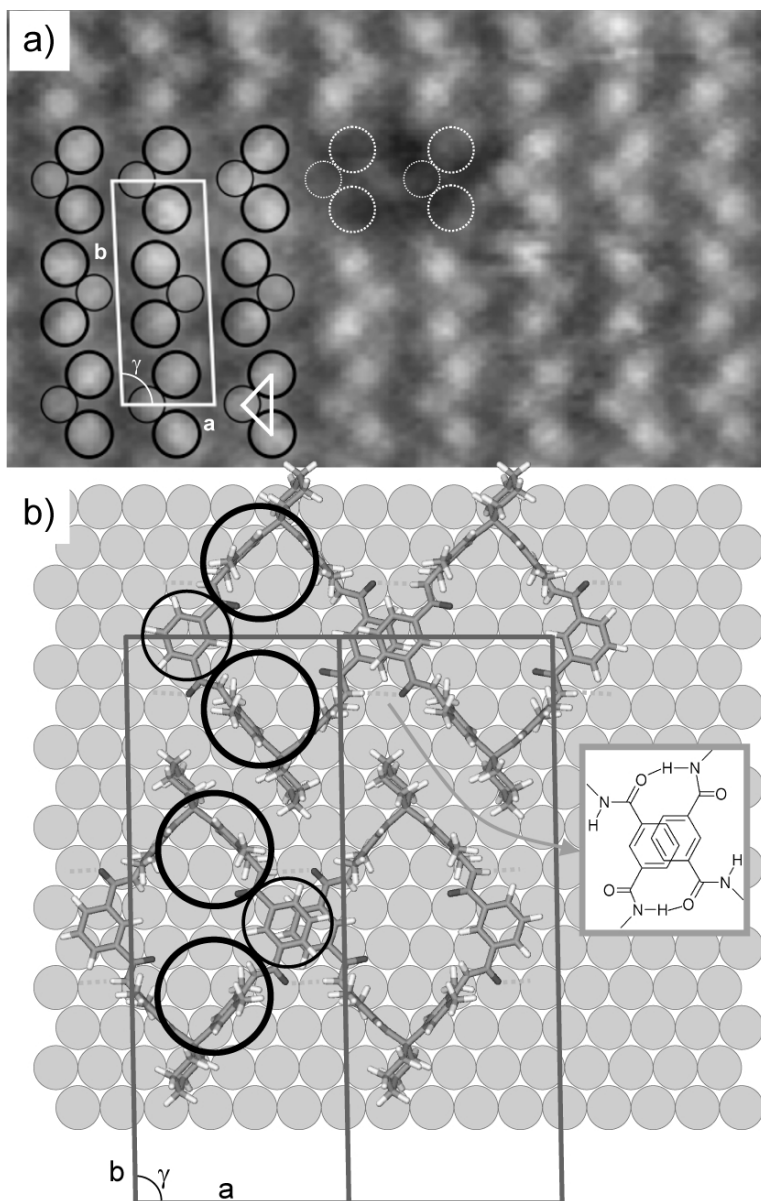


Fig. 2. (a) STM image of the α structure of TLM on Au(111) recorded at room temperature. Each molecule causes three protrusions in the image, which are arranged in the shape of a chevron. The unit cell is indicated. In the middle of the image there is a defect with two missing molecules. Scan size: $11.3 \text{ nm} \times 6.73 \text{ nm}$, ($U_{\text{sample}} = 1.36 \text{ V}$, $I = 1.5 \text{ pA}$). (b) Stick model of the α structure. The unit cell and the protrusions seen in STM images are indicated. The hydrogen bonds between the NH- and the carbonyl groups which stabilize this structure are indicated by dashed lines

From the stick model it can be seen that the structure consists of rows of molecules which are built up from partially overlapping (stacked) molecules. There are two molecules per unit cell. As a consequence of the overlap, the principal planes of the macrocycles are not parallel to the surface, but inclined by about 20° . In the STM image (see Fig. 2) each molecule contributes three protrusions which stem from the upper half of the inclined molecules. The two stronger protrusions result from methyl groups located on two benzene rings, which are about perpendicular to the plane of the macrocycle. The smaller protrusion stems from a benzene ring on the “corner of the molecule” which lies on top of the respective ring of the next molecule along the chain.

The reason for this formation of linear chains of molecules is the formation of hydrogen bonds between the next neighbour molecules, as it is illustrated in Fig. 2. Each molecule is bonded to its two neighbours along both directions of the chain via two hydrogen bonds which form between carbonyl and NH groups. For completeness we mention that in addition to this α structure, there exists a second structure similar to the α structure, which is named as β structure and which was also described in detail in ref. [7]. In this β structure, the TLM molecules are also arranged in hydrogen-bonded aggregates. However, the average number of hydrogen bonds per molecule is reduced by one third with respect to the α structure.

3.2. The Chiral η Structure

3.2.1. Preparation and Thermodynamic Stability

A third structure, which is completely different as compared to the two structures described above, is obtained if a sample with the α structure is heated at 400 K and subsequently quenched to 80–90 K. This structure is illustrated in Fig. 3 and will be named as η structure in the following. It is also long range ordered and forms well ordered large domains on the Au(111) surface. These domains consist of chiral aggregates which show six protrusions each. An example of a right-handed and a left-handed aggregate is shown in Fig. 3(b) and (d), respectively. Within one domain, we observed only one type of chirality for these aggregates, and thus the domains have to be considered as chiral, too. We note that the η structure is only obtained by this preparation process if the surface coverage is not too high, i.e., below the coverage required for the formation of a complete monolayer of the α structure. Otherwise the β structure preferentially forms.

From the preparation route of the η structure and from STM observations, we conclude that this structure forms from the α structure, that is present at room temperature, at elevated temperatures (400 K). If the sample is cooled down to room temperature slowly, we did not observe the η structure, but only the α and β structures. However, if the sample is quenched to low temperatures, the η structure is preserved at low temperatures due to kinetic hinderance. In principle it should be possible to observe the η structure also at high temperatures (400 K). However this was not possible due to experimental reasons. We finally note that the η structure was considerably more fragile with respect to interactions with the STM tip than the α and β structure. This indicates that the lateral bonding between the molecules by hydrogen bonds which stabilizes the α and β structures is not present for the η structure.

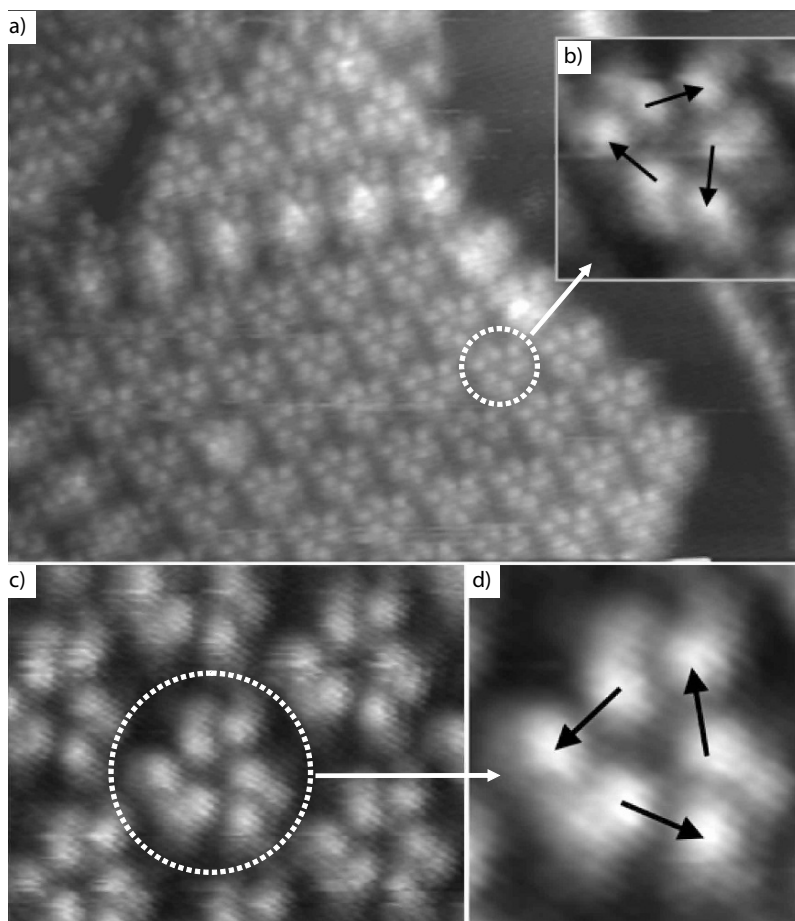


Fig. 3. STM images of the chiral η -structure, recorded at 80–90 K. **(a)** Image of a domain with right handed aggregates ($33.5 \text{ nm} \times 23.2 \text{ nm}$, $U_{\text{sample}} = 1.25 \text{ V}$, $I = 2.0 \text{ pA}$). **(b)** Enlarged detail from (a), as indicated by the dotted circle ($3.39 \text{ nm} \times 3.30 \text{ nm}$), showing one right handed aggregate. **(c)** Image of a domain with left handed aggregates ($10.1 \text{ nm} \times 6.42 \text{ nm}$, $U_{\text{sample}} = 1.25 \text{ V}$, $I = 2.4 \text{ pA}$). **(d)** Enlarged detail from (c) ($3.35 \text{ nm} \times 3.37 \text{ nm}$), showing one left handed aggregate

3.2.2. Formation of Chiral Aggregates

In Fig. 4(c) a hardsphere model of the complete unit cell of the η structure is shown. Within the error of the experiment, the angle γ of the unit cell is determined as 120° , and the unit-cell vectors have an equal length of $a = 3.0 \pm 0.1 \text{ nm}$ (see Fig. 4(c)). The structure is thus within error hexagonal, which fits to the threefold rotational symmetry of the chiral aggregates, that form the basis of the unit cell. The space group is $p3m1$. There are three molecules per unit cell, which covers an area of $7.80 \pm 1.0 \text{ nm}^2$. This yields a surface area of $2.60 \pm 0.3 \text{ nm}^2$ per **TLM**. The value corresponds well to the estimated footprint of the flat lying **TLM**

moieties. For comparison, the surface area per molecule in the α and the β structure is $2.35 \pm 0.19 \text{ nm}^2$ and $2.26 \pm 0.22 \text{ nm}^2$, respectively. This means that the η structure is the structure of the lowest molecular density on the surface, which is about 10 – 20% smaller as compared to the other two structures.

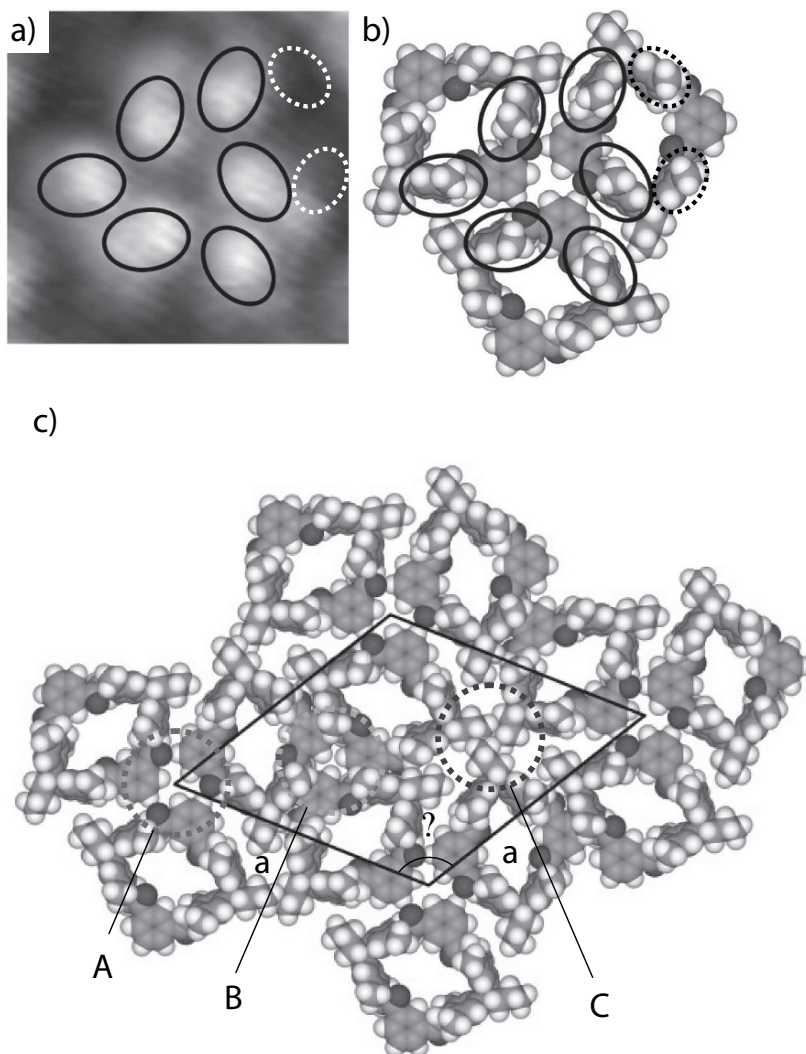


Fig. 4. (a) Explanation of the STM protrusions seen for a left-handed aggregate. The six dominant protrusions are indicated by black ellipses. (b) Corresponding hard sphere model of an aggregate consisting of three molecules. The dotted ellipses and circles in (a) and (b) indicate secondary small protrusions which are seen only, if the contrast of the STM image is strongly enhanced. These are discussed in text. (c) Hard sphere model of the unit cell of the η -structure for left handed aggregates. The unit cell is indicated by the black lines. The high symmetry sites marked by A, B and C are discussed in the text

This latter fact becomes understandable, if the hardsphere model of the chiral aggregates which form the η structure is considered. Fig. 4(b) shows such a model for a right-handed aggregate. The aggregates consist of three **TLM** molecules which form a cyclic trimer. There is a threefold rotational axis at the centre of the trimer. For this model, we made two assumptions. The first is that the molecular geometry of the **TLM** macrocycle in the η structure is similar to that which was successfully used in the model of the α structure [7]. The second assumption concerns the protrusions in the STM image. As described above, the two main protrusions in the STM image of the α structure are due to two methyl groups on two benzene rings which are roughly perpendicular to the surface. We assume that these methyl groups are also responsible for the dominant protrusions in the STM images of the η structure.

As illustrated in Fig. 4(b), we obtain a good agreement between the positions of the protrusions observed in the STM image with those predicted on the basis of the shown hard sphere model. However, we also see from the hardsphere model that the two methyl groups located on the two benzene rings which are further away from the centre of the chiral aggregate do *not* lead to such pronounced protrusions in the STM images (see the dotted ellipses in Fig. 4(b)). Small local maxima are detected at these positions only, if the contrast in the STM image is artificially strongly enhanced. Two explanations for this observation can be considered. First, the two noted benzene rings may be slightly tilted out of the vertical orientation into the plane of the surface, which brings the methyl groups closer to the surface. As an additional consequence the ring planes of the macrocycles would be slightly tilted with respect to the surface, and the molecular geometry would, hence, slightly differ from that shown in Fig. 4(b). Secondly, it is further conceivable that local groups of the **TLM** rings are partially closer to the surface due to the formation of chemical bonds between the amide groups and the Au(111) surface in the region indicated by the dotted ellipse in Fig. 4(b). This could also cause that the noted methyl groups are not seen as protrusions. This possibility of a formation of chemical bonds to the Au surface will be discussed in more detail further below.

3.2.3. Interactions Involved in the Formation of the Chiral Aggregates

The interesting question is of course, which interactions between the molecules are present and cause the formation of the described cyclic trimers. Since the resolution of the structural details in our STM images is limited we can only give some speculative ideas on the basis of the hardsphere model of the lateral arrangement of the macrocycles that is shown in Fig. 4(c). We note that the geometry of the macrocycles in this model has not been optimized, e.g., by density functional theory calculations, as it was done for the other structures in ref. [7]. Local tilts of the ring segments can be expected due to the above noted flexibility of the molecule, and the exact local configuration of the macrocycles, hence, likely differs from that illustrated in Fig. 4(c). Nevertheless we find that there are three high symmetry sites within the structure, which are labelled as A, B, and C. There exists a threefold rotational axis at all three sites. For all three sites A, B and C, we discuss the formation of hydrogen bonds between carbonyl and NH groups of adjacent molecules.

At the site A, van der Waals interactions and weak CH–O bonds between the C=O and the hydrogen on the phenyl rings appear to be possible. However stronger hydrogen bonds between the C=O and the NH groups are not possible here, since the latter are oriented away from this site. The site C is formed by three cyclohexylidene groups of three macrocycles, and can be excluded for the formation of hydrogen bonds, while reasonably strong Van-der-Waals interactions may play a role in stabilizing the assembly here. The site B possibly offers the best possibilities for hydrogen bond formation between NH groups and phenyl rings [18], and for π - π interactions between the phenyl rings of the next in the β structure neighbouring **TLM** molecules, after small geometric distortions of the ring geometry. However, hydrogen bonds between NH groups and phenyl groups are generally only weak [18].

Therefore, we suppose that the van der Waals interaction between the macrocycles, and possibly also the π - π interactions between the phenyl rings, at the site B play a more important role for the lateral ordering than hydrogen bonds. In addition, it is conceivable that the CH–O bonds between the isophthalic acid units and the phenyl rings at site A are relevant and in particular induce the chiral arrangement via the local geometry at this site (see Fig. 4(c)). Concerning the intermolecular bonding, the η structure, hence, differs considerably with respect to the α and β structures that are laterally held together by hydrogen bonds between NH and carbonyl groups.

Finally, we comment on the possibility of chemisorptive bonds between the molecule and the surface. Since the surface area per molecule in the η structure is larger than in the α or β structure, the interaction between the molecule and the underlying Au surface is presumably stronger and more relevant for the η structure than for the former two structures. Indeed, for a chemically similar, but smaller macrocycle, the formation of chemisorptive bonds between the carbonyl oxygen atoms and the Au(111) surface was recently deduced by photoemission and high-resolution electron loss spectroscopy by Whelan et al. [19]. However, the macrocycle investigated by Whelan et al. does not exhibit the methyl groups which can act as spacer groups between the ring plane of the molecule and the surface for our macrocycle [20]. Hence the bond formation between the carbonyl oxygen and the Au surface is considerably easier for the macrocycle investigated by Whelan et al., compared to the one investigated here.

Nevertheless, for our macrocycles, it may be possible that conformational changes occur which lead to a partial orientation of the dimethylphenyl groups into the plane of the ring and, hence, allow direct contact of the carbonyl oxygen atoms with the surface. In particular at the high sample temperatures (400 K) required for the formation of the η structure, conformational changes of the **TLM** molecules can be thermally activated. As a consequence, chemisorptive O–Au bonds of two carbonyl groups in one half of the **TLM** molecule may form and bring one half of the macrocycle closer to the surface, while the other half is still further away due to the vertically oriented methyl groups. As a result, the ring plane of **TLM** molecules is in a tilted geometry with respect to the surface. This tilted geometry and the noted orientation of the dimethylphenyl groups (into the ring plane) in the half of the molecule that is oriented away from the position A (see Fig. 4(c)) do nicely explain the above described STM images of the chiral aggregates.

From a detailed analysis of our STM images we further find, that the two highest protrusions of each **TLM** molecule appear to be not fully symmetric to each other. This means, that the corresponding parts of the **TLM** molecule differ slightly in their geometry and electronic structure. Thus we conclude that the individual macrocycles are chiral in the adsorbed state [2]. The formation of chiral aggregates in the η structure may, hence, be understood as a self-organized process that optimizes the packing of the tilted molecules on the surface in order to optimize the lateral interactions between the molecules and the interaction with the Au(111) surface, via the formation of two Au-O bonds per molecule after conformational changes. Evidently, this self organization requires some space and can only take place if the surface coverage is not too high as it was observed.

As noted above, the η structure forms at high temperatures. The α structure is obtained again, if the sample is held at room temperature. Hence, the α structure exhibits the smaller free energy at room temperature, which indicates that the lateral intermolecular hydrogen bonds which stabilize the α structure overcompensate the O-Au bonds that are formed in the η structure. On the other hand, one has to conclude that entropic contributions stabilize the η structure at high temperatures. These may be contained in larger thermal vibrations of the macrocycle segments, which are less possible in the α structure due to the stronger intermolecular bonds in this structure.

4. Conclusions and Summary

We have found the monolayers of large achiral macrocycles, which are used for the synthesis of mechanically interlocked molecules, to self-organize on the Au(111) surface in long range ordered structures. In one of these structures, chiral aggregates of three molecules form which are ordered in long range ordered domains. These domains are present on the surface in a racemic mixture. Since the free molecules are not chiral, this system constitutes an example for surface-induced chirality. The formation of the chiral aggregates seems to be a complicated self-organized process which involves conformational changes of the macrocycles, intermolecular interactions, and bonding to the substrate.

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) through the research centre 624: "Chemical Templates". C.A.S. thanks the Fonds der Chemischen Industrie for a Dozentenstipendium.

References

1. E. Umbach, M. Sokolowski, and R. Fink, *Applied Physics A: Materials Science & Processing* **63**, 565 (1996).
2. S. M. Barlow and R. Raval, *Surf. Sci. Rep.* **50**, 201 (2003).
3. B. A. Hermann, L. J. Scherer, C. E. Housecroft, and E. C. Constable, *Advanced Functional Materials* **16**, 221 (2006).

4. J. V. Barth, J. Weckesser, C. Cai, P. Günter, L. Bürgi, O. Jeandupeux, and K. Kern, *Angewandte Chemie International Edition* **39**, 1230 (2000).
5. V. Balzani, A. Credi, and M. Venturi, *Molecular Devices and Machines* (Wiley-VCH, Weinheim, 2003).
6. K. H. Ernst, in *Topics in Current Chemistry* (Springer Verlag, Berlin, 2006), Vol. 265, p. 209.
7. I. Kossev, W. Reckien, B. Kirchner, T. Felder, M. Nieger, C. A. Schalley, F. Vögtle, and M. Sokolowski, *Advanced Functional Materials* **17**, 513 (2007).
8. C. A. Hunter, *Journal of the American Chemical Society* **114**, 5303 (1992).
9. F. Vögtle, S. Meier, and R. Hoss, *Angewandte Chemie International Edition in English* **31**, 1619 (1992).
10. S. Ottens-Hildebrandt, S. Meier, W. Schmidt, and F. Vögtle, *Angewandte Chemie International Edition in English* **33**, 1767 (1994).
11. R. Hoss and F. Vögtle, *Angewandte Chemie International Edition in English* **33**, 375 (1994).
12. O. Lukin and F. Vögtle, *Angewandte Chemie International Edition* **44**, 1456 (2005).
13. P. Ghosh, O. Mermagen, and C. A. Schalley, *Chemical Communications*, 2628 (2002).
14. T. Felder and C. A. Schalley, *Angewandte Chemie International Edition* **42**, 2258 (2003).
15. P. Ghosh, G. Federwisch, M. Kogej, C. A. Schalley, D. Haase, W. Saak, A. Lützen, and R. M. Gschwind, *Organic & Biomolecular Chemistry* **3**, 2691 (2005).
16. C. A. Schalley, T. Weilandt, J. Brüggemann, and F. Vögtle, *Topics in Current Chemistry* **248**, 141 (2004).
17. C. A. Schalley, W. Reckien, S. Peyerimhoff, B. Baytekin, and F. Vögtle, *Chemistry – A European Journal* **10**, 4777 (2004).
18. T. Steiner, *Angewandte Chemie* **114**, 50 (2002).
19. C. M. Whelan, F. Cecchet, R. Baxter, F. Zerbetto, G. J. Clarkson, D. A. Leigh, and P. Rudolf, *J. Phys. Chem. B* **106**, 8739 (2002).
20. I. Kossev, S. Fahrenholz, A. Görling, W. Hieringer, C. A. Schalley, and M. Sokolowski, *Synthetic Metals* **147**, 159 (2004).

Surface Resonant Raman Spectroscopy at Indium-Nanowire-Terminated Si(111)

N. Esser¹, K. Fleischer², S. Chandola^{1,2}, and J. McGilp²

¹ ISAS-Institute for Analytical Sciences, Department Berlin, Albert-Einstein-Str. 9, 12489 Berlin, Germany

² School of Physics, Trinity College Dublin, Dublin 2, Ireland

Abstract. In this article we analyse the surface vibrational modes of In terminated Si(111) surfaces by Raman spectroscopy. Surface Resonant Raman Spectroscopy allows us to identify a number of surface phonons with high spectral precision. The phase transition of the (4×1) to (8×2) surface structure is found to be accompanied by characteristic changes of the surface phonons. The surface phonon modes are discussed with respect to various structural models suggested.

1. Introduction

The vibrational properties of a material are closely related to its atomic structure. To date, a significant body of information concerning the structure of quite different condensed matter systems such as molecules, solids or surfaces have been collected by vibrational spectroscopy. One of the most traditional spectroscopy methods in this regard is Raman Spectroscopy (RS) [1]. First described by C.V. Raman in 1928, it is nowadays a powerful technique used in a diversity of different disciplines for analysing gases, fluids and solids. On the other hand it has, until recently, rarely been employed as a surface analysis tool. High Resolution Electron Energy Loss Spectroscopy (HREELS) [2,3] and Helium Atom Scattering (HAS) [4–6], in contrast, are preferably used for surface vibrational spectroscopy.

However, Raman Spectroscopy has in recent years been successfully applied to probe surface phonons as well [7–11]. Much of the Raman work on surface vibrational modes has been obtained by the study of Sb monolayer terminated (110) surfaces of III-V semiconductors. Surface vibrations of Sb terminated III-V(110) surfaces were compared to ab-initio phonon calculations performed by different theoretical approaches to test the validity of the model approximations [11]. Accordingly, Surface Resonant Raman Spectroscopy can be used to study the surface structure formation on semiconductor surfaces [12]. In particular the accurate Raman frequencies as well as the Raman selection rules are linked to the surface structure and thus are valuable to validate different competing structural models.

In this paper we discuss Raman modes recorded on the In-nanowires on Si(111) (4×1) and (8×2) , the two reconstructions known to occur at RT and LT. The surface phonon modes are discussed with respect to available other experimental and theoretical results, in particular with regard to the controversial discussion of the atomic structure of the (8×2) reconstruction.

2. Experimental Methods

The Raman measurements were performed using a setup in near back scattering geometry attached to a UHV vessel. A schematic of the setup is shown in Fig. 1. The measurements were performed at a base pressure of 8×10^{-11} mbar. The UHV vessel was equipped with a liquid helium cooling stage with integrated direct current heating, a Knudsen cell for In evaporation, LEED, AES, STM and optical windows. Vicinal Si(111) with an offcut of 1° towards $[-1-12]$ were used. The formation of the single domain (4×1) surface and the transition into the $(4 \times 1)-(8 \times 2)$ surface phase transition was monitored in situ with Reflectance Anisotropy Spectroscopy [13].

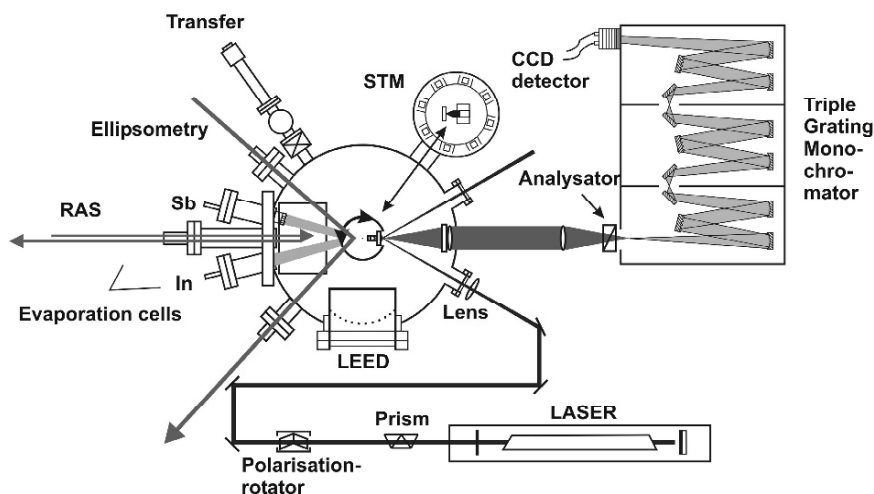


Fig. 1. Experimental Raman-UHV setup. A triple grating monochromator and Ar/Kr- ion lasers are used. The sample is placed inside an UHV vessel which is equipped with heating and cooling facilities, LEED, STM, evaporation sources and additional windows for Ellipsometry and Reflectance Anisotropy Spectroscopy

The incident laser beam was directed onto the sample at an incident angle of 50° with respect to the surface normal. At the semiconductor surface the incident light is diffracted such that the propagation direction inside the crystal is only few degrees off the normal. This ensures the “near-backscattering”-geometry. The scattered light was focussed onto the entrance slit of a triple monochromator and detected by a liquid nitrogen cooled CCD array. The frequency scales of the Raman spectra were calibrated by using Ar- and Kr- plasma lines.

Raman spectra were taken with a Kr ion laser operated at 647 nm (1.91 eV). The spectral resolution was about 1.5 cm^{-1} . In order to correct the Raman spectra for apparatus artefacts and to ensure comparability of spectra on clean and monolayer terminated samples, the Raman intensities were normalized to the symmetry allowed bulk TO phonon of Si.

Reflectance Anisotropy Spectroscopy (RAS) measures the difference in reflectance, at near normal incidence, of light linearly polarised in two orthogonal directions at the surface plane of a cubic material. With a three-domain surface of equal statistical weight, no anisotropy would be observed because of domain averaging. Consequently, the amplitude of the RAS signal is maximum if the surface is single domain [13]. Deposition at 400°C was controlled by maximising the main In-related RAS feature at 2eV. After cooling to RT, LEED patterns showed a single domain (4×1) reconstruction.

3. Results and Discussion

3.1. Raman Selection Rules

As a result of symmetry considerations the Raman selection rules describe for which polarisation of incoming and scattered light a certain phonon mode is Raman active (termed as “allowed”) or not (termed as “forbidden”). The selection rules are given as Raman tensors which are tabulated for all irreducible presentations of the crystallographic point groups [1].

Silicon crystals (diamond structure) belong to the point group Oh. For Raman backscattering on the (111) surfaces the principal axes of light polarization are the $[1 \bar{1} 0]$ and the $[1 1 \bar{2}]$ crystal directions. Deformation potential scattering of the bulk TO mode is then symmetry allowed in any polarization configuration, i.e., for polarizations of incident and scattered light (E_i, E_s) along ($[1 \bar{1} 0], [1 1 \bar{2}]$), along ($[1 \bar{1} 0], [1 \bar{1} 0]$), and along ($[1 1 \bar{2}], [1 1 \bar{2}]$), respectively [1].

Different selection rules apply for the surface phonons modes, since the termination of the 3D-crystal imposes a symmetry reduction. A single domain indium nanowire terminated Si(111) refers to the point group Cs. The corresponding normal modes group into A' and A'' surface modes which are symmetry allowed under parallel or perpendicular polarization configuration, respectively [10]. The Raman tensors in the coordinate system $x = [1 \bar{1} 0]$, $y = [1 1 \bar{2}]$ are given by [10]:

$$R(A') = \begin{pmatrix} a & 0 \\ 0 & b \end{pmatrix}$$

$$R(A'') = \begin{pmatrix} 0 & c \\ c & 0 \end{pmatrix}$$

A' -modes appearing under the ($[1 \bar{1} 0], [1 \bar{1} 0]$) and ($[1 1 \bar{2}], [1 1 \bar{2}]$) configurations refer to tensor components a and b , respectively. A'' -modes appearing under the ($[1 1 \bar{2}], [1 \bar{1} 0]$) or ($[1 \bar{1} 0], [1 1 \bar{2}]$) polarization configurations both refer to tensor component c . Consequently the surface Raman spectra differ for the three inequivalent polarization configurations [12]. The difference in the two possible A' scattering configurations (components a , b)

results from the fact that the surface unit cell is anisotropic, with the In chains extending along the $[1\ -1\ 0]$ direction. Raman spectra shown in the following correspond to tensor component “a”. The surface structure is shown in Fig. 2 for the (4×1) and (4×2) reconstructions, according to a model calculation [14]. Please note that the (8×2) structure follows from the (4×2) structure if the pairwise displacement of In atoms, as indicated by arrows in Fig. 2(b), is shifted by half a lattice constant along $[1\ -1\ 0]$ in adjacent In zig-zag chains.

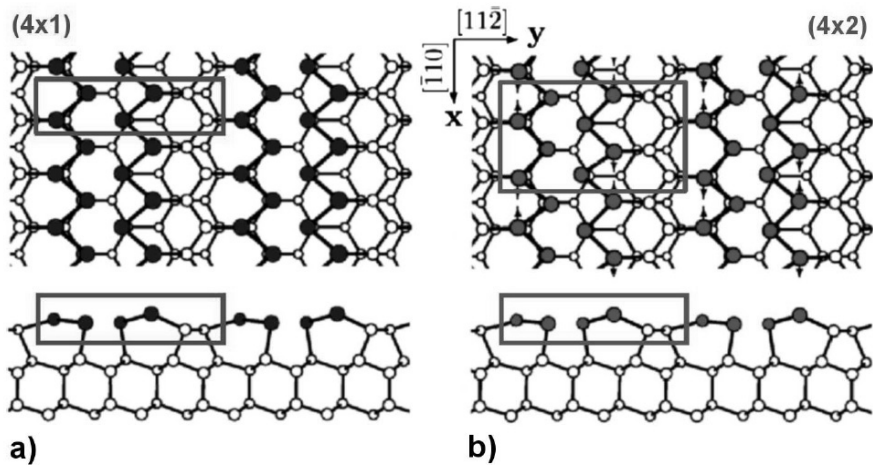


Fig. 2. Schematics of the (4×1) (a) and (4×2) (b) surface structures according to the model of Wang et al. [14]. The unit cells are marked by the red and blue boxes

3.2. Surface Resonance Effects

Due to the large penetration depth of light, the experimentally recorded Raman spectra are a superposition of bulk and surface phonon excitations. However, the Raman scattering cross section depends significantly on the resonance of incident and scattered light with electronic states [1]. As demonstrated by Santos et al. [15] surface phonons couple predominantly to surface electronic states: Since the atomic displacements related to surface phonons are confined to few topmost atomic layers, the deformation potential scattering is mediated by surface electronic states. Accordingly, bulk modes scatter predominantly via the bulk electronic states. For the Raman experiments on Si the bulk resonance is fulfilled at the E1-bulk critical point of 3.4 eV [16]. The In-nanowire terminated Si surface gives rise to distinct electronic band structures. Optical transitions of the surface are revealed by RAS spectra, as shown in Fig. 3. Strong surface related optical transitions appear in the spectral range between 1.8 and 2.1 eV, well separated from the E1 band gap of Si. Consequently, the surface phonons are favourably recorded under surface resonant conditions, using exciting laser lines close to the surface electronic transitions.

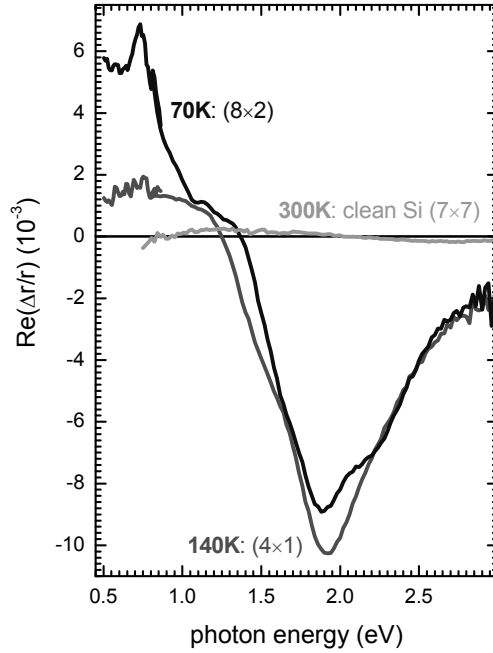


Fig. 3. Reflectance Anisotropy spectra obtained on the clean Si(111) substrate as well as on the In nanowire terminated surface at RT and 140K, respectively. The surface optical response shows strong, distinct features for the (4×1) and (8×2) surface phases. Raman spectroscopy is performed with a Kr laser line at 1.91eV, in resonance to the surface optical absorption.

3.3. Surface Phonon Modes of In-nanowire Terminated Si(111)

Surface phonon modes were already measured for the (4×1) and (8×2) phases with HREELS at 300 and 90K respectively. A mode at 60 meV (484 cm^{-1}) was observed for the (4×1) phase, and two modes at 61 meV (492 cm^{-1}) and 33 meV (266 cm^{-1}) were observed for the (8×2) (see Tab. 1) [17]. Surface Raman spectroscopy reproduces these modes and reveals many additional modes. Raman spectra of (8×2) and (4×1) samples are shown in Fig. 4. Strong modes at 435 cm^{-1} and 59 cm^{-1} as well as weaker modes at 33, 65, 150, 474, and 493 cm^{-1} are observed for the (4×1) surface. The bulk Si TO mode at 520 cm^{-1} is not shown Fig. 4 since it is approximately 500 times larger than the full scale. The surface phonon modes are grouped in two distinct frequency regions: In the low frequency range, up to 100 cm^{-1} , the surface vibrational modes involve mainly displacements of the In atoms of the outer atomic layer. The higher frequency modes above 250 cm^{-1} involve, to the contrary, dominant displacements of the Si atoms in between the In-zig-zag chains. Both kinds of surface modes are separated in frequency since the atomic mass of In (115 amu) is much larger than that of Si (28 amu).

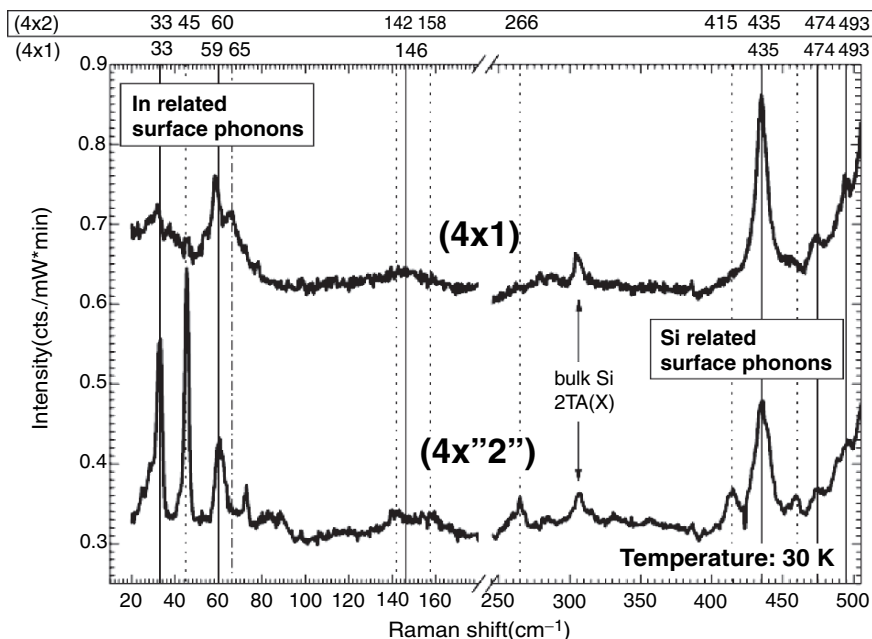


Fig. 4. Comparison of Raman spectra of the (4×1) and (8×2) phases at 30K. The (4×1) phase was conserved at 30K by a very small surface contamination. At room temperature Raman spectra of such samples showed no significant differences from those of clean samples. The lines mark the structures related to the (4×1) phase, additional modes for the (8×2) phase are marked with dotted lines. All measurements were taken at 647 nm and incoming and scattered polarisation along $[0\ 1\ \bar{1}]$ direction

On formation of the LT phase, significant differences in the spectra were observed, especially in the low frequency region. Very sharp modes appear at 33 and 45cm^{-1} , while the mode at 65cm^{-1} cannot be distinguished anymore. At higher energies new modes are observed at 266 , 415 and 459cm^{-1} . Thus the formation of the LT phase is accompanied by the retention of the RT phase modes at similar intensities and frequencies (which is a remarkable observation in itself) and the appearance of new modes in the immediate vicinity of the RT phase modes. The atomic configurations of (4×1) and (8×2) reconstructions must therefore be very similar. The larger number of (8×2) surface modes as compared to the (4×1) structure is no surprise since by the enlargement of the surface unit mesh from (4×1) to (8×2) the number of atoms per unit cell rises by the factor of four: In the outermost atomic layer, the (4×1) cell contains 4 In and 2 Si atoms, the (4×2) contains 8 In and 4 Si and the (8×2) 16 In and 8 Si atoms. We expect more surface modes to exist than those identified in the present set of spectra. This will depend on the photon related Raman cross section, as well as spectrometer

Table 1. Overview of A' surface phonon modes, in cm^{-1} , measured for both phases at 30 K. The line width of a mode is given in brackets. The energy difference for the (4×1) -mode at 484 cm^{-1} visible with HREELS is due to a temperature related shift, since the (4×1) HREELS data were taken at 300 K

(4×1)		$(4 \times "2")$	
RS (30 K)	HREELS ¹⁷	RS (30 K)	HREELS ¹⁷
33 (20)	-	33 (3)	-
-	-	45 (2)	-
59 (3)	-	60 (6)	-
65 (18)	-	-	-
146 (50)	-	142 (12)	-
-	-	158 (15)	-
-	-	266 (8)	266
-	-	415 (8)	-
435 (10)	-	435 (13)	-
-	-	459 (11)	-
474 (11)	-	474 (14)	-
493 (12)	484	493 (15)	492

sensitivity and spectral resolution. In particular broad modes may be composed by the superposition of adjacent eigenmodes.

In a recent ab-initio DFT-GGA-calculation by Bechstedt et al. [18] the surface phonon modes of the In-Si(111) (4×1) structure was calculated. Surface modes of A' and A'' symmetry were identified and eigenfrequencies as well as displacement patterns determined. Based on the displacement patterns the modes were characterized as surface phonons and surface resonances involving mainly In-In-, In-Si or Si-Si-vibrations (see Table 2). The calculation shows that in fact the low frequency modes are associated with In-In- and the high frequency modes with Si-Si- displacements. However, no one-by-one correspondence between Raman modes and calculated modes can be established since the eigenfrequencies of most of the modes differ significantly.

Table 2. Symmetry, character and eigenfrequency of calculated surface modes (taken from Ref.[18])

Character	A'	A''
In surface mode	31, 42, 54	21, 55
In/Si surface mode	104, 109	79
In/Si resonance mode	93, 129	51
Si/Si resonance mode	140, 303, 314, 394	81, 109
Si surface mode	255, 411	421

3.4. Implications to Surface Structure

The limited agreement between experiment and ab-initio calculation shows that the structure formation of the In nanowires on silicon is still not satisfactorily understood. In particular, approximations inherent to DFT slab calculations appear problematic and, moreover, the structural changes upon the phase transition into the (8×2) structure are under discussion. A change of 2% in phonon eigenfrequency in modes common to both reconstructions would suggest very little change in In-In-bond lengths on forming the (8×2) phase, in contrast to the severe structural changes suggested by in other works [19, 20]. We suggest that bonding arrangements, inherent in hexagon or trimer formation, should result in a new set of significantly different surface modes, which was clearly not observed by Raman.

While large changes in atomic positions are not supported, the formation of a charge density wave driven restructuring is more likely. A doubling of the surface unit cell induced by small changes in the atomic positions would give rise to backfolding of the surface phonon branches within the reduced Surface Brillouin Zone. As the phonon branches are expected to show dispersion, the backfolding would lead to the appearance of new phonon modes at the centre of the SBZ, with the original mode being retained at an unchanged energy. The modes at 33 and 45 cm^{-1} , 415 and 435 cm^{-1} , together with the separation of the 150 cm^{-1} mode into two, lend themselves to this interpretation. While the CDW mechanism can not directly be proven, our Raman results comply well with a restructuring without substantial modification of the bonding configuration in the surface layer.

4. Summary

In conclusion, we identified surface phonon modes for Indium-nanowire terminated Si(111) surfaces by Surface Resonant Raman spectroscopy. The eigenfrequency of the surface phonons were analysed and compared to HREELS results. The appearance of new surface phonon modes upon phase transition into the (8×2) surface phase is attributed to the change in periodicity, i.e., backfolding of surface phonon dispersion branches. The atomic structure of the (8×2) surface phase

remains still an issue to discussion. We would like to note that the accurate Raman frequencies represent a sensitive test of the accuracy of ab-initio calculation methods, which have not yet lead to a satisfactory structure model.

Acknowledgements

The authors acknowledge financial support by the Irish Higher Education Authority, IRCSET Grant No. SC/2003/223.

References

1. Light Scattering in Solids Vol. II, ed. by M. Cardona, G. Güntherodt, Springer Verlag Berlin, Heidelberg, New York (1982).
2. H. Nienhaus, Phys. Rev. B **56** (1997) 13194.
3. H. Ibach, D.L. Mills, Electron Energy Loss Spectroscopy and Surface Vibrations, Academic Press (1982).
4. G. Benedek and J.P. Toennies, Surf. Sci. **299** (1994) 587.
5. E. Hulpke, Helium Atom Scattering from Surfaces, Springer Series in Surface Sciences 27 (1992).
6. W. Kress, F.W. de Wette, Surface Phonons, Springer Series in Surface Science 21, (1991).
7. N. Esser, M. Köpp, P. Haier, W. Richter, J. Electron Spectrosc. **64/65** (1993) 85.
8. K. Hinrichs, A. Schierhorn, P. Haier, N. Esser, W. Richter and J. Sahm, Phys. Rev. Lett. **79** (1997) 1094.
9. M. Hünermann, J. Geurts and W. Richter, Phys. Rev. Lett. **66**, (1991) 640.
10. N. Esser, W. Richter, Raman Scattering from Surface Phonons, in: Light Scattering in Solids Vol. VIII, Topics in Applied Physics 76, ed. by M. Cardona, G. Güntherodt, Springer Verlag Berlin, Heidelberg, New York (2000).
11. N. Esser, K. Hinrichs, J.R. Power, W. Richter, J. Fritsch Phys. Rev. B **66** (2002) 075330.
12. K. Fleischer, S. Chandola, N. Esser, W. Richter, J. McGilp, Phys. Rev. B. **76** (2007) 205406.
13. K. Fleischer, S. Chandola, N. Esser, W. Richter, J.F. McGilp, Phys. Stat. Sol. (a) **188** (2001) 1411.
14. S. Wang, W. Lu, W.G. Schmidt, J. Bernholc, Phys. Rev. B **68** (2003) 035329.
15. P.V. Santos, N. Esser, M. Cardona, W.G. Schmidt, F. Bechstedt, Phys. Rev. B **52** (1995) 12158.
16. A. Compaan, H.J. Trodahl, Phys. Rev. B **29** (1984) 793.
17. K. Sakamoto, H. Ashima, H.W. Yeom, W. Ushida, Phys. Rev. B **62** (2000) 9923.
18. F. Bechstedt, A. Krivosheeva, J. Furthmüller, A.A. Stekolnikov, Phys. Rev. B **68** (2003) 193406.
19. C. Gonzales, F. Florez, J. Ortega, Phys. Rev. Lett. **96** (2006) 136101.
20. A.A. Stekolnikov, F. Bechstedt, W.G. Schmidt, Phys. Rev. Lett. **98** (2007) 026105.

The Properties of Nano-Hexaferrite Sr-La Prepared by Citrate-Gel Method

Dang Le Minh,¹ Le Thanh Cong,¹ Luu Tuan Tai, and Nguyen Hanh²

¹ Faculty of Physics- Hanoi University of Sciences – Vietnam National University of Hanoi

² Hanoi University of Technology

Abstract. Nano-Hexaferrite $\text{SrFe}_{12}\text{O}_{19}$ has been prepared using the Citrate-gel method. The crystalline structure, the particle size and the magnetic property were investigated by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), as well as Vibrating Sample Magnetometer (VSM). The influence of the La concentration on the particle size and properties of the samples has been examined. The presented results show that the Intrinsic Coercivity (H_c) and the Magnetization M (at $H = 13.5$ kOe) were higher than those of the samples prepared by ceramic technology.

1. Introduction

The pure Ba, Sr hexagonal ferrites or the ones including La as a dopant have been investigated and produced by ceramic technology for a long time. The energy product $(BH)_{\max}$ of about 4–5 MGOe ($B_{\text{sr}} = 4550$ G; $B_{H_c} = 3200$ Oe) [1] can be achieved. However, in order to use it for modern technique such as micro-electro mechanical systems (MEMS), micro-wave absorption, biomedical applications ..., the materials must have nano-particle size and high magnetic properties. For this reason the magnetic nano-particles including soft and hard nano-ferrites have attracted much attention of the scientists in the world.

In this paper, our results on the properties of the Sr-La nanoferrites prepared by citrate-gel method are reported. We have systematically studied the influence of the ratio of Sr/Fe, the concentration of La as a dopant substituting Sr, as well as the heat treatment temperature on the properties of the samples.

2. Experimental Methods

The samples of $(\text{SrO})_{1-x}(\text{La}_2\text{O}_3)_{x/2} \cdot 6 \text{Fe}_2\text{O}_3$ ($x = 0.00; 0.02; 0.04; 0.06; 0.08$) and $[\text{SrO} \cdot (n \cdot \text{Fe}_2\text{O}_3)]$ ($n = 5.2; 5.3; 5.5; 5.7; 6.0$) were prepared using the citrate-gel method. The raw materials (PA) are: $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{La}(\text{NO}_3)_3$ and Citric acid (CA). The raw materials with the given compositions dissolved into the mixed solution and then heated at 80°C with magnetic mixing for 8 hours. During this process, NH_4OH was added to the solution until a pH of about 7 was reached and a gel was formed. The gel was dried at $80\text{--}100^\circ\text{C}$ for 24 hours into the xerogel. The xerogel was heated at 300°C – 500°C – 700°C – 900°C and 1100°C for 2 hours. The crystal structure was examined using a X-ray diffractometer Siemens D-5000. The magnetic properties were studied with a Vibrating Sample Magnetometer (VSM).

3. Results and Discussion

All samples were sintered at the temperature range of $(3, 5, 7, 9, 11) \times 10^2$ °C and the XRD patterns (Fig. 1) have shown that the hexagonal phase $\text{SrFe}_{12}\text{O}_{19}$ has been formed at 700°C that is much lower than the respective one in [6,7].

Figure 2 shown the XRD patterns of the samples $\text{SrO}_n\text{Fe}_2\text{O}_3$ ($n = 5.2; 5.3; 5.5; 5.7; 6.0$) heated at 900°C for 2 h. The main phase in the samples was hexagonal ferrites phase ($\text{SrFe}_{12}\text{O}_{19}$).

Refined peak shape parameters were used for the calculation of the crystal size and the lattice strain by various single line methods and multi-order procedures. Methods based on full-width-half-maximum (FWHM) and integral breadths were described in detail among others by Klug & Alexander [2] and Ziegler [3].

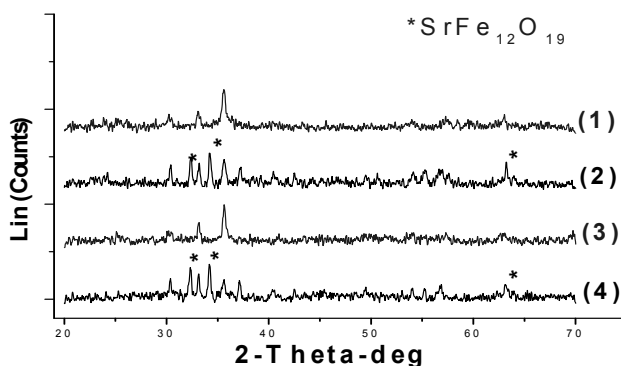


Fig. 1. The XRD patterns of the samples with $n = 5.7$ (1,2); 5.2 (3,4) sintered at 500°C and 700°C

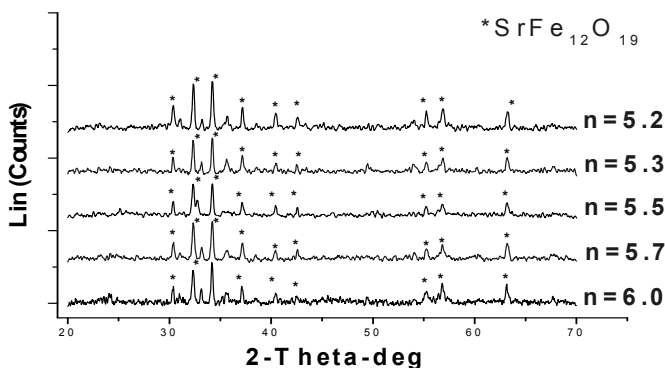


Fig. 2. The XRD patterns of the samples with $n = 5.2; 5.3; 5.5; 5.7; 6.0$ sintered at 900°C

WINFIT utilized the single line variance approach of Arkai & Toth [4]. Additionally, a procedure for separation of size and strain proposed by Dehlez et al. [5] was available. From the Pearson exponent of the PSF, the contribution of Gaussian and Lorentzian components can be calculated, which are assumed to be proportional to size broadening and strain broadening of the crystallites respectively. Finally, size and strain parameters were calculated by Fourier analysis with results as shown in Table 1 and Table 2.

Table. 1. Crystal Size according to Fourier analysis for the samples $(\text{SrO})_x (\text{La}_2\text{O}_3)_{0.5x} (6\text{Fe}_2\text{O}_3)$

Sintering temperature °C	Crystal Size (nm)
300	34
500	35
700	–
900	36
1100	46

Table. 2. Crystal Size according to Fourier analysis for the samples $\text{SrO } n.\text{Fe}_2\text{O}_3$ sintered at 900°C

n	Crystal Size (nm)
5.2	27
5.3	22
5.5	18
5.7	21

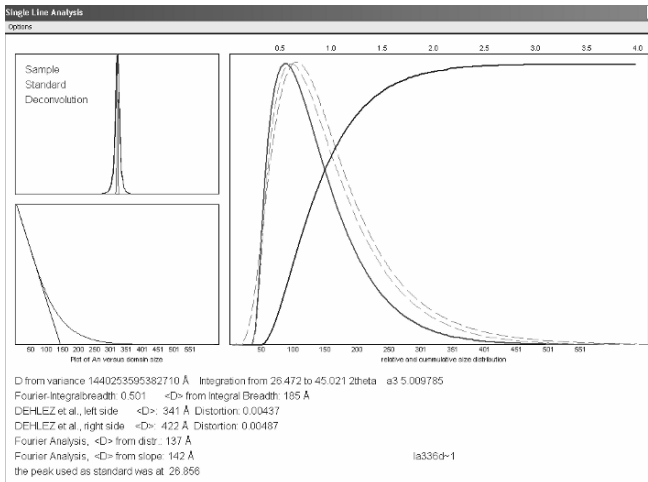


Fig. 3. A typical size distribution for the sample $(\text{SrO})_x (\text{La}_2\text{O}_3)_{0.5x} (6\text{Fe}_2\text{O}_3)$ calculated at 300°C

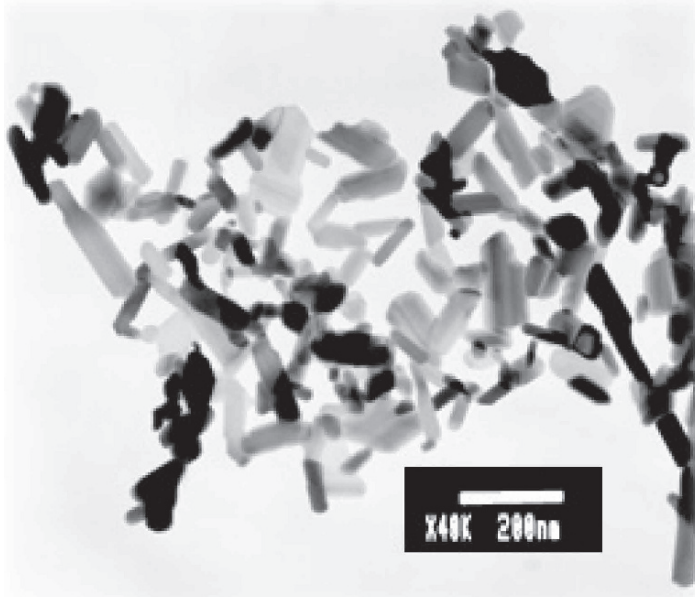


Fig. 4. The TEM photography of the sample $\text{SrO.5.2 Fe}_2\text{O}_3$ sintered at 900°C for 2 h

As in Fig. 4 shown the particles have a needle shape with the ratio (diameter/length) of about (30/200) nm. According to Stoner-Wohlfarth, generally, the coercivity H_C can be determined as following :

$$H_C = a (K_1/I_s) + b (N_{\perp} - N_{\parallel}) I_s + c \lambda_s (\tau/I_s)$$

K: Crystal anisotropy constants; N: Demagnetization factors; I_s : Saturation Magnetization; λ_s : Saturation magnetostriction; τ : inner-stress

The first term is the contribution of the crystal anisotropy, the second is the contribution of the particle shape anisotropy and the third is the contribution of the inner-stress which can be neglected.

In the case of needle particles, the second term is accountable for strong increased H_C value of the sample. For this reason this material is used as magnetic powder for producing anisotropic magnets, which will have a very high energy product $(BH)_{\max}$.

The M-H loops (by VSM) of the samples $\text{SrO.n Fe}_2\text{O}_3$ ($n = 5.2; 5.3; 5.5; 5.7; 6.00$) sintered at $900, 1100^\circ\text{C}$ shown in the Fig. 5 (a, b) and some of magnetic parameters are listed in Table 3

The highest H_C of the samples can be more than 6kOe. This value is decreased when increasing the sintering temperature due to increasing of particle size.

The influence of substituted La for Sr in the samples $(\text{SrO})_{1-x}(\text{La}_2\text{O}_3)_{0.5x} 6 \text{ Fe}_2\text{O}_3$ ($x = 0.00; 0.02; 0.04; 0.06; 0.08$) on their properties was shown in Table 4.

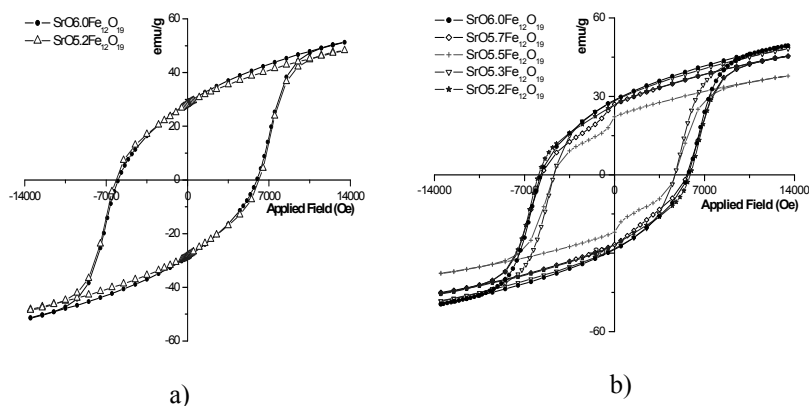


Fig. 5. The M-H loops of the samples $\text{SrO} \cdot n \text{Fe}_2\text{O}_3$ (a) $n = 5.2$; 6.00 sintered at 900°C . (b) The samples sintered at 1100°C

Table 3. The magnetic parameters of the samples $\text{SrO} \cdot n \text{Fe}_2\text{O}_3$ (by VSM at $H_{\max} 13.5\text{kOe}$)

n	$T_s 900^\circ\text{C}$		$T_s 1100^\circ\text{C}$	
	$H_C(\text{Oe})$	$M(\text{emu/g})$	$H_C(\text{Oe})$	$M(\text{emu/g})$
5.2	6121	48.35	5894	45.44
5.3	4695	49.58	4698	48.25
5.5	4704	32.89	4698	37.82
5.7	5849	46.70	5616	45.45
6.0	5958	51.39	5739	49.43

Table 4. The magnetic parameters of the samples $(\text{SrO})_{1-x}(\text{La}_2\text{O}_3)_{x/2} 6 \text{Fe}_2\text{O}_3$ (by VSM at $H_{\max} 13.5\text{kOe}$)

n	$T_s 900^\circ\text{C}$		$T_s 1100^\circ\text{C}$	
	$H_C(\text{Oe})$	$M(\text{emu/g})$	$H_C(\text{Oe})$	$M(\text{emu/g})$
0.00	5958	51.39	5739	49.43
0.02	5441	54.41	4393	54.40
0.04	5579	34.50	5865	28.84
0.06	5894	57.70	5920	57.94
0.08	5781	54.11	5888	57.52

The substitution of La for Sr leads to the unconsiderably change of H_C but to increasing of magnetization M . This may be caused by substituting of La^{+3} for Sr^{+2} and thus Fe^{+3} are transferred to Fe^{+2} in $4f_2$ site, as a result, the magnetic moment of the sample is increased.

4. Conclusion

The samples of Hexaferrites $SrFe_{12}O_{19}$ have been prepared using the citrat-gel method. The influence of the ratio of Fe/Sr and of the substitution of La for Sr are investigated. It is shown that the hexagonal ferrite crystal size is about $(20 \div 40)$ nm and have the needle shape with the ratio (diameter/length) of $(30/200)$ nm. The temperature at which the hexagonal ferrite phase is formed is about $700^\circ C$. The sample $SrO.5.2Fe_2O_3$ sintered at $900^\circ C$ for two hours has a rather high coercivity H_C around 6 kOe. The substitution of La for Sr leads to the increasing of the magnetization (M) of the samples.

References

1. N.K. Dung, D.L. Minh, B.T. Cong, N. Chau, N.X. Phuc The influence of La_2O_3 substitution on the structure and properties of Sr hexaferrite. Proceedings of the 7th ICF, September 3–6, 1996 Bordeu, France , C113–C114 .
2. P.H. Klug, E.L. Alexander (1974): X-ray diffraction procedures for polycrystalline and amorphous materials, p. 966.
3. G. Ziegler (1981): Charakterisierung keramischer Pulver durch ein röntgenographisches Messverfahren. – *Keramische Zeitschrift*, 33, 287-290.
4. P. Arkai, M.N. Toth (1983): Illite crystallinity: Combined effects of domain size and lattice distortion. – *Acta Geologica Hungaria*, 26, 341-358.
5. R. Dehlez, T.H. de Keijser, J.I. Langford, D. Louer, E.J. Mittemeijer, & E.J. Sonneveld (1993): Crystal imperfection broadening and peak shape in the Rietveld method. – in: Young, R.A. (ed.): The Rietveld method. – International Union of Crystallography monographs on crystallography, 5, 30-57.
6. J.F. Wang, C.B. Ponton, R. Grössinger, I.R. Harris “A study of La-sustituted strontium hexaferrite by hydrothermal synthesis” *Journal of Alloys and Compounds* 369 (2004) 170-177.
7. T.T.V. Nga, T.D. Hien, N.P. Duong and T.D. Hoang “Structural and magnetic properties of $SrLa_xFe_{12-x}O_{19}$ ($x = 0 \div 0.15$) prepared by sol-gel method.” Proceeding of the 1st IWOFM- 3rd IWONN Conference, Halong, Vietnam, December 6-9, 2006

Glucose Sensor Based on Multi-Wall Carbon Nanotubes Doped Polypyrrole

T.T.N. Lien¹, L.H. Bac¹, T.D. Lam², and P. Q. Pho¹

¹ Institute of Engineering Physics (IEP), Hanoi University of Technology,
No 1 Dai Co Viet, Hai Ba Trung, Hanoi, Vietnam
Email: lientruong-iep@mail.hut.edu.vn

² Faculty of Chemical Technology, Hanoi University of Technology,
No 1 Dai Co Viet, Hai Ba Trung, Hanoi, Vietnam

Abstract. In this paper, we describe the preparation of electrochemical glucose sensors based on the glucose oxidase (GOx), which is immobilized into multi-wall carbon nanotubes (MWCNTs) doped polypyrrole (PPY) membrane during electropolymerization of polypyrrole film. The morphology of the MWCNTs doped polypyrrole film was characterized by scanning electron microscopy (SEM). Glucose is detected by using electrochemical impedance spectroscopy (EIS). An increase in the glucose concentration results in a decrease in the faradic charge transfer resistance (R_{CT}) obtained from the EIS measurements. The results indicate that the electroanalytical PPY/MWCNTs-GOx film was highly sensitive and suitable for glucose biosensors based on GOx.

1. Introduction

Biosensors are in the forefront of current research in the area of bioanalytical chemistry. Unlike conventional chemical sensors, the incorporation of enzymes with transducers allows one to fabricate highly sensitive and selective enzyme-based biosensors. These devices rely on the interaction of a biocatalyst, usually an isolated and purified enzyme, with the analyte. Among all the enzyme-based biosensors, glucose biosensor is most widely studied because of its importance in the monitor of blood glucose for treatment and control of diabetes. For this glucose sensor a unique working mechanism was proposed based on direct electron transfer between the enzyme glucose oxidase (GOx) and the conducting polymer. Among known conducting polymers, polypyrrole is most frequently used in the commercial applications [1] due to the high conductivity, long term stability of its conductivity and the possibility of forming homopolymers or composites with optimal mechanical properties. Therefore, the polypyrrole is usually used as material which associates bioreceptor and transducer of a biosensor. On the other hand, carbon nanotubes (CNTs) have gained considerable attention in recent years because of their remarkable electrical and mechanical properties, which have made them extremely attractive for a wide range of sensing applications from structural materials [2] to nanoelectronic components [3]. The ability of CNTs-modified electrodes to promote electron-transfer reactions has been documented in connection with important biomolecules [4].

In this paper, an electrochemical method is developed to produce glucose sensor based on the enzyme glucose oxidase (GOx), which is immobilized into multi-wall carbon nanotubes doped polypyrrole (PPy) membranes. Glucose was detected based on electrochemical impedance spectroscopy measurements.

2. Experimental

2.1. Chemical and Reagents

Reagents used were of analytical grade or the highest commercially available purity and used as supplied without further purification. Pyrrole monomer (99%, Aldrich Chemical Co.) was distilled under reduced pressure. Glucose oxidase (GOx), β -D-glucose and sodium chloride was purchased from Merck. All solutions were prepared with deionized water of resistivity not less than 18 M Ω cm. The multi-wall carbon nanotubes (MWCNT, ~95% purity), prepared by Chemical vapor deposition, were obtained from Nanolab (China). The diameter of a MWCNT is in the range of 40–60 nm and their length is 1–2 micrometers.

2.2. Electrodes Preparation

The MWCNT (5g) were functionalized with carboxylic acid groups by ultrasonication in a 3:1 sulfuric-acid/nitric-acid mixture (80 ml) for 24 h at 40°C, in accordance to previously described protocols [5]. The resulting suspension was diluted with deionized water and was centrifuged. The pretreated CNT were washed for several times, filtered with 0.1M NaOH (to reach neutrality of pH 7.0), and dried at 60°C overnight. The desired amount of the functionalized carbon nanotubes (cMWCNTs) (usually 3 mg/ml) was added in deionized water and ultrasonicated for about 15 min to form a uniform black solution. Pyrrole (usually 0.5 M) was added to the cMWCNTs solution. The PPy-cMWCNTs film was electrochemically deposited on the gold microelectrode at a fixed potential and time (usually +0.7 V versus Ag/AgCl for 30 min) in the pyrrole-cMWCNTs solution. Some electropolymerization experiments involved growing the polymer by cycling the potential at 20 mV/s (from 0.0 to 0.9 V versus Ag/AgCl for 30 scans). A pure PPy film (using NaCl 0.5 M) was obtained by the same procedure described above without the addition of cMWCNTs and the action of ultrasonication.

The amount of GOx 3 mg/ml was added in pyrrole-cMWCNTs solution and ultrasonicated for about 15 min to form a uniform pyrrole-cMWCNTs-GOx solution. The pyrrole-cMWCNTs-GOx film was deposited at a fixed potential of +0.7 V versus Ag/AgCl for 30 min. The PPy/Cl, PPy/Cl/GOx, PPy/cCNTs, and PPy/cCNTs-GOx films were washed with deionized water several times and stored in the buffer solution (pH 7) at 4°C prior to use.

2.3. Electrochemical Measurements

All electrochemical experiments in this work were performed using a computer-controlled Autolab PGSTAT12 system (Eco Chemie B.V., Utrecht, The Netherlands). The electrochemical cell consisted of three electrodes. Gold or platinum microelectrodes were used as the working electrode. While platinum foil was used as the auxiliary electrode and either Ag/AgCl 3M KCl was used as the

reference electrode. The electrolyte and the monomer (pyrrole) were mixed together and then the solution was purged with nitrogen for ten minutes to remove oxygen from the solution.

All impedance measurements were performed in the frequency range 10 kHz to 10 mHz using a 10 mV alternating voltage superimposed on DC potential. Evaluation and simulation were carried out with Zview software.

3. Results and Discussion

3.1. Formation of Electrodes

Cyclic voltammetry was used during the polymerization of pyrrole on micro-electrode. Figure 1 shows the voltammetric profiles for the PPy growth in the presence of GOx using the chloride and cMWCNTs dopants. A normal polymer growth, with increasing current upon repetitive scanning is observed in the both presence of chloride and CNT. The current signals in the presence of CNT are smaller than those observed in the presence of chloride, reflecting the more facile entrapment of the small inorganic anion.

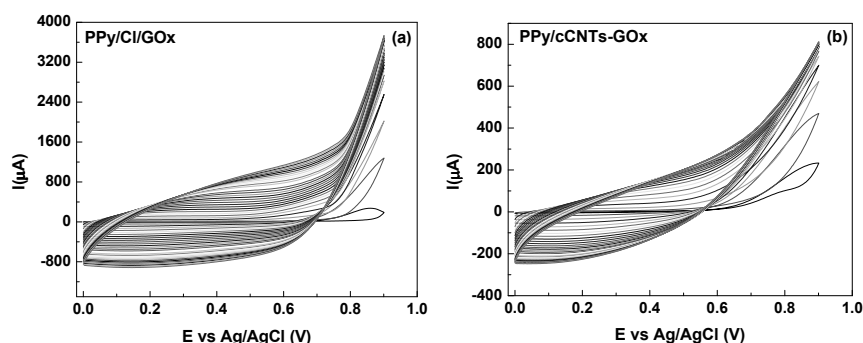


Fig. 1. Repetitive cyclic voltammograms recorded during the electropolymerization of polypyrrole in the absence of 0.5 mg/ml glucose oxidase, using different dopants: (a) 0.5 M NaCl, (b) 3 mg/ml MWCNTs. Monomer, 0.5 M pyrrole. Scan rate: 20 mV/s

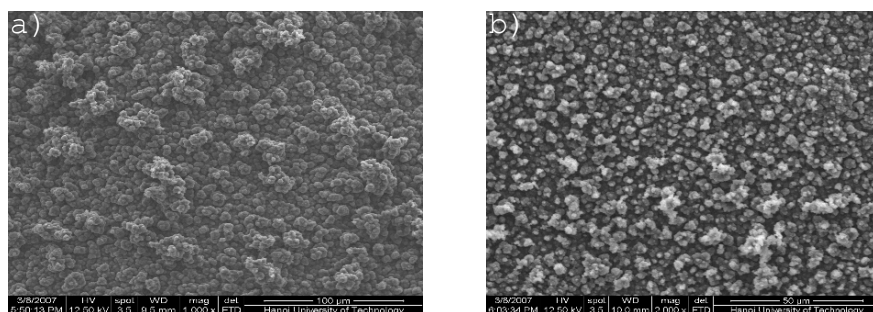


Fig. 2. Scanning electron microscopy (SEM) micrographs for PPy/Cl film in the absence (a) and presence (b) of 0.5 mg/ml glucose oxidase. The films were prepared by cycling the potential at 20 mV/s (from 0.0 to 0.9 V for 50 scans). Monomer 0.5 M pyrrole and 0.5 M NaCl

Scanning electron microscopy (SEM) was used for characterizing the morphology of the PPy/Cl, PPy/Cl/GOx and PPy/cMWCNTs-GOx films. Figure 2 shows the morphology of PPy/Cl films prior to (Fig. 2a) and after (Fig. 2b) GOx immobilized into PPy membrane. The morphological changes in the polymer structure from those observed in the absence and presence of enzyme indicated that the enzyme was incorporated into the conductive polypyrrole membrane. In the Fig. 3 one can observe that the morphology of the PPy-cMWCNTs-GOx nanocomposite film surface with bundles of cMWCNTs is covering the PPy. This result indicates that there is incorporation of cMWCNTs within the PPy films during the electropolymerization. Such morphology is in agreement with previous studies of conducting polymer/CNT composites [6-8]. The diameter of the individual PPy/CNT fibrils is significantly larger than that of the corresponding MWCNT alone (40–60 nm). From the images of cauliflower PPy and PPy nanowires, it was clear that PPy nanowires had a large number of microgaps and micropores, which provided an important morphological.

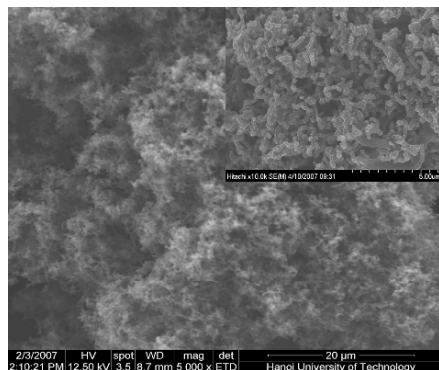


Fig. 3. Scanning electron microscopy (SEM) micrograph for the electrode surface using PPy/cCNTs-GOx film, prepared by using 3 mg/ml cMWCNT, 0.5 mg/ml GOx and 0.5 M pyrrole at +0.7 V versus Ag/AgCl for 30 min

3.2. Glucose Measurements

Electrochemical impedance spectroscopy (EIS) can be used to investigate the properties of a systems impedance and reveal the change of electrochemical systems and interfaces to provide valuable information on charge transport phenomena [9-11]. All electrochemical impedance measurements of PPy electrodes were recorded in glucose solutions with concentration change from 0 to 170 mM in the frequency range from 10 kHz and 10 mHz with an ac amplitude of 10 mV.

Figure 4 presents the Nyquist plot of a PPy/Cl/GOx electrode recorded in 40 mM glucose solution in the frequency range from 10 kHz to 10 mHz. The impedance spectrum includes a semicircle in the high frequency region corresponding to the electron transfer limited process and a linear part at the

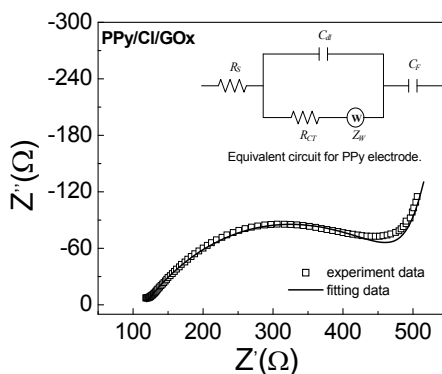


Fig. 4. Nyquist plot of electrochemical impedance spectra of PPy/Cl/GOx electrode recorded in 40 mM glucose concentration in the frequency range from 10 kHz to 10 mHz. Symbols show experimental data and line shows the fitting data using Zview software. The inset shows equivalent circuit for PPy electrode

low frequencies resulting from the diffusion limited electrochemical process [12]. The diameter of the semicircle exhibits the electron transfer resistance of the modified layer, which shows its blocking behavior of the electrode. The increase or decrease in its value exactly characterizes the modification of the electrode surface. The impedance data were fitted using the Zview software (see in Fig. 5). A modified Randles' equivalent circuit [13, 14], shown in the inset of Fig. 4, was found to fit adequately the data over the entire measurement frequency range. The fitted curves were also shown in Fig. 4 (solid line), indicating the good agreement between the circuit model and the measurement system, especially in the higher frequency range. The circuit includes the following four elements: (1) the ohmic resistance of the electrolyte solution, R_s ; (2) the Warburg impedance, Z_W ; (3) C_{dl} , associated with the double layer, which reflects the interface between the assembled film and the electrolyte solution. This element can also be replaced by the constant phase element impedance [15], Z_{CPE} ; (4) R_{CT} , the electron transfer resistance [16]. Ideally, Z_W and R_s represent the properties of the electrolyte solution and diffusion of the redox probe, thus they are not affected by modifications occurring on the electrode surface [17]. R_{CT} accounts for the partial charge transfer from strongly adsorbed specimen into the electrode and decreases with increase in their concentration and applied electrochemical potential. The charge transfer resistance R_{CT} and double layer capacitance C_{dl} can be related to the amount of β -D-glucose adsorbed onto the PPy/GOx electrode surface [18]. The inverse of charge transfer resistance, $1/R_{CT}$, is directly proportional to the surface charge density of the β -D-glucose adsorbing onto the electrodes.

The EIS measurements of PPy/Cl/GOx electrode recorded in different β -D-glucose solution concentrations are presented in Fig. 6. a. The R_{CT} were attracted using Randles' equivalent circuit and the Zview software. The variation of $1/R_{CT}$ versus glucose concentration produced a calibration curve with a short linear behavior, i.e. 0–20 mM as shown in Fig. 6 (b). The results show that the values of the R_{CT} gradually decrease upon addition of glucose to the solution. This confirmed the success of immobilization of glucose on the electrode. Figure 7 (a) shows the complex plane plots obtained on an Au/PPy/Cl/GOx electrode for different concentration of β -D-glucose from 40 to 130 mM. We also observed the decrease in R_{CT} due to increasing the glucose concentration (see Fig. 7 (b)). The value of R_{CT} is lowest at 130 mM glucose concentration ($R_{CT} = 267\Omega$).

The EIS measurements of PPy/cCNTs-GOx electrode recorded in different β -D-glucose solution concentrations from 0 mM to 10 mM are also presented in Fig. 8. The inset shows a calibration curve obtained using $1/R_{ct}$ as a function of

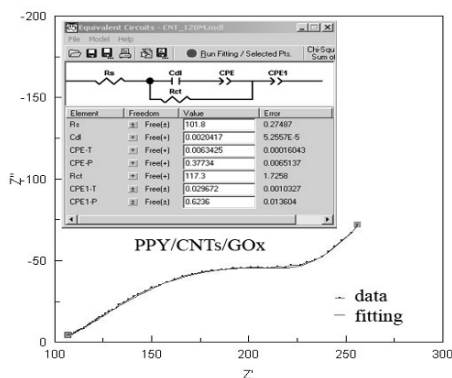


Fig. 5. Nyquist plot of electrochemical impedance spectra of PPy/cCNTs-GOx electrode recorded in 120 mM glucose concentration in the frequency range from 10 kHz to 10 mHz. Symbol shows experimental data and line shows fitting data using Zview program

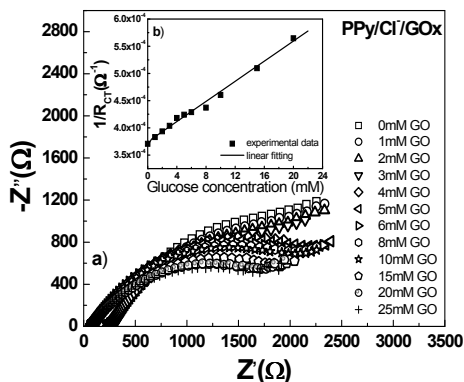


Fig. 6. (a) Complex plane plots obtained on Au/PPy/Cl⁻/GOx electrode for difference concentrations of β-D-glucose in buffer solution (pH 7.2), $E_{DC} = 0.32$ V vs. Ag/AgCl, $E_{ac} = 10$ mV and frequency from 10 kHz to 10 mHz. (b) The calibration curve obtained using $1/R_{CT}$ as a function of glucose concentration C (from 0 mM to 20 mM) at $E_{DC} = 0.32$ V vs. Ag/AgCl with the linear regression equation: $Y(\Omega) = 3.74 \times 10^{-4} + 9.26 \times 10^{-6} C$ (mM)

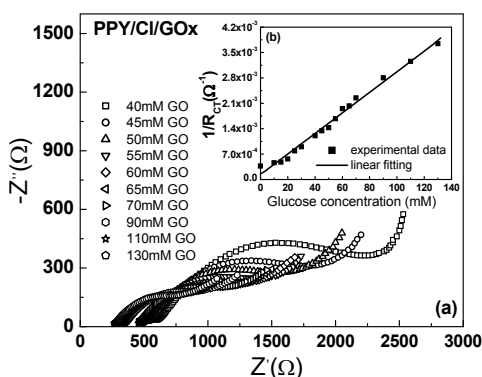


Fig. 7. (a) Complex plane plots obtained on Au/PPy/Cl⁻/GOx electrode for difference concentrations of β-D-glucose in buffer solution (7.2 pH), $E_{DC} = 0.32$ V vs. Ag/AgCl, $E_{ac} = 10$ mV and frequency from 10 kHz to 10 mHz. (b) The calibration curve obtained using $1/R_{CT}$ as a function of glucose concentration C (from 0 mM to 130 mM) at $E_{DC} = 0.32$ V vs. Ag/AgCl with the linear regression equation: $Y(\Omega) = 1.32 \times 10^{-4} + 2.84 \times 10^{-5} C$ (mM)

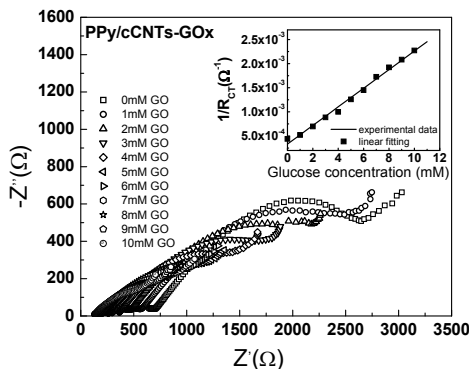


Fig. 8. Complex plane plots obtained on Au/PPy/cCNTs-GOx electrode for difference concentrations of β-D-glucose in buffer solution (7.2 pH), $E_{DC} = 0.34$ V vs. Ag/AgCl, $E_{ac} = 10$ mV and frequency from 10 kHz to 10 mHz. The inset shows calibration curve obtained using $1/R_{ct}$ as a function of glucose concentration C (from 0 mM to 10 mM) at $E_{DC} = 0.34$ V vs. Ag/AgCl with the linear regression equation: $Y(\Omega) = 3.32 \times 10^{-4} + 1.92 \times 10^{-4} C$ (mM)

glucose concentration C (from 0 mM to 10 mM) at $E_{DC} = 0.34$ V vs. Ag/AgCl by using the following linear regression equation: $Y(\Omega) = 3.32 \times 10^{-4} + 1.92 \times 10^{-4} C$ (mM). The CNTs-doped PPy exhibits dramatically different electronic properties compared to PPy/Cl. From Table 1, R_{CT} of PPy/Cl electrodes were lower than that of PPy/CNTs, which indicated that PPy nanowires have a better ionic and electronic conductivity. We also observed the decrease in R_{CT} during increase of the glucose concentration (see Fig. 9).

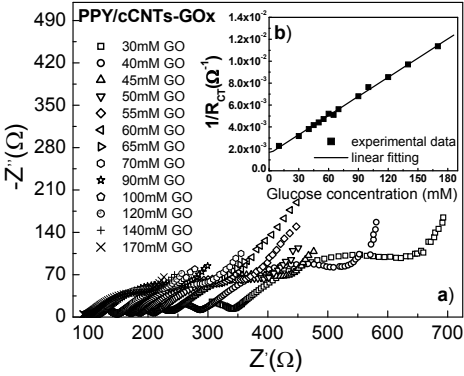


Fig. 9. (a) Complex plane plots obtained on Au/PPy/cCNTs-GOx electrode for difference concentrations of β -D-glucose in buffer solution (7.2 pH), $E_{DC} = 0.34$ V vs. Ag/AgCl, $E_{ac} = 10$ mV and frequency from 10 kHz to 10mHz. (b) The calibration curve obtained using $1/R_{ct}$ as a function of glucose concentration C (from 10 mM to 170 mM) at $E_{DC} = 0.34$ V vs. Ag/AgCl with the linear regression equation: $Y(\Omega) = 1.50 \cdot 10^{-3} + 5.83 \cdot 10^{-5} C$ (mM)

Table 1. The values of R_{CT} for PPy/Cl and PPy/CNTs electrodes

β -D-Glucose concentration n (mM)	R_{CT} (Ω)		β -D-Glucose concentration (mM)	R_{CT} (Ω)	
	PPy/Cl	PPy/CNTs		PPy/Cl	PPy/CNTs
0	2691	2273	30	1111	316
1	2605	1913	40	830	263
2	2535	1432	45	745	240
3	2471	1128	50	700	227
4	2386	1000	55	597	212
5	2352	794	60	512	192
6	2327	689	65	493	196
7		579	70	445	178
8	2283	520	90	357	147
9		480	100		131
10	2167	440	120		117
15	1958		130	267	
20	1768		140		103
25	1270		170		88

4. Conclusion

This work demonstrated the preparation of PPy/Cl (in bulk) and PPy/CNTs (in nanowires) electrodes for glucose biosensors by an electrochemical method. Based on the presented studies, it proves that the electrochemical impedance spectroscopy can be used for detection of glucose. In comparison with bulk PPy electrodes, PPy nanowires have a higher conductivity.

Acknowledgements

The authors gratefully acknowledge the receipt of a grant from the Flemish Interuniversity Council for University Development cooperation (VLIR UOS) which enabled them to carry out this work.

References

1. G. Natta, G. Mazzanti, P. Corradini, *Atti. Acad. Naz. Lincei, Cl. Sci. Fis. Mat. Rend.* (1958), 25, 8, 3,
2. R.R. Schlittler, J.W. Seo, J.K. Gimzewski, C. Durkan, M.S.M. Saifullah, M.E. Welland, *Science* 292 (2001) 1136–1139.
3. S.J. Tans, A.R.M. Verschueren, C. Dekker, *Nature* 393 (1998) 49–52.
4. C.-X. Cai, J. Chen, *Anal. Biochem.* 325 (2004) 285–292.
5. Z. Wang, J. liu, Q. liang, Y. Wang, G. Luo, *Analyst* 127 (2002) 653.
6. G. Chen, M. Shaffer, D. Colbey, G. Dixon, W. Zhou, D. Fray, A. Windle, *Adv. Mater.* 12 (2000) 522.
7. Z. Wei, M. wan, T. Lin, L. Dai, *Adv. Mater.* 15 (2003) 136.
8. Yu-Chan Tsai, Shih-Ci Li, Shang-Wei Liao, *Biosensors and Bioelectronics* (2006).
9. S.H. Lim, J. Wei, *Chem. Phys. Lett.* 400 (2005) 578–582.
10. D. Mishra, J. Farrell, *Environ. Sci. Technol.* 39 (2005) 645–650.
11. R. K. Shervedani, A.H. Mehrjardi, N. Zamiri, *Bioelectrochemistry* 69 (2006) 201–208.
12. R.J. Pei, Z.L. Cheng, E.K. Wang, X.R. Yang, *Biosens. Bioelectron.* 16 (2001) 355–361.
13. J.B.B. Randles, *Discuss. Faraday Soc.* 1 (1947) 11–19.
14. F. Patolsky, M. Zayats, B. Katz, I. Willner, *Anal. Chem.* 71 (1999) 3171–3180.
15. Y. Hou, S. Helali, A. Zhang, N. Jaffrezic-Renault, C. Martelet, J. Minic, T. Gorjankina, M.-A. Persuy, E. Pajot-Augy, R. Salesse, F. Bessueille, J. Samitier, A. Errachid, V. Akimov, L. Reggiani, C. Pennetta, E. Alfinito, *Biosens. Bioelectron.* 21 (2006) 1393–1402.
16. A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York, 2000.
17. L. Yang, Y. Li, *Biosens. Bioelectron.* 20 (2005) 1407–1416.
18. Wright, J.E.I., Cosman, N.P., Fatih, K., Omanovic, S., Roscoe, S.G., *J. Electroanal. Chem.* 564 (2004) 185–197.

Structural and Spectral Properties of Curcumin and Metal- Curcumin Complex Derived from Turmeric (*Curcuma longa*)

Vu Thi Bich¹, Nguyen Thi Thuy¹, Nguyen Thanh Binh¹, Nguyen Thi Mai Huong², Pham Nguyen Dong Yen², and Tran Thanh Luong²

¹ Center for Quantum Electronics, Institute of Physics and Electronics, VAST
10, Daotian Road, Badinh District, Hanoi, Vietnam
E-mail: vtlich@iop.vast.ac.vn

² Institute of Applied Materials Science in HCM City, VAST
1, Mac Dinh Chi, District 1, Ho Chi Minh City, Vietnam
E-mail: tthanhluong@yahoo.com

Abstract. Structural and spectral properties of curcumin and metal- curcumin complex derived from turmeric (*Curcuma longa*) were studied by SEM and vibrational (FTIR and Raman) techniques. By comparison between curcumin commercial, fresh turmeric and a yellow powder obtained via extraction and purification of turmeric, we have found that this insoluble powder in water is curcumin. The yellow compound could complex with certain ion metal and this metal-curcumin coloring complex is water soluble and capable of producing varying hues of the same colors and having antimicrobial, cytotoxicity activities for use in foodstuffs and pharmacy. The result also demonstrates that Micro-Raman spectroscopy is a valuable non-destructive tool and fast for investigation of a natural plant even when occurring in low concentrations.

1. Introduction

Curcuminoid is a natural yellow-orange compound derived from the root of *Curcuma longa*. This compound has been employed for a long time as dye, medicine and food additive in the Asian countries. Today it is also used as spice, in curry, and as food dye (E100) and preservative [1]. The medicinal activity of curcuminoid has been known since ancient times. Curcuminoid has powerful antioxidant and HIV antiproteases activities, anti-inflammatory and cancer preventive properties and it may help in Alzheimer's Disease (AD) [2].

The goal of our research is to get a deeper understanding of the structural and spectral properties of curcuminoid derived from turmeric on molecular level and to find a mechanism of action in AD. In this paper we investigate the structural and spectral properties of different types of curcumin: curcumin commercial, yellow powder extracted and purified from turmeric, a metallo-curcumin complex and fresh turmeric by SEM and vibrational (FTIR and Raman) techniques. The Raman technique also has been used for rapid and non-destructive plant analysis. From which we could achieve information about the microstructure, chemical composition and also the distribution of this specific compounds in the fresh curcuma root.

2. Experimental Methods

Materials. *Extraction and isolation of curcuminoid.* The curcuminoid was obtained by extraction and isolation from a rhizome of turmeric (*Curcuma longa*) as described in detail in [3]. The thin cut rhizome of turmeric purchased from a local market was air-dried and powdered after removal of the essential oils by water steam distillation. The powdered turmeric (500 g) was extracted three times with ethyl acetate (1500 ml). The crystal was filtered and washed with alcohols. Recrystallization from acetone afforded the curcumin. Yield: 1,25%.

Synthesis of metallo-curcumin complex. The metallo-curcumin complexes were prepared by a reaction of curcuminoid with certain metal ions [4]. A solution (5 mmol) of metal salt (ZnCl_2 , SnCl_2 , MgCl_2) and methanol (20 ml) was added drop wise at 50°C to a solution of curcuminoid (10 mmol) in methanol and acetone (1:1, 50 ml). After complete addition the reaction mixture was stirred for 2–3 h until the color was changed. The pH of the mixture was adjusted to 7.5–9.5 using ammonia to precipitate the metal complexes. The precipitate is filtered and washed with water and finally rinsed with methanol. The wet cake is dried at $70\text{--}80^\circ\text{C}$. The yield is 4,3% of manganese, 14,1% of zinc and 33,1% of tin complex with curcuminoids.

Curcumin was purchased from Fluka Chemical Co. (Sigma- Aldrich Co.) and used as received for comparison.

Apparatus. The content of curcuminoid was determinate by gas chromatography system HP 5890 and the metal content was analyzed on a Thermo Quest-CE Instrument [5]. The surface morphology of samples were obtained on a Field Emission Scanning Electron Microscope, S-4800, Hitachi. FTIR spectra were recorded on a Nicolet in the $4000\text{--}400\text{ cm}^{-1}$ range with 32 scans in using the KBr pellet technique. Spectral resolution was 4 cm^{-1} . The Raman spectra were scanned on a confocal Labram Raman Micro- spectrometer Dilor-Jobin Yvon-Spex, equipped with a detector CCD in the range of $100\text{--}1800\text{ cm}^{-1}$. For excitation, we used the red line (632.8 nm) of a He-Ne laser.

3. Results and Discussion

Curcuminoid. *Structure Description.* The curcuminoid was obtained by extraction and isolation from a rhizome of turmeric (*Curcuma longa*). Chemical analysis by gas chromatography shows that this yellow compound is a mixture of 51,1% curcumin I, 32,6% curcumin II (mono demethoxy curcumin) and 6,1% curcumin III (bis demethoxy curcumin) [3]. Molecule of curcumin have a conjugated symmetrical structure with single (--C--C--) and double (--C=C--) bonds alternately. They have two benzene rings, two methoxy and particular two hydroxy groups. Curcumin can exist in at least two tautomeric forms: keto and enol. In the central part of the molecule it can have a C=O and a C--OH group for the enol form and two C=O groups for the keto form.

Vibrational spectra. The Raman with 632.8 nm excitation and FTIR spectra obtained in solid state of curcumin (Fluka Co.) and curcuminoid were presented in Figure 1 and Figure 2 respectively.

The Raman spectra in the range of 100–1800 cm^{-1} and the FTIR spectra in the range of 400–4000 cm^{-1} of curcuminoid indicate the global characteristic vibrational groups. In comparison between curcumin (Fluka Co.) and curcuminoid we have seen that almost vibrational modes of these samples are the same. This

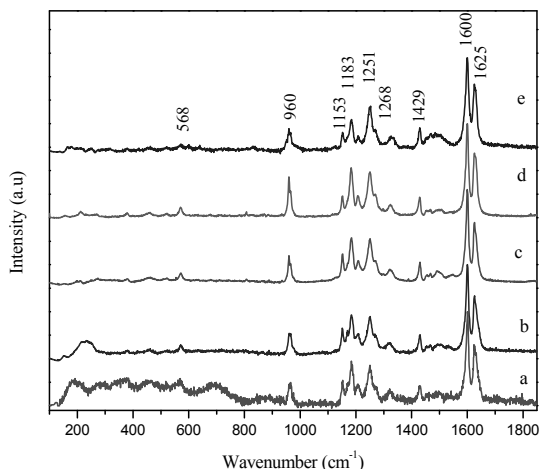


Fig. 1. Raman spectra of (a) curcumin (Fluka Co.), (b) curcuminoid, (c) Mg-cur., (d) Zn-cur. and (e) Sn-cur. complexes

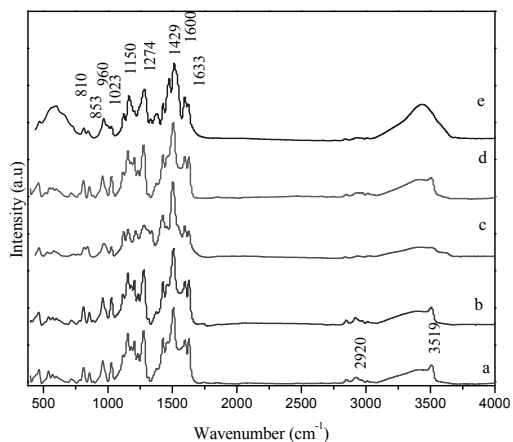


Fig. 2. FTIR spectra of (a) curcumin (Fluka Co.), (b) curcuminoid, (c) Mg-cur., (d) Zn-cur. and (e) Sn-cur. complexes

confirms that the chemical structure of curcuminoid obtained from turmeric is comparable with curcumin. In the highest frequency region both phenolic $\nu(\text{OH})$ vibrations of the curcumin have calculated frequency at 3595 cm^{-1} by [6], but in practice this band could be shifted downwards due to the intramolecular and intermolecular hydrogen bonds. In the Figure 2 we have seen this $\nu(\text{OH})$ sharp band at 3515 cm^{-1} (IR). Moreover, for enolic $\nu(\text{OH})$ mode the theoretical spectra predicts a strong band at 2979 cm^{-1} , but we have not seen this band neither in the IR nor in Raman spectra. We know that the diketo form is preferred in solid phase and the enol form in solution [5]. In our case all spectra were carried out in solid state, for this reason all our IR and Raman spectra of obtained curcuminoid show only bands of the diketo form. In the region from $2700\text{--}3000\text{ cm}^{-1}$ (IR) we have seen few bands with low intensity which are assigned to the aliphatic C-H stretches. In the middle region, a strong band at 1623 cm^{-1} (IR) and 1625 cm^{-1} (Raman) can be assigned to $\nu(\text{C}=\text{C})$ of the benzene ring. The observed shoulder at 1633 in IR and 1638 in the Raman spectrum is a characteristic band of C=O vibrations of the diketo form. Furthermore we have found a very strong band at 1600 cm^{-1} in this region. In agreement with the author in [6] we refer it to a mixing of $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{O})$ of the benzene ring. The most prominent band in the IR spectrum is at 1509 cm^{-1} , while the corresponding Raman band at 1507 cm^{-1} is weak. These are attributed to highly mixed vibrations (Table 1). Most bands in frequency region $1400\text{--}1490\text{ cm}^{-1}$ are highly mixed, except one very clear band at 1429 cm^{-1} (IR and Raman). This band is assigned to deformation vibrations of the two methyl groups. In IR spectra one band and one shoulder at $1274/1250\text{ cm}^{-1}$ and one very weak band at 1183 cm^{-1} are attributed to the in plane deformation vibrations of (CCH) of phenyl rings and skeletal in plane deformations, respectively. In the Raman spectra we have seen the same vibration at nearly the same frequencies ($1270/1250\text{ cm}^{-1}$ and 1183 cm^{-1}) with very high intensity at 1183 cm^{-1} . In the range of $1320\text{--}1200\text{ cm}^{-1}$ the observed bands at 1322 cm^{-1} (Raman)/ 1314 cm^{-1} (IR) and at 1206 cm^{-1} (Raman, IR) can be attributed to $\nu(\text{C}-\text{O})$ and $\delta(\text{C}=\text{C}-\text{H})$ of interring chain, respectively [4]. In this region the vibrations of the phenyl group are strongly mixed with skeletal ones. For this reason one prominent band at 1152 cm^{-1} in both IR and Raman spectrum was assigned also to (C-O-C) vibration. The IR bands at 1023 , 810 and 713 cm^{-1} and one Raman band at 886 cm^{-1} could be assigned to $\nu(\text{C}-\text{H})$ out of plane vibration of the aromatic ring. In the same region we have seen IR bands at 960 and 853 cm^{-1} which were attributed to $\nu(\text{C}-\text{O})$ vibrations. In the range of $700\text{--}400\text{ cm}^{-1}$ we could see deformation vibrations of both benzene rings and the out of plane vibrations of both OH groups which are at 460 cm^{-1} (Raman) and 466 cm^{-1} (IR). The low frequency region we assign to torsion vibrations. These bands were very weak because of the absorption of the lattice modes. We could see more clearly about these vibrations if we will use the laser line that approaches the electronic levels corresponding to metallic transitions in the near-UV. All observed IR and Raman frequencies of obtained curcuminoid, curcumin (Fluka Co.) and metallo-curcumin complexes are listed in Table 1.

Table 1. Observed Raman (632.8 nm excitation) and FTIR frequencies in wavenumbers (cm^{-1}) of the curcumin (Fluka Co.) and curcuminoid and metallo-curcumin complex studied

Curcumin (Fluka Co.)		Curcuminoid		Metallo-cur. complex		Assignment
<i>Raman</i>	<i>IR</i>	<i>Raman</i>	<i>IR</i>	<i>Raman</i>	<i>IR</i>	
	3518		3519		3519	$\nu(\text{OH})$
	3419		3413		3422	$\nu(\text{OH})$
	3006		3006		3006	
	2918		2920		2920	$\nu(\text{C-H})$
	2848		2848		2848	
1630	1633	1638	1633	1631	1633	$\nu(\text{C=O})$ of ketone groups
1625	1623	1625	1623	1626		mixing $\nu(\text{C=O})$ and $\nu(\text{C=C})$
1600	1600	1600	1600	1600	1600	$\nu(\text{C=C})$ benzene ring
	1509	1507	1509	1507	1506	mixing of vibrations
		1492		1491		
	1465	1466		1468	1465	mixing of vibrations
		1454		1454		
1428	1429	1429	1429	1429	1427	$\delta(\text{CH}_3)$
1322	1314	1322	1314	1322	1329	$\nu(\text{C-O})$
1270	1270	1268	1274	1270	1274	$\delta(\text{C-O-C})$
1250	1250	1251	1250	1250		
1206	1207	1208	1207	1207	1213	$\delta(\text{C=C-H})$
1183	1183	1182	1183	1183		$\delta(\text{C-O-C})$
1152	1153	1150	1153	1153	1163	$\delta(\text{C-O-C})$
	1023		1023		1027	$\nu(\text{C-H})$
				966sh		Me-O
962	960	960	960	960	963	$\nu(\text{C-O})$
886						$\nu(\text{C-H})$
	853		853	853	859	$\nu(\text{C-O})$
	810	805	810	805	812	$\nu(\text{C-H})$
	723		725		725	$\nu(\text{C-H})$
569	554	568	536	570	600	Out-of-plane def. of benz. ring and OH group
		518		518		
456		460	466	459	467	
376		378		387		Torsion
280				270		
		247				
		233				
		212		210		

Fresh turmeric. In spite of that curcumin is present in the root in an amount of only 3–5%, we have seen clearly in Figure 3 that it dominates in the Raman spectrum and that the characteristic bands occur almost at the same positions as for the curcumin and curcuminoid in the Figure 1. The most intense bands appearing at 1633 and 1602 cm^{-1} in the spectra are vibrations of the (C=C) and mixing $\nu(\text{C}=\text{O})$ with $\nu(\text{C}=\text{C})$ of the benzene ring and the bands at 1190 and 976 cm^{-1} are due to C-O-C and C-O-H, respectively. Figure 3 shows the Raman spectra and the image of one transverse section of fresh curcuma roots with the points where we have taken corresponding Raman spectra. From this figure we can see that the highest concentration of the dyeing substance was observed in the core (A and B points) and it is lower in outer or near the skin (C point) of the curcuma root.

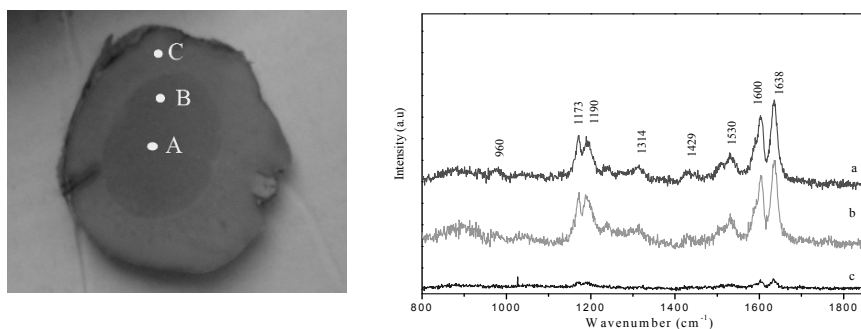


Fig. 3. Raman spectra and the image of one transverse section of fresh curcuma roots: at (a) the center point in the core, (b) outer point in the core and (c) in near the skin

Metal-curcumin complex. All obtained metallo-curcumin coloring complexes (Zn-cur., Mg-cur. and Sn-cur.) have been investigated by Raman and FTIR spectra in solid state. We will pay attention all regions in which there is indication of appearance either of metal-ligand structures like metal-oxygen or metal-nitrogen groups or enhance in the intensity of the bands assigned to $\nu(\text{C}=\text{O})$ when the metal could break a double bond $\text{C}=\text{O}$ of ketone groups and bonding with oxygen. In comparison between curcuminoid and metallo-curcumin complexes (Figure 1 and Table 1) we have seen that almost characteristic bands of the Raman spectra were in the same positions (in the frequencies and also in intensities). Below 500 cm^{-1} we have seen some weak bands but it is very difficult to attribute them to Me-N or Me-O vibrations, except one shoulder at 966 cm^{-1} which could be assigned to Me-O normally appearing belongin at this frequency (Table 1). By FTIR analysis we could not see any band g to metal-oxygen bond. But we could predict that if the metal ions used possess the ability to attract the ion pair electrons on oxygen atoms of the curcumin molecule to form a complex, the (C-O) bonds must increase.

From IR spectrum in Figure 2 we have seen that $I_{960\text{cm}^{-1}}/I_{1023\text{cm}^{-1}} \sim 1$ in the case of curcumin (Fluka Co.) and curcuminoid. But in the case of metallo-curcumin complexes this ratio is changed. For Mg-curcumin and Sn-curcumin this ratio is nearly ~ 2 . While this ratio was not changed for the Zn-curcumin complex. The same explanation applies also for the ratio of intensities between 853 and 810cm^{-1} frequencies (we note that 960 and 810cm^{-1} are characteristic bands of C-O bond and 1023 and 853cm^{-1} are characteristic bands of C-H). Thus using IR techniques, we quantify curcumin an affinity for manganese, zinc, and tin ions. It is shown that Zn^{2+} was little binding, but Mg^{2+} and Sn^{2+} ions could bind at least two curcumin molecules. This conclusion can be confirmed by investigations of the morphology of these samples by SEM (Figure 4).

Scanning Electron microscopy. The surface morphology of curcuminoid and all obtained metallo-curcumin copmplexes (Mg-cur., Zn-cur. and Sn-cur. complexes) were examined by SEM and shown in panel a, b, c and d of Figure 4.

Our curcuminoid shows rods or plaque in the dimension of a micron (a). These plaques become much more porously (in the case of Mg-cur. (b) and Sn-cur. complexes (d) in Figure 4). In the case of Zn-curcumin complex (c) we have seen small broken plaques. Thus the curcuminoid readily binds the Mg^{2+} and Sn^{2+} in contrast to Zn^{2+} . In addition these metallo- curcumin coloring complexes are water soluble. These properties gave us the idea to use the curcuminoid for removing the metal ions in the brain so it reduces plaque formation which is formed in the brain and causes Alzheimer's Disease (AD).

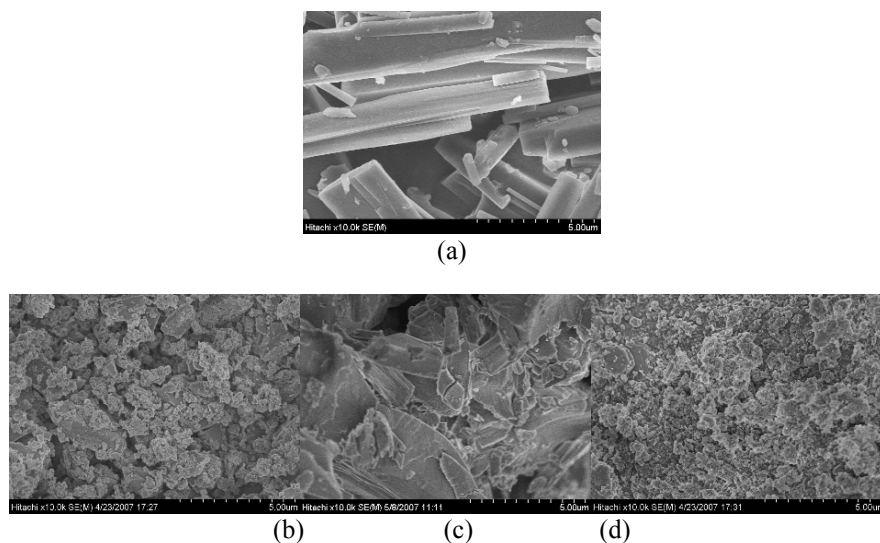


Fig. 4. SEM image of the surface morphology of (a) curcuminoid, (b) Mg-cur., (c) Zn-cur. and (d) Sn-cur. complexes

4. Conclusions

All vibrational assignments in detail on molecular level of the compound which was obtained by extraction and isolation from a rhizome of turmeric (*Curcuma longa*) and its metallo-curcumin complexes for a deeper understanding of the microstructure is presented. In addition the surface morphology was studied by SEM. An easy binding to metal ions has been given us an idea to use the curcuminoid for removing the metal ions in the brain so it reduces plaque formation which is formed in the brain and causes Alzheimer's Disease (AD). We can also note that Micro-Raman spectroscopy is a valuable tool for non-destructive and fast investigations of natural plants even for compounds occurring in low concentrations. Besides due to the intense curcumin bands this technique allows us to determine the distribution of specific compounds.

Acknowledgements

The financial support of the National Fundamental Research Program on Physics N. 4 030 06 is gratefully acknowledged.

References

1. B.B. Aggarwal, A. Kumar, M.S. Aggarwal, and S. Shishodia, In: Preuss H, ed. Phyto-pharmaceuticals in Cancer Chemoprevention. Boca Raton: CRC Press; (2005) 349
2. Larry Baum and Alex Ng, J. Alzheimer's Disease, 6-4 (2004) 367
3. Tran Thanh Luong, Nguyen Duc Hai and Pham Nguyen Dong Yen, Reports and SRW of IMS, HCM-Brand (2002)
4. Tran Thanh Luong, Nguyen Duc Hai, Pham Nguyen Dong Yen and Nguyen Thi Mai Huong, J. Med. Mat. 11-4 (2006) 159.
5. AOAC 2002(965.09) Application Note No 622 Thermo Quest-CE Instrument
6. T.M. Kolev, E.A. Velcheva, B.A. Stamboliyska and M. Spiteller, Int. J. Quant. Chem. 102, (2005) 1069

***In-situ* Chemically Polymerized PANi-SWNTs Composites: Characterizations and Gas Sensing Feature**

Duong Ngoc Huyen

Institute of Engineering Physics, Hanoi University of Technology

No. 1 Daicoviet, Hanoi, Vietnam

E-mail: duonghuyen@mail.hut.edu.vn

Abstract. An experiment has been made in order to study the impact of SWNTs in *in-situ* chemically polymerized PANi-SWNTs composites. It is found that the SWNTs surface plays a role of nucleation sites for PANi growth. The presence of SWNTs enhances the degree of polymerization and increase the conductivity (polaron or bipolaron lattice) of PANi. When radiated by a near-infrared laser (1064 nm) the dried materials emit strong fluorescent bands in mid-infrared region which are assumed to be the transitions from the π -orbital (highest occupied molecular orbital) to polaron and bipolaron lower levels. The bands are speculated to arise from charge transfer interactions between the PANi and SWNTs, which brings new polaron and bipolaron levels into the band gap of PANi. The PANi-SWNTs also exhibits an improvement in NH_3 gas sensing characterization in comparison to neat SWNTs and PANi. The results are interpreted as a modification in the chemical and electronic structure of PANi.

1. Introduction

Polyaniline (PANi), a pi-conjugated polymer, has been the subject of intense experimental and theoretical studies because of its outstanding states of oxidation and protonation. Depending on the degree of oxidation and protonation, the conductivity of PANi can be tuned in a large range from conductor to insulator [1–7].

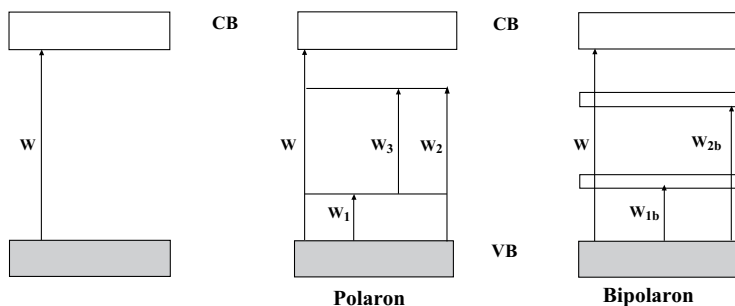


Fig. 1. Simplified band models used to describe polaron, bipolaron levels and allowed transitions. The transition w corresponds to the π to π^* transition of the benzenoid unit. The transitions w_1 , w_{1b} and w_2 , w_{2b} are the transitions of polaron and bipolaron states, respectively. The transition w_3 is transition from lower into the upper binding polaron

The charge carriers responsible for PANi conductivity are polaron and bipolaron arising from chemical doping, charge injection, or electronic defects within the π -orbitals backbone. Figure 1 depicts a simplified model of the formation of polaron and bipolaron in band gap of PANi. The energy levels of the π -orbital (highest occupied molecular orbital) and of the π^* -orbital (lowest unoccupied molecular orbital) form the valence band and conduction band, respectively [8, 9]. The electron-phonon coupling results in a gap between valence and conduction band. In the single charged case two localized polaron levels are created in the gap. With the number of polaron level increasing the discrete levels are combined into a lower and upper band (bipolaron). Depending on the state of electronic occupation, the possible allowed transitions W , w_1 , w_2 , w_3 , w_{1b} and w_{2b} are described in the model, see Fig 1. The transitions W , w_2 , w_3 , and w_{2b} are mostly in the violet and visible region. On the other hand, the transition from valence band to lower polaron (bipolaron) level w_1 and w_{1b} gives rise to a band in the infrared region as shown in photoinduced absorption and chemical doping spectra [8, 10].

Single-wall carbon nanotubes (SWNTs) also exhibit excellent electrical properties which are somewhat comparative to that of PANi. Both materials show a strong interaction via dono-acceptor binding as evidence of a relatively high dispersion of CNTs into aniline [11,12]. The combination of SWNTs and PANi in a composite is expected to improve their unique characterizations. Based on these considerations, an effort has been made in order to study the effect of SWNTs on characteristics of *in-situ* chemically polymerized PANi-SWNTs composites which were synthesized with chemical treatment of SWNTs in acidic aqueous solution of HCl under bath ultrasonic. In this paper, SEM images, FTIR and Raman spectra of the composites are measured and analyzed. Gas sensing characteristics are tested to evaluate the impact of SWNTs. Some most relevant results are presented and discussed in this report.

2. Experimental Procedure

Commercial AP grade SWNTs (mean diameter about 1.2 nm) from ILJIL Co. Korea, were used as starting materials. Aniline 99.5% (Aldrich. Co.) as monomer, ammonium persulphat (APS, Kanto Chemical Co. Inc.) as oxidant were used to synthesis PANi. All the materials were used as received.

PANi was chemically synthesized with the following routine: 30 ml of aqueous solution of 1.0 M acid and 0.2 M aniline was mixed with 30 ml of aqueous solution of 0.2 M APS at temperature of 0°C [13-15]. The synthesis of *in-situ* chemically polymerized PANi-SWNTs composites was carried out in two steps. Firstly, 20 mg SWNTs were chemically purified in 5 ml HCl (37%) acid at 120°C for 3 h in an ultrasonic bath. Secondly, aniline and distilled water were added to the acidic solution containing purified SWNTs to have an aqueous solution of 1.0 M acidic and 0.2 M aniline. The procedure then was made following the routine as that of PANi. The synthesis was carried on in an ultrasonic bath in order to increase the rate of polymerization. The color of the mixture was gradually changed from transparent, colorless to blue, and to dark blue-green indicating the emeraldine base and salt polyaniline formed in the solution. After a certain duration, the reaction was terminated by pouring ethanol into the mixture. The resulting PANi and PANi-SWNTs composites were filtered out, washed repeatedly

with distilled water and with dilute acidic solution. After dried, the products were characterized using SEM, FTIR, and Raman spectra.

Gas sensitivity was determined using a PANi-SWNTs or PANi layer coated on interdigitated Pt electrodes. The test sample was put in a closed chamber with installed electrodes, gas inlet, and outlet. The sensing signal was monitored and analyzed by a personal computer. The sensitivity is determined as a change in resistance of the PANi-SWNTs or PANi layer between Pt electrodes as follows:

$$S = \frac{R - R_0}{R_0}, \quad (1)$$

where R_0 and R are the layer resistances in open air and upon exposure to the target gas, respectively.

3. Results and Discussions

Experiments indicate that the morphologies of PANi and PANi-SWNTs composites have different features. As can be seen from SEM images in Fig. 2, PANi without SWNTs grows in granular structure, the orientation of PANi is planar and random. On the other hand, in PANi-SWNTs composites PANi firmly grows on the surface of SWNTs and the orientation of PANi is perpendicular to the SWNTs surface. The potential mechanism of the formation of PANi film and colloids seems to be applicable to explain the different structure here. In pure PANi, the oxidation of aniline produces aniline oligomers. Due to its hydrophobic the PANi oligomers separate from aqueous solution and then adsorb themselves to form nuclei and to grow. The resulting PANi then has a granular form. In the case of PANi-SWNTs composites, the aniline oligomers are adsorbed and anchored at strong binding sites on SWNTs surface [16]. The oligomers stimulate the growth of the PANi chain and then form a nucleus. The strong bond between SWNTs and PANi via donor-acceptor interaction is accounted for the growing mode [11, 12]. By the auto-acceleration mechanism, new oligomers form and the polymerization proceed, PANi particles grow. In PANi-SWNTs composites, SWNTs play a role of nucleation sites for PANi growth. Depending on the synthesis condition, the preferable anchoring sites give the different morphology.

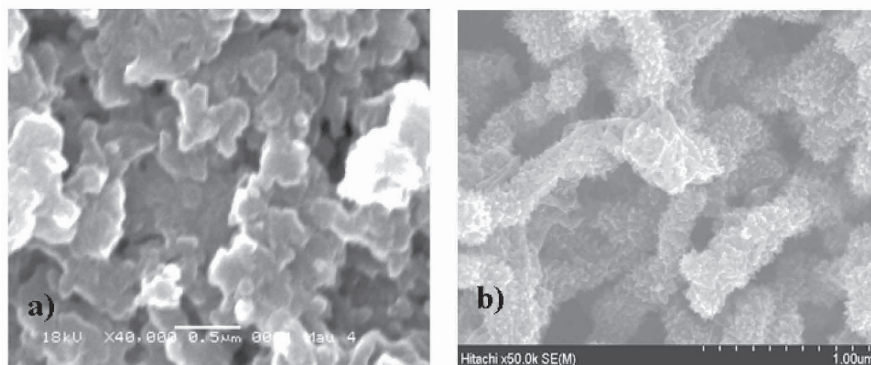


Fig. 2. SEM images of PANi (a) and *in-situ* chemically synthesized PANi-SWNTs composites (b)

The interaction between SWNTs and PANi is expected to affect the electronic structures of both PANi and SWNTs.

The FTIR spectra of PANi and the PANi-SWNTs are shown in Fig. 3. The vibration modes standing for PANi emeraldine are clearly observed. The bands around $1478\text{--}1485\text{ cm}^{-1}$ and $1577\text{--}1580\text{ cm}^{-1}$ are assigned to the benzenoid and quinoid moiety, respectively. The semiquinoid indicating the change in quinoid to benzenoid form, i.e. the protonated structure is assigned to the adsorption band at 1300 cm^{-1} . The strong band at around $1173\text{--}1175\text{ cm}^{-1}$ is assigned for the vibration mode of (N=Q=N) which is considered as degree of delocalization of electrons. As can be seen from Fig. 3, the relative ratio of quinoid vibration intensity (1577 cm^{-1}) and benzenoid vibration intensity (1485 cm^{-1}) in PANi-SWNTs is higher than that of PANi (1580 and 1478 cm^{-1} , respectively). The semiquinoid vibration mode peaking at 1300 cm^{-1} in the composite is more intensive. The feature indicates the fact that in the composites the PANi has more quinoid and semiquinoid structure than the neat PANi, or in the other words the interaction between PANi and SWNTs promotes and/or stabilizes quinoid form. From chemical view of consideration, SWNTs enhance the degree of polymerization of PANi. A slight blue-shift in vibration modes of PANi is also found in the composite. The shift is assumed as modifications in PANi chemical structure.

The Raman spectrum of starting dispersed SWNTs acidic solution contains the line of 1593.5 cm^{-1} standing for the G-line (in-plane stretching E_{2g} mode) of CNTs while that of starting Ani solution contains 1649.1 , 1206.4 , 797 , 721.8 cm^{-1} modes standing for ANi. As can be seen from Fig. 4, the vibration modes of both SWNTs and PANi at around 1590 cm^{-1} appear in Raman spectra of PANi-SWNT composites. The band in the region of 1500 cm^{-1} was attributed mainly to the benzenoid (B) ring stretching vibration while the band near 1600 cm^{-1} is related to the quinoid (Q) structure of the PANi chain. The intensity of the benzenoid ring stretching vibration is less than that of the quinoid. Both the 1590 and 1500 cm^{-1} absorption bands exhibit an increase in intensity and a red shift during the protonation process. The red-shift is an indication of

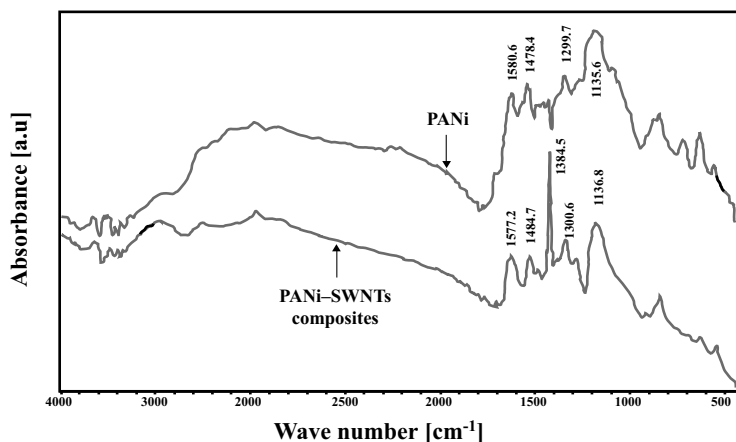


Fig. 3. FTIR spectra of PANi and *in-situ* chemically synthesized PANi-SWNTs composites

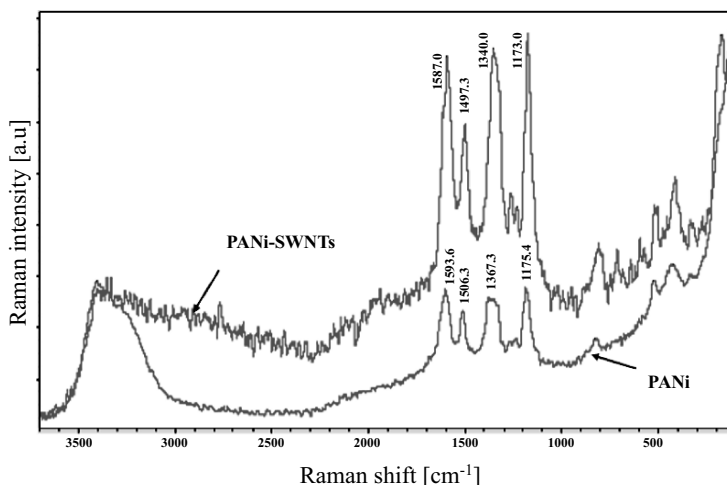


Fig. 4. Raman spectra of PANi and *in-situ* chemically synthesized PANi-SWNTs composites

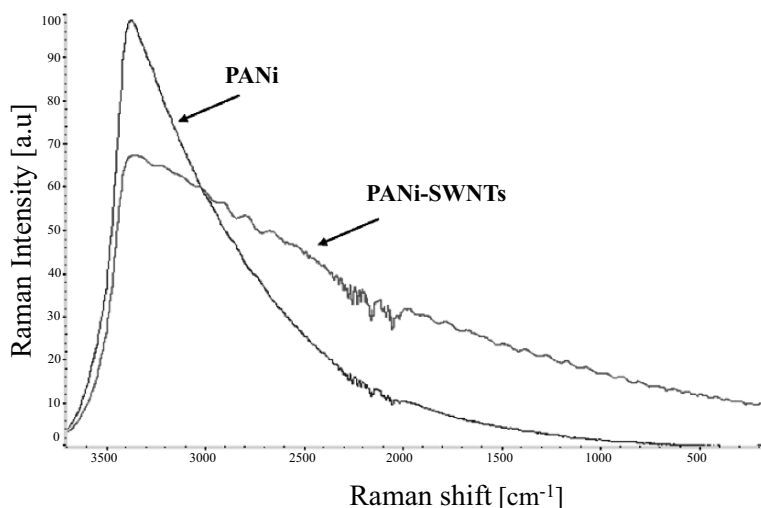


Fig. 5. Fluorescent bands of PANi and PANi – SWNTs composites excited by 1064 nm laser

the change of a benzenoid structure to the polaron lattice in the polymer chain. The 1170 cm^{-1} band can be assigned to a vibration mode of B - NH = Q structure, which is formed during the protonation process and indicates the existence of positive charges on the chain and the distribution of the dihedral angles between the Q and B rings. This band increases with the degree of doping of the polymer backbone. The band at 1170 cm^{-1} was attributed to an electronic-like band and was considered as a measure of the degree of delocalization of electrons. In PANi-SWNTs composites, the stretching vibration modes are slightly shifting towards the red region indicating

a higher conducting structure (polaron lattice). As a dopant, the presence of SWNTs enhances the conductivity of the PANi.

Excitation by 1064 nm laser from Raman Nicolet 6700, the dried PANi and PANi-SWNTs composites emit broad bands peaking at around 3400 cm^{-1} (0.42 eV) as shown in Fig. 5. This band is assumed to be the superimposition of N-H, O-H stretching modes and the optical transition w_1 and w_{1b} (as shown in Fig. 1) from highest occupied molecular orbital (HOMO) to lower polaron level or bipolaron band [17, 18]. The width of the transition band is broadened toward the red region (red shift) when SWNTs are added. The feature has been frequently observed in both FTIR and Raman spectra and are speculated to arise from charge transfer interactions between the PANi and SWNTs. The interaction brings new polaron and bipolaron levels into the band gap of PANi, as a result the fluorescent band broadens toward red region.

Experiments found that the conductivity of both PANi and *in-situ* chemically synthesized PANi-SWNTs composites are sensitive to ambient change. Using a vacuum pump to change the air pressure, the conductivity of the materials are varied. As shown in Fig. 6, the resistance of materials increases as air pressure reduces (the vacuum pump on). The main reason accounting for the change in conductivity is the adsorption of oxygen, water vapour and variety of gas molecules which are available in air. The interaction between gas molecules and PANi/SWNTs results in the formation of shallow levels in their band gaps (chemical doping) and then alters their conductivity (in open air, both SWNTs and PANi are p-type semiconducting materials). From physical view of consideration, the conductivity of PANi and SWNTs will change again if we change the gas concentration (the pump on or off) or add some other gases. As an example, the resistance of PANi and SWNTs increases upon exposure to NH_3 gas whose sensing feature is shown in Fig. 7. The reason for the reduction of free carriers (hole) in PANi and SWNTs is the addition of electrons from adsorbed NH_3 molecules into their valence band. As can be seen from the plot, the sensitivity of the PANi-SWNTs composite at low NH_3 concentration is higher but at high NH_3 concentration the sensitivity of PANi is higher. The saturation of gas adsorption is assumed to be the reason. The most striking point is the good recovery of PANi-SWNTs composite. As shown in Fig. 8, after the gas is off the resistance of

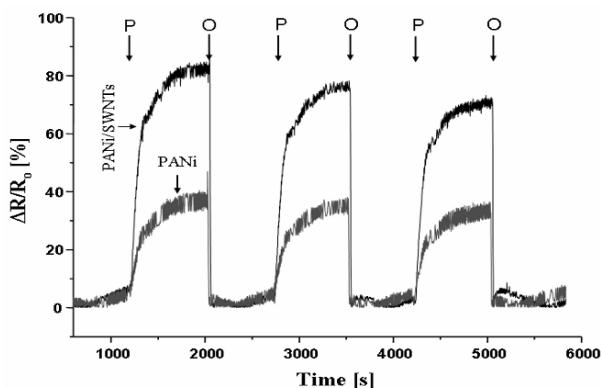


Fig. 6. Resistance of PANi and PANi-SWNTs as function of air pressure (P: pump on, O: open air)

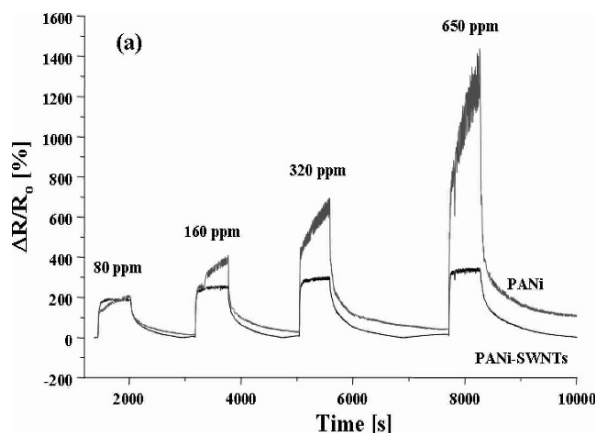


Fig. 7. Conductivity of PANi and PANi-SWNT composite as function of NH_3 concentration

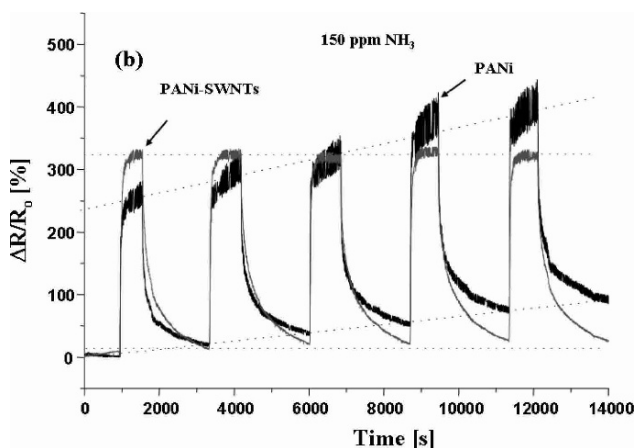


Fig. 8. Repeatability of PANi and PANi-SWNT composite upon exposure to 150ppm NH_3

the composite completely returns to the origin. The improvement is assumed to be due to the larger surface area, larger sensing sites due to the modification of electronic structure as a result of PANi-SWNTs interaction.

4. Conclusion

In *in-situ* chemically polymerized PANi-SWNTs composites, SWNTs and SWNTs bundle surfaces are found to play the role of nucleation sites for PANi growth. In FTIR and Raman spectra, the intensities and band positions assigned for absorption and vibration modes of SWNTs and PANi are varied. The presence of SWNTs in the composites affects the polymerization and chemical bonding structure of PANi. From

the chemical view of consideration, SWNTs enhance the degree of polymerization and increase the conductivity (polaron or bipolaron lattice) of PANi. The PAN-SWNTs interaction brings new polaron and bipolaron levels into the band gap of PANi. PANi-SWNTs composites also exhibit high gas sensitivity, fast response and perfect recovery. The modification in electronic structure of PANi and SWNTs in the composite is assumed as the reason for the improvement.

Acknowledgement

The author gratefully acknowledges financial support from Project 405206 and the National Nano Program.

Reference

1. G. G. Wallace et al., *Conductive electroactive polymers*, Technomic Pub. Co., 1997.
2. D. Han et al., *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 259, 179, 2005.
3. E. Erdem, M. Karakýsla and M. Sacak, *European Polymer Journal*, 40, 785, 2004.
4. D. N. Debarnot. and F. P. Epailard, *Analytica Chimica Acta*, 475, 1, 2003.
5. J. Janata and M. Josowics., *Nature Mater.* 2, 19, 2003.
6. N. E. Agbor, M. C. Petty, A. P. Monkman, *Sensors and Actuators B*, 28, 173, 1995.
7. G. Li et al., *Electrochem Solid-State Lett.*, 7 (10), H44, 2004.
8. M. Wohlgenannt, X. M. Jaing and Z. V. Vardeny, *Phys. Rev. B* 69, 241201, 2004.
9. R. Holze, *Advanced Functional and Polymers*, Vol. 2, Gordon and Beach Sci. Pub., 172, 2001.
10. R. A. J. Janssen et al., *Chem. Phys.* 103 (2) 8 788, 1995.
11. H. Zengin et al., *Adv. Mater.*, 14, 1480, 2003.
12. J. E. Huang, X. H. Li, J. C. Xu, H. L. Li, *Carbon* 41, 2731, 2003.
13. N. E. Agbor, M. C. Petty, A. P. Monkman, *B* 28, 173, 1995.
14. D. Han et al., *Colloids and Surfaces A: Physicochem. Eng. Aspects* 259, 179, 2005.
15. E. Erdem , M. Karakýsla, M. Sacak, *European Polymer Journal* 40, 785, 2004.
16. J. Stejskal, and I. Sapurina, *Pure Appl. Chem.*, Vol. 77, No. 5, 815, 2005.
17. M. Wohlgenannt, X. M. Jaing and Z. V. Vardeny, *Phys. Rev. B* 69, 241201, 2004.
18. D. N. Huyen, Ng. X. Chien, *Proc. 3rd IWONN*, Halong, 2006.

Design, Simulation and Experimental Characteristics of Hydrogel-based Piezoresistive pH Sensors

Thong Quang Trinh¹, Jorge Sorber², and Gerald Gerlach²

¹ Institute for Engineering Physics (IEP), Hanoi University of Technology (HUT),
1 Daicoviet Road, Haibatung District, Bohobox-100000 Hanoi, Vietnam
E-mail: thongtq97@yahoo.com

² Institute for Solid-State Electronics (IFE), Technische Universitaet Dresden (TUD),
Helmholtzstr. 18, D-01062 Dresden, Germany
E-mail: gerlach@ife.et.tu-dresden.de

Abstract. This paper presents the investigations of a novel type of piezoresistive pH sensors exploiting the chemo-mechanical energy conversion due to hydrogel swelling. pH-sensitive poly(vinyl alcohol)-poly(acrylic acid) (PVA-PAA) hydrogel is used for this aim. The pH sensor has been designed including a commercial piezoresistive pressure sensor chip, a hydrogel layer, and a rigid grid. Behaviour of pH sensor under swelling of polymer hydrogel has been simulated using finite element method (ANSYS). The sensor simulations have been performed using the experimental material parameters of PVA-PAA hydrogel. The sensor characteristics including the silicon diaphragm deflection and output voltage have been measured. There were good relative agreements between simulations and experimental results.

1. Introduction

Polymer hydrogels have been known for long time as a so-called smart material due to their ability of large, reversible volume changes in response to various external stimuli, such as temperature, pH, solvent concentration, and electric field. Nowadays, hydrogels are becoming more and more interesting for applications in sensors and actuators [1-6]. Researches on gel-based sensors and actuators were focused mostly on device design and fabrication. However, a systematic investigation of the material properties and the implementation into appropriate models combined with the simulation of the complex device behaviour has not been delved yet.

In this paper, we present our development of a pH sensor exploiting the swelling property of PVA-PAA hydrogel by mechano-electrical transduction via a silicon piezoresistive pressure transducer chip. The general sensor principle is as follows: The swelling state of a hydrogel will change due to pH value changes causing the flexible plate bending. It results in the change of membrane stress leading to the resistance change of the integrated piezoresistors and consequently the appropriate Wheatstone bridge output voltage. For silicon piezoresistive sensors, the output voltage can be theoretically determined as [7]:

$$U_{\text{out}} = -\frac{1}{2}U_{\text{in}}(\pi_{\parallel} - \pi_{\perp})(\sigma_{\parallel} - \sigma_{\perp}) = -\frac{1}{2}U_{\text{in}}(\pi_{\parallel} - \pi_{\perp})\sigma_{\text{Res}} \quad (1.1)$$

where U_{in} is the applied voltage, $\pi_{\parallel}$ and $\pi_{\perp}$ the parallel and perpendicular piezoresistive coefficients, $\sigma_{\parallel}$ and $\sigma_{\perp}$ the membrane longitudinal and transverse stresses, σ_{Res} the piezoresistors' stress.

Our investigations will combine both the material characteristics of PVA-PAA hydrogel and the behaviour of the hydrogel-based sensor obtained by modeling and simulation as well as the experiments using the real fabricated sensors.

2. Material Model of PVA-PAA Hydrogel

For the aim of producing pH sensors, which rely on the hydrogel swelling, a good understanding of the appropriate material model is required that enable the calculation of the sensor behaviour. Based on the free swelling experiments and mechanical tests, a visco-hyperelastic model is possibly applied for PVA-PAA hydrogel. The hyperelasticity can be described by a Mooney-Rivlin model with two parameters [8]:

$$W = C_1(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + C_2(\lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2} - 3) \quad (2.1)$$

where $\lambda_1, \lambda_2, \lambda_3$ are the principal stretch ratios, and C_1 and C_2 material parameters characterizing the instantaneous response of the hyperelastic material. Here C_1 and C_2 are related to the initial shear modulus, G_0 :

$$G_0 = 2(C_1 + C_2) \quad (2.2)$$

while the viscoelasticity can be expressed by a Prony's series for the shear modulus [9]:

$$G(t) = G_0 \left[1 - \sum_{i=1}^n g_i \left(1 - e^{-\frac{t}{\tau_i}} \right) \right] \quad (2.3)$$

where g_i and τ_i are material parameters characterizing the relaxation behaviour which is a property of viscoelasticity.

The material parameters C_1, C_2, g_i and τ_i were determined by mechanical tests, i.e., uniaxial tensions [10] combined with the curve fitting procedures using a software for finite element method (FEM) called ANSYS. The calculated values of these parameters are summarized in Table 1. All these parameters will be used as input data for the simulation of the hydrogel-based pH sensor characteristics.

Table 1. Material parameters characterizing the viscohyperelasticity of PVA-PAA hydrogel

Constant	C_1 [MPa]	C_2 [MPa]	g_1	g_2	g_3	τ_1 [s]	τ_2 [s]	τ_3 [s]
Value	0.15	0.06	0.147	0.1433	0.2337	18.975	261.069	1476.9

3. Sensor Modeling and Simulation

Sensor modeling and behaviour simulation were carried out by finite element method (FEM) using the ANSYS 8.1 software package [8]. The purpose of the simulation work was to predict the pH sensor characteristics.

3.1. Sensor Design

The structure of the piezoresistive pH sensor would include three components which are directly connected with each other. The hydrogel layer is considered as a thin square slab. It is placed between the upper flexible bending plate of the chip and a lower rigid grid (Figure 1). The grid contains a number of small holes, which are supposed as channels for transferring the solution to be analyzed.

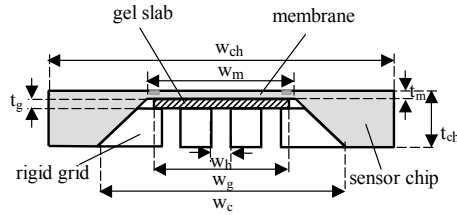


Fig. 1. Cross-section of hydrogel-based piezoresistive pH sensor, W_{ch} chip size, W_c cavity size, W_m membrane width, W_g gel width, W_h hole size, t_{ch} chip thickness, t_m membrane thickness, and t_g gel thickness

3.2. Sensor Modeling

In this work, a FE model was adjusted to the real dimensions of the commercial silicon piezoresistive sensor chips (Table 2).

Table 2. Geometrical parameters used for pH sensor modeling

Quantity	w_{ch} [μm]	w_m [μm]	w_c [μm]	w_g [μm]	w_h [μm]	t_{ch} [μm]	t_m [μm]	t_g [μm]
Value	5100	3100	3800	1300	200	380	20	30–50

The sensor model was built by the parametric modeling facility provided by the ANSYS Parametric Design Language (APDL) using macros which allow design changes relatively easily. In our work, only a quarter of the model was considered for the numerical analysis due to the chip symmetry. The sensor model was built using three elements. The SOLID45 is used to model the silicon chip and the rigid grid. The HYPER58 is employed for modeling the hydrogel slab, which is a solid but has hyperelastic properties. It describes the large and elastic deformation of the hydrogel. The CONTAC49 is applied to realize the contact of the surfaces between hydrogel, silicon membrane, and rigid grid within the sensor structure.

Two simulation procedures have been established to calculate the static and the dynamic response of hydrogel-based sensors. The static simulation enables to calculate the instantaneous sensor response subjected to the given strains

corresponding to the pH range of 5.5 to 11. The dynamic simulation is carried out to compute the time-dependent characteristics.

3.3. Simulation Assumptions

Due to the isotropic deformation of PVA-PAA hydrogels, an equivalent strain has been introduced using the thermal expansion term offered by ANSYS to describe the strain due to chemical swelling [8]. The simulation was performed only for the swelling process of the hydrogel, but did not consider any temperature influences. Additionally, the following assumptions have been used for the sensor simulation:

- (i) The reference state of hydrogel is considered as that one at pH 1.
- (ii) Calculations are applied for gel swelling process from pH 1 to higher pH values.
- (iii) The sensor is assumed to be fixed at the bottom. The grid is considered to be so rigid that it is not significantly deformed by hydrogel swelling process.

3.4. Simulation Results

The FE sensor model obtained by ANSYS is shown in Figure 2 (left side).

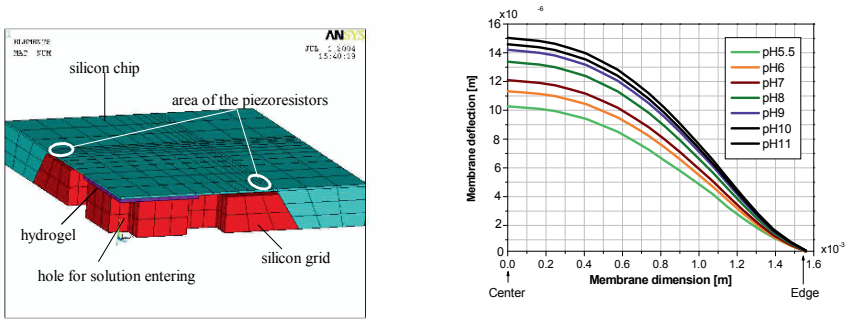


Fig. 2. Sensor FE model (left) and membrane deflection profiles (right)

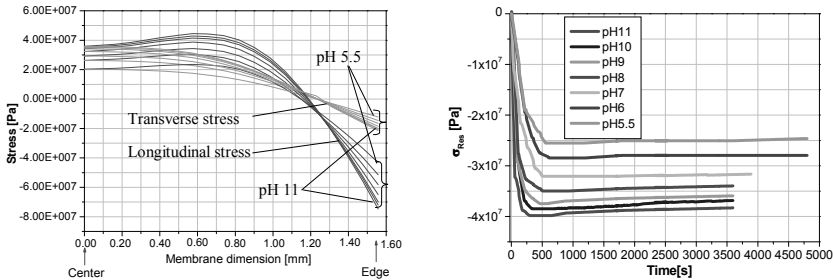


Fig. 3. Longitudinal and transverse membrane stresses profiles (left) and pH-dependent transient stress within the piezoresistors (right)

The simulations were performed for sensors with the hydrogel thickness of 30, 40, and 50 μm . The membrane deformations in different pH solutions from 5.5 to 11 are obtained from the finite element static analysis (FEA). A typical case of the membrane deflection is shown in the right side of Figure 2 corresponding to the gel thickness of 40 μm . As expected, the membrane bending exhibits the shape of a curved shell. The center membrane deflections of this case have been calculated in the range of 10.2 to 15.1 μm . Another important result obtained from static analysis is the membrane stress distributions both of longitudinal and transverse stress along the axis from the membrane centre to edge. This analysis results are shown in Figure 3 (left side). It can be seen that the longitudinal stress gradient is higher than the transverse one.

The FEA dynamic analyses result in the time-dependent response of the membrane stress within the piezoresistor after a step-like change from pH 1 to higher pH values as shown in Figure 3 (right side). Consequently, the sensor output voltage is determined using equation (1.1). In this case, the supplied voltage U_{in} is assumed to be 5 V for convenience of the comparison with the measurements. The calculated maximum values and the time-dependence of the sensor output voltages due to the hydrogel swelling in different pH solutions are presented in Figure 4. Here, the sensor output voltage at pH 1 was supposed as reference state and assumed to be zero. The operation range is determined by the maximum calculated voltage compared to the reference state.

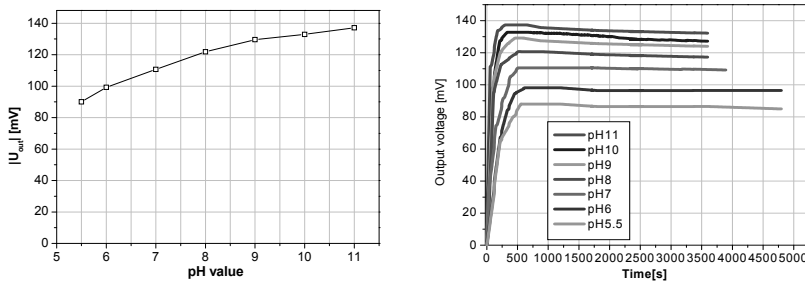


Fig. 4. Predicted maximum values (*left*) and time dependence of output voltage (*right*) vs. pH values (for case of 40 μm gel thickness)

4. Experimental Verification

Relying on the mentioned design, pH sensors have been realized using the rigid grids made of silicon and fabricated by micromachining technology. The membrane deflection and output voltage characterizing the sensor performance have been experimentally verified using those manufactured pH sensors.

The membrane deflection measurements were carried out by the nanofocus microscan profilometer (Nanofocus AG, Oberhausen, Germany). The left picture in Figure 5 presents a measured result corresponding to 40 μm hydrogel thickness.

It revealed that the sensor, namely the silicon diaphragm, exhibited a sufficiently good response to the PVA-PAA hydrogel swelling. The corresponding values of the centre membrane deflections are between 9.1 and 14.3 μm for pH values of 5 to 11.

Comparing with the simulation results, a relatively good agreement with experimental results was obtained as shown in the right picture of Figure 5.

The sensor long-term output voltage has been measured using so-called pulse-wise and step-wise pH excitation regimes between pH 1 and pH 4...11. One of the measurement results is shown in Figure 6.

These pictures demonstrate the sensor response to pH value changes for both measurement regimes. The output voltage increases with increasing pH. A transition occurs between pH 4 and pH 5. It is because the pH value rises above the dissociation constant of PAA ($\text{pK}_a = 4.7$). It means that the ionization process of polycarboxylic groups within the polymer network happened and created the electrostatic repulsion force leading to the significant increase of the swelling degree. In most cases, the polycarboxylic groups were fully ionized at pH 11. The maximum sensor output voltage of this case is in the range of 75 to 130 mV corresponding to a pH range of 5.5 to 11.

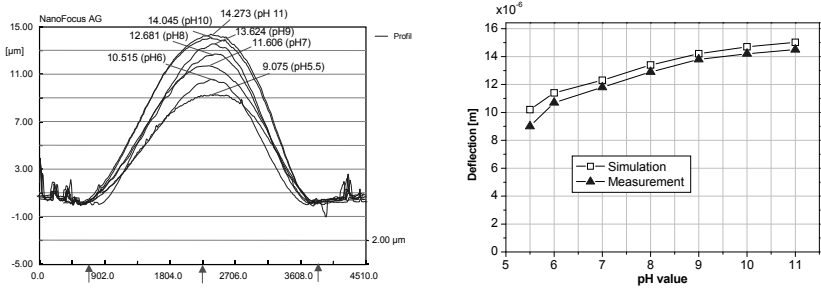


Fig. 5. Measured sensor membrane deflections (left) and comparison of center membrane deflection values with simulation (right)

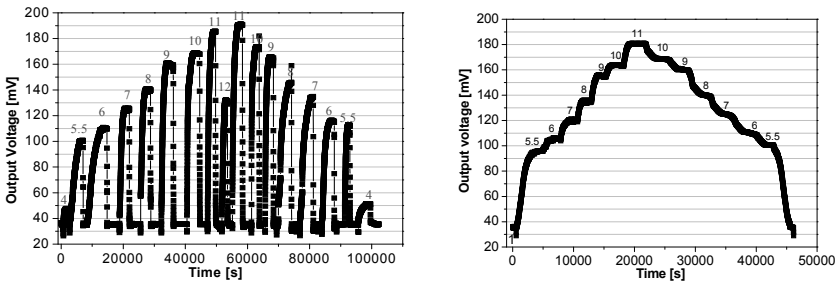


Fig. 6. Sensor long-term output voltage, left is pulse-wise and right step-wise cycling (gel thickness: 40 μm , parameter: pH value)

All the sensor output characteristics according to the gel thickness of 30 to 50 μm obtained from simulation and experiment are summarized in Table 3. Once again, these results also disclose that the experimental characteristics appeared to be well-suited for the calculations.

Table 3. Simulated and measured sensor output voltage in pH range of 5.5 to 11

Gel thickness (μm)	Output voltage (mV)	
	Simulation	Measurement
30	75...125	65...120
40	85...140	75...130
50	100...155	95...145

5. Conclusion

In this work, the behaviour of a pH sensor relying on the swelling of PVA/PAA hydrogel has been investigated theoretically and experimentally. A viscohyper-elastic model has been applied for the hydrogel. The sensor behaviour has been modeled and simulated successfully by finite element analysis using the analogy of chemical swelling and thermal extension. Some main characteristics of pH piezoresistive sensor have been computed including membrane deflection, membrane stress, and consequently sensor output voltage. The experimental verifications have pointed out that a relatively good agreement between simulation and measurement results of both the sensor membrane deflection and the output voltage could be reached.

Acknowledgements

This work was supported by Vietnamese Government via Ministry of Education and Training and German Research Council (DFG) as project C11 of SFB 287. The simulation and measurements were performed at the Institute for Solid-State Electronics (IFE) of Dresden University of Technology.

References

1. D. De Rossi, M. Suzuki, Y. Osada, and P. Morasso, *Journal of Intelligent Material Systems and Structures*, Vol. 3, 75, 1992.
2. Z. Liu, P. Calvert, *Advanced Materials*, Vol. 12, 288, 2000.
3. K.-F. Arndt, D. Kuckling, and A. Richter, In *Polymers for Advanced Technologies*, Vol. 11, 496, 2000.
4. R. Bashir, J. Z. Hilt, O. Elibol, A. Gupta, and N.A. Peppas, *Applied Physics Letters*, Vol. 81, 3091, 2002.
5. I.S. Han, et. al., *Macromolecules*, Vol. 3, 1271, 2002.
6. S. Herber, W. Olthuis, and P. Bergveld, *Sens. and Act. B*, Vol. 91, 378, 2003.
7. G. Gerlach, and W. Doetzel, In *Einführung in die Mikrosystemtechnik*, Fachbuchverlag im Carl Hanser Verlag, Munich, Wien, 2006.
8. P. Kohnke, *ANSYS Theory Reference*, Rel. 5.7, ANSYS Inc., Cannonsburg, 1999.

9. Y.C. Fung, In *Biomechanics: Mechanical Properties of Living Tissues*, 2nd ed. Springer-Verlag, New York, 1993.
10. Trinh Quang Thong, In *Hydrogel-based Piezoresistive pH Sensors*, TUD Press, Dresden, Germany, 2006.

Optimization of the Thermostable Nanogel Systems for High Temperature Reservoir Application

Nguyen Phuong Tung, Nguyen T. Phuong Phong, Nguyen Hoang Duy,
and Nguyen T. Quynh Anh

Institute of Applied Materials Science, 1 Mac Dinh Chi St., 1st Dist.,
Ho Chi Minh City, Viet Nam
E-mail: nptung@vast-hcm.ac.vn

Abstract. We designed experiments to find optimal thermostable nanogel systems that meet the requirements for use in high temperature oilfield reservoirs. The Response Surface Method is used to build second-order regression functions that correlate statistically gel strength and gelation time with the experimental parameters, like clay concentration and crosslinker concentration. Via in situ intercalative free-radical copolymerization, nanogels have been prepared from acrylamido-2-methylpropane sulfonic acid (AMPS), acrylamide (AM) (weight ratio of which in nanogel systems equals to 1:1) and montmorillonite-alkyl ammonium clay. The mixture of Hexamethylenetetramine (HMTA)/Phenyl acetate (PhAc) was used as a crosslinking system. The Lagrange multiplier method is used to optimise the resulting statistical model and to determine the maximum value of gel strength with the constraint of gelation time for practical applications. After a gelation time of 10.8 hours and storage for 32 days at 150°C the gel strength can reach up to 96%. The optimal nanogel has a clay concentration of 0.55% and a HMTA/PhAc mixture concentration of 0.80%. The characteristics of these nanogel systems meet the requirements for the use as water isolating materials in the White Tiger basement reservoir and provide a good basis for the further design of similar gels.

1. Introduction

In our recent works [1, 2, 3, 4, 5], several thermostable polymer nanogel systems were designed for water shut-off in the harsh conditions (high temperature, granite fractured stone-collector ...) which can be found in the production wells of the White Tiger basement reservoir. However, there were some limitations of the existing polymer such as degradation (thermal, mechanical, shear...) and polymer rheology. In order to overcome these weaknesses, this study was conducted to select the optimal nanogel systems based on AMPS-AM copolymer-clay using a statistical model by employing the Response Surface method and optimizing this model by using the Lagrange multiplier method.

2. Experimental

2.1. Chemicals

- Nanofil 757 (Montmorillonite sodium clay), a commercial chemical from Sub-Chimie-Germany;
- Acrylamide monomer (AM) 99%, Aldrich;
- Acrylamido-2-methylpropane sulfonic acid (AMPS) 98%, Lubrizol;
- Potassium peroxydisulfate 99.5%, China;
- Hexamethylenetetramine (HMTA) 99%, Aldrich;
- Phenylacetate (PhAc) 99%, Aldrich;
- Acetic acid 99%, China.

2.2. Apparatus and Equipments

- Glass vials (Thick wall glass pressure tubes employing a thread of a Teflon cap with an O-ring seals were used. These tubes are available from ACE GLASS – Catalog. N° 8648-04-USA).
- Oven Shellox (USA)
- The test equipment for medium nitrogen pressure made by the Fine Mechanical Workshop-Institute of Applied Mechanics-VAST
- Scanning Electronic Microscopy JSM-5500 (Japan)
- Digital Programmable Water Bath Brookfield TC-100 (USA).

3. Results and Discussion

3.1. Nanopolymer Synthesis

The nanopolymer was synthesized by standard *in-situ* polymerization techniques. The strategy of the synthesis is described in Fig. 1. First, separated clay ($<2\mu\text{m}$) was swollen in the mixture solution of AM and AMPS monomers by strong dispersion with magnetic stir in a 1000 ml glass beaker [6]. Second, the initiator

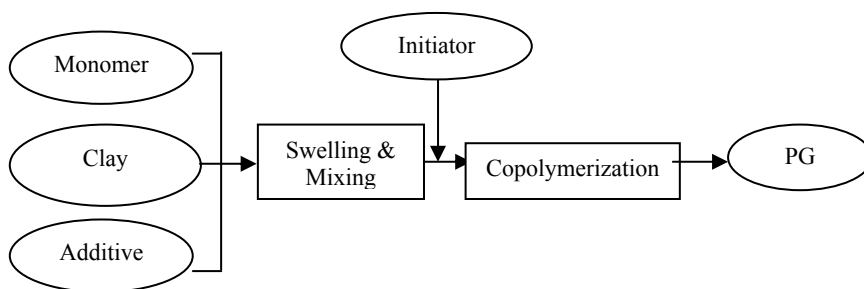


Fig. 1. Synthesis of preformed gel (PG)

(Potassium peroxydisulfate, $K_2S_2O_8$) and NH_4Cl were added into a composition of 4.0% AM + 4.0% AMPS + 0.3% $K_2S_2O_8$ + 1.0% NH_4Cl + 0.3–1% clay + deionized water. The reaction was initiated by heating the solution to 60°C. The polymerisation mechanism is strongly exothermic and self accelerating yielding large amounts of ammonia. The reaction is finished in half an hour and followed by aging at room temperature. Analyzing the final product by TEM technique illustrated in Fig. 2 shows that the clay is well-dispersed within the polymer matrix.



Fig. 2. TEM picture of nanopolymer

3.2. Polymer Gelation

In bottle tests, gel samples including nanopolymer, crosslinkers and additives were aged at desired temperatures in a laboratory oven at 150°C for 32. For sample screening under nitrogen pressure, the 15 ml thermostable test tubes were filled with 5 ml gelant and then put in small stainless-steel containers with tightly fitting O-ring screw caps. The valve of the cap was connected to a balloon filled with nitrogen. A small amount of water was added into these containers to create the thermal transparent medium. The Nitrogen pressure was kept at 7 atm in the containers to avoid boiling of both water and gelant. The temperature was increased from 35°C to 140°C and then to 150°C with a rate of 1°C/2 min. The samples were taken out every hour during the first days, daily during the first week and weekly during the first month for analysis. After cooling down and releasing of the nitrogen pressure, the tubes were opened and the gelling rate was recorded according to Marathon code [7]. The last sample was evaluated after storage at 150°C for 32 days. The appearances of the gel samples are shown in Fig. 3. They were rigid and yellow. Perhaps “ringing gels” with strong and excellent elongation recovery like rubber have been formed. The morphological investigation of these gels by the SEM technique is shown in Fig. 4. In the SEM images, the 3-dimensional network structure of these gels is clearly visible.

The crosslinkers used in this study were HMTA and PhAc as a replacement of Phenol and Formaldehyde. These crosslinkers have multi-functional groups, which can build a complex three dimensional network with $-CONH-$ bridges during the gelation process [8]. They provide a slow gelation even at high temperature and produce rigid, stable gels. The crosslinker concentration is critical for the structure and properties of the gel. The resulting gels are stronger with increasing crosslinker concentration due to the formation of a denser network.

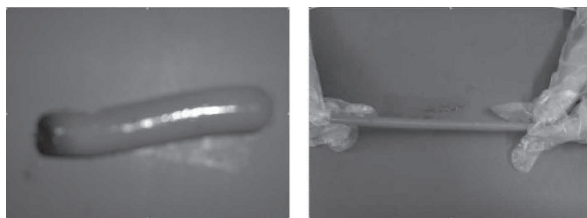


Fig. 3. Appearance of nanogels after thermal aging

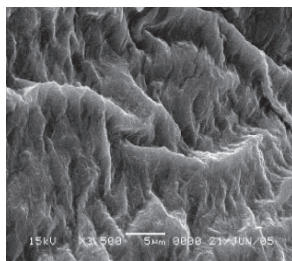


Fig. 4. SEM picture of nanogel after aging 150°C (32 days).

In previous works [4, 5], we have investigated the effect of the crosslinkers (HMTA and PhAc) on gelation time and gel strength. We found that the most suitable HMTA/Phenylacetate ratio for crosslinking reaction was about 2/5. In this study a series of experiments are performed and analyzed statistically to find the optimal nanogel systems.

3.3. Optimisation of Gelation Process

Optimization and control of gelation processes require a strong knowledge of the correlation between experimental variables and the properties of the resulting copolymer. Statistical analysis of the experimental data was done by home written software which was implemented in the computer language Pascal. The measured response functions are gelatin time and gel strength. Gelatin time is defined as the time needed for the gel forming solution to reach gel strength level *G* according to the Marathon code. Gel strength depends on two factors: water content separated from the gel system and the hardness of the gel [7].

Based on some screening tests of the nanogel system, the experimental variables were chosen to design the experiments of gelation process using the Box – Hunter method to find out the optimal conditions for gelling systems. In these experiments the clay concentration (Z1) was varied from 0.3% to 1%, the HMTA concentration was varied from 0.1% to 0.3% and the PhAc concentration was varied from 0.25% to 0.75% (HMTA/PhAc ratio was always set to 2:5). Variables that were assumed to remain constant included the aging process from 30°C to 140°C (with a temperature rate of 5°C/10 minutes and storage at 150°C for 30 days).

The experimental variables Z_i were converted into variables X_i following the equation:

$$X_i = \frac{Z_i - Z_i^0}{\Delta Z_i}$$

The exponential regressive equation (according to Box and Hunter)

$$Y = b_0 + b_1X_1 + b_2X_2 + \dots + b_nX_n + b_{12}X_1X_2 + \dots + b_{n1,n}X_{n1,n} + b_{11}X_1^2 + \dots + b_{nn}X_{nn}^2 \quad (1)$$

is estimated by standard exponential regressive methods. The parameter b_0 is defined as

$$b_0 = a_1 \sum_{j=1}^N Y_j - a_2 \sum_{i=1}^k \sum_{j=1}^N X_{ij}^2 Y_j; \quad b_i = a_3 \sum_{j=1}^N X_{ij} Y_j; \quad b_{ii'} = a_4 \sum_{j=1}^N X_{ij} Y_j;$$

$$b_{ii} = a_5 \sum_{j=1}^N X_{ij}^2 Y_j + a_6 \sum_{i=1}^k \sum_{j=1}^N X_{ij}^2 Y_j - a_7 \sum_{j=1}^N Y_j$$

The regression was done using the experimental data shown in Table 1, yielding the following results:

(a) Gelation time:

With $b_0 = 12.05$; $b_1 = -1.24$; $b_2 = -1.23$; $b_3 = -0.82$; $b_{12} = 0.02$; $b_{13} = 0.02$; $b_{23} = -0.02$; $b_{11} = -0.39$; $b_{22} = 0.35$; $b_{33} = -0.16$ in which the coefficients b_{12} , b_{13} , b_{23} are nonsense.

Optimal equation in the X coordinate system:

$$\hat{Y}_1 = 12.053 - 1.239X_1 - 1.234X_2 - 0.816X_3 - 0.39X_1^2 + 0.352X_2^2 - 0.16X_3^2 \quad (2)$$

Optimal equation in the Z coordinate system:

$$\hat{Y}_1 = 12.022 + 26.61Z_1 - 39Z_1^2 - 26.42Z_2 + 35.2Z_2^2 + 9.44Z_3 - 16Z_3^2 \quad (3)$$

(b) Gel strength:

With $b_0 = 95.22$; $b_1 = 2.38$; $b_2 = 1.71$; $b_3 = 1.42$; $b_{12} = -0.13$; $b_{13} = -0.13$; $b_{23} = -0.13$; $b_{11} = -2.26$; $b_{22} = -2.79$; $b_{33} = -4.21$ in which the coefficients b_{12} , b_{23} , b_{13} are nonsense.

Optimal equation in the X co-ordinate system:

$$\hat{Y}_2 = 95.222 + 2.376X_1 + 1.714X_2 + 1.421X_3 - 2.264X_1^2 - 2.794X_2^2 - 4.209X_3^2 \quad (4)$$

Optimal equation in the Z coordinate system:

$$\hat{Y}_2 = -123 + 250.16Z_1 - 226.4Z_1^2 + 128.9Z_2 - 279.4Z_2^2 + 477.2Z_3 - 420.9Z_3^2 \quad (5)$$

The response surfaces of gel strength and gelation time were illustrated in Fig. 5 and Fig. 6.

Table 1. Code matrix of gelation process using the Box- Hunter method

[illegible]

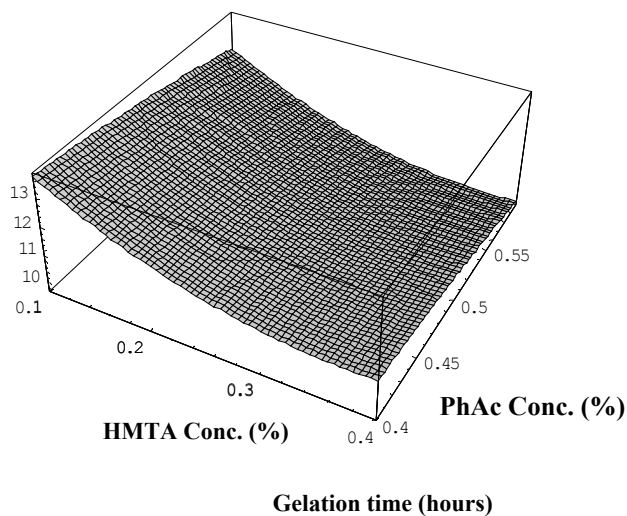


Fig. 5. Response surface of gelation time as a function of HMTA and PhAc concentration

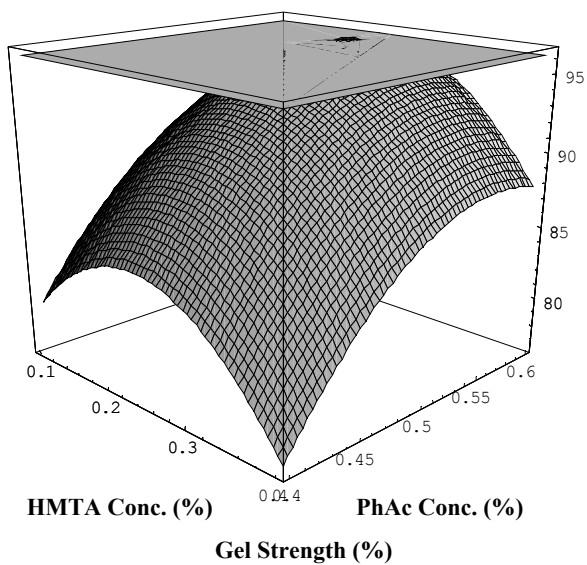


Fig. 6. Response surface of gel strength as a function of HMTA and PhAc concentration

3.4. Application of the Lagrange Multiplier Method to Determine the Optimal Gel System

A nanogel system which can be applied in oilfield treatments must meet two requirements: (a) the formed nanogel must be stable at reservoir conditions for a long time; (b) the gelation time must be long enough to allow gelant injection into the reservoir (from 10 to 13 hours according to the White Tiger basement reservoir characteristics and Vietsopetro company's technical requirements [9, 10]). Therefore we want to find out the maximum gel strength with the gelation time as a constraint using the Lagrange multiplier method. According to the Kuhn – Tucker theory [11], the maximum value of a function $y = f(X) = f(X_1, X_2, \dots, X_n)$ constrained by the functions $g_i(X) = b_i$ ($i = 1, \dots, M$) can be found using the following Lagrangian function:

$$L(X, \lambda) = f(X) + \sum \lambda_i (g_i(X) - b_i)$$

in which, λ_i are the Lagrange multipliers.

The maximal values of $f(X)$ under the conditions mentioned above are found by solving the following equation system:

$$\frac{\partial L}{\partial X_j} = 0 \quad \text{for all } j$$

$$\frac{\partial L}{\partial \lambda_i} = 0 \quad \text{for all } i$$

For our problem, the optimal equations of gelation time and gel strength are given by:

$$\text{Gelation time: } \hat{Y}_1 = 12.053 - 1.239X_1 - 1.234X_2 - 0.816X_3 - 0.39X_1^2 + 0.352X_2^2 - 0.16X_3^2$$

$$\text{Gel strength: } \hat{Y}_2 = 95.222 + 2.376X_1 + 1.714X_2 + 1.421X_3 - 2.264X_1^2 - 2.794X_2^2 - 4.209X_3^2$$

The Lagrangian function is

$$L(X, \lambda) = \hat{Y}_1 + \lambda (\hat{Y}_2 - b)$$

or

$$L(X, \lambda) = 95.222 + 1.2.376X_1 + 1.714X_2 + 1.421X_3 - 2.264X_1^2 - 2.794X_2^2 - 4.209X_3^2 + \lambda(12.053 - 1.239X_1 - 1.234X_2 - 0.816X_3 - 0.39X_1^2 + 0.352X_2^2 - 0.16X_3^2 - b) \quad (6)$$

In this equation λ is the Lagrange multiplier and b the gelation time.

To find out the maximum gel strength the equations are solved as follows:

$$\frac{\partial L}{\partial X_1} = -2.376 - 4.528X_1 + \lambda(-1.239 - 0.78X_1) = 0 \quad (7)$$

$$\frac{\partial L}{\partial X_2} = 1.714 - 5.588X_2 + \lambda(-1.234 + 0.704X_2) = 0 \quad (8)$$

$$\frac{\partial L}{\partial X_3} = 1.421 - 8.418X_3 + \lambda(-0.816 - 0.32X_3) = 0 \quad (9)$$

$$\frac{\partial L}{\partial \lambda} = 12.053 - 1.239X_1 - 1.234X_2 - 0.816X_3 - 0.39X_1^2 + 0.352X_2^2 - 0.16X_3^2 - b = 0 \quad (10)$$

The equation system above was solved numerical on a computer with constraints of $X \in [-1, 1]$ and $b \in [10, 13]$. The results are shown in Table 2. After a gelation time of 10.8 hours and storage of the gel for 32 days at 150°C the gel strength reaches 96% with a composition of 0.55 % clay, 0.23 % HMTA and 0.57 % PhAc.

Table 2. The calculation results through Lagrange method

X_1	X_2	X_3	Z_1 (%)	Z_2 (%)	Z_3 (%)	Gelation time (Hours)	Gel Strength (%)
0.52	0.31	0.17	0.55	0.23	0.57	10.8	96.2

4. Conclusion

The optimal conditions of gelation time and gel strength by combining two response functions to form a desired function via Lagrange multipliers were determined. Using this function, the optimal composition of a gel system which has gelation time and gel strength suitable for application in high temperature oilfield reservoirs like the White Tiger reservoirs, was determined. This method proofed to be useful to optimize and control gelation time and gel strength in a way that satisfies the technical requirements of oil producing companies.

Acknowledgments

This work was supported by the National Research & Development program DTNN KC.02/06–10; the VAST marine and marine construction R & D program.

References

1. Nguyen Phuong Tung et al., *Research of Polyacrylamide Gel Application for Water Shut off in High Temperature Reservoir*, SPE 72120, The Improved Oil Conference, Kuala Lumpur, Malaysia, October 8th–9th, 2001.
2. Nguyen Phuong Tung et al., *Design Polymer Gel Systems to Use for Water Shut off In Production Wells Of The White Tiger Basement Reservoir*, Proceeding of the 30th PetroVietnam Anniversary Conference, Vol.1, 2005.
3. Nguyen Phuong Tung et al., *Design of Polyacrylamide Based Nanogel Systems Used for Improved Recovery in High Temperature Reservoir*, Proceeding of the 12th Regional Symposium on Chemical Engineering (RSCE), pp. 207-212, Ha Noi, Vietnam, 2005.
4. Nguyen Phuong Tung et al., *Design of the Thermostable Nanogel Systems for Using in The White Tiger Basement Reservoir to Increase Crude Oil Production Effectiveness*, Proceeding of the 1st IWOFFM – 3rd IWONN Conferences, Halong, Vietnam, 2006.
5. Nguyen Phuong Tung et al., *Optimization of gel system for high temperature reservoir application*, Proceeding of the 12th Regional Symposium on Chemical Engineering (RSCE), pp. 69-73, Ha Noi, Vietnam, 2005.
6. Baojun Bai, et al., *Preformed Particle Gel for Conformance Control: Transport through Porous Media and IOR Mechanisms*, SPE 89468, The Symposium on Improved Oil Recovery held in Tulsa, Oklahoma, U.S.A 17th–21st April, 2004.
7. Sydansk, R.D. and Southwell, G. P., *More than 12 years' experience with a successful conformance-control polymer-gel technology*, SPE:66558, SPE Production and Facilities, November 2000.270-278
8. Dovan, H.T, et al., *Delaying Gelation of Aqueous Polymers at Elevated Temperatures Using Novel Organic Crosslinkers*, SPE 37246, the International Symposium on Oilfield Chemistry, Houston, Texas, February 18–21, 1997.
9. Tran Hong Phong, *Problem of Water Isolation in Production Wells at The White Tiger Basement Reservoirs*, Symposium of Improved Oil Recovery, Vung Tau, Viet Nam, September, 2002, in Vietnamese.
10. Technical Requirements for the Contractor of the R&D and Industrial Testing Project (2002), Vietsovetro.
11. J.C. Miller, Wygggeston and Queen Elizabeth 1 College, Leicester, *Statistics for Analytical Chemistry*, Third Edition.

Discovery of Nanotubes in Ancient Damascus Steel

Marianne Reibold^{1*}, Peter Paufler¹, Aleksandr A. Levin¹, Werner Kochmann², Nora Pätzke¹, and Dirk C. Meyer¹

¹ Institut f. Strukturphysik, *Triebenberg Lab., FR Physik, Technische Universität Dresden, D-01062 Dresden, Germany

E-mail: paufler@physik.tu-dresden.de

² Krüllsstr. 4b, D-06766 Wolfen, Germany

Abstract. Using high-resolution electron microscopy, we have found in a sample of Damascus sabres from the 17th century both cementite nanowires and carbon nanotubes. These might be the missing link between the banding and ancient recipes to make that ultrahigh carbon steel. The sample considered belonged to the wootz-type of Damascus steel which is fundamentally different from welded Damast. The nanotubes have only been revealed after dissolution of the sample in hydrochloric acid. Some remnants showed not yet completely dissolved cementite nanowires, suggesting that these wires were encapsulated by carbon nanotubes. Only recently, considerable progress has been achieved in reproducing the process of making the characteristic pattern of wootz. We propose a connection between impurity segregation, nanotube formation, nanotube filling with cementite, cementite wire growth, and formation of large cementite particles. Needless to say that the presence of a nanostructure will have an impact upon the mechanical properties.

1. Introduction

Damascus blades featured two qualities not found in European steels at that time: an attractive wavy-like banding, known today as Damast, an extremely sharp edge (according to the legend a sword could slice through a silk handkerchief floating in the air) (cf., e.g., [1-4]). When talking about the damast pattern three kinds of technologies have to be distinguished carefully: (i) false damast, (ii) artificial or welded, (iii) genuine or wootz-based. False damast (i) is made by a treatment of the surface region of a steel blade only (for example by etching or scratching). It can easily be identified when looking at the cross section. Type (ii) is obtained when thin steel blades of different carbon content are welded by repeated forging and folding. This technology is widespread giving rise to spectacular patterns, the formation of which depends mainly on the flow of material during forging. In this sense it may be called artificial. In what follows we will restrict ourselves on the type (iii), whose Damast pattern appears after forging a cake-like piece of ultrahigh carbon crucible steel. The formation of the pattern depends on the formation of cementite (Fe_3C) particles of a certain size, shape and spatial distribution. It is just this process of formation, obviously representing a complex combination of plastic deformation, diffusion and phase transitions, that still needs further exploration.

How was genuine Damascus steel done ? It is generally agreed that those ingots of crucible steel were made in ancient India ('wootz') and Central Asia ('bulad'), then sold to the Near East and to Europe for forging. Details of the blade production were kept secret. At the end of the 18th century the ability to produce this type of steel got lost. Numerous attempts have been made since that time to reproduce this quality. Thanks modern methods of analysis, progress has been achieved on a trial-and-error basis [5–6]. The processes behind pattern formation at nanoscale, however, are still subject of controversy.

2. Experimental Methods

Our analytical methods have been applied to samples of genuine Damascus sabres. We were lucky to get them from the Berne Historical Museum. There are a few earlier reports dealing with samples of the identical sabres [7–10]. They are documented as product of the famous blacksmith Assad Ullah (17th Century) [7, 11].

We have collected data for phase analysis using optical microscopy, high resolution transmission electron microscopy (HRTEM; Philips CM200FEG) and X-ray diffraction. Furthermore, elemental analysis with the aid of optical spectrometry and electron beam microanalysis as well as nanohardness measurements have been performed. For details of our methods and the results we refer to [12–16]. Though several metallographic studies of this material have been published by other authors, no HRTEM has been applied to historic specimens.

3. Results and Discussion

Focussing on the results of HRTEM, apart from the presence of microscopic particles of cementite already known from the early works of [17], a pronounced structuring of the material at nanoscale has been observed. One component of this

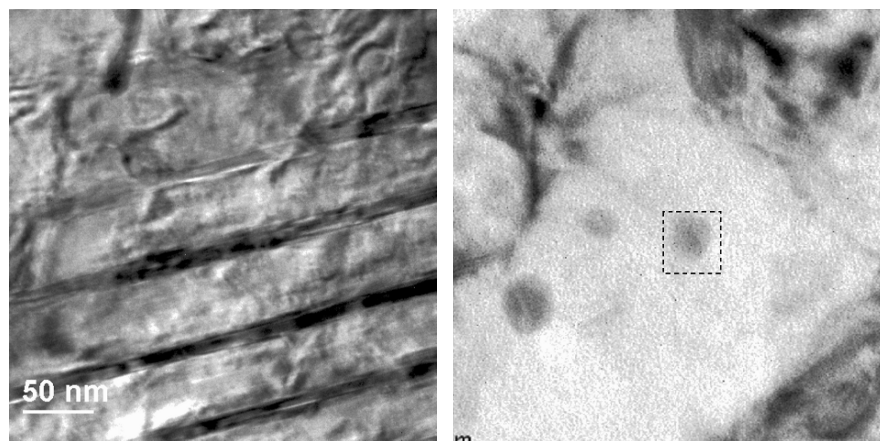


Fig. 1. TEM image of cementite nanowires in a Damascus sabre. Left panel: The dark stripes indicate wires of several hundreds nanometers in length. Right panel: View showing an almost circular cross section (dotted)

is the appearance of wire-like objects of cementite structure (Figs. 1–4). They are locally ordered in colonies of parallel wires, changing orientation in neighboured regions. Their spacing is of the order of 100nm. From earlier work on conventional steels cementite plates or laths have become known already, however, on a much larger microscopic scale. The spacing of lattice planes in high-resolution mode has been used to identify the structure (see, e.g., Fig. 2).

The mechanical effect of wire-like obstacles may be anticipated from Fig. 4, where dislocations are tangled between them.

To check a previous proposal made by Kochmann (cf. [13]) presuming carbon nanotubes in this Damascus steel, a small remnant (ca. $2 \times 3 \times 4$ mm) of the sample, also investigated by [12–14], was dissolved completely in HCl (20%) for one week in a glass evaporating dish. Unlike iron and iron carbide, carbon should

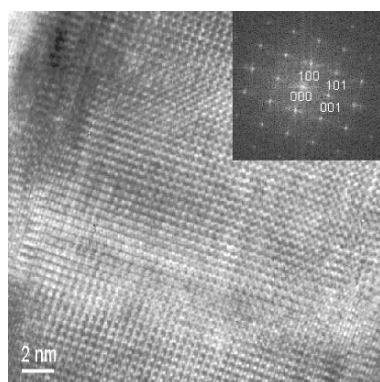


Fig. 2. Nanowire of Fig. 1 in high-resolution mode
Inset : Fourier transform. Reflections ($d = 0.4434$ nm, 0.3342 nm and 0.4900 nm) are indexed as Fe_3C 001, 101 and 100, respectively

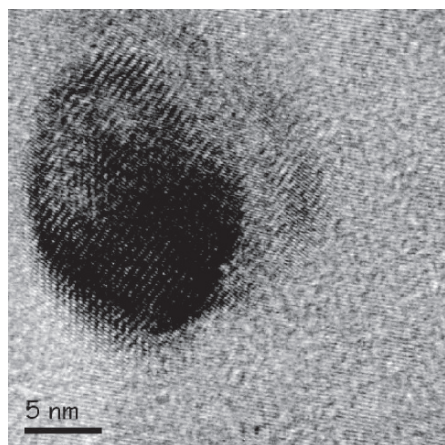


Fig. 3. Same as Fig. 2 for cross section of a cementite nanowire piercing the image plane

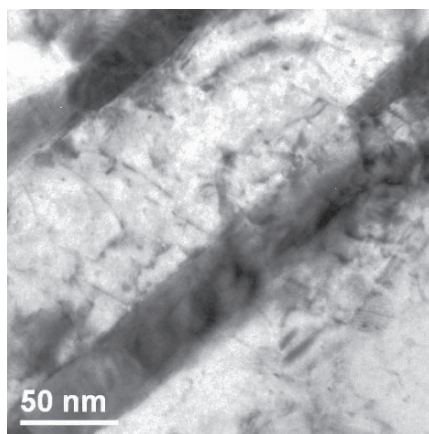


Fig. 4. Dislocation lines tangled at nanowires in a sample prior to annealing. Two samples are marked by arrows. No. 1 shows a straight section between the wires and No. 2 is bent around a wire

be retained. With the aid of a copper grid covered by an amorphous carbon layer the remnants were picked up from the acid and investigated by HRTEM (Figs. 5–7). This experiment has been repeated about one year later dissolving a second sample. Cylindrical remnants found this way were of two types: (i) straight (Fig. 5) and bent (Fig. 6) homogeneous particles and (ii) embedded particles (Fig. 7). Determination of the lattice spacings and consideration of the chemical processing let us conclude that the particles found are carbon nanotubes occasionally filled with cementite. This mode of nanostructuring is also suggested looking at Fig. 8, which was obtained from our most recent sample not yet dissolved in HCl. The formation of carbon nanotubes and nanowires in steel

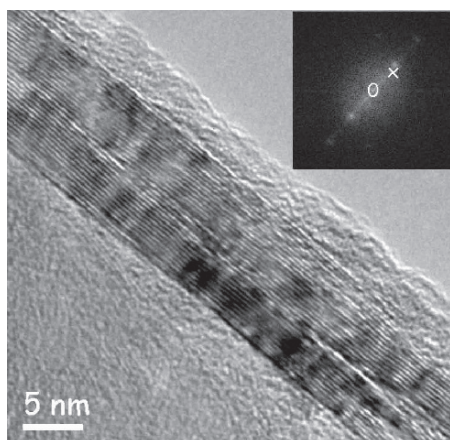


Fig. 5. Straight homogeneous remnant with a fringe spacing of 0.342 nm, which is characteristic of carbon nanotubes, in this case multiwalled

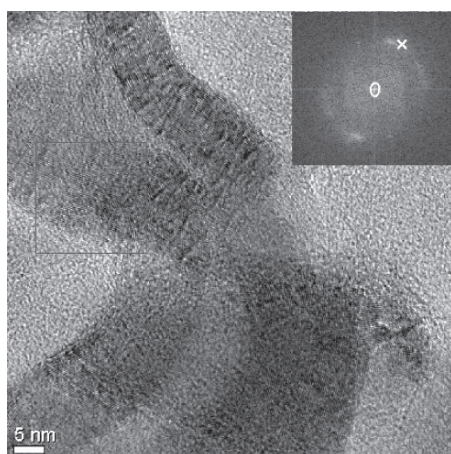


Fig. 6. Bent homogeneous remnants with a fringe spacing of 0.349 nm, which is characteristic of carbon nanotubes

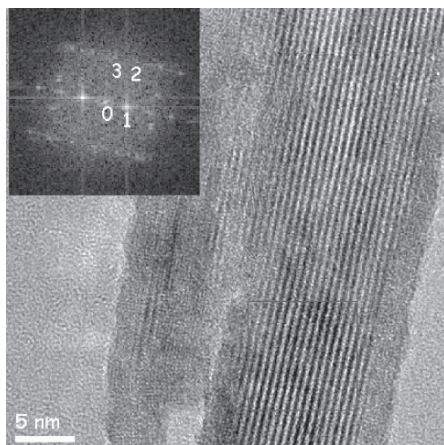


Fig. 7. Embedded remnant with a fringe spacing of 0.63 nm, which is characteristic of cementite. It is embedded in an almost structureless surrounding, which prevented dissolution

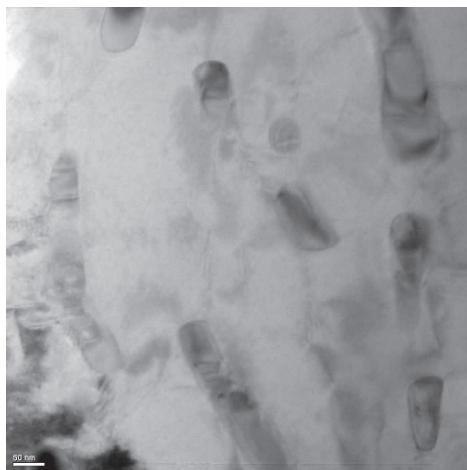


Fig. 8. Wire-like particles consisting of an outer wall partly filled with a dense material. TEM image of a preliminary study of sabre No. 9 (according to Zschokke [7]) showing similar nanostructuring like sabre No. 10

during a thermomechanical treatment has not yet been observed. Taking ancient recipes of wootz-technology into account, we have speculated that organic additions with the aid of metallic catalysts might have given rise to this carbon nanotube formation [15, 19]. Recent results of wood research (group of Barry Goodell) seem to support this route[18].

4. Conclusions

The nanostructure of an ancient steel sample opens a new view upon the formation of the Damast pattern. The formation of carbon nanotubes could be a missing link between the role of impurities and the existence of cementite particles. Moreover,

the effect on the special mechanical properties of Damascus steel deserves further investigation.

Acknowledgements

Authors thank the Historical Museum Berne for supply of the samples and Ms. Heide Müller for help with the TEM-preparation.

References

1. J. Piaskowski, *O stali damascenskiej*. Wroclaw 1974.
2. J. Wadsworth and O.D.Sherby, *Progr. Mater. Sci.* **25**, 35,1980
3. J.D. Verhoeven, *Scientific American* **284**(1), 74,2001
4. A. Feuerbach, *JOM* **58**(5),48, 2006
5. J.D. Verhoeven, *Steel research* **73**, 356, 2002
6. J. Wadsworth, *MRS Bulletin* **27**, 980, 2002
7. B. Zschokke, *Rev. de Métallurgie* **21**, 635,1924
8. J. Piaskowski, *J.Hist.Arabic Sci.* **2**, 3, 1978
9. J.D. Verhoeven, and L.L. Jones, *Metallogra phy* **20**, 153,1987
10. J.D. Verhoeven, A.H. Pendray, and W.E. Dauksch, *JOM* **50**, 58, 1998
11. R. Zeller, *Jahrbuch des Bernischen Historischen Museums* **4**, 24, 1924
12. A.A. Levin; D.C. Meyer, M. Reibold, W. Kochmann, N. Pätzke, and P. Paufler, *Cryst. Res.Technol.* **40**, 905, 2005
13. W. Kochmann, M. Reibold, R. Goldberg, W. Hauffe, A.A. Levin, D.C. Meyer, T. Stephan, H. Müller, A. Belger, and P. Paufler, *J.Alloys & Comp.* **372**, L15, 2004
14. M. Reibold, A.A. Levin, D.C. Meyer, P. Paufler, and W. Kochmann, *Intl. J. of Materials Research* **97**, 1172, 2006
15. M. Reibold, P. Paufler, A.A. Levin, W. Kochmann, N. Pätzke, and D.C. Meyer, *Nature* **444**, 286, 2006
16. W. Kochmann, P. Paufler, M. Reibold, A.A. Levin, and D.C. Meyer, *Sitzungsber. Leibniz-Sozietät* **85**, 109, 2006
17. N. Belaiew, *J. Iron Steel Inst.* **97**, 417, 1918; **104**, 181,1921
18. <http://woodscience.umaine.edu/goodell/nanotubes.html>
19. L.A. Chernozatonskii, V.P. Val'chuk, N.A. Kiselev, O.I. Lebedev, A.B. Ormont, and D.N. Zakharov, *Carbon* **35**, 749, 1997

Materials Research with Energetic Heavy Ions at GSI

Reinhard Neumann

Gesellschaft für Schwerionenforschung (GSI), Planckstraße 1,
64291 Darmstadt, Germany

Abstract. Materials research at the Gesellschaft für Schwerionenforschung (GSI) in Darmstadt, Germany, employs the energetic heavy-ion beams from the large accelerators operated by GSI, and encompasses a broad spectrum of basic and applied aspects. This article gives an overview of the main topics and illustrates them with some recent results. Phase transitions have been stimulated in graphite and zircon by simultaneous exposure to high pressure and heavy ions. The damage trails caused by energetic heavy ions along their trajectories in materials such as organic polymers and mica are transformed by chemical etching into channels with diameters down to the nanometer scale. These pores can serve as model systems for biological ion channels and, furthermore, represent promising devices for biosensor applications. Metal and semimetal nanowires have been created by filling etched ion tracks in polymer foils, related studies focusing on electrical, optical, and thermal properties of single nanowires. The heavy-ion microprobe is able to target a sample with a single ion including uranium, having specific kinetic energies up to 12 MeV/amu, with a precision of about 1 μm . Single-ion irradiation of individual cell nuclei in a cell culture is one of the objectives under investigation.

1. Introduction

GSI, a member of the *Hermann von Helmholtz Association of German Research Centers*, operates several accelerators for heavy ions, namely the HLI high-charge injector, the UNILAC linear accelerator, and the SIS heavy-ion synchrotron. These facilities generate ion beams of all elements, in the case of the SIS even in all charge states up to bare uranium nuclei. The kinetic energies amount to 1.4 MeV/amu at the HLI, 4 to 12 MeV/amu at the UNILAC, and approx. 50 MeV/amu to 1 GeV/amu (for light elements up to 2 GeV/amu) at the SIS. The GSI Materials Research Department utilizes the available ion species and kinetic energies to perform irradiations of a variety of materials and to pursue a wide spectrum of aims. This brief overview addresses a few examples representing the main topics being performed in cooperation with numerous German and foreign partners [1].

A broad field is dedicated to basic research and concerns heavy-ion induced alterations in solids such as lattice defects or phase transitions, for example influenced by simultaneous exertion of high pressure or by low sample temperature. Thus, for the first time, solid samples being exposed to a high pressure in a diamond anvil cell were irradiated with relativistic heavy ions which propagated through several mm of diamond to reach the sample.

Other activities encompass aspects both of basic and applied research. Heavy ions with high kinetic energy generate long, absolutely straight damage trails, so-called latent tracks, along their trajectories. These tracks can be transformed, by means of chemical etching, into narrow channels with diameters down to the nanometer scale. By irradiation of a polymer foil with only a single ion, one obtains a single-pore membrane, particularly suitable to study the flow of electrolytic ion current and the translocation of objects such as biological molecules.

Filling a material into these channels makes it possible to produce, depending on the deposition parameters, poly- or single-crystalline nanowires. Among the wire characteristics investigated are electrical resistance and thermal instability, but also quantum effects caused by the restricted geometry.

A heavy-ion microprobe operated with the UNILAC beam is employed for irradiation sensitivity tests of objects such as microelectronic circuits or biological cells. This probe is able to place single heavy ions, including uranium, having energies of up to 12 MeV/amu, with a precision of the order of one micrometer. This allows, for example, the irradiation of individual cells in a cell culture with single ions.

2. Research Activities

2.1. Heavy-ion Induced Material Alterations

Energetic heavy ions passing through a solid deposit their kinetic energy in small fractions almost exclusively via interaction with the electrons of the target. This very rapid energy transfer stimulates fast processes, in many materials causing damage trails along the ion trajectories. There occurs a broad range of alterations from point defects to complete amorphization.

GSI Materials Research applies a variety of tools and methods in order to meet the conditions suitable for specific experiments and to characterize samples prior and subsequent to irradiation with ions. Thus, a helium decompression cryostat has been installed in the beamline of the UNILAC irradiation site, allowing ion exposure at fixed sample temperatures from 5 K up to room temperature. Before and after irradiation, the samples can be studied in situ by means of an optical spectrometer [2].

When impinging on the surface of a solid, an ion creates in many cases a tiny damage at the impact site which can be analyzed efficiently only by high-resolution microscopy. Figure 1 displays micrographs of tracks on the surface of highly oriented pyrolytic graphite (HOPG) acquired with a scanning tunneling microscope [3]. The surface had been irradiated by uranium ions under crazing incidence. On their way into the bulk, the projectiles lifted up some of the surface material, causing a bulge that diminishes with increasing penetration depth.

A series of experiments has been started recently using relativistic heavy ions from the SIS heavy ion synchrotron [4]. In these studies, a solid sample is mounted in a diamond anvil cell and simultaneously exposed to high pressure and energetic heavy ions. This arrangement is illustrated schematically in Fig. 2, taken

from [4]. The ions exit the SIS beam line through a thin metal window, travel about half a meter through ambient air and then traverse the front diamond and the pressurized sample.

One of the first materials to be investigated was HOPG. Transmission electron microscopy images of the sample after the ion exposure did not show, in contrast to ion irradiation without external pressure, any individual tracks but exhibited complete amorphization and partial recrystallization of randomly oriented graphite bands. This result was very surprising also due to the fact that the fluence of 1×10^{11} ions/cm² had been sufficiently low to be far from the situation of track overlapping.

Further exciting findings concern the mineral zircon, ZrSiO_4 . The sample transformed to the high-pressure phase reidite at a pressure significantly lower than that necessary without ion bombardment. This phase transition was revealed by additional lines typical of reidite in the Raman spectrum. Figure 3 shows a section of the zircon spectrum recorded (a) before and (b) after ion irradiation, displaying bands of reidite in (b).

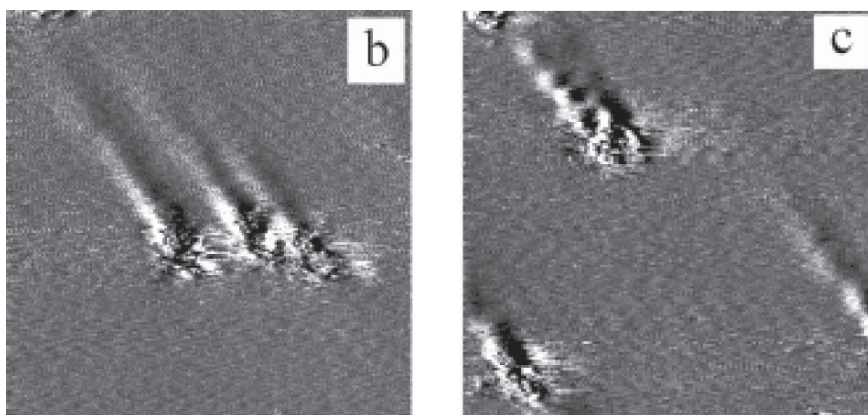


Fig. 1. Scanning tunneling microscopy images ($48 \text{ nm} \times 48 \text{ nm}$) of highly oriented pyrolytic graphite, irradiated with 2.64 GeV uranium ions under grazing incidence. The direction of ion propagation is from bottom right to top left (taken from [3]).

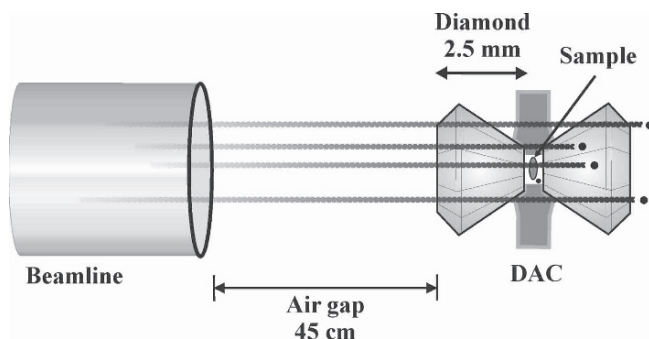


Fig. 2. Scheme for the exposure of a diamond anvil cell, containing a pressurized sample, to relativistic heavy ions from the GSI heavy-ion synchrotron [4].

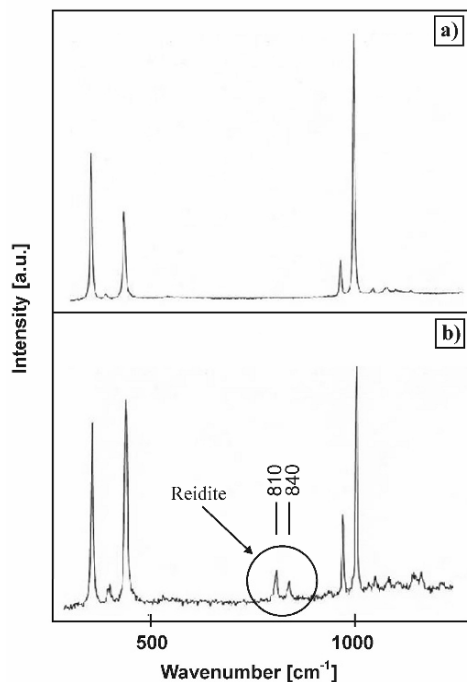


Fig. 3. A section of the Raman spectrum of pressurized zircon (a) prior and (b) subsequent to irradiation with 2×10^9 uranium ions/cm². The pressure amounted to 14.2 GPa. New bands of the high-pressure phase reidite at 810 and 840 cm⁻¹ occur in (b) [4]

2.2. Nanopores and Nanowires

In a number of radiation-sensitive materials such as organic polymers and mica, the ion-induced damage trails, also called latent tracks, are transformable by chemical etching into channels with diameters down to the nanometer scale. For this purpose, the foil containing latent tracks with a certain area density, in many cases preferably only a single track, is inserted in an electrolytical cell and serves as a diaphragm dividing the cell into two separated compartments. A schematic view of this experimental arrangement is depicted in Fig. 4. (from [5]). The left chamber is filled with an etchant, whereas the right one contains a stopping solution which is neutralizing the etching solution in the pore tip after breakthrough to keep the diameter as small as possible.

After removing the stopping solution, the size of the apertures at both sides of the pore can be increased in a controlled manner by continuing the etching process. The channel geometry, in particular cylindrical or conical with various opening angles, can be determined by choosing specific etching parameters with respect to the membrane material, such as etchant, pH value, temperature, and applied voltage.

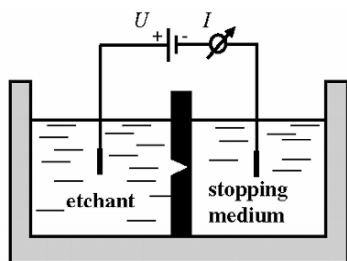


Fig. 4. Schematic view of an electrolytical cell [5]

Detailed studies have focused on the fabrication and analysis of membranes containing a single conical nanochannel [6]. These membranes are characterized by a pronounced permselectivity for ions in aqueous solutions. The selective transmission originates from charged ligands on the inner wall of the nanopore that interact electrostatically with ions traversing the channel, leading to rectifying current-voltage characteristics. The left diagram in Fig. 5 displays experimental current-vs.-voltage curves recorded with a single conical nanopore in a polyethylene terephthalate membrane. The radii of the small and large pore apertures amounted to 3 and 200 nm, respectively. The electrolyte was unbuffered KCl at pH 5.6, whose concentration was varied from 1 to 0.01 M. Theoretical modeling of these data provided satisfying agreement as illustrated in the right diagram of Fig. 5 (for details see [6]). These nanopores can serve as model systems for biological ion channels and, furthermore, represent promising devices for bio-sensor applications.

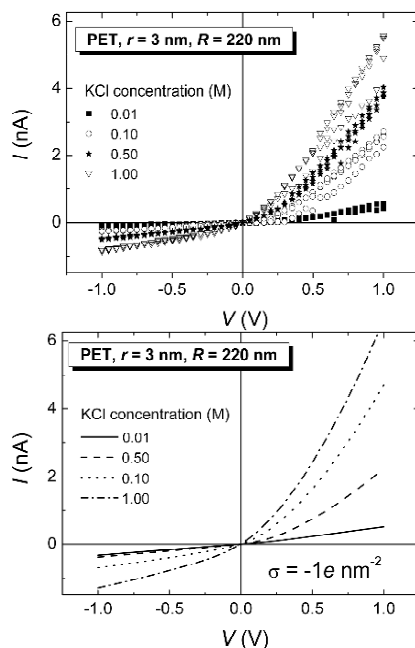


Fig. 5. Current-vs.-voltage curves for different parameters, (left) experiment and (right) theory [6]

Polymer membranes containing ion track-etched nanopores can also be used as templates for the controlled fabrication of poly- and single-crystalline nanowires. The group of materials employed so far at GSI comprises Cu, Au, Bi, Ni, Co, and Pt. For the purpose of wire fabrication, a membrane is first covered on one side with a thin gold layer, subsequently reinforced by a Cu layer, and then inserted in an electrolytical cell containing a suitable electrolyte. Nanowires are grown electrochemically inside the nanopores starting from the Au/Cu layer used as an electrode. Depending on the voltage and temperature at which the deposition takes place, the wires will be fine- or coarse-grained, or even single-crystalline.

Using 30- μm thick membranes, wires with lengths of the order of 30 μm and diameters down to 30 nm have been produced, these wires thus having an aspect ratio of 10^3 . The analysis of the crystallinity of a gold wire with diameter 40 nm by means of high-resolution transmission electron microscopy is illustrated in Fig. 6. The single-crystalline lattice becomes visible under high magnification and is confirmed via electron diffraction [7].

A major aspect of nanowire research concerns so-called finite-size and quantum-size effects [8, 9] expected when the geometrical wire dimensions approach the size of characteristic parameters such as the electron mean free path and the Fermi wavelength. Bismuth is particularly suitable since these parameters are remarkably large even at room temperature. Further favourable properties of Bi are the small effective electron mass and the very low charge carrier density. With decreasing Bi nanowire diameter, conduction band and valence band recede from each other, and the solid undergoes a transition from a semimetal to a semiconductor.

Single cylindrical Bi nanowires of different diameters were consecutively placed on an infrared (IR) transparent substrate and irradiated with monochromatic IR light from the ANKA synchrotron radiation source at Karlsruhe Research Center, Germany. When tuning the IR wavelength, the wires showed an

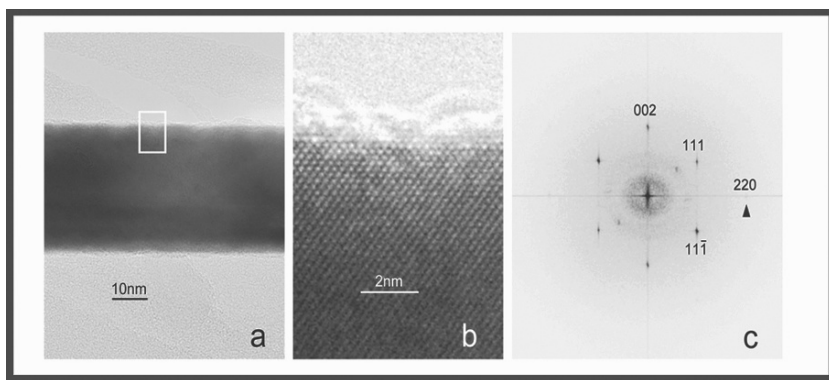


Fig. 6. Characterization of a single-crystalline gold nanowire: **(a)** Wire section imaged with high-resolution transmission electron microscopy at low magnification. **(b)** Framed area in **(a)** displayed with large magnification visualizing the gold lattice. **(c)** Electron diffraction pattern recorded from area **(b)** [7]

IR absorption edge which shifted to higher wavenumbers (i.e., to shorter wavelengths) as a function of decreasing wire diameter [9]. The absorption spectra of wires with diameters 400, 160, 120, 60, and 30 nm are depicted in Fig. 7. The absorption thresholds are estimated by extrapolating the edges by straight lines down to the points of intersection with the abscissa. This absorption behaviour is ascribed to interband transitions, and the blueshift is interpreted as a quantum-size effect originating from the diameter-dependent splittings and shifts of the energy bands.

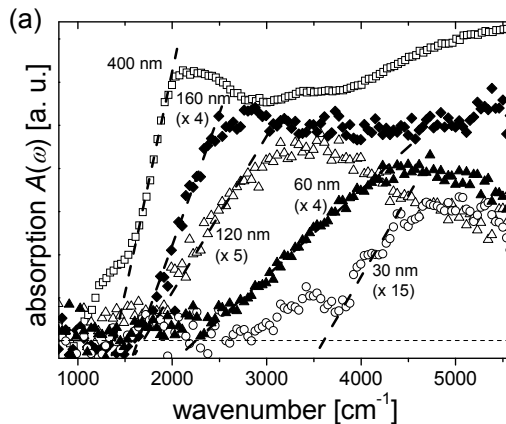


Fig. 7. Infrared absorption spectra of single Bi nanowires [9].

2.3. Heavy-ion Microprobe

As already briefly mentioned before, the GSI heavy-ion microprobe is capable of irradiating objects with single ions with an accuracy of about $1\ \mu\text{m}$. Therefore, it has been used frequently for mapping of radiation-sensitive sites in micro-electronic circuits with the aim of examining the reliability for space applications. A further very important activity concerns the irradiation of individual living cells with single ions [10, 11]. It is possible to automatically recognize and target an ensemble of about hundred cells within several seconds. The fate of the cells subsequent to ion exposure is followed by employing staining and fluorescence microscopy. In particular, the behaviour and development of cells that were hit and of those that were not hit by an ion can be tracked and compared for an extended time period. The precise targeting and damage visualization is optimally illustrated in Fig. 8, displaying a stained cell nucleus and its damage sites caused by ion irradiation [12].



Fig. 8. Confocal laser microscopy image of stained (red in original) nucleus of a human fibroblast cell (diameter $\sim 15\ \mu\text{m}$) irradiated with the GSI ion microprobe. Each area indicated by a circle was targeted by four He ions with kinetic energy $4.8\ \text{MeV/amu}$. The sites hit by ions were revealed by the cell reaction to the DNA damage via staining (yellow in original) a protein involved in damage repair (This picture was taken from the front page of [12]. Courtesy GSI and biophysics & materials research team).

3. Outlook

While the activities described in this article will be continued and further developed, materials research is facing additional major challenges, since GSI is presently strongly involved in a very large and ambitious project: the *Facility for Antiproton and Ion Research (FAIR)* [13]. Supported by more than a dozen countries and by numerous external research groups, GSI is working towards the construction of a heavy-ion double synchrotron, of collector, storage, and cooler rings, a fragment separator, and a variety of big caves with irradiation sites and experimental arrangements. The UNILAC and SIS will be employed as injectors for these future accelerators. The GSI biophysics and materials research groups have jointly elaborated the so-called BIOMAT project, focusing in both fields on experiments with high-energy and high-intensity ion beams. For this purpose, a dedicated experimental cave is planned, which will be shared also with atomic physics groups. The scientific goals of materials research within FAIR concentrate on the effects induced by heavy ions with kinetic energies up to $10\ \text{GeV/nucleon}$ when traversing a solid, and further on the simultaneous exposure of large solid samples (i.e. with centimeter dimensions rather than only of some $10\ \mu\text{m}$) to high pressure and ion irradiation (see [BIOMAT]).

Acknowledgements

The fruitful worldwide cooperations with numerous partners are gratefully acknowledged.

References

1. For the complete, continuously updated publication list of GSI Materials Research see www.gsi.de.
2. K. Schwartz, A.E. Volkov, K.-O. Voss, M.V. Sorokin, C. Trautmann, and R. Neumann, *Thermal spike effect on defect evolution in NaCl irradiated with light and heavy ions at 8 and 300 K*, Nucl. Instr. and Meth. **B 245**, 204, 2005.
3. J. Liu, R. Neumann, C. Trautmann, and C. Müller, *Graphite irradiated by swift heavy ions under grazing incidence*, Nucl. Instr. and Meth. **B 193**, 259, 2002.
4. U.A. Glasmacher, M. Lang, H. Keppler, F. Langenhorst, R. Neumann, D. Schardt, C. Trautmann, and G.A. Wagner, *Phase transitions in solids stimulated by simultaneous exposure to high pressure and relativistic heavy ions*, Phys. Rev. Lett. **96**, 195701, 2006.
5. Z. Siwy, P. Apel, D. Baur, D.D. Dobrev, Yu.E. Korchev, R. Neumann, R. Spohr, C. Trautmann, K.-O. Voss, *Properties of synthetic nanopores with transport properties analogous to biological channels*, Surf. Sci. **532-535**, 1061, 2003.
6. J. Cervera, B. Schiedt, R. Neumann, S. Mafé, and P. Ramírez, *Ionic conduction, rectification, and selectivity in single conical nanopores*, J. Chem. Phys. **124**, 104706, 2006.
7. S. Karim, M.E. Toimil-Molares, A.G. Balogh, W. Ensinger, T.W. Cornelius, E.U. Khan, and R. Neumann, *Morphological evolution of Au nanowires controlled by Rayleigh instability*, Nanotechnology **17**, 5954, 2006.
8. T.W. Cornelius, M.E. Toimil-Molares, R. Neumann, and S. Karim, *Finite-size effects in the electrical transport properties of single bismuth nanowires*, J. Appl. Phys. **100**, 114307, 2006.
9. T.W. Cornelius, M.E. Toimil-Molares, R. Neumann, G. Fahsold, R. Lovrincic A. Pucci, and S. Karim, *Quantum size effects manifest in infrared spectra of single bismuth nanowires*, Appl. Phys. Lett. **88**, 103114, 2006.
10. P. Barberet, M. Heiss, G. Du, B. E. Fischer, G. Taucher-Scholz, *The GSI heavy ion microbeam: A tool for the investigation of cellular response to high LET radiations*, Acta Physica Polonica A **109**, 329, 2006.
11. G. Du, B. Fischer, P. Barberet, M. Heiss, *A fast online hit verification method for the single ion hit system at GSI*, Radiation Protection Dosimetry doi:10.1093/rpd/ncl435, 2006.
12. GSI Scientific Report 2004 (GSI Report 2005-1, June 2005).
13. For a concise description of FAIR, see for example Nuclear Physics News **16**, No. 1, 2006.

Nanoantennas for Surface Enhanced Infrared Spectroscopy

F. Neubrech, M. Klevenz, F. Meng, and A. Pucci¹

¹Kirchhoff-Institut für Physik, University of Heidelberg, Im Neuenheimer Feld 227, 69120 Heidelberg, Germany
E-mail: pucci@kip.uni-heidelberg.de

Abstract. Infrared spectroscopy is not only a powerful tool for the study of vibrational modes, it is also very effective for the investigation of metal nanoobjects such as films, wires, and dots. Metal films with thickness in the nm range can be studied with transmittance spectroscopy, which, via the development of the plasmon resonances, allows for the observation of their morphological development. Individual metal islands have their plasmon resonance in the visible range and only a weak tail of that resonance in the infrared. But nevertheless they can be detected with the help of adsorbate absorption lines. Their signals appear increased for molecules on metal islands. More signal enhancement is expected for metal particles at resonance, like metal nanorods with a length in range of infrared wavelengths that show a typical antenna resonance in the infrared related to considerable enhancement of the electromagnetic field.

1. Introduction

Infrared (IR) spectroscopy is an analytical method more than 100 years old [1]. But it still is a method at the frontiers of science. Reasons are the long time continuously used for further improvements of the method and, as a consequence, its high technical standard that allows the detection of intensity changes of 10^{-4} and better, which is below monolayer sensitivity. The method is almost non-destructive and, particularly under vacuum conditions, it can be applied as an in situ for the observation and control of growth processes of nanofilms and nanoparticle arrays. In the case of metal nanoobjects, the signal is due to the absorption by charge carriers [2, 3, 4, 5] that extends into the visible range. Moreover, in combination with IR microscopy the method can be extended to the spectroscopy of single nanoobjects. [6] For adsorbate-on-metal systems IR spectroscopy has the advantage to study both the charge carriers and the adsorbate vibrations within one experiment [3, 7, 8, 9, 10, 11] and to exploit field enhancement. The experimental basics of the following examples are given for example in Ref. [2, 3, 4, 5].

2. Metal Island Films

In the IR region the long-wavelength tail of the plasmon resonance of metal islands can be investigated. If the number of islands is too small to see this tail directly in the IR spectrum it is possible to detect adsorbate signals because of surface enhanced IR absorption (SEIRA) [7, 11, 12]. The main contribution to

SEIRA comes from electromagnetic field enhancement in the vicinity of the metal particle. Far from resonance this enhancement is less than a factor of 10. [12] In Fig. 1 and Fig. 2 we show that enhancement is sufficient to detect adsorbates from residual gas on a growing metal film. In this experiment some parts of the evaporator were not completely outgassed, which gave a high hydrocarbon pressure. The IR spectra clearly show C-H stretch vibrations (in the range between 2850 cm^{-1} and 2950 cm^{-1}) appearing during film growth. Different to the growth at a pressure below 10^{-9} mbar where at 10 nm average thickness a smooth films has formed, [5, 11, 13] the hydrocarbons seem to induce three-dimensional particle growth indicated by the nearly dispersion-less spectrum at 10 nm in Fig. 1. [14] It corresponds to a metal film close to the percolation threshold. With atomic force microscopy it turned out that this film really was consisting of densely packed nearly spherically particles [13].

The electromagnetic field between densely packed metal islands may be strongly enhanced over a large frequency range because such an ensemble has an extremely broad resonance from the visible to the IR [14]. As a consequence for IR transmittance spectroscopy of metal-island films close to the percolation threshold, all IR active vibration lines from adsorbates between metal islands become particularly strong. [7, 8] According to the distribution of the nearfield enhancement, the SEIRA signals are maximum between metal islands at their smallest distance. SEIRA enhancement factors up to 2000 are experimentally proven [15] but have to be considered as average values over ensembles of more or less randomly packed islands. It is important to note, that the enhancement clearly depends also on the dielectric function of the particles [7, 8].

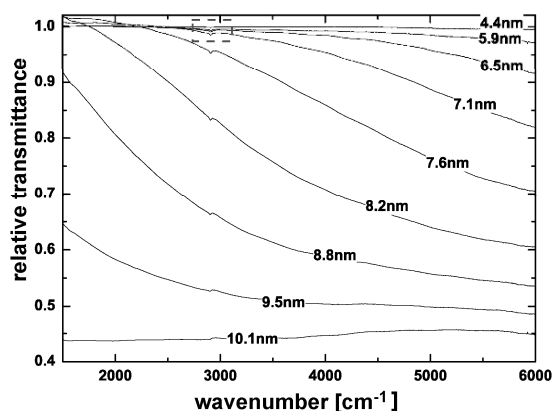


Fig. 1. Selection of relative transmittance spectra measured during deposition of Ag on UHV-cleaved MgO(001) at 300 K. The average film thickness is given for each curve. The pure substrate was used as reference. Due to the hot evaporator the pressure was increased to 5×10^{-8} mbar from hydrocarbons. The range of respective vibration bands is marked for the lower film thicknesses, for the higher thickness a vibrational feature at about 2900 cm^{-1} is clearly visible

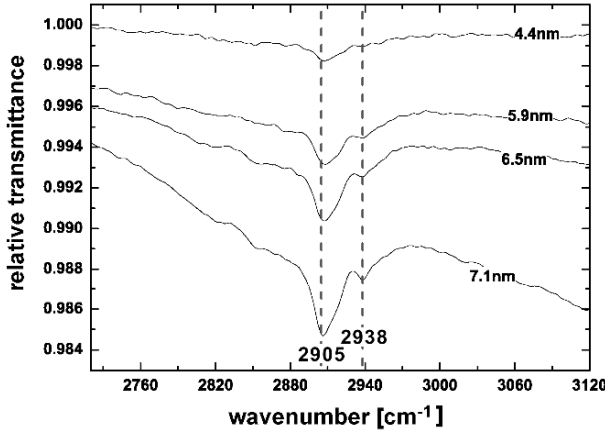


Fig. 2. SEIRA from hydrocarbons on Ag-island films during growth (average Ag thickness is given for each curve). Typical C-H stretch vibrations are indicated (in cm^{-1})

3. Nanowire Resonances

Nanowires or nanorods with length of microns have their main resonance in the IR, [6] which opens the way to further increase of field enhancement for SEIRA. For example, rod-like lead particles grown on a specially prepared Si (335) surface under ultra-high vacuum conditions (UHV) as a consequence of anisotropic diffusion [16, 17] show such antenna resonance (Fig. 3). Under ideal conditions (diameter small compared to length L , ideal metal) the resonance wavelength λ can be described with the following formula

$$\lambda / n_{\text{eff}} = 2L \quad (1)$$

with n_{eff} as the refractive index around the wire. [6] With

$$n_{\text{eff}} = \sqrt{n_{\text{Si}}^2 + 1} \quad (2)$$

and the refractive index n_{Si} for the silicon substrate a length of about $1 \mu\text{m}$ for the rods gives a resonance, which is in agreement with the atomic force microscopy image. For polarization perpendicular to the wire only the IR spectrum typical for metal islands is observed. From the signal strength of the antenna resonance the extinction cross section σ_{ext} can be estimated from the relative transmittance (T_{rel}) spectrum via the relation

$$1 - T_{\text{rel}} = 2\sigma_{\text{ext}}\rho / (n_{\text{Si}} + 1) \quad (3)$$

With a rod diameter of about 100 nm and an area density $\rho \approx 5 \times 10^{-7} \text{ nm}^{-2}$ of wires (from [17] and from atomic force microscopy) a scattering cross section of about 10 times the geometrical one follows, which indicates field enhancement (of about a factor of 3 in the farfield). Field enhancement in the nearfield will be investigated with adsorbate vibrations in our next experiments.

IR spectroscopy of individual nanowire resonances in comparison to theoretical calculations with the Boundary Element Method [18] have clarified that the detailed resonance curve is sensitive not only to the diameter but also to the metal dielectric function in the IR [6, 19].

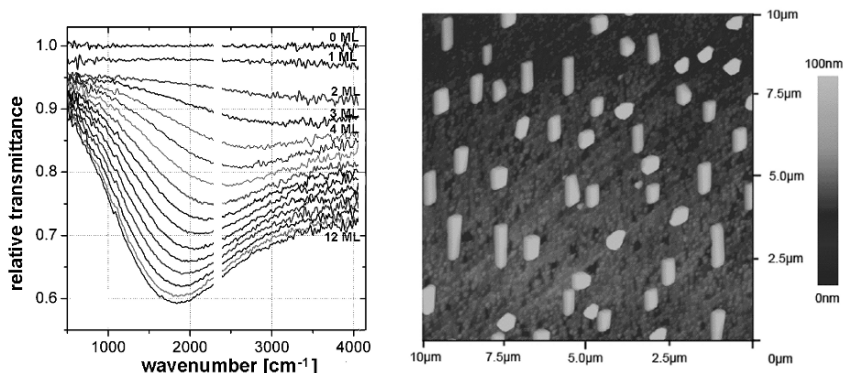


Fig. 3. Relative transmittance spectra T_{rel} of growing Pb nanorods on Si(335)/Au at room temperature (left). The electric field is polarized along the long axis of the rods. The average thickness for the final spectrum corresponds 15 monolayers (ML) lead. On the right an atomic force microscopic image is shown. It is taken in air immediately after the UHV preparation.

Acknowledgements

Financial support by the DFG (Deutsche Forschungsgemeinschaft) is gratefully acknowledged. The authors thank Gerhard Fahsold (Heidelberg), Javier Aizpurua (San Sebastian), and Mietek Jalochofski (Lublin) for valuable discussions.

References

1. E.F. Nicols, *Physical Review*, Vol. **1**, 1, 1893.
2. G. Fahsold, A. Bartel, O. Krauth, N. Magg, and A. Pucci, *Physical Review B* Vol. **61**, 14108, 2000.
3. G. Fahsold, M. Sinther, A. Priebe, S. Diez, and A. Pucci, *Physical Review B* Vol. **65**, 235408, 2002.
4. Pucci, F. Kost, G. Fahsold, and M. Jalochofski, *Physical Review B* Vol. **74**, 125428, 2006.
5. F. Meng and A. Pucci, *physica status solidi (b)* vol. **244**, 3739, 2007.

6. F. Neubrech, T. Kolb, R. Lovrincic, G. Fahsold, A. Pucci, J. Aizpurua, T.W. Cornelius, M.E. Toimil-Molares, R. Neumann, S. Karim, *Applied Physics Letters* Vol. **89**, 253104, 2006.
7. Priebe, M. Sinther, G. Fahsold, and A. Pucci, *The Journal of Chemical Physics* Vol. **119**, 4887, 2003.
8. Pucci, *physica status solidi (b)* Vol. **242**, 2704, 2005.
9. G. Fahsold, M. Sinther, A. Priebe, S. Diez, and A. Pucci, *Physical Review B* Vol. **70**, 115406, 2004.
10. M. Hein, P. Dumas, M. Sinther, A. Priebe, A. Bruckbauer, A. Pucci, and A. Otto, *Surface Science* Vol. **600**, 1017, 2006.
11. F. Meng, G. Fahsold, and A. Pucci, *physica status solidi (c)* Vol. **2**, 3963, 2005
12. Priebe, *Thesis*, University of Heidelberg 2002.
13. Meng, *Thesis*, University of Heidelberg 2007.
14. S. Berthier and J. Peiro, *Journal de Physique III France* Vol. **7**, 537, 1997.
15. D. Enders and A. Pucci, *Applied Physics Letters* Vol. **88**, 184104 2006.
16. M. Klevenz, *Diploma thesis*, University of Heidelberg 2007.
17. e.g. M. Jalochoowski and E. Bauer, *Surface Science*. **480**, 109, 2001.
18. J. Aizpurua, G.W. Bryant, L.J. Richter, F.J. Garcia de Abajo, B.K. Kelley and T. Mallouk, *Physical Review B* Vol. **71**, 235420, 2005.
19. F. Neubrech, J. Aizpurua, S. Karim, T.W. Cornelius, and A. Pucci, in “*Nanostructures in Electronics and Photonics*”, ed. by F. Rahman, World Scientific Publishing 2008, p. 209- 222.

Ultrafast Switching of Coherent Electronic Excitation: Great Promise for Reaction Control on the Femtosecond Time Scale

Matthias Wollenhaupt, Tim Bayer, Andrea Klumpp, Cristian Sarpe-Tudoran, and Thomas Baumert

University of Kassel, Institute of Physics, Center for Interdisciplinary Nanostructure Science and Technology (CINSaT), Heinrich-Plett-Str. 40, 34132 Kassel, Germany
E-mail: wollenha@physik.uni-kassel.de

Abstract. We report on a physical mechanism of coherent control with shaped intense femtosecond laser pulses. To this end we study photoelectron spectra from the multi-photon ionization of potassium atoms using tailored femtosecond laser pulses. Our results are interpreted in terms of Selective Population of dressed states (SPODS). Two realizations of SPODS by Photon Locking and Rapid Adiabatic Passage are discussed. A physical picture of SPODS based on the interplay of the laser electric field and the atomic wave function is presented. In addition, coherent control of a larger molecule (isopropyl alcohol) by shaped femtosecond laser pulses is demonstrated experimentally.

1. Introduction

With the advent of femtosecond laser pulses the temporal aspect of the interplay of light and molecular dynamics came to the fore and became experimentally accessible. The beauty of femtochemistry lies in our ability to observe [1] and to manipulate [2,3] ultrafast processes as they occur. Shaped femtosecond optical laser pulses [4] are the suitable tools to exert microscopic control on molecular dynamics at the quantum level. Fig. 1 depicts the concept of quantum control exerted by suitably shaped femtosecond laser pulses.

Initially, the quantum system is in the ground state $|i\rangle$. The dynamics induced by specifically designed laser pulses (three examples of which are depicted in Fig. 1) drives the system towards one of the possible final states $|f\rangle$. This particular target state represents for instance a specific excitation in an atom or molecule which initiates a desired physical process or chemical reaction. Important requirements for applications of quantum control are (1) the ability to address different target states, i.e. *tunability* among the manifold of final states, and (2) to ensure that only one of the final states is populated, i.e. high *selectivity* among the final states. The combination of pulse-shaping techniques with closed loop adaptive feedback learning algorithms [5–8] allows to optimize virtually any conceivable observable as reviewed for example in [9,10]. However, it is not always possible to deduce the underlying physical mechanism from the electrical fields obtained by this procedure. Therefore, the need to bridge the gap between the efficient ‘black box’ closed loop optimal control methods and detailed understanding of the physical processes especially in strong laser fields is quite

evident. To that end we combine femtosecond laser techniques with atomic-/molecular beam techniques and photoelectron-/ion detection techniques [11] in order to investigate the physical mechanism of strong field quantum control on simple systems with well characterized shaped pulses. So far we have extended weak field methods to free electrons [12]. New techniques making use of polarization control in molecular multi-photon excitation [13] and shaped intense laser pulses for molecular alignment [14,15] open further dimensions in this field.

Within this context, shaped *resonant* intense pulses are of special interest, as this class of pulses is of *general importance*. Resonant control scenarios will be the dominant pathways as shorter and shorter pulses with ultra broad spectra become available. Figure 2 shows the general picture of the physical principles of resonant strong field control. In this scenario, control is exerted via the intermediate resonant state $|r\rangle$. In general, strong laser fields give rise to an energy

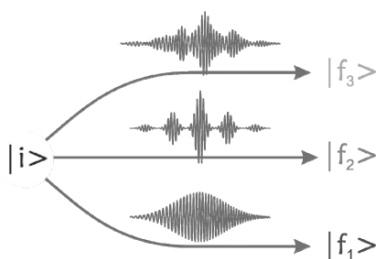


Fig. 1. Principle of quantum control by shaped femtosecond laser pulses: control is obtained by the design of pulse shapes that guide the quantum system from an initial state $|i\rangle$ to different final states $|f_i\rangle$ with high efficiency and high selectivity

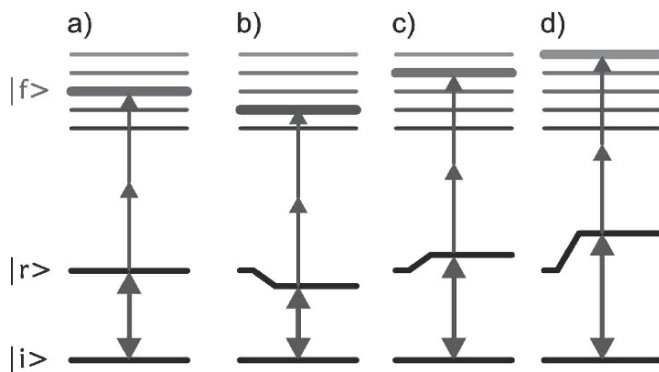


Fig. 2. Quantum control of multi-photon processes via an intermediate resonant state: (a) shaped resonant laser pulses are used to steer the initial population in state $|i\rangle$ via the intermediate resonant state $|r\rangle$ to an individual target state $|f\rangle$ within a manifold of final states. (b) and (c) selective population transfer is obtained by manipulating the energy of the resonant state $|r\rangle$. (d) selection of a particular target state among the manifold of final states is achieved by tuning the intermediate resonant states into resonance with the desired target state

splitting of the resonant state into two (so called *dressed*) states in the order of $\hbar\Omega$, where Ω describes the Rabi-frequency. The decisive step in switching among different final electronic states is realized by manipulation of dressed state energies and dressed state populations. By suitable phase shaping of the driving laser field, it is possible to populate only one of these two (dressed) states [16], i.e., to realize *Selective Population of Dressed States* (SPODS). Effectively, population of a single dressed state corresponds to a controlled energy shift of the resonant state into a desired direction as illustrated in Fig. 2(b) and (c). In Fig. 4(b), a physical picture for population of a single dressed state is given. Generally, during laser *excitation* the driving laser field precedes the atomic dynamics by a phase of $\pi/2$. However, in the case of SPODS the wave function of the superposition state $|\psi(x,t)|^2$ and driving laser field are perfectly in-phase (no phase shift) or anti-phase (phase shift of π). This is exemplified in the upper (lower) panel of Fig. 4(b) for selective population of the upper (lower) dressed state. Depending on the orientation of the atomic dipole with respect to the laser field vector $\mathcal{E}$ the interaction between the atomic dipole and the laser field gives rise to a positive or negative energy contribution. By variation of the laser intensity the energy splitting can be controlled and thus a particular target state among the manifold of final states are addressed (cf. Fig. 2(d)) providing tunability.

2. Experimental

An experimental implementation of resonant strong field control is shown in Fig. 3(a). This approach makes explicit use of the manipulation of the temporal phase of a pulse sequence with attosecond precision [17]. Sequences of pulses are generated by sinusoidal phase modulation in frequency domain [4,18,19] with our home-built pulse shaper [20]. The shaped pulses are allowed to interact with potassium atoms in an atomic beam. Photoelectron spectra for different pulse shapes are measured using a Time-Of-Flight (TOF) electron spectrometer. Experimentally we make use of a 1+2 REMPI process on potassium atoms (see Fig. 3(b)). An intense fs-laser couples coherently the $4s$ and $4p$ states and at the same time ionizes the system in a two photon process. The shape of the photoelectron spectra reflects the temporal phase of the excited state amplitude [11]. In particular, the photoelectron spectra map the dressed state population. During the time evolution, the dressed states are characterized by a time-dependent energy splitting giving rise to the observed Autler-Townes (AT) splitting [21] in the photoelectron spectra. Employing two-photon ionization as the non-linear probe step precludes averaging over the intensity distribution within the laser focus since the ionization probability is highest in the spatial region of highest laser intensity. This technique permits us to overcome the common problem of washing out intensity dependent strong field effects.

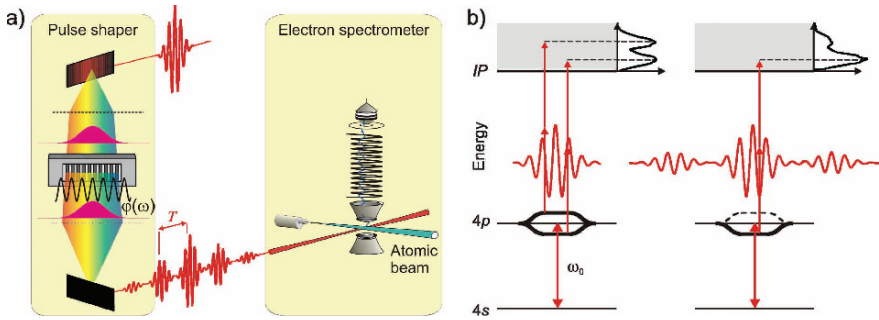


Fig. 3. (a) Schematic of the experimental set-up: tailored pulse trains are created via applying a phase mask in the Fourier plane of our pulse shaper [20]. In the case discussed here, the spectrum of our femtosecond laser pulse (785 nm, 30 fs, 0.35 – 2 μ J) is phase-modulated in frequency domain with a sinusoidal phase function $\phi(\omega) = A \sin[(\omega - \omega_0) T + \phi]$ with $A = 0.2$, $T = 170$ fs and $\omega_0 = 2.40 \text{ fs}^{-1}$ to produce a sequence of pulses in time domain separated by T . The pulses are focused on a potassium atomic beam. The resulting photoelectrons are detected with a magnetic bottle Time of Flight photoelectron spectrometer. (b) Schematic of the excitation scheme (potassium-atoms): The bare states are indicated with thin lines. Thick lines illustrate the dressed state splitting during the interaction giving rise to a symmetric Autler Townes splitting (left). Selective population of a dressed state with a tailored pulse train is shown in the right panel, leading to a strongly asymmetric Autler Townes doublet

3. Results and Discussion

Figure 4 shows two realizations of SPODS on potassium atoms using (a) phase-locked double pulses and (c) chirped femtosecond laser pulses. In both cases the experimentally observed photoelectron spectra are in good agreement with our simulations [19]. The results shown in Fig. 4(a) have been discussed in the bare state picture [17] and with the help of dressed states [16]. Briefly, the first pulse creates a coherent electronic superposition state. Depending on the relative optical phase of the second pulse either the upper or the lower dressed states are populated with high selectivity as seen in the alternating peaks in the photoelectron spectra. This realization of SPODS is based on Photon Locking [22]. An alternative realization of SPODS shown in Fig. 4(c) is based on Rapid Adiabatic Passage (RAP) [23,24] by chirped laser pulses. In our experiment chirped pulses are created by quadratic spectral phase modulation. By variation of the chirp parameter, we can switch between the population of the upper and the lower dressed state. Up-chirped pulses lead to population of lower dressed state and vice versa. Making use of adaptive feedback learning algorithms we are able to control the dressed state population by more than 90% as seen by the corresponding suppression of one AT component [16].

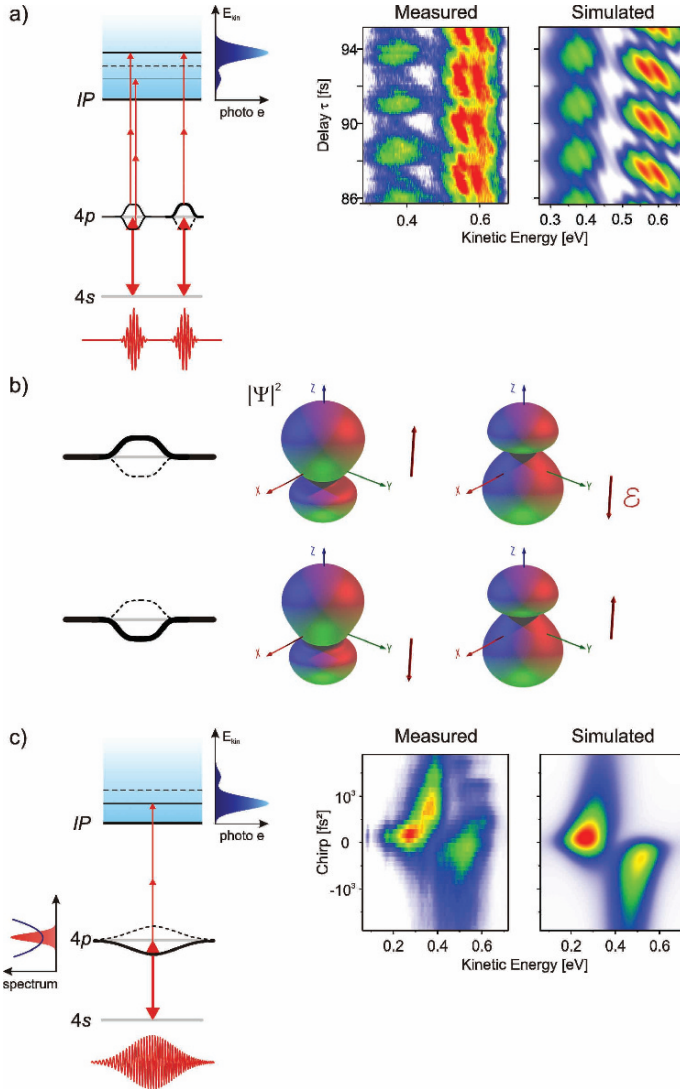


Fig. 4. Selective population of dressed states (SPODS) on potassium atoms via (a) Photon Locking in a two-pulse experiment and (c) Rapid Adiabatic Passage (RAP) using chirped pulses. Measured photoelectron spectra (false colour representation) as a function of the pulse parameters (a) delay and (c) chirp are in good agreement with the simulated results. (b) population of a single dressed state manifests itself by in-phase or anti-phase oscillations of the wave function of the superposition state $|\Psi(x,t)|^2$ with respect to the driving laser field vector $\mathcal{E}$. Examples for two orientations of the electrical field vector $\mathcal{E}$ with respect to the wave function during selective population of the upper dressed state (upper panel) and lower dressed state (lower panel) are shown

With the help of tailored pulse trains we demonstrate that SPODS is highly selective, tunable (up to 250 meV) and robust [25]. In Fig. 5 experimental results – obtained with a pulse train created by applying a sine mask in the Fourier plane of the pulse shaper (see Fig. 3) – are displayed.

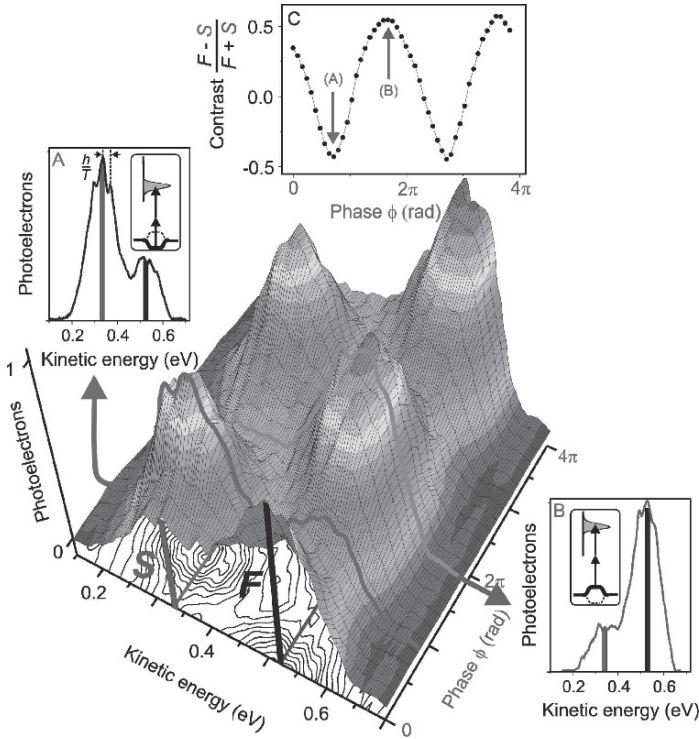


Fig. 5. The Selective Population of Dressed States (SPODS) is directly mapped into the measured photoelectron spectra by variation of the phase ϕ . The maximum of the asymmetric photoelectron distribution alternates between 0.33 eV and 0.52 eV. These results are obtained at a laser energy of $W = 0.5 \mu\text{J}$. A section through the distribution along the energy axis at $\phi = 0.7 \pi$ – indicated with the violet trajectory – yields the photoelectron spectrum (A) where the lower dressed state is selectively populated as depicted in the inset to (A). Fringes in the spectrum with an energy separation of h/T arise from the interference of free electron wave packets [12] launched during the different pulses. Selective population of the upper dressed state is achieved at $\phi = 1.7 \pi$ as indicated with the magenta trajectory and plotted in spectrum (B). The signal of the slow photoelectrons at 0.33 eV (S) and the fast photoelectrons at 0.52 eV (F) – as indicated with the red and blue bars – is obtained as a function of the phase ϕ by taking a section through the distribution along the phase coordinate. The contrast of F and S, i.e., $(F-S)/(F+S)$ as shown in (C) is a measure of the selectivity of dressed state population. The phases corresponding to the highest selectivity for population of the lower dressed state – spectrum (A) – and the upper dressed state – spectrum (B) – are indicated with violet and magenta arrows respectively

Besides the experimental demonstration of SPODS on atoms, theoretical studies on potassium dimers (K_2) have been performed [25,26]. These studies confirm the applicability of strong field control by SPODS to molecules. In particular, the insights into the physical mechanism of strong field control obtained on atoms can be used to design shaped laser pulses to efficiently switch the final population among different electronic states of a diatomic molecule. For applications to chemistry, it is particularly important to validate coherent control strategies on larger molecules. As a first step, we investigate the mass spectra – measured with a TOF spectrometer – from dissociation of isopropyl alcohol (C_3H_8O) using a pulse sequence. The results shown in Fig. 6 show pronounced variations in the molecular ion yield upon variations of the phase ϕ in the pulse sequence. In these experiments we simultaneously measured the atomic ion yield of K^{39} and K^{41} at about $7.8\ \mu s$ and $8.1\ \mu s$ respectively. Here no significant variations of the ion-yield with the phase ϕ were found as expected since ion detection integrates over all accessible final electronic states. This result confirms that neither scattering losses or spectral/spatial cross-sensitivities are introduced by our pulse shaper. These observations show that control on the molecular dynamics of isopropyl alcohol is exerted by the optical phase of the shaped pulse.

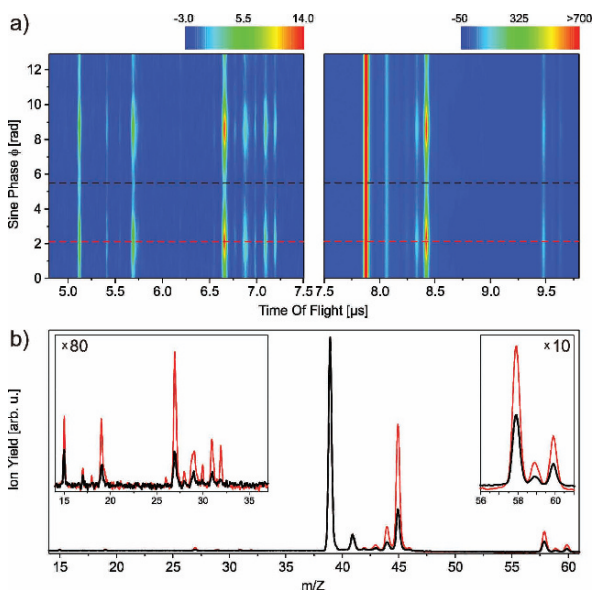


Fig. 6. (a) false color representation of TOF - mass spectra from the dissociation of isopropyl alcohol (C_3H_8O) using a pulse sequence. Shaped laser pulses are generated by sinusoidal spectral phase modulation of $E = 10\ \mu J$, $\lambda = 790\ nm$, $\Delta t = 30\ fs$ pulses using a phase function $\varphi(\omega) = 0.5 \sin[50\ fs(\omega - 2.4\ fs^{-1}) + \phi]$. The phase ϕ is varied within 4π . (b) sections through the mass spectra at $\phi = 2\ rad$ (red) and $\phi = 5.5\ rad$ (black) exhibit a strong variation of the molecular ion yield. At $m = 45\ u$ ($C_2H_5O^+$) a variation in the molecular ion yield by a factor of 3 is observed. The insets show a magnification of the spectra. The atomic ion yield of K^{39} ($7.8\ \mu s$) and K^{41} ($8.1\ \mu s$) measured simultaneously shows no variation with the phase ϕ

However, so far it is not fully clear whether the physical mechanism underlying our observations on isopropyl alcohol is based on SPODS. Currently, other physical mechanisms such as spectral interference [27,28] can not be ruled out. In future we will carry out systematic studies on the intensity dependence of phase control of larger molecules. Intensity dependent phase effects as observed in strong field control of atoms [17] and molecules [26] provide a critical test to discriminate weak field control scenarios such as spectral interference from strong field control exemplified by SPODS.

4. Conclusions

Since switching between selective population of either dressed states occurs within a few femtoseconds, this technique is also interesting for applications in the presence of decoherence processes. SPODS can be realized with very different pulse shapes making use of diverse physical mechanisms ranging from Photon Locking [17,25,29] – to Rapid Adiabatic Passage [24]. In this sense, SPODS provides a unifying framework to describe resonant strong field control scenarios. We believe that SPODS is at play in many other circumstances as well, for instance in adaptive closed loop experiments [16,30,31]. Because SPODS combines high selectivity (more than 90% as observed in our experiments) and tunability (several hundred meV) with efficient population transfer, relevant applications to chemistry – so far investigated theoretically [25,26] – are within reach. Initial studies on mass spectra from dissociation of isopropyl alcohol using pulse sequences show pronounced phase effect.

Acknowledgements

We want to thank the Deutsche Forschungsgemeinschaft - DFG - for financial support.

References

1. A.H. Zewail, *J Phys Chem* **104**, 5660, 2000.
2. M. Shapiro and P. Brumer, in *Principles of the Quantum Control of Molecular Processes*, 1 ed., (John Wiley & Sons, Hoboken, New Jersey, 2003).
3. S.A. Rice and M. Zhao, in *Optical control of molecular dynamics*, (Wiley, New York, 2000).
4. A.M. Weiner, *Rev Sci Instr* **71**, 1929, 2000.
5. R.S. Judson and H. Rabitz, *Phys Rev Lett* **68**, 1500, 1992.
6. T. Baumert, T. Brixner, V. Seyfried, M. Strehle, and G. Gerber, *Appl Phys B* **65**, 779, 1997.
7. D. Meshulach, D. Yelin, and Y. Silberberg, *Opt Comm* **138**, 345, 1997.
8. C.J. Bardeen, V.V. Yakolev, K.R. Wilson, S.D. Carpenter, P.M. Weber, and W.S. Warren, *Chem Phys Lett* **280**, 151, 1997.
9. H. Rabitz, R. de Vivie-Riedle, M. Motzkus, and K. Kompa, *Science* **288**, 824, 2000.

10. T. Brixner, T. Pfeifer, G. Gerber, M. Wollenhaupt, and T. Baumert, in *"Femtosecond Laser Spectroscopy"*, Edited by P. Hannaford (Springer Verlag, 2005), Chap. 9.
11. M. Wollenhaupt, V. Engel, and T. Baumert, *Ann Rev Phys Chem* **56**, 25, 2005.
12. M. Wollenhaupt, A. Assion, D. Liese, C. Sarpe-Tudoran, T. Baumert, S. Zamith, M.A. Bouchene, B. Girard, A. Flettner, U. Weichmann, and G. Gerber, *Phys Rev Lett* **89**, 173001-173001-4, 2002.
13. T. Brixner, G. Krampert, T. Pfeifer, R. Selle, G. Gerber, M. Wollenhaupt, O. Graefe, C. Horn, D. Liese, and T. Baumert, *Phys Rev Lett* **92**, 208301-208301-4, 2004.
14. C. Horn, M. Wollenhaupt, M. Krug, T. Baumert, R. de Nalda, and L. Banares, *Phys Rev A* **73**, 031401-031401-4, 2006.
15. R. de Nalda, C. Horn, M. Wollenhaupt, M. Krug, L. Banares, and T. Baumert, *J Raman Spectroscopy* **38**, 543, 2007.
16. M. Wollenhaupt, A. Präkelt, C. Sarpe-Tudoran, D. Liese, and T. Baumert, *J Opt B* **7**, S270-S276, 2005.
17. M. Wollenhaupt, A. Assion, O. Bazhan, C. Horn, D. Liese, C. Sarpe-Tudoran, M. Winter, and T. Baumert, *Phys Rev A* **68**, 015401-015401-4, 2003.
18. M. Wollenhaupt, A. Assion, and T. Baumert, in *Springer Handbook of Lasers and Optics*, Edited by F. Träger (Springer Science and Business Media, 2007), Chap. 12.
19. M. Wollenhaupt, A. Präkelt, C. Sarpe-Tudoran, D. Liese, T. Bayer, and T. Baumert, *Phys Rev A* **73**, 063409-063409-15, 2006.
20. A. Präkelt, M. Wollenhaupt, A. Assion, C. Horn, C. Sarpe-Tudoran, M. Winter, and T. Baumert, *Rev Sci Instr* **74**, 4950, 2003.
21. S.H. Autler and C.H. Townes, *Phys Rev* **100**, 703, 1955.
22. E.T. Sleva, I.M. Xavier Jr., and A.H. Zewail, *JOSA B* **3**, 483, 1985.
23. N.V. Vitanov, T. Halfmann, B.W. Shore, and K. Bergmann, *Ann Rev Phys Chem* **52**, 763, 2001.
24. M. Wollenhaupt, A. Präkelt, C. Sarpe-Tudoran, D. Liese, and T. Baumert, *Appl Phys B* **82**, 183, 2006.
25. M. Wollenhaupt, D. Liese, A. Präkelt, C. Sarpe-Tudoran, and T. Baumert, *Chem Phys Lett* **419**, 184, 2006.
26. M. Wollenhaupt and T. Baumert, *J Photochem Photobiol A* **180**, 248, 2006.
27. D. Meshulach and Y. Silberberg, *Nature* **396**, 239, 1998.
28. A. Präkelt, M. Wollenhaupt, C. Sarpe-Tudoran, and T. Baumert, *Phys Rev A* **70**, 063407-063407-10, 2004.
29. M. Wollenhaupt, A. Präkelt, C. Sarpe-Tudoran, D. Liese, and T. Baumert, *J Mod Opt* **52**, 2187, 2005.
30. A. Assion, T. Baumert, M. Bergt, T. Brixner, B. Kiefer, V. Seyfried, M. Strehle, and G. Gerber, *Science* **282**, 919, 1998.
31. R.J. Levis, G.M. Menkir, and H. Rabitz, *Science* **292**, 709, 2001.

InGaAsP/InP Semiconductor Optical Amplifiers and their Some Nonlinear Effects

Vu Doan Mien^{1,2}, Vu Thi Nghiem¹, Tong Quang Cong² and Pham Van Truong¹

¹ Institute of Materials Science, Vietnamese Academy of Science and Technology,
18, Hoang Quoc Viet st., Cau Giay, Hanoi, Vietnam
E-mail: mienvd@ims.vast.ac.vn

² College of Technology, National University of Vietnam, 144 Xuan Thuy, Cau Giay,
Hanoi, Vietnam

Abstract. Experimental investigations of four-wave mixing (FWM) in Semiconductor Optical Amplifier (SOA) modules have been performed. SOA modules were prepared based on 1550 nm InGaAsP/InP SOA chips. The distributed-feedback (DFB) laser modules based on the 1.55 μm InGaAsP/InP BH $\lambda/4$ phase-shifted DFB laser chips have also been prepared for the light sources. The dependence of the FWM effect on the frequency detuning between pump and probe signals, SOA dc operating currents and input pump signal power were studied. The FWM effect is the result of nonlinear interactions between the medium and the optical fields, some physical FWM mechanisms are proposed for the observed effect.

1. Introduction

Wavelength Division Multiplexing (WDM) is one of the most important technologies in modern fiber optic telecommunication systems. Wavelength converters are essential devices to exploit the full fiber bandwidth in a wavelength division multiplexed network. Four-wave mixing (FWM) in semiconductor optical amplifiers (SOA) is a strong candidate to implement this function [1, 2, 3, 4]. Semiconductor gain mediums, like the active layer of an SOA or a semiconductor laser, have third-order nonlinear susceptibility which is considerably larger than those observed in optical fibers. FWM in SOAs also can be used for other applications in modern all-optical fiber optic networks. At the same time, studying FWM in SOAs one can understand and eliminate FWM noises in WDM systems. In this paper we report the preparation of the SOA, DFB laser modules and the experimental investigation of FWM effects in the prepared SOA modules.

2. Results and Discussion

Angled-facet Semiconductor Optical Amplifier (SOA) and DFB laser module preparation. In this work we used the 1 mm angled-facet (tilted) 1550 nm InGaAsP/InP SOA chips which were designed and fabricated at the Heinrich-Hertz Institute (HHI) in Berlin. They have a buried heterojunction structure with a tensile strained layer (0.15%) to keep the polarization dependence as small as possible. In order to prevent back reflection the SOA was designed 7° off axis with

respect to the crystal axis (that is why it is called angled-facet) and the facets are anti-reflection (AR) coated with a $\text{TiO}_2/\text{SiO}_2$ double layer. AR coating was done by RF sputtering with *in-situ* control of the reflection spectra. The facet reflection coefficient is expected to be lower than 10^{-4} as the result of both effects of angled-facet and anti-reflection coating. We prepared SOA modules based on such 1 mm-long SOA chips at the Institute of Materials Science (VAST), Hanoi. The SOA chip was soldered on the gold plated diamond heat sink, then the heat sink was soldered on a copper plate attached to the peltier cooler. In some cases, the SOA chips were attached to the gilded copper heatsink with electrically conducting epoxy EPO-TEK H20E. The electrical contacts were made of $25\mu\text{m}$ gold wires by ultrasonic welding and the thermal sensor was also attached to the copper plate for controlling the SOA temperature. Fiber-to-fiber optical coupling was performed. In order to have good coupling efficiency between 9/125 single mode fibers and the SOA chip we tapered the fibers using electrical arc. The fibers were coupled at 23° angle relatively to the crystal axis in order to have the best coupling efficiency. The tapered fiber with the tip diameter of about $15\mu\text{m}$ gives a coupling efficiency of about 25%. The fibers were fixed to the copper plate with epoxy Araldite 1014 and the capping process completed the SOA module preparation.

The results of the characterization showed that SOA modules have 3dB-ASE bandwidth $\Delta\lambda \sim 35$ nm with the maximum at 1540 nm (at operating current $I = 60$ mA). The ASE spectra are shown in figure 1a for different operating current of the SOA module ($RBW = 0.01$ nm). Here the ripples due to the residual reflection are < 1 dBm. Figure 1b shows the dependence of the SOA optical gain on optical output power at two operating currents $I = 60$ mA and $I = 80$ mA, the small signal gains are about 12 dB and 17 dB and the saturation output powers are around -5 dBm and -1 dBm, respectively. The 3dB saturated gain is achieved at rather low output power, the nonlinearity effects are, thus, not too difficult to be observed. The dependence of gain on input light polarization is still rather high (~ 4 dB) and the SOA noise figure is about 12 dB.

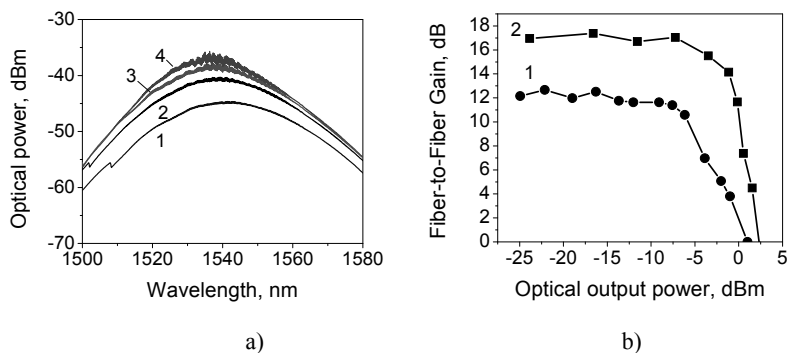


Fig. 1. (a) ASE spectra of SOA module at operating current of 50 mA (1), 60 mA (2), 70 mA ($T = 27^\circ\text{C}$); b) Dependence of Fiber-to-Fiber gain on optical output power at SOA operating current of 60 mA (1) and 80 mA (2) ($T = 27^\circ\text{C}$)

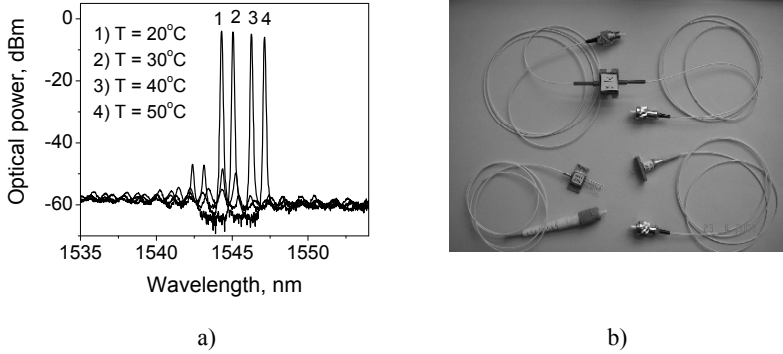


Fig. 2. (a) Optical spectra of the prepared DFB laser module at different temperatures ($I = 20$ mA); (b) Image of the prepared SOA and DFB laser modules

Normally, as pump light source in FWM experiments the DFB laser must have high enough output power. Here we prepared the DFB laser modules based on the $1.55\ \mu\text{m}$ InGaAsP/InP BH $\lambda/4$ phase-shifted DFB laser chips with an integrated $200\ \mu\text{m}$ spot-size converter region [5]. The DFB laser chips were also fabricated at Heinrich-Hertz Institute (HHI). The laser chips were attached to the gilded copper heatsink also with electrically conducting epoxy EPO-TEK H20E and the contacts were also made by ultrasonic welding $25\ \mu\text{m}$ gold wires. The 9/125 single mode fiber was butt-coupled to this chip with the coupling efficiency of about 40% due to the integrated waveguide (spot-size converter) region while the coupling efficiency between the tapered fiber and the DFB laser chip without integrated waveguide was $20 \div 25\%$ [6]. We prepared both cooled and uncooled DFB laser modules. The threshold currents of the DFB laser modules are smaller than 5 mA at room temperature and their output power can be developed up to 10 dBm and the operating current can be increased up to 100 mA. By changing the temperatures of the DFB laser modules with the thermoelectric cooler control unit (temperature stability: $\pm 0.1^\circ\text{C}$) we can have different wavelengths of the probe signal as shown in Fig. 2a. The coefficient of the wavelength shift with temperature was defined as $d\lambda/dT = 0.09\ \text{nm}/^\circ\text{C}$. From the optical spectra we can see a good side mode suppression ratio ($>40\ \text{dB}$) of the DFB laser module. Figure 2b shows the images of our prepared SOA and DFB laser modules.

Four-wave mixing in SOAs. In a typical FWM experiment, a strong pump wave at frequency ω_p and a weak probe wave at ω_s are combined and coupled to the waveguide modes of the SOA, which is a traveling wave amplifier. Dynamic gain and index gratings are formed due to the beating of the pump and probe waves, at a detuning frequency given by $\Omega = \omega_p - \omega_s$. The pump and the probe waves are subsequently scattered by these gratings which give rise to the FWM sidebands ω_c , as shown in Fig. 3a. In this figure $P_p(0)$ and $P_s(0)$ are the optical power of pump and probe waves at the SOA input, and $P_p(L)$, $P_s(L)$ and $P_c(L)$ are the optical power of the pump, probe and conjugate waves at the SOA output respectively while $P_N(L)$ is the ASE optical noise power.

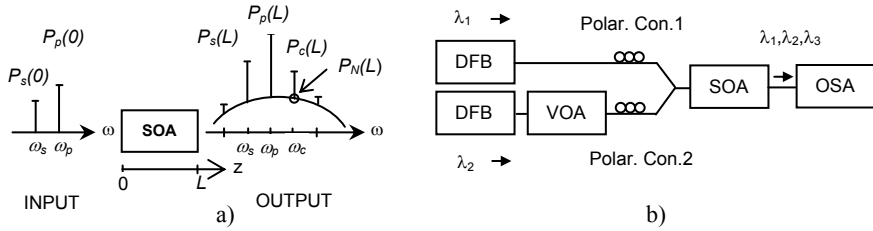


Fig. 3. (a) Generation of the FWM sidebands in a SOA; (b) Experimental setup for FWM measurements

Our experimental setup for studying the FWM effect in SOAs is shown in Fig. 3b. Pump (λ_1) and probe or signal wave (λ_2) from the 1550 nm DFB laser modules are combined in a 50:50 optical coupler before entering the SOA. The isolators were put at the DFB laser module outputs to prevent the back reflection to the lasers. To vary the intensity of the pump or probe wave without the change of their wavelength we used the variable optical attenuator (VOA). The polarization of the pump and probe waves could be changed with the fiber polarization controllers. The temperature of the DFB laser modules and SOA could be changed and stabilized ($\pm 0.1^\circ\text{C}$) with the peltier coolers. The optical spectra of the pump, probe and conjugate (FWM) (λ_3) waves at the SOA's output were measured with an optical spectrum analyzer (OSA) Advantest Q8384 ($RBW = 0.01$ nm). Both pump and probe waves were dc signals in our experiments.

FWM efficiency depends strongly on the polarization of the pump and probe waves. With the rotation of the fiber coils in the polarization controllers we could have the maximum efficient FWM (maximum intensity of conjugate wave λ_3) as shown in Fig. 4a when the polarization of the pump and probe wave are the same. The relative intensity ratio between pump and probe waves was also changed with VOA for observing the change in intensity of the conjugate wave ($\lambda_3 = 1541.58$ nm). The frequency detuning between the pump ($\lambda_1 = 1543.42$ nm) and the probe ($\lambda_2 = 1545.25$ nm) waves in this case is $\Omega = 230$ GHz ($\Delta\lambda = 1.84$ nm). The same detuning between the FWM conjugate wave and the pump wave is observed. The higher order FWM waves are also observed but with much smaller intensity. The detuning shown in Fig. 4a is a negative one because the pump frequency is higher than the probe frequency. We also observed the case of positive detuning when the pump frequency became lower than the probe frequency. In this case the conjugate wave λ_3 is at the right side of the wave λ_2 . Keeping the constant ratio between the intensities of the input pump and probe waves we changed the detuning between the pump and probe frequencies by changing the temperature of the DFB laser module (which gives the probe wave signal) with the peltier cooler. Each time the conversion efficiency of FWM in SOA was calculated by the following formula [1,2]:

$$\eta(\text{dB}) = 10 \log_{10} \frac{P_c(L)}{P_s(0)} \quad (1)$$

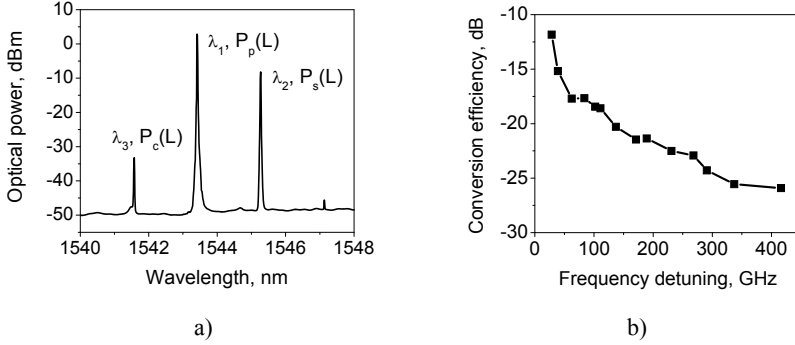


Fig. 4. a) FWM in the prepared SOA module: $P_p(0) = 1.4$ dBm, $P_s(0) = -10.7$ dBm, $I_{SOA} = 70$ mA ($T = 25^\circ\text{C}$); b) Dependence of the FWM conversion efficiency on the frequency detuning at $I_{SOA} = 70$ mA ($T = 25^\circ\text{C}$) and $P_p(0) = 1.7$ dBm, $P_s(0) = -10.7$ dBm

where $P_c(L)$ is the optical power of the conjugate wave at the output of the SOA which depends much on the SOA length L , and $P_s(0)$ is the optical power of the probe wave at the SOA input.

The dependence of the conversion efficiency on the frequency detuning for the SOA operating current $I = 70$ mA ($T = 25^\circ\text{C}$) is shown in Fig. 4b where the input power of the pump and probe waves were kept constant ($P_p(0) = 1.7$ dBm, $P_s(0) = -10.7$ dBm). The conversion efficiency of FWM decreases with increasing frequency detuning. We could have a maximum detuning of about 3.3 nm in the wavelength by changing the temperature of the probe laser source with the peltier cooler while the temperature of the pump laser source was kept at 20°C . To achieve more detuning one needs to have a tuning laser.

For detuning frequencies less than a few gigahertz, the largest contribution to the FWM susceptibility is due to carrier density modulation (CDM) which arises from the beating of the pump and probe waves. The intensity beating due to the pump and the probe leads to a pulsation of the population inversion in the medium. This pulsation of the total carriers leads to a gain modulation as seen by the traveling waves, which gives rise to the FWM sidebands. Due to the slow recovery of the carrier density, determined by the carrier lifetime τ_s , which is on the order of several hundred picoseconds, the efficiency of FWM mediated by CDM drops off for frequency detunings much larger than 10 GHz. At the large detuning frequencies, that is suitable for our case, the gain and index gratings are formed by intraband processes, such as carrier heating (CH) and spectral hole burning (SHB) [1]. Instead of a pulsation of the total carriers in the conduction and valence bands of the semiconductor, the occupation probabilities of the individual transition levels are modulated to form the gain and index gratings that give rise to the FWM sidebands. The pulsation of the occupation probabilities create distortions in the equilibrium Fermi distribution functions of the carriers, which relax back to their equilibrium state through different scattering processes, such as CH and SHB. SHB arises from carrier-carrier scattering which tend to

restore a quasi-equilibrium Fermi distribution function. Typically, carriers scatter each other at a time scale, τ_{SHB} , which is of the order of 50–100 femtoseconds. The quasi-equilibrium Fermi distribution function is characterized by a temperature which is different from the lattice temperature. The relaxation to the lattice temperature is through the emission of optical phonons with a time constant due to carrier-phonon scattering lifetime, τ_{CH} , which is of the order of 0.5–1 picoseconds. Thus the relaxation of the carriers can be explained as a three step process: (1) the carriers first scatter with each other to create a quasi-equilibrium Fermi distribution which has a temperature T_x that is different from the lattice temperature (SHB), (2) the temperature of the carriers then relaxes to the lattice temperature through carrier-phonon scattering (CH) and (3) the carriers then recombine through stimulated recombination.

The conversion efficiency of FWM depends on the SOA saturated gain G_{sat} , the input pump power $P_p(0)$ (in dBm) and the detuning as given by the following formula [1]:

$$\eta(\Omega) = 3G_{sat} + 2P_p(0) + 20 \log_{10} \left| \sum_{m=1}^3 c_m \cdot \frac{1}{1 - i\Omega \tau_m} \right| \quad (2)$$

where τ_m is the lifetime of the above processes CDM, CH and SHB which correspond to $m = 1, 2$ and 3 , respectively, and c_m is the complex coupling coefficient. The conversion efficiency strongly depends on the length of the devices through the saturation of SOA. In our case we have fixed the SOA length so that the saturated gain increases when the SOA dc operating current increases as shown in Fig. 1b.

Figure 5a shows the dependence of the FWM conversion efficiency on the SOA operating current at the fixed frequency detuning ($\lambda_1 = 1543.38$ nm, $\lambda_2 = 1544.40$ nm, $\Omega = 128$ GHz) and the fixed optical powers of the input pump and probe waves ($P_p(0) = 1.7$ dBm and $P_s(0) = -9.77$ dBm). The higher SOA operating

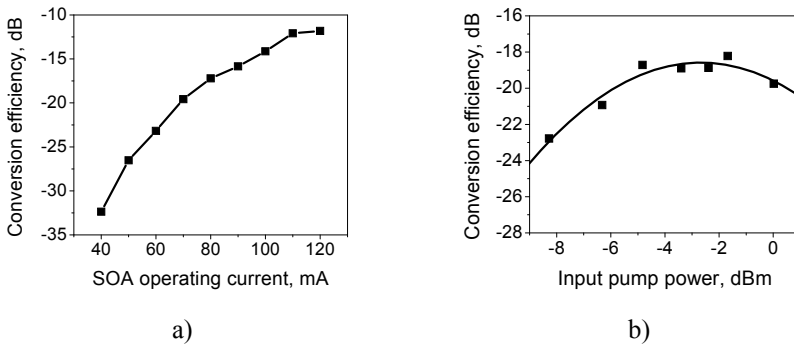


Fig. 5. a) Dependence of the FWM conversion efficiency on the SOA operating current when $P_p(0) = 1.7$ dBm and $P_s(0) = -9.77$ dBm ($T = 25^\circ\text{C}$); b) Dependence of the FWM conversion efficiency on the input pump power ($I_{SOA} = 70$ mA, $P_s(0) = -8.8$ dBm, $\Omega = 90$ GHz) ($T = 25^\circ\text{C}$)

current gives a higher SOA optical gain so that the optical power of the conjugate wave is higher and, as a consequence, the FWM conversion efficiency is higher. For a longer SOA chip ($>1\text{mm}$) it is expected to have a more efficient FWM. When keeping the probe signal power ($P_s(0) = -8.8\text{ dBm}$), the SOA operating current ($I_{SOA} = 70\text{ mA}$) and the detuning ($\lambda_1 = 1544.53\text{ nm}$, $\lambda_2 = 1545.24\text{ nm}$, $\Omega = 90\text{ GHz}$) constant, an increase of the input pump signal power $P_p(0)$ at first results in an increase in the conversion efficiency. Higher input pump power ($\sim -2\text{ dBm}$) will saturate the SOA and cause reduction of the gain so that the conversion efficiency decreases with increasing $P_p(0)$ as shown in Fig. 5b. When the pump signal power was kept constant a change of the probe signal power caused a little change in the conversion efficiency.

3. Conclusion

Semiconductor Optical amplifier (SOA) and DFB laser modules operating in the region of $1.55\text{ }\mu\text{m}$ have been prepared based on the angled-facet InGaAsP/InP SOA chips and InGaAsP/InP BH $\lambda/4$ phase-shifted DFB laser chips with integrated spot-size converter region. A four-wave-mixing effect was observed experimentally by using the prepared SOA and DFB laser modules. The dependences of the FWM conversion efficiency on the frequency detuning, SOA optical gain and input pump power have been investigated which show the qualitative behavior of this third – order nonlinear effect in the semiconductor optical amplifier. This effect can be used for many functional applications of SOA in fiber optic communication such as in WDM technology.

Acknowledgements

The authors express sincere thanks to the National Council on Natural Sciences for its financial support and Dr. H. Venghaus and Dr. H. Heidrich from HHI for their support in providing SOA and DFB laser chips.

References

1. J. Zhou, N. Park, J.W. Dawson, K.J. Vahala, M.A. Newkirk and B.I. Miller. *IEEE Photonics Technology Letters*, Vol. 6, No. 1, pp. 50–52, 1994
2. S. Diez, C. Schmidt, R. Ludwig, Hans. G. Weber, K.f. Obermann, S. Kindt, I. Kolchanov and K. Peterman. *IEEE Journal of Selected Topics in Quantum Electronics*, Vol. 3, No. 5, p. 1134 – 1145, 1997.
3. J. Zweck, C.R. Menyuk. *Optics Letters*, Vol. 27, No. 14, pp. 1235-1237, 2002 .
4. A. Bilenca, R. Alizon, V. Mikhelashvili, D. Dahan, G. Eisenstein, R. Schwertberger, D. Gold. *IEEE Photonics Technology Letters*, Vol. 15, No. 4, p. 563, 2003,
5. K. Janiak, J. Kreissl, S. Fidorra, T. Hartwich, Rehbein, G. Wache, and H. Heidrich. *Proceedings of the 2004 International Conference on Indium Phosphide and Related Materials*, Kagoshima, Japan, 31/5-4/6, 2004, p. 476–479
6. V.D. Mien, P.V. Truong and V.N. Hai. *Proceedings of the 6th National Physics Conference*, Hanoi, Vietnam, 23-25/11/ 2005, Vol. 2, pp. 819–823

Simulation and Lock-In Phase Analysis in Photoreflectance Modulation Spectroscopy of GaAs And Photoreflectance Investigations of The Heterojunction Structure $\text{Al}_x\text{Ga}_{1-x}\text{As}(\text{N}^+)/\text{GaAs}(\text{P}^-)/\text{GaAs}(\text{P}^+)$

Nguyen Thi Ngoc Ha¹, Truong Kim Hieu¹, Le Hong Vu¹, Huynh Sa Hoang¹,
Pham Thanh Tam¹, and Vuong Trung Kien¹

¹ University of Natural Sciences -VNU-HCM 227 Nguyen Van Cu Street,
5 District, Ho Chi Minh City, Viet Nam.
E-mail: ntnha@hcmuns.edu.vn.

Abstract. The photoreflectance (PR) is a sensitive optical method for examining the surface and interface properties of semiconductors. The important substrates that are available for light emitting technology are GaAs and InP. In this report, we simulate PR Spectra of GaAs in two cases: single-layer model (surface field is homogeneous in depth d), and multi-layer model (surface field decreases with depth d). By the multi-layer model, we received simulation results that are very similar to the experimental results. Important semiconductor materials exploited in optoelectronics are the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloys which are lattice matched very well to GaAs substrates. With the multi-layer model we simulated the PR spectra of the heterojunction structure $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}/\text{GaAs}$ ($x = 0.05$) for heterojunction- LEDs. The two-channel (X,Y) lock-in phase analysis is one of the most powerful methods for studying multi-component PR spectra. In this report, we set up the phase diagram in three-dimensions: X(E), Y (E) and E (energy of photon) coordinates. The 3-D phase diagrams indicate the number of the spectral components in a multi-component PR spectra (Franz-Keldysh oscillation-FKO; Exciton or Low-energy oscillation interference-LEOI).

The PR spectra experiment: our optical system is placed in front of the monochromator and has a scalable and tidiness structure. Collecting and processing data are automatically controlled by a PC. The controlled-program has a simple, easy used GUI (graphic user interface) simulated PR spectra of the heterojunction structure $\text{Al}_{0.05}\text{Ga}_{0.95}\text{As}(\text{n})/\text{GaAs}(\text{p}^-)/\text{GaAs}(\text{p}^+)$. These spectra include three separated parts: The PR with the maximum $E_0 = 1.487$ eV that shows the interface $\text{Al}_{0.05}\text{Ga}_{0.95}\text{As}(\text{n})/\text{Air}$, and the PR with $E_0 = 1.42$ eV correlates to the interface $\text{Al}_{0.05}\text{Ga}_{0.95}\text{As}(\text{n})/\text{GaAs}(\text{p}^-)$. Especially, the peak with $E_0 = 1.381$ eV in the experimental spectra points out the radiative recombination transition transition band-impurity (acceptor Si) in the $\text{GaAs}(\text{p}^+)$ -layer.

1. Introduction

1.1. Photoreflectance Modulation Spectroscopy [1,2]

Modulation spectroscopic techniques, which are sensitive to the optical properties of solids, are the oscillations in the vicinity of the optical transition energies at critical points, so-called Franz-Keldysh (FK) oscillations. By most useful method for the analysis of epitaxial layers for compound semiconductor devices. Photoreflectance (PR) spectroscopy can be a non-destructive and contact-less inspection technique because of the optical modulation of the built-in electric field by modulated photo excitation.

In the PR technique, a modulated laser beam with an energy above the band gap of the material being studied creates the photoinduced variation in the built-in electric field. For a case of an n-type semiconductor, because of the pinning of the Fermi energy at the surface, there exists a space-charge layer. The occupied surface states contain electrons from the bulk. Photoexcited electron-hole pairs are separated by the built-in field, with the minority carrier (holes for this case) being swept toward the surface. At the surface, the holes neutralize the trapped charge, reducing the built-in field.

When the low-field criteria are not satisfied, the dielectric function can exhibit the Franz-Keldysh oscillations.

$$\frac{\Delta R}{R}(E) \approx \frac{1}{E^2(E - Eg)} \exp \left[-\frac{\Gamma \sqrt{E - Eg}}{(\hbar\Omega)^{3/2}} \right] \cos \left[\frac{4}{3} \left(\frac{E - Eg}{\hbar\Omega} \right)^{3/2} \right] \quad (1.1)$$

E is the photon energy; Γ is the broadening parameter ;

$\hbar\Omega$ is the electro-optic energy given by: $\hbar\Omega = \left(\frac{e^2 \hbar^2}{2\mu} F_s^2 \right)^{1/3}$

F_s is the magnitude of the electric field: $F_s = \frac{\sqrt{2e\mu}}{\hbar} \hbar\Omega^{3/2}$

μ is the reduced interband effective mass in the direction of the field.

1.2. The PR Spectra of $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ as Multilayer [2, 3, 5, 6, 7].

In this model, the surface layer of the semiconductor is divided into j plane-parallel layers. The field F_v is assumed to be constant within each layer v . Then the complex refractive index (n, k) in each layer is defined as $\overline{N}_v = \overline{N}(F=0, E) + \Delta \overline{N}_v(F_v, E)$.

In this case, the reflectance signal is calculated from the formula:

$$\frac{\Delta R}{R}(E) = \frac{|\overline{r}_0|^2 - \text{Re}(R_0)}{\text{Re}(R_0)}; \quad R_0 = \left[\frac{\overline{N} - \overline{N}_L}{\overline{N} + \overline{N}_L} \right]^2 \quad (1.2)$$

The results of calculations in the context of the multilayer model are shown in Fig. 1. As can be seen, consideration of the inhomogeneity of the electric field gives rise to a negative low-energy peak, a flattening and energy shift of the main peak, and additional damping of the Franz–Keldysh oscillations. For comparison with the calculation model (dash line), the single spectra of PR typical of GaAs samples is shown by the solid line in Fig. 2.

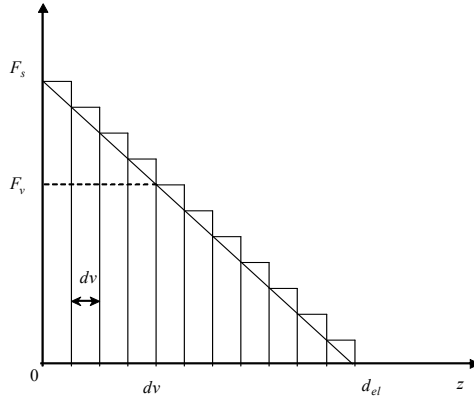


Fig. 1. The field F_s is reduced with depth

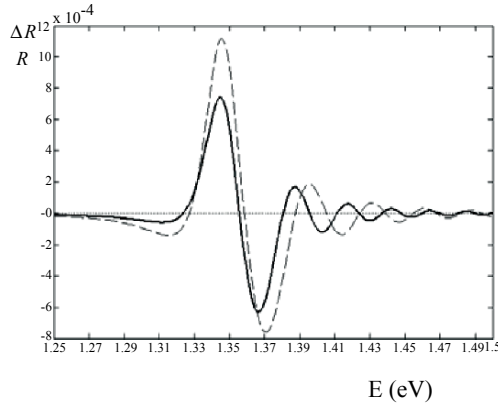


Fig. 2. The PR of GaAs with the model calculation (dash line) and experiment signal (solid line)

1.3. The Theory of Heterostructures Multilayer PR Spectra [3, 4, 5, 6].

There are a few methods of the heterostructures multilayer PR spectra. The first one uses the fact that we have many signals from different depths in the sample. In this case, the PR signal consists of three subsignals in Fig. 3:

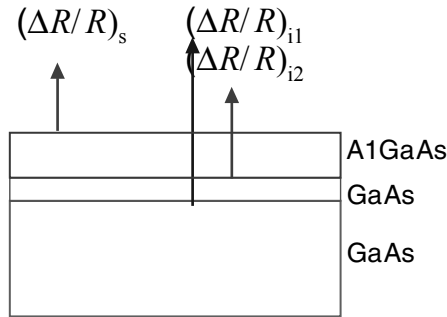


Fig. 3. The PR subsignals of surface and interfaces

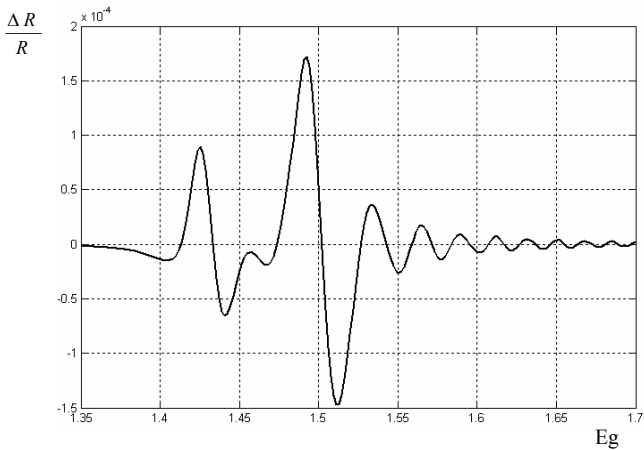


Fig. 4. The PR of $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}/\text{GaAs}$

$$\left(\frac{\Delta R}{R}\right) = \left(\frac{\Delta R}{R}\right)_s + A \left[\left(\frac{\Delta R}{R}\right)_{i1} + \left(\frac{\Delta R}{R}\right)_{i2} \right] \tag{1.3}$$

$\left(\frac{\Delta R}{R}\right)_s$: PR signal of $n - \text{Al}_x\text{Ga}_{1-x}\text{As}$ / Air

$\left(\frac{\Delta R}{R}\right)_{i1}, \left(\frac{\Delta R}{R}\right)_{i2}$: PR signal of the interfaces.

These subsignals are given with the accuracy of a constant factor A - the decrease coefficient of PR signal from interfaces.

2. Experimental Methods

2.1. The Experimental Set-up [7]

The automated instruments in our set-ups were a monochromator that was equipped with a stepper motor, a lock-in amplifier. The conventional photo-reflectance apparatus uses a mechanical chopper (210Hz) to modulate the laser lights.

We have two laser which have different power, one goes to the sample, one goes to the lock-in amplifier to make a reference signal. The modulation of the sample is produced by photoexcitation of electron-hole pairs created by the 10 mW laser. The laser light will have a characteristic wavelength corresponding to radiation with an energy above the band gap of the sample studied to assure that an adequate number of electron-hole pairs are photoexcited to produce the PR signal.

In the Fig. 5, a beam of light from the lamp is hitting the sample surface in the same area as the impinging laser light. The signal separator, connected to the detector, separates the signal into two components. The DC component is proportional to $I_0 R$, and AC component is proportional to $I_0 \Delta R$. The AC component is measured with a lock-in amplifier. A computer divides the AC signal by the DC component giving the PR spectra as Fig. 6.

In Fig. 7 show that the multilayer PR spectra is very similar to the experimental PR spectra. We also calculated $x = 0,5$ as a suitable parameter.

These spectra include three separated parts: the PR spectrum with the maximum $E_0 = 1.48, \text{ eV}$ that shows the interface $\text{Al}_{0.05}\text{Ga}_{0.95}\text{As}(\text{n})/\text{Air}$, and the PR spectrum with $E_0 = 1.42 \text{ eV}$ correlates to the interface $\text{Al}_{0.05}\text{Ga}_{0.95}\text{As}(\text{n})/\text{GaAs}(\text{p}^-)$. Especially, the peak with $E_0 = 1.38, \text{ eV}$ in the experimental spectrum points out the radiative recombination transition band-impurity (acceptor Si) in the $\text{GaAs}(\text{p}^+)$ -layer.

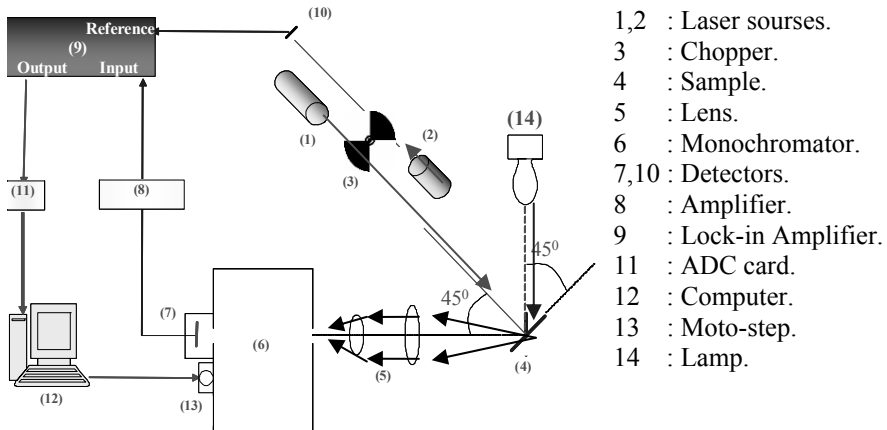


Fig. 5. The experimental set-up

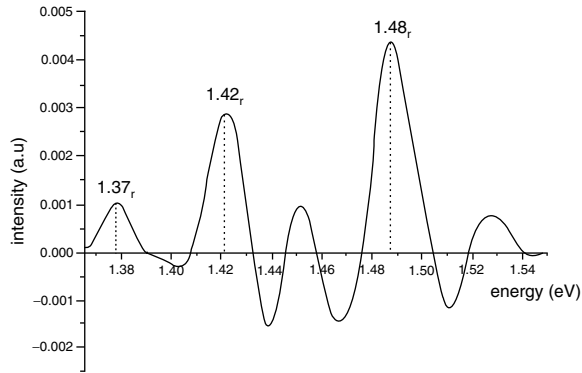


Fig. 6. The experimental PR spectra $\text{Al}_{0.05}\text{Ga}_{0.95}\text{As}/\text{GaAs}/\text{GaAs}$ at room temperature

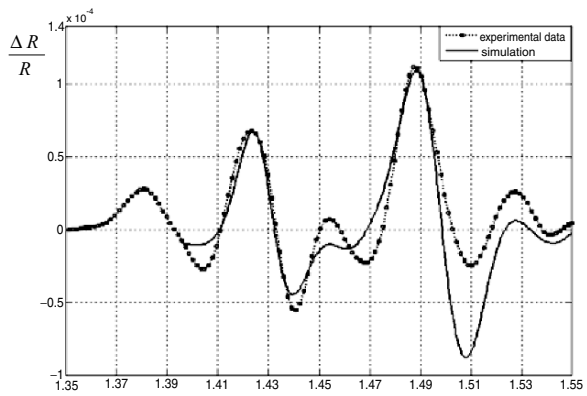


Fig. 7. The PR of $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}/\text{GaAs}$ with the calculation (dash line) and experiment signal (solid line).

3. Lockin-Phase Analysis of PR Spectra[1,2]

The use of a two-channel lock-in amplifier whose output is a complex signal consisting of a signal in phase with the modulation and a second imaginary component shifted relative to it by 90° , leads to the result that the PR spectra, with the time dependence of the reflection signal $R(t)$ taken into account, is described as follows:

$$\frac{\overline{\Delta R}}{R}(E, F_s, \tau, \omega) = \frac{\Delta R}{R}(E, F_s) \frac{2}{\pi(1 + \omega^2 \tau^2)} (1 - i\omega\tau) \tag{1.4}$$

where E is the photon energy, F_s is the electric field intensity, and $\omega = 2\pi f$ is the modulation frequency. The time dependence $R(t)$ yields the phase delay δ of the photorefectance signal relative to the phase of the modulating light. The lock-in amplifier defines the amplitude of the first Fourier component of the input signal at the reference frequency and for the preset phase. Using a two-channel lock-in amplifier, one can determine either the component of the signal in phase with the reference frequency (X) and the component shifted by 90° (Y), or the amplitude $r(E)$ and phase $\delta(E)$ of the modulated variable signal relative to the modulating signal: $\frac{\Delta R}{R}(E) = r(E)e^{i\delta(E)} = x(E) + iy(E)$. The phase of the signal δ is defined as the angle between the phase of the scattered modulating light and the PR signal.

$$\tan \delta = \frac{Y(E)}{X(E)} = \frac{\text{Im}(1 - i\omega\tau)}{\text{Re}(1 - i\omega\tau)} = -\omega\tau \quad (1.5)$$

with:

$$X(E) = \sum_{j=1}^n X(E)_j$$

$$Y(E) = \sum_{j=1}^n Y(E)_j$$

τ is the time constant.

The simulated shape of the 3D phase diagram is an indication of the complex character of the PR signal. (Franz-Keldysh oscillation-FKO; Exciton or Low-energy oscillation interference-LEOI).

In Fig. 8, on the (OXY) plan, the solid line is Franz-Keldysh effect. The dash line is the projection of two components PR on the plan (X,Y,O). This projection is the 2D phase diagram shown in Fig. 9.

In case of the one component PR spectra (example: FKO component), the shape of 2D phase is linear.

From simulated results, base on 3D phase diagram, we suggest a method to determine components of the complex PR spectra:

- Determining the FKO component:

In Fig. 8, the (ABC) plan is called the plan of FKO. The 2D phase diagram is a linear line as Fig. 9.

- Determining the other components:

In Fig. 8, the exciton component peak is D. This peak is not on (ABC) plan. So, if the 3D phase diagram of PR spectra has peaks which are not on the plan of FKO, these PR spectra have more than one component.

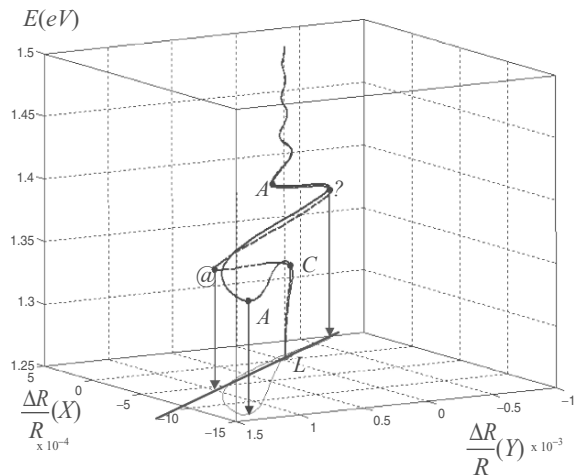


Fig. 8. The simulated shape of the 3D phase diagram of complex PR spectra

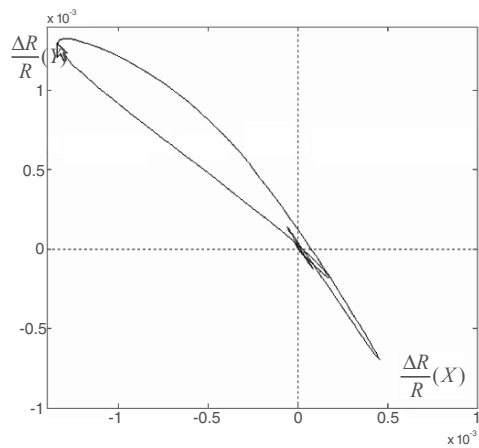


Fig. 9. The shape of the 2D phase diagram of complex PR spectra

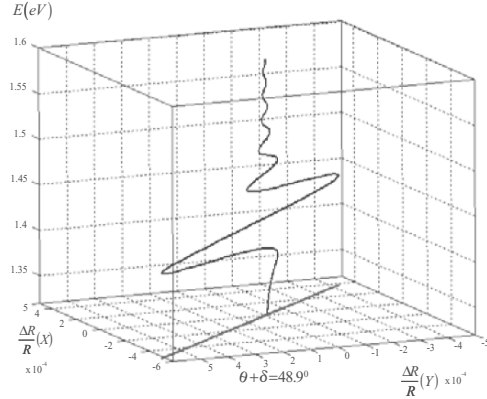


Fig. 10. The shape of the 3D phase diagram of FKO PR spectra

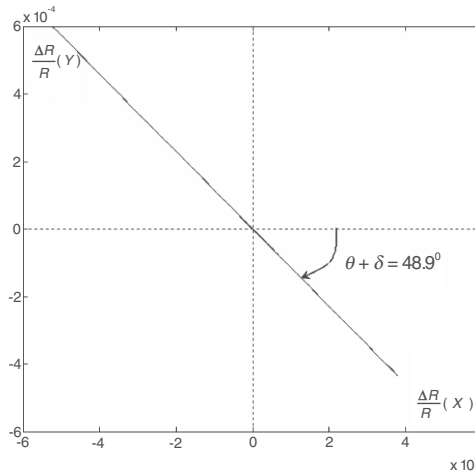


Fig. 11. The shape of the 2D phase diagram of FKO PR spectra

4. Conclusion

- From the theory of photoreflectance modulation spectroscopy, we have simulated heterostructures multilayer PR spectra $Al_x Ga_{1-x} As/GaAs/GaAs$. The simulated PR is very similar to the experiment PR at room temperature.
- To determine components of the complex PR by Lockin- phase analysis, we have used the 3D phase diagram instead of the 2D phase diagram of other authors [1]. This makes the determining PR components easily.

Reference

1. A.V. Ganzha, V. Kuz'menko, V. Kircher, J. Schreiber, and S. Hildebrandt, *Lock-in phase analysis of n-GaAs photoreflectance spectra*. Semiconductors **32**, 272–277, American Institute of Physics, (1998).
2. Jan Misiewicz, Piotr Sitarek, Grzegorz Sęk, Robert Kudrawiec, “*Semiconductor heterostructures and device structures investigated by photoreflectance spectroscopy*”, Materials Science, Vol. 21, No. 3, (2003).
3. J. Singh, “*Semiconductor Optoelectronics*”, McGraw Hill International Editions, (1995).
4. Kenneth A. Jones, “*Optoelectronik*”, VCH – Weinheim, (1992).
5. Pham Thanh Tâm “*Simulation and lock-in phase analysis in photoreflectance modulation spectroscopy of InP and heterostructures multilayer Ga_{1-x}Al_xAs/GaAs/GaAs*”, BSc Thesis, University of Natural Science, HCM city, Viet Nam, (2006).
6. Vương Trung Kiên, “*Photoluminescence and photoreflectance investigations of hetero-junction structures Ga_{1-x}Al_xAs/GaAs/GaAs and InP*”, BSc Thesis, University of Natural Science, HCM city, Viet Nam, (2006).
7. W. Kircher, R. Kuzmenko, S. Hidebrandt, and J. Schreiber, “*Comprehensive theoretical-model for the simulation of photoreflectance spectra from gallium arsenide*”, J. Appl. Phys. **83**, 4447 (1998); DOI:10.1063/1.367205

Principally Basic Effects of Laser on the Bulk Semiconductor Bands

N. Vinh Quang

Institute of Physics and Electronics, 10 Dao Tan, Hanoi, Vietnam
E-mail: nvquang@iop.vast.ac.vn

Abstract. Overcoming mathematical difficulties, it is finally solved the last case (the real-symmetry bands of zinc-blend structure bulk semiconductors interacting with the non-linearly polarized laser) of the very long-standing problem (the effects of external field on crystal spectrum), initiated by L.D. Landau 77 years ago.

The existence of a qualitatively new effect, which is simultaneously removing the s (spin index) and l - h (light, heavy holes) degeneracy, is theoretically proved. The “configuration” of the splitting of main quasi-band edges is strongly dependent on the polarization character of laser and is changed when the frequency changes from the values smaller than (or equal to) the band gap to the ones greater the band gap. The numerical evaluation shows that the effect is sufficiently strong for observation, for which a pump- probe experiment is proposed.

For the first time, paying attention to the uniqueness of the main quasi-band conception, all of the principally basic effects are clearly classified.

1. Introduction

The problem “the effects of external electromagnetic field on the electronic states and spectrum in a crystal” is many-year long- standing 77 years ago, in 1930 L.D. Landau initiated the investigation of the problem by considering a time-independent magnetic field case [1]; in 1940 W.V. Houston examined the time-independent electric field case [2]; studying the time-dependent case is begun from 1969 when V.M. Galitskii [3], other authors and N. Vinh Quang [4-6] considered the case of linearly polarized electromagnetic wave; in [7] the case of circularly polarized laser interacting with the Wurtzite structure semiconductors is solved; the “last” unsolved case is a one of non-linearly polarized wave interacting with the real-symmetry bands of Zinc-blend structure bulk semiconductors. That case is most mathematically complicated, since the l - h degeneracy causes the essential difficulties as in the exciton problem [8]. In addition, in the “last” case Hamiltonian is not invariant for the time-inversion, therefore there is no degeneracy like the Kramer one [9], hence, we have to take into account s (spin index) degeneracy simultaneously. This is why that “last” case is unsolved up to now. In this paper, overcoming mathematical difficulties, it is finally solved the” last “case. A qualitatively new effect that is the s - l - h splitting due to elliptically polarized laser is found. The numerical evaluation is made to show that the effect can be observed

by the experiment, which is proposed. Its low dimension case is discussed. Using the uniqueness of main quasi-band notion [7], all of the principally basic effects are clearly classified. In this paper, the system of the atomic units is used.

2. *S-L-H* Splitting

It is taken from Kane's band theory [10, 11] the electron's Bloch wave functions. As in [4] we determine a state $\varphi(\underline{r}, t)$ of the crystal in the field $\vec{A}(t)$ from the time-dependent Schrödinger equation with the Hamiltonian

$$\begin{aligned} H(t) &\equiv H_o + H_{\text{int}}; H_o \equiv \frac{\hat{P}^2}{2m} + V(\underline{r}) + \frac{1}{4m^2} [\hat{\sigma} \nabla V(\underline{r})], \\ H_{\text{int}} &\equiv \frac{1}{m} e \vec{A}(t) \hat{Q} + \frac{1}{2m} e^2 A^2(t); \hat{Q} \equiv \hat{P} + \frac{1}{4m} [\hat{\sigma} \nabla V(\underline{r})], \end{aligned} \quad (2.1)$$

where $m, -e, \hat{P}$ and $\hat{\sigma}$ are the mass, charge, the momentum and spin operator of the electron, respectively; $V(\underline{r})$ is the crystal potential.

The set of equations for defining coefficients $a_{n\vec{k}\delta}$ in the expansion of the wave function $\varphi(\underline{r}, t)$ into the set of eigen-functions is obtained in [12]. Using the Kane's functions it is found that the spin index (+)[-] stationary state of *c*-band mix only the spin index (+)[-] ones of *h*-band and the spin index (-)[+] ones of *l*-band.

In [12] the existence of a qualitatively new effect, which is simultaneously removing the *s* (spin index) and *l-h* (light, heavy holes) degeneracy, is just theoretically proved without using RWA (rotating wave approximation) for circularly polarized laser.

Now we complete the problem by considering the "last part" of the "last case": the one of elliptically polarized laser. Then field is

$$\vec{A}(t) = (\vec{i} \cos \omega t - \vec{j} \sin \omega t) A_0; \quad \vec{i} \perp \vec{j}; |\vec{i}| = |\vec{j}| = 1, \quad (2.2)$$

where g is real number describing elliptical degree.

Repeating the formalism developed in [12], 3 different dispersion relations of the main quasi-bands are obtained:

$$\begin{aligned} E_{c(+)}(\underline{k} \rightarrow 0, A_0) &= E_c(\underline{k} \rightarrow 0) + u_-(\delta) \alpha_1(\delta_1, \delta_2) + [1 - u_-(\delta)] \alpha_2(\delta_1, \delta_2) \\ E_{h(+)}(\underline{k} \rightarrow 0, A_0) &= E_h(\underline{k} \rightarrow 0) + \alpha_3(\delta_1, \delta_2) + \delta_1 \\ E_{l(-)}(\underline{k} \rightarrow 0, A_0) &= E_l(\underline{k} \rightarrow 0) + u_-(\delta) \alpha_2(\delta_1, \delta_2) + [1 - u_-(\delta)] \alpha_1(\delta_1, \delta_2) + \delta_2, \end{aligned} \quad (2.3)$$

where

$$\begin{aligned}
 \alpha_1(\delta_1, \delta_2) &= \frac{2}{\sqrt{3}}(-p)^{1/2} \cos \frac{\theta}{3} - \frac{v}{3}, \\
 \alpha_2(\delta_1, \delta_2) &= -\frac{2}{\sqrt{3}}(-p)^{1/2} \cos \left(\frac{\pi}{3} + \frac{\theta}{3} \right) - \frac{v}{3}, \\
 \alpha_3(\delta_1, \delta_2) &= -\frac{2}{\sqrt{3}}(-p)^{1/2} \cos \left(\frac{\pi}{3} - \frac{\theta}{3} \right) - \frac{v}{3}, \\
 \theta &= \arccos \left(-\frac{3^{3/2}}{2} q / (-p)^{3/2} \right); \quad \pi \geq \theta \geq 0, \\
 v &\equiv \delta_1 + \delta_2; \quad s \equiv \delta_1 \delta_2 - (\Lambda_1^2 + \Lambda_2^2); \quad t \equiv -(\delta_1 \Lambda_1^2 + \delta_2 \Lambda_2^2), \\
 p &\equiv -\frac{v^2}{3} + s; \quad q \equiv 2 \left(\frac{v}{3} \right)^3 - \frac{vs}{3} + t, \\
 u_-(y) &\equiv \begin{cases} 1; & y \geq 0 \\ 0; & y < 0 \end{cases}, \quad (2.4)
 \end{aligned}$$

with

$$\begin{aligned}
 \delta &\equiv E_G - \omega, \delta_1 \equiv E_c - E_h - \omega, \delta_2 \equiv E_c - E_l - \omega, \\
 \Lambda_1 &\equiv -i\sqrt{2} \frac{e}{m} A_0 Q(g+1), \Lambda_2 \equiv -i\sqrt{\frac{2}{3}} \frac{e}{m} A_0 Q(g-1), \quad (2.5)
 \end{aligned}$$

Q being a Kane's parameter.

Three others equal

$$\begin{aligned}
 E_{c(-)}(\underline{k} \rightarrow 0, A_0) &= E_c(\underline{k} \rightarrow 0) + u_-(\delta) \alpha_1(\delta_2, \delta_1) + [1 - u_-(\delta)] \alpha_2(\delta_2, \delta_1), \\
 E_{h(-)}(\underline{k} \rightarrow 0, A_0) &= E_h(\underline{k} \rightarrow 0) + u_-(\delta) \alpha_2(\delta_2, \delta_1) + [1 - u_-(\delta)] \alpha_1(\delta_2, \delta_1) + \delta_1, \\
 E_{l(+)}(\underline{k} \rightarrow 0, A_0) &= E_l(\underline{k} \rightarrow 0) + \alpha_3(\delta_2, \delta_1) + \delta_2, \quad (2.6)
 \end{aligned}$$

where the $\alpha_1(\delta_2, \delta_1)$, $\alpha_2(\delta_2, \delta_1)$, $\alpha_3(\delta_2, \delta_1)$ are determined from (2.4) by the replacement $\delta_1 \leftrightarrow \delta_2$.

From (2.2) – (2.6) it follows that the s and l - h degeneracy at the top of l - h bands are simultaneously removed.

When $\omega > E_G$ the “configuration” of the split main quasi-band edges is

$$E_{h(-)}(\underline{k} \rightarrow 0, A_0) > E_{l(-)}(\underline{k} \rightarrow 0, A_0) > E_{l(+)}(\underline{k} \rightarrow 0, A_0) > E_{h(+)}(\underline{k} \rightarrow 0, A_0) \quad (2.7)$$

When $\omega \leq E_G$ the “configuration” of the split main quasi-band edges is

$$E_{l(+)}(\underline{k} \rightarrow 0, A_0) > E_{h(+)}(\underline{k} \rightarrow 0, A_0) > E_{l(-)}(\underline{k} \rightarrow 0, A_0) > E_{h(-)}(\underline{k} \rightarrow 0, A_0) \quad (2.8)$$

Thus, the “configuration” of the split main quasi-band edges is strongly changed when the frequency ω continuously changes from $\omega \leq E_G$ to $\omega > E_G$. The results for the case with the field

$$\underline{A}(t) = (\underline{i}g \cos \omega t + \underline{j} \sin \omega t) A_0 \quad (2.9)$$

are obtained from the above obtained results by the following substitutions:

$$c(+) \leftrightarrow c(-); \quad h(+) \leftrightarrow h(-); \quad l(+) \leftrightarrow l(-) \quad (2.10)$$

Thus, the polarization character of the field plays an important role in s - l - h splitting effect.

The reason of the s - l - h splitting is the fact that the Hamiltonian $H(t)$ is time-periodic simultaneously being not invariant for time inversion, while the states must be classified according to the representation of the symmetry group of $H(t)$. The elliptical case is different from the circularly one only quantitatively but not qualitatively.

In order to make clear the practical significance of the s -splitting of c -band and s - l - h splitting let us now calculate these effects for *InSb*. Using the band parameter as in [13]:

$$\begin{aligned} E_G &\approx 0,237 \text{ eV}, \\ Q^2 &\approx 25 \text{ eV} \end{aligned} \quad (2.11)$$

when the field has intensity $E_0 \cong 6,75 \cdot 10^4 \text{ V/cm}$ and $g=1$ we obtain the following essential results.

For $\omega > E_G$:

$$\begin{aligned} [\Delta E_c(\underline{k} \rightarrow 0)]_s &\cong 58 \text{ meV}, \\ \Delta_{h(-)l(-)} &\cong 40 \text{ meV}, \\ \Delta_{l(-)l(+)} &\cong 92 \text{ meV}, \\ \Delta_{l(+)h(+)} &\cong 18 \text{ meV}. \end{aligned} \quad (2.12)$$

When $\omega \leq E_G$

$$\begin{aligned} [\Delta E_c(\underline{k} \rightarrow 0)]_s &\cong 40 \text{ meV}, \\ \Delta_{l(+)h(+)} &\cong 18 \text{ meV}, \\ \Delta_{h(+)l(-)} &\cong 25 \text{ meV}, \\ \Delta_{l(-)h(-)} &\cong 58 \text{ meV}. \end{aligned} \quad (2.13)$$

Hence, s - l - h splitting should be observed by the following pump-probe experiment. Let a sample of $InSb$ be irradiated by the circularly polarized laser beam of $E_0 \cong 6,75 \cdot 10^4 V/cm$ with the frequency just smaller than 237 meV then we study the absorption spectrum of the additional weak linearly polarized light [20] with the frequency near 18 meV waiting for the peak, which should be appeared due to the transitions from the main quasi-band h (+) to the main quasi-band l (+).

The particular feature of the s - l - h splitting effect, namely, the change of the “configuration” of the splitting of main quasi-band edges under the continuous changes of the frequency from $\omega \leq E_G$ to $\omega > E_G$ could be used for determining exactly the band gap.

Since any arbitrarily directed time-independent electric field cannot cause s - l - h splitting (see Kramer’s theorem [9]), the s - l - h splitting is a qualitatively new effect and could not be considered as a high-frequency Franz-Keldysh effect [14,15].

As a principally basic effect, the s - l - h splitting has a significant sense. It is important not only for the theories of optical and transport processes associated with intense electromagnetic wave (for instance, laser annealing, the generation of a strong field in semi conducting lasers [16] etc.), but also for studying the discrete symmetries in electrodynamics [17].

In addition, since the change of the electron spectrum has essential influence on the superconductivity’s properties of semiconductor, the s - l - h splitting may be important in studying the high-Tc superconductivity’s non-equilibrium mechanism in semiconductors [18].

3. Principally Basic Effects

Due to the uniqueness of the main quasi-band conception [7] we are able to classify clearly all of the principally basic effects of lasers on the bulk semiconductor bands that are the shifts, field-induced-gaps (FIG), l - h splitting, s -splitting and s - l - h splitting. The s -splitting and s - l - h splitting are qualitatively new and could not be considered as a high-frequency Franz-Keldysh effect.

i. Shifts of the main quasi-band edges [4–7, 12]

When the frequency is greater than the band gap, the C (V) edges are shifted to the side of lower (higher) energy.

When the frequency is smaller than (or equal to) the band gap, the C (V) edges are shifted to the side of higher (lower) energy.

ii. Field-induced-gaps (FIG) [3-6]

They appear at the resonant points when the frequency is greater than the band gap.

iii. l-h splitting [5-6]

It appears in the linearly polarized wave case.

iv. s-splitting [7]

It appears in the non-linearly polarized wave case in the Wurtzite structure semiconductors.

v. s-l-h splitting [12]

It appears in the non-linearly polarized wave case in Zinc-blend structure semiconductors.

These principally basic effects, the Landau sub-zone, and the Franz-Keldysh shift are the most interesting ones of “the effects of external electromagnetic field on the electronic states and spectrum in a crystal”, which together with the effects of the hydrostatic pressure, and uniaxial stresses have to form an irreplaceable chapter in a book on optical properties in semiconductors [8] and [19].

4. Discussion

In future, the low dimension [21] case of the effects will be considered later for studying the relaxation and dephasing quantum kinetics for a quantum dot and for a quantum well [22] optically excited by laser.

Acknowledgment

This work is made with contributions of Truong Ngoc Chinh and Pham Hong Phong. The author would like to thank Prof. Do Tran Cat for his helpful interest to this paper. This work is supported by Vietnamese Ministry of Science and Technology – the natural science basic research program 40 28 06

References

1. L.D. Landau, *Z.Phys.*, Vol. 64, 629, 1930
2. W.V. Houston, *Phys.Rev.* Vol. 57, 184, 1940
3. V.M. Galitskii, S.P. Goreslavskii and V.F. Elesin, *Zh. eksper.teor. Fiz.*, Vol. 57, 207, 1969
4. N. Vinh Quang, *Phys. Stat. Sol (b)*, Vol. 90, 597, 1978
5. N. Vinh Quang, *J de Physique* Vol. 43, 113, 1982
6. N. Vinh Quang, *Czech.J.Phys.*, Vol. B35, 86, 1985
7. N. Vinh Quang, *Sol. Stat. Commun.*, Vol. 64, 1089, 1987
8. F. Bassani, G. Pastori Parravicini, *Electronic states and Optical transition in Solid*, Pergamon Press, ch.8, 1975.

9. H. Kramers, *Proc. Acad. Sci. Amsterdam*, Vol. 33, 959, 1936
10. E.C. Kane, *J. Phys. Chem. Solids*, Vol. 1, 249, 1957
11. E.C. Kane, in *Semiconductors and Semimetals*, Vol. 1, 1966
12. N. Vinh Quang, *Laos J.A.S.*, Vol.1, 125, 2006
13. C. Herman and Weisbush, *Phys. Rev.*, Vol. B15, 823, 1977
14. W.Z. Frans, *Naturforsch*, Vol. 13, 484, 1958.
15. K.V. Keldysh, *Zh.eksper.teor.Fiz.*, 1138, 1958
16. V.M. Galitskii and V.F. Elesin, *Zh.eksper.teor.Fiz*, Vol. 68, 216, 1975
17. V.I. Strajev and N. Vinh Quang, *Soviet Nucl.J.*Vol.16, 614, 1972
18. Iu.V. Kopaev, in *High Tc superconductivity problem*, Ed. By V.L. Ginzburg and D.A. Kirjnitx, "Nauka", Moscow.1977
19. H. Haug and S.W. Koch, *Quantum Theory of the Optical and Electronic Properties of Semiconductors*, 4th ed., World Scientific, Singapore, 2004
20. G.M. Arutynyan, E.M. Kazaryan, and G.R. Minasyan, *Fiz.Tver.Tela*, Vol. 9, 2568, 1976
21. F.T. Vasko and A.V. Kuznetsov, *Electronic States and Optical Transitions in Semiconductor Heterostructures*, Springer, 1999.
22. O.T. Vu, H. Haug and S.W. Koch, *Phys. Rev. B*, Vol. 73, 205317, 2006

Controlling the Bragg Wavelength Spectral Profile Expansion of FBG Sensors by Nano-Particle Coated Layers

Pham Van Hoi*, Pham Thanh Binh, Ha Xuan Vinh, and Tran Thi Cham

National Key Laboratory for Electronic Materials and Devices, Institute of Materials Science, VAST of Vietnam, 18 Hoang Quoc Viet Rd., Cau Giay Dist., Hanoi, Vietnam
E-mail: hoipv@ims.vast.ac.vn

Abstract. This paper presents the results of a detailed study of spectra profile expansion of Bragg wavelength on the embedded fiber-Bragg-grating (EFBG) and the method for controlling it for optical sensors. The fiber-Bragg-grating (FBG) was coated by nano-particle layers with various thicknesses (600–2000 nm) and bonded to substrates of various materials with a large thermal expansion coefficient. With this embedding method, the variation of the line-width expansion of Bragg wavelength with cooling down FBG has been controlled. The nano-EFBG morphology was investigated by FE-SEM and the nano-EFBG sensors are studied in ambient from 77K (liquid nitrogen) to 393K. The expansion of spectral profile caused by transverse loading from nano-particle/embedded layers, can be changed in the range of 0.1–1.3 nm between before and after cooling down. This result may be used for the strain-temperature sensors, but has potential application in FBG dispersion compensation devices.

Key word: Nano particles • embedded fiber Bragg grating • fiber optic sensors

1. Introduction

Wavelength tuning of fiber Bragg gratings (FBGs) by lateral or transverse load, temperature and/or vibration is attractive for optical sensing [1–6]. The wavelength response characteristic of the FBG upon temperature, lateral and transverse load is highly dependent on the surrounding media, its configuration and the contact conditions. As we known, by fixing FBG on a substrate with a large thermal expansion coefficient, the sensitivity of temperature FBG sensor can be enhanced to 1.5–15 times that of pure FBG [5, 7–9]. But, Reid and Ozcan [10] demonstrated that an FBG embedded in composite material at 4.2K–300K showed the same temperature dependence as that of non-embedded FBG sensors, because the composite materials had small thermal expansion coefficients. Suresh and Tjin had been developed the embedded FBG with two layers from carbon composite and deformable materials for shear force sensors with a linear variation of the wavelength shift [11]. Therefore, selection of substrate materials is especially important for embedded FBG sensors. For EFBG temperature sensors, when the contact surface between embedded material and glass fiber is homogeneous and smooth, there is no significant change in the profile of both spectra, before and

after cooling down [8]. But in practice, contact surface between substrate and FBG has micron-size roughness. From this non-homogeneous contact surface, the transverse load would be changed from point to point along the FBG, when sensor is cooling down, and it is caused a significant change in the line-width of Bragg wavelength between before and after cooling down [12].

In this paper, we propose use of nano-particles thin film of CdSe as a controlled-roughness layer on FBG and it is embedded in different materials with various thickness and configuration, for a fiber optic sensory application. We examined several types of embedded FBG sensors in the large temperature range (from 77 K to 393 K). The line-width expansion of Bragg wavelength, which depend upon thickness of nano-particle coated layer and bonded material substrate, has been studied and discussed. We compared the experimental spectra expansion of Bragg wavelength caused by transverse load with a theoretical one.

2. Experimental Procedure

In our work, the FBG was written by holographic method using a KrF-Excimer laser (248 nm) and Talbot interferometer. The optical fiber was a commercial photosensitive germanosilicate single-mode fiber. An FBG has one or multi-grating (maximum 5 grating at different Bragg wavelength) into one fiber. The Bragg wavelength at room temperature was in the range of 1530–1550 nm (the spacing between each Bragg wavelength was of 5 nm for FBG-array), a reflectivity was of 75–90% and a Full-width-half-maximum (FWHM) bandwidth was of 0.15–0.30 nm. The length of FBG was 15 mm. The broad-band light source was an Amplified Spontaneous Emission (ASE) from Erbium-doped Fiber Amplifier (EDFA). The spectral measurement was performed with a reflection scheme using 1550 nm- fiber optic circulator. The reflection spectrum was observed with an Optical Spectrum Analyzer (Advantest Q8384), which has spectra resolution of 0.01 nm. The shift of Bragg wavelength induced by the change of temperature is [8]:

$$\frac{\Delta\lambda_B}{\lambda_B} = [(1 - p_e)\alpha + \xi]\Delta T \quad (1)$$

Where $\alpha = (1/\Lambda) (\delta\Lambda/\delta T)$ is the linear thermal expansion coefficient, P_e is the photo-elastic constant ($P_e \cong 0.22$ [6]) and $\xi = (1/n_{\text{eff}}) (\delta n_{\text{eff}}/\delta T)$ is the thermo-optic coefficient of fiber, respectively. The coefficients α and ξ are not linearly depending on temperature in a large range. For germanosilicate fibers, α is so small ($0.5 \times 10^{-6} \cdot \text{K}^{-1}$) that the effect of the thermal expansion is one order less than that of the thermo-optic refractive index change ($\xi \cong 10^{-5} \cdot \text{K}^{-1}$).

If the effect of thermal expansion is large enough, the temperature sensitivity of the FBG sensor can be proportional to the thermal expansion coefficient.

When FBG is embedded into materials, transverse strain may arise that will also shift the period of the grating. In addition, the non-homogeneous of contact surface between FBG and substrate causes the perturbation of transverse loading along the fiber, when the temperature is cooling down. This perturbation of strain

on fiber provides expansion of spectral profile of Bragg wavelength. The shift of Bragg wavelength by pressure can be calculated by following formula [13]:

$$\frac{\Delta\lambda}{\lambda_B} = \left[-\frac{1-2\nu}{E} + \frac{n_{eff}^2}{2E} (1-2\nu)(2p_{12} + p_{11}) \right] \Delta P \quad (2)$$

Where: ν is Poisson's ratio, p_{11} and p_{12} are components of strain-optic tensor, and E is modulus of elasticity. The FBGs were assembled as shown in figure 1. In our experiment we used colloidal nano-particles of CdSe with size of 6–10 nm for coating FBG with effective thickness from 600 nm to 2000 nm. The epoxy (OCI – USA Inc.) and the large thermal expansion materials such as copper, Teflon were used as substrate. The configurations of substrate are rectangular and/or cylinder with various sizes. The embedded FBG was inserted into metallic housing and put into various environment temperatures such as Dewar vessel containing liquid nitrogen, ice or boiled water and/or thermal furnace. The use of FBG array permits to study in detail the change of spectra line-width of reflection light in various temperatures. The measurement was performed in thermal equilibrium during several scanning times of optical spectrum analyzer (more than 10 minutes).

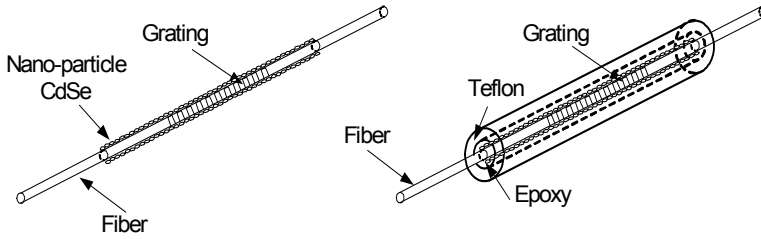


Fig. 1. Schematic of FBG temperature sensors: The FBG coated by nano-particle CdSe with thickness of 600–2000 nm (left) and Nano-particle coated FBG is bonded into an epoxy cylinder ($d = 3$ mm) coated by Teflon cylinder with $d = 10.3$ mm

3. Results and Discussions

Figure 2a shows SEM images of micro-bending and micro-size roughness of contact surface between glass fiber and epoxy substrate of epoxy/Teflon embedded FBG sensor. The micro-bending of tens-micron radius provides optical loss of reflection power and the micron-size roughness on contact surface provide the perturbation of transverse strain on fiber that causing change of spectral profile of Bragg wavelength. Figure 2b demonstrates the SEM image of fiber coated by nano-particle of colloidal CdSe with thickness about 2 microns. This nano-particle layer can control the level of homogeneous of contact surface between fiber and embedded materials. Figure 3 presents the experimental results of wavelength shifts of different materials-substrate embedded FBG sensors in low temperature range (77–360K). At room temperature range (301–360 K) the Bragg wavelength shift of non-embedded FBG was of 0.648 nm and the average temperature

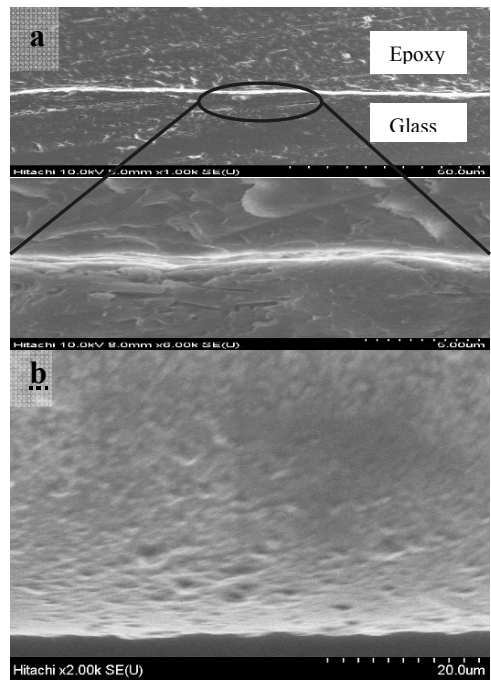


Fig. 2. SEM – images of non-homogenous surface between epoxy and glass fiber in epoxy/ Teflon embedded FBG (a) and CdSe-Nano-particle coated FBG (b)

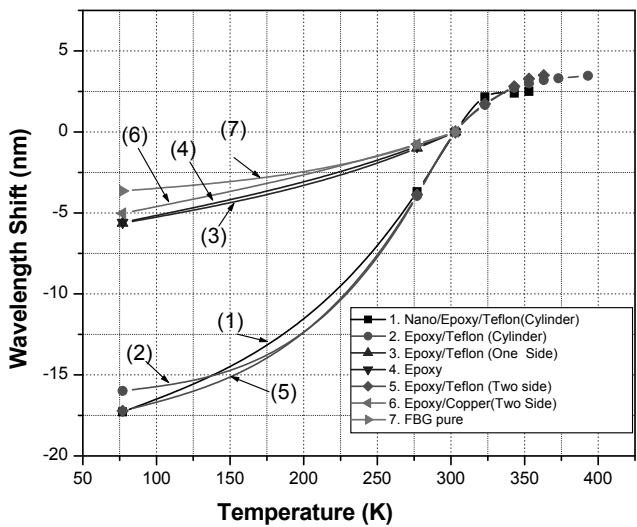


Fig. 3. Wavelength shifts of different material–substrate embedded FBG with temperature from 77K to 370 K

sensitivity corresponds to 11.3 pm.K^{-1} . At low temperature range (77–301 K) the Bragg wavelength shifted by 3.49 nm (from 1539.63 nm to 1536.14 nm). For non-embedded FBG, there is no significant change in the line-width spectra and in reflection peak level before and after cooling down. This result is well comparable to sensitivity value of typical silica FBG [8]. It is remarkable, that when FBG bonded into epoxy, the Bragg wavelength was slightly shifted to long-wavelength zone (for example the Bragg wavelength shift about 0.2 nm in our case). Figure 4 shows the experimental wavelength shifts of one FBG bonded into epoxy cylinder with diameter of 3 mm (fig. 4a) and the other coated by 2-micron layer of nano-CdSe and epoxy (fig 4b) at 301 K, 277 K and 77 K. Both types of EFBG had been

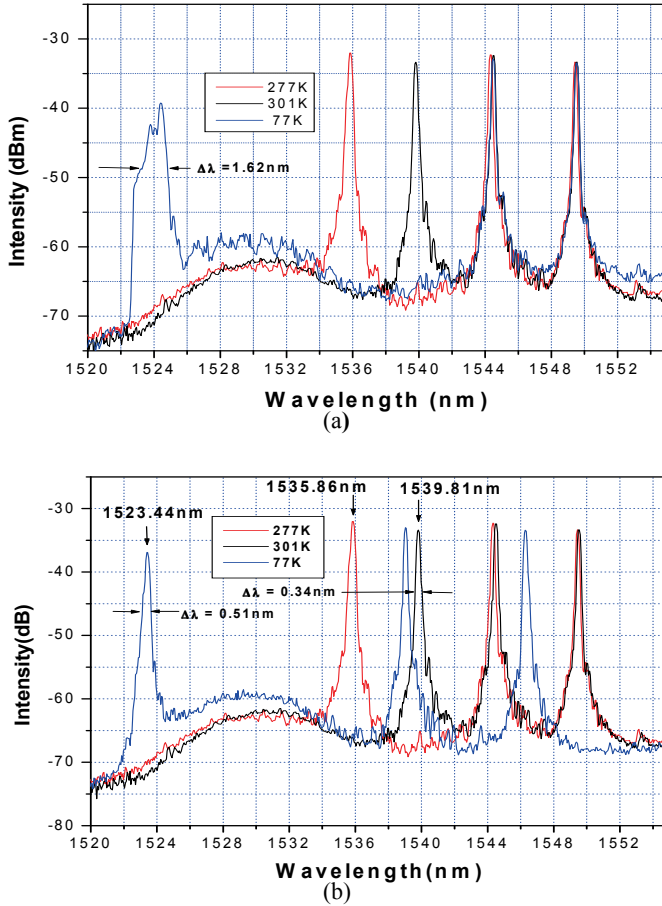


Fig. 4. The expansion of spectral profile of epoxy/Teflon substrate FBG was of 1.62 nm (a) and of CdSe-nano epoxy/Teflon -embedded FBG was of 0.51 nm (b) observed after some times cooling down

coated by Teflon cylinder with diameter of 10.3 mm. The sensitivity of both epoxy/Teflon substrate sensors is the same value (about 164 pm.K^{-1} at room temperature and average sensitivity corresponds to $71\text{--}73 \text{ pm.K}^{-1}$ from room temperature to liquid nitrogen temperature). The signal peak level decreased by some decibel (3–5 dB) and it is considered to be micro-bending induced in the coating of the fiber (see Fig. 2). A significant change in the spectral profile of Bragg wavelength of EFBG, when the sensors inserted into liquid nitrogen several times, has been observed.

To study the line-width expansion of Bragg wavelength, two group of EFBG sensors were taken. The epoxy/Teflon embedded FBG with rectangular and cylinder configurations were taken for the first group. The nano-CdSe coated layer/epoxy/Teflon embedded FBGs were in the second one. The nano-CdSe effective thickness was of 600, 1000, 1500 and 2000 nm. The characteristics of various embedded FBG upon the temperature is shown in Table 1.

The spectra line-width of EFBG has been compared with that of non-substrate FBG at the same temperature. The spectra line-width at -10dB was increased from 0.3 nm for non-substrate FBG to 1.62 nm and to $0.4\text{--}0.51$ nm for the epoxy/Teflon and nano-CdSe coated/epoxy/Teflon sensors, respectively. We can explain this effect by the micron-size space between the fiber and the surrounding materials, which made non-homogeneous contact surface of FBG. The micron-size roughness on contact surface can be provided a perturbation of transverse strain from point-to-point along the fiber, when the embedded FBG was cooling down. This perturbation of transverse strain caused the non-homogeneous change of Bragg periods of the FBG. We used the value of ν , p_{11} and p_{12} , E for silica glass fiber from reference [13], and the n_{eff} changed from 1.444 at room temperature to 1.441 at 77 K for calculation of transverse pressure on FBG. The calculation result of ΔP changed from 10.4 to 136.9 MPa is well comparable to elasticity condition of strain on silica glass fibers.

Table 1. Characteristics of various embedded FBG temperature sensors

Type of Sensors	T_0 (°K)	λ_0 (nm)	T_s (°K)	λ_s (nm)	Wave-length shift (nm)	Line-width at -10dB (nm)	Average sensitivity (pm/°K)
Epoxy-embed.FBG	301	1529.90	77	1524.32	5.58	1.1	24.91
Epoxy-copper FBG	301	1550.00	77	1544.91	5.08	1.2	22.68
Epoxy-Teflon FBG (one side)	301	1550.00	77	1544.36	5.64	1.2	25.18
Epoxy-Teflon FBG (two side)	301	1550.20	77	1532.78	17.42	1.54	77.78
Epoxy-Teflon FBG (cylinder)	301	1539.89	77	1523.91	15.98	1.62	71.34
Nano-CdSe coated/ Epoxy-Teflon FBG	301	1539.81	77	1523.44	16.37	0.51	73.08
Non-embed. FBG	301	1539.63	77	1536.14	3.49	0.3	15.58

4. Conclusion

Nano-embedded-FBG temperature sensors for large temperature range (from 77K to 373K) have been developed. Nano-EFBG sensors using epoxy/Teflon cylinder configuration achieved the high-sensitivity coefficient of 164 pm.K^{-1} at room temperature and of 73 pm.K^{-1} at large range from 77 K to 373 K, respectively. The expansion of spectra line-width of EFBG sensors at low temperature changed from 0.1 to 1.3 nm and it depended upon thickness of nanoparticle coated layers. This phenomenon may be explained by a perturbation of transverse strain along the fiber, which caused by micron-size space between fiber and surrounding materials.

Acknowledgment

This work was supported by the Vietnamese Physics Research Program for 2006-2007.

References

1. C.R.Giles, "Light wave applications of fiber Bragg gratings", Light wave Technol., **15**, (1997), 1391-1404.
2. A.D. Kersey, M.A. Davis, H.J. Patrick, M. LeBlanc, K.P. Koo, C.G. Askins, M.A. Putnam, E.J. Friebele, "Fiber grating sensors", Light wave Technol., **15**, (1997), 1442-1463.
3. S. Ekannelopoulos, V.A. Handrek, A.J. Rogers, "Simultaneous strain and temperature sensing with photo generated in-fiber gratings", Optic.Lett. **20**, (1995), 333-335.
4. S.W. James, M.L. Dockney, R.P. Tatum, "Simultaneous independent temperature and strain measurement using in-fiber Bragg grating sensors", Electron.Lett. **32**, (1996), 1133-1134.
5. A. Inoue, M. Shigehara, M. Ito, M. Inai, Y. Hattori, T. Mizunami, "Fabrication and application of fiber Bragg grating-a review, Optoelectron. Dev. Technol., **10**, (1995), 119-130.
6. S.C. Tjin, J.Z. Hao, Y.Z. Lam, Y.C. Ho and B.K. Ng, "A pressure sensor using fiber Bragg grating", Fiber Int. Opt. **20**, (2001), 59 -69.
7. G. Meltz, W.W. Morey, "Bragg grating formation and germanosilicate fiber photo-sensitivity", Proc. SPIE, **1516**, (1992), 185-199.
8. T. Mizunami, H. Tatehata, H. Kawashim, "High-sensitivity cryogenic fiber-Bragg-grating temperature sensors using Teflon substrates", Meas. Sci. & Tecnol., **12**, (2001), 914-917.
9. S. Gupta, T. Mizunami, T. Yamao, T. Shimomura, "Fiber Bragg grating cryogenic temperature sensors", Appl. Opt., **35**, (1996), 5202-5205.
10. M.B. Reid, M. Ozcan, "Temperature dependence of fiber optic Bragg gratings at low temperatures", Opt. Eng., **37**, (1998), 237-240.
11. R. Suresh, S.C. Tjin, "Effects of dimensional and material parameters and cross-coupling on FBG based shear force sensor", Sens. & Actuators A, No. **120**, (2005), 26-36.
12. Nguyen Thu Trang, Do Thanh Huu, Pham Van Hoi, Pham Thanh Binh, Ha Xuan Vinh, Chu Thi Thu Ha, "Improvement of temperature Sensitivity of fiber-Bragg-grating

- sensors using large thermal expansion coefficient material substrates*", Proc. of Vietnam National Conf. on Optics and Spectroscopy 2006 (in press)
13. O. Frazao, R. Romero, F.M. Araujo, L.A. Ferreira, J.L. Santos, "*Strain-temperature discrimination using a step spectrum profile fiber Bragg grating arrangement*", Sens. & Actuators A, No. 120, (2005), 490-493.
 - 14 M.G. Xu, L. Reekie, Y.T. Chow, J.P. Dakin, "*Optical in-fiber grating high pressure sensor*", Electronics Letters, 29, no. 4, (1993), 398-399.

Controlled Cantilever-Tips Adapted from the Scanning Probe Microscopies as Active Working Elements in Smart Systems

Michael Hietschold¹, Falk Müller², Anne-Dorothea Müller², and Thomas Gessner³

¹ Solid Surfaces Analysis Group, Institute of Physics, Chemnitz University of Technology, D-09107 Chemnitz, Germany

E-mail: hietschold@physik.tu-chemnitz.de

² Present address: Anfattec AG, D-08606 Oelsnitz(V), Melanchthonstr. 28, Germany

E-mail: mailbox@anfattec.de

³ Center for Microtechnologies, Chemnitz University of Technology, D-09107 Chemnitz, Germany

E-mail: thomas.gessner@zfm.tu-chemnitz.de

Abstract. We report on the design, fabrication and application of a novel MEMS device consisting of two cantilever-tip tongues which can be deflected electrostatically independent from each other. The MEMS/NEMS chip is embedded in a complete scanning probe microscopy environment. We demonstrate operation as non-contact AFM, EFM, and the accomplishment of a temporary device by controlled deposition of the tips on a Si surface.

1. Introduction

Scanning probe microscopies (as atomic force or scanning tunneling microscopy) have revolutionized not only nano-scale analytics but also provided real tools for active working in the nano-world. Despite of this tremendous progress a basic deficiency is preventing a large-scale and even industrial application: there is always only one single element in action. Therefore the technique needs to be extended to multiple-tip operation to gain efficiency and speed by proper parallelization. Actually, controlled cantilever-tips are ideal active working elements for smart systems. The huge field of applications covers topographic reading and more complex highly local physical and chemical analysis as well as active interaction with and modification of sample surfaces on the μm , nm and even atomic scale.

Till now, only a few attempts going towards parallelization have been undertaken [1, 2] with the only exception of the famous “millipede” from IBM [3, 4]. The latter is a unique array comprising 1024 single cantilevers for simultaneous data storage and reading. This is a NEMS device of a highly involved but also highly specialized kind.

We will present here a complementary approach using only a (very) few cantilevers but ensuring high versatility and especially individuality of each single cantilever probe.

2. Concept of a Double-Cantilever Device

General Set-Up: It is based on electrostatically driven cantilever tongues with integrated probe tips. They can be moved independently from each other as can be measured their individual deflection. A completely adapted microscope-environment including mechanical stage, electronics and digital control has been developed to operate the device. The main intention in the past has been operation as non-contact AFM with extension to scanning electrical force microscopy (EFM).

Figure 1 shows a SEM image of a MEMS/NEMS chip with the two cantilever tongues. The tongues are made from a Si wafer. This part is bonded on a Pyrex chip carrying metallic electrodes. Applying a voltage between one cantilever tongue and its counter electrode, the tongue can be attracted (i.e. retracted from the sample) in a controlled manner. An optimized pattern of holes in the cantilever tongue minimizes damping during movement in air at ambient pressure.

Detection of Cantilever Elongation: Usually, the cantilever elongation is detected by a laser beam which is reflected from the outermost end of the cantilever. Since the geometries of both tongues are a little bit different from each other, their eigen-frequencies will also be slightly different which allows discrimination of the

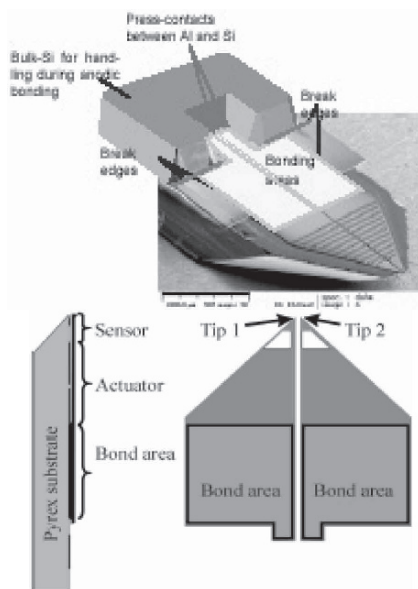


Fig. 1. (Left) Top view of the MEMS/NEMS chip showing the Si unit (upper half) bonded onto a Pyrex glass chip (lower half) with electrodes (not visible for below the Si tongues) which allow independent elongation of the Si cantilevers and capacitive sensing of their elongation. The free-standing part of the Si tongues carries a pattern of holes and in their foremost parts the integrated probe tips (not visible at this magnification). The bulk-Si parts are broken away in the next step giving access to the electrical contacts on the back-part of the Pyrex. (Right): schematic representation of the MEMS chip in side and top view.

signals belonging to the single cantilever tongues in the non-contact modus. This laser-beam deflection approach is nowadays fairly well accepted and used widespread. But it has the clear disadvantage that some part of the sample surface close to the probing tip is illuminated unintentionally. For local electrical measurements on semiconductor surfaces this turns out to be a major obstacle because of additional uncontrolled carrier generation.

To avoid this an independent capacitive detection has been included here. It is realized for the non-contact AFM by measuring the displacement current due to the change in the distance between the foremost (sensing) parts of the oscillating cantilever tongues and their counter-electrodes.

Cross-talk between the cantilevers has been investigated. It is mainly due to air-flow in and out of the gap between the cantilever tongues and their fixed counter-walls (as has been demonstrated in HV). This effect prevents a further reduction of the distance between the probing tips.

Design of Probing Tips: They are integrated in the outermost end of the cantilever tongues, and have to be fabricated highly reproducible with a very sharp apex, which determines the lateral resolution.

Figure 2 shows electron microscopy images of the tips fabricated by anisotropic etching. Their total length is $3\text{ }\mu\text{m}$, and the apex radii are less than 10 nm . The mutual distance between the two tips on the neighboring ends of the cantilever tongues is about $10\text{ }\mu\text{m}$. The flank angle can be further reduced till to about 10° by additional finishing. It could be shown that these tips can be further modified e.g. by electron-beam deposition of metallic super-tips. This procedure should allow to fabricate also magnetic tips suitable for magnetic force microscopy (MFM).

Microscope Environment: To have a really functioning microscope, there has to be supplied an environment comprising a mechanical stage fitting to the MEMS chip and allowing to level it with respect to the sample surface plane as well as corresponding electronics and software. More details about these (macroscopic) components can be found in [5–10].

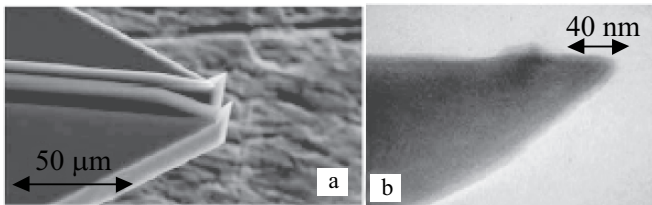


Fig. 2. SEM and TEM images of the integrated probe tips on the outermost part of the cantilever tongues. The faint skin around the tip at high-resolution is a contamination layer

3. Applications

Imaging of Test Samples: Imaging of the surface topography in the non-contact AFM mode requires external excitation of the cantilevers (by applying an ac signal between the cantilever-tongue and its counter-electrode) near to their mechanical eigenfrequency – here in the order of 20 kHz . Approaching the range

of the van der Waals interaction there acts an additional vertical force gradient which shifts the effective eigenfrequency of the cantilever. The topography is obtained by adjusting the mean height of the probe tip so that either the amplitude or the phase shift of the cantilever movement are preserved. We could demonstrate such a type of non-contact imaging by both of the cantilever tongues on test structures [5,6].

Electrical force microscopy (EFM) is a scanning probe method which allows local electrical characterization of the sample surface in addition to non-contact AFM topography [11]. Basically there is applied an additional signal

$$U = U_{dc} + U_{ac} \sin \omega_{el} t$$

between the cantilever-tip and the sample surface. This leads to electrostatic forces modulated with ω_{el} as well as a second harmonics. We have been able to implement this method using the MEMS/NEMS structure presented with the additional requirement of a sufficient electrical conductivity of the cantilever tongues which can be ensured by proper doping of the Si and metallization of the tip.

Figure 3 shows EFM on a special test sample: a regular pattern of doped dots on a Si wafer surface leading to a square lattice made of the doped dots with $1\ \mu\text{m}$ distance between the dots as well as diameter of the dots. This example shows that the doping profile can be measured with sub- μm resolution.

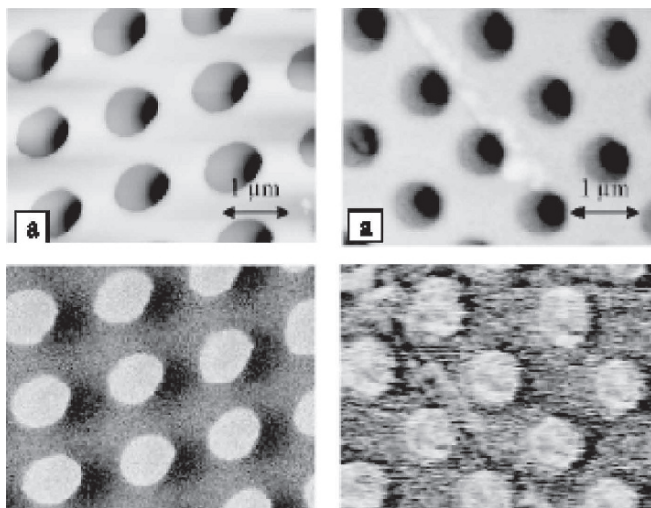


Fig. 3. EFM imaging of a test sample as described in the text. Upper row: Topography; Lower row: EFM-signal (2^{nd} harmonics representing the vertical gradient of the tip-sample capacitance); Left-hand side: Conventional AFM; Right-hand side: obtained using one of the cantilever tongues of the MEMS structure

Temporary Devices: A completely different type of experiment demonstrating the versatility of the concept is illustrated in Fig. 5. The metallized tips are put in a controlled manner on a Si surface. Furthermore two biases are applied: one between the two tips and another one between the sample and one of the tips. At the points of contact there appear Schottky diodes and the whole set-up is nothing else than a transistor (a MESFET).

We have measured I-V-characteristics as shown in Fig. 4 and compared them with a simple simulation of this temporary device [9] which disappears as soon as the tips are retracted.

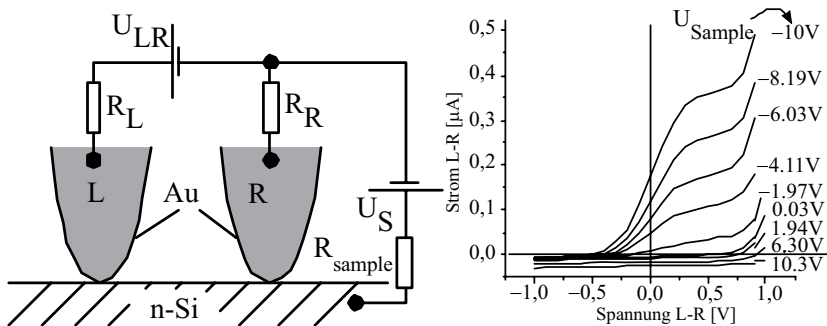


Fig. 4. Schematic set-up (left) and I-V characteristics (right) of a temporary MESFET device (the voltage on the axis is that one applied between the tips corresponding to the source-drain voltage whereas the different curves belong to different values of the voltage between the right tip R and the sample corresponding to the drain-gate voltage)

4. Summary and Outlook

We have presented a double-cantilever probe device which has been shown to be able to image in a non-contact AFM mode surface topography with a resolution of vertically about 1 nm and laterally about 10 nm. Furthermore this device has been successfully modified into a EFM. An experiment using the two probe tips for a controlled contact to a Si wafer has resulted in a temporary MESFET.

The versatility of the underlying concept is expected to allow further extensions towards multiple-tip devices having more than two tips as well as tips functionalized in a different manner. Already as few as four to five tips would allow an astonishing variety of experiments as 4-point measurements on crystallites, electrical screening during BEEM (ballistic electron emission microscopy) or combined electrical and magnetic measurements using individually functionalized tips. We are convinced that smart systems incorporating one or even more controlled probe tips will open access to a huge field of applications. Smart systems integration [12] will enable a convenient usage of such kind of instruments.

Acknowledgements

The authors acknowledge financial support from Deutsche Forschungsgemeinschaft (SFB 379) and Saxonian Ministry of Science and Arts.

References

1. S. Akamine, T.R. Albrecht, M.J. Zdeblick, C.F. Quate. IEEE Electr. Dev. Lett. **10**, 490, 1989.
2. H. Kawakatsu, D. Saya, A. Kato, K. Fukushima, H. Toshiyoshi, H. Fujita. Rev. Sci. Instrum. **73**, 1188, 2002.
3. M. Despont, J. Brugger, U. Drechsler, U. Dürig, W. Häberle, M. Lutwyche, H. Roithuizen, R. Stutz, R. Widmer, G. Binnig, H. Rohrer, P. Vettiger. Sens. & Actu. A **80**, 100, 2000.
4. P. Vettiger, G. Cross, M. Despont, U. Drechsler, U. Dürig, B. Gostmann, W. Häberle, M.A. Lantz, H.E. Rothuizen, R. Stutz, G.K. Binnig. IEEE Trans. Nanotechnol. **1**, 39, 2002.
5. M. Hietschold, F. Müller, A.-D. Müller, M. Reuter, J. Wibbeler, B. Loebner, Th. Gessner. Scanning **23**, 78, 2001.
6. A.-D. Müller, F. Müller, J. Middeke, J. Mehner, J. Wibbeler, Th. Gessner, M. Hietschold. Microel. Reliab. **42**, 1685, 2002.
7. M. Hietschold, A.-D. Müller, F. Müller, J. Mehner, B. Löbner, Th. Gessner. Scanning **52**, 97, 2003.
8. A.-D. Müller, F. Müller. Elektror no. 10, 68, (2003).
9. F. Müller, A.-D. Müller, M. Hietschold, Th. Gessner. Curr. Appl. Phys. **5**, 629, 2005.
10. F. Müller, A.-D. Müller, M. Hietschold, Th. Gessner. Jap. J. Appl. Phys. **45**, 1974, 2006.
11. M. Hietschold, A.-D. Müller, F. Müller. Proc. SPIE **4412**, 191, 2001.
12. T. Gessner (Ed.). *Smart Systems Integration 2007, Paris, March 27-28, 2007*. VDE Verlag 2007

Design and Fabrication of a Miniaturized Three-Degree-of-Freedom Piezoresistive Acceleration Sensor Based on MEMS Technology Using Deep Reactive Ion Etching

Vu Ngoc Hung¹, Nguyen Van Minh¹, Le Van Minh¹, Nguyen Huu Hung¹, Chu Manh Hoang¹, Dzong Viet Dao², Ranjith Amarasinghe², Bui Thanh Tung², and Susumu Sugiyama²

¹ International Training Institute for Materials Science, Hanoi University of Technology,
1 Dai Co Viet, Hanoi, Vietnam,
E-mail: hungvungoc@itims.edu.vn

² Graduate School of Science and Engineering, Ritsumeikan University, 1-1-1 Noji Higashi,
Kusatsu, Shiga 525-8577, Japan,
E-mail: dzung@se.ritsumei.ac.jp

Abstract. This paper presents the design and the fabrication of a miniaturized three-degree-of-freedom piezoresistive acceleration sensor based on MEMS technology using deep reactive ion etching. Finite element method (FEM) using the ANSYS program has been applied to study the mechanical and electrical behavior of the device. The fabricated sensor with the dimension $1 \times 1 \times 0.45 \text{ mm}^3$ can detect simultaneously three components of the linear acceleration at the frequency bandwidth 100 Hz.

1. Introduction

Micromachined silicon accelerometers have great advantages concerning the sensitivity, the size, the productivity with batch fabrication processes utilizing IC technology, micromachining technology and low power consumption. In recent years, however, for many applications such as automobile applications, space navigation systems, robot motion monitoring systems, portable microsystems, biomedical applications, and etc., reduction of chip size and increase of sensitivity of silicon based accelerometers have been in the focus of study. Various types of silicon accelerometers based on piezoelectric, piezoresistive and capacitive principles have been developed [1–9]. Piezoelectric accelerometers have a fast response but do not respond to a constant acceleration. Capacitive accelerometers have a dc response, a low drift, and very low-temperature insensitivity, but the detected signal is difficult to measure because of the parasitic capacitance of connecting leads. Piezoresistive accelerometers have a dc response, simple read-out circuits, high sensitivity, high reliability, and low cost in addition to the potential for mass production. Nowadays, multi-degree-of-motion sensing devices are highly demanded in many applications such as in the biomechanical field, robotics, and human gesture recognition system applications [10].

In this work, we present a miniaturized three-degree-of-freedom piezoresistive acceleration sensor with overall active device area of $1 \text{ mm} \times 1 \text{ mm}$. The device

was fabricated on n-type single crystal silicon-on-insulator (SOI) wafer by using bulk micromachining technology.

2. Design of the Acceleration Sensor

2.1. Accelerometer Structure

Silicon acceleration sensors generally consist of a seismic mass attached to a fixed frame by suspension beams. The structure of the sensor is shown in Fig. 1. The seismic mass is suspended on the four surrounding beams, which are fixed to the frame at the middle. Si piezo-resistors are located at suitable places of the surface of the sensing beams. When an external acceleration is applied to the chip, the seismic mass will be displaced due to the inertial force. The resistance of Si piezoresistors will be changed due to the deformation of sensing beam by this displacement. The resistance variations of resistors will be converted into electrical signals by using imbalance of excited Wheatstone bridge circuits. In our design, the sensing beam of the accelerometer has the dimension $340 \times 60 \times 10 \mu\text{m}^3$. The overall size of the sensor chip is $1000 \times 1000 \times 450 \mu\text{m}^3$.

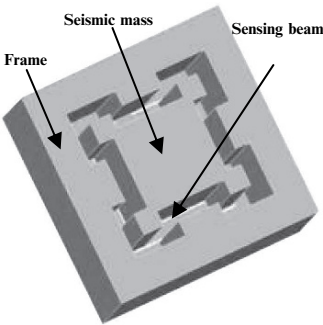


Fig. 1. 3-D model of the acceleration sensor

2.2. Structural Analysis by FEM

The mechanical sensitivity and the resonance frequency greatly depend on the geometric properties of the sensor. Simulation using finite element method (FEM) has been performed to verify mechanical behaviors of the structure as well as to optimize the design. The ANSYS software has been used for the analysis of the motion of the seismic mass, the mechanical stress in the beams and the resonance frequency of the sensor. In order to simplify the calculation, the frame is not modeled with the condition that pedestals are built at the middle of beams. The structures are meshed in such a way that a high density of elements is available where the deformation was expected to be very high, such as the clamped edge of the suspension beam.

The ANSYS Block Lanczos solver is used for the mode analysis. The resonance frequencies gained by the FEM are listed in table 1, and the mode shapes are represented in Figure 2.

Table 1. Resonance frequencies of the accelerometer

	Frequency (Hz)	Description
Mode 1	46494	Vibration in the Z-direction
Mode 2	600110	Vibration in the Y-direction
Mode 3	600110	Vibration in the X-direction

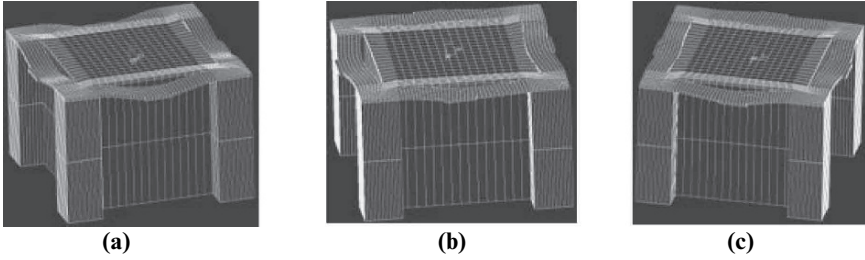


Fig. 2. Vibration in the Z-direction mode due to the linear acceleration A_z (a), vibration in the X-direction mode due to the linear acceleration A_z (b) and vibration in the Y-direction mode due to the linear acceleration A_z (c)

In order to define the optimal positions of the piezoresistors in the sensing beams, it is necessary to perform stress analysis. The distributions of longitudinal stress components on the top surface of the Si sensing beams due to application of accelerations are illustrated in Figure 3. The FEM result shows that on the top surface of beam the stress components other than the longitudinal one are very small so that it can be neglected. The distributions of longitudinal stress induced by vertical acceleration A_z on the four beams are similar and symmetrical. In the case of horizontal accelerations (A_x or A_y), the maximal longitudinal stress on the beams being perpendicular to the acceleration direction is larger than that on the beams being parallel to the acceleration direction. Thus, for measurement of acceleration A_x the piezoresistors are arranged on the Y-oriented beams, and vice versa. It is shown that the maximum stresses do not occur near the clamped edge of the sensing beam, possibly due the fact that the structure is really in the condition of large deflection.

Based on the finite element analysis presented, the piezoresistors to measure each component of acceleration have to be arranged on region of the sensing beams so that the longitudinal stress induced by that acceleration is largest (Fig. 4). In order to avoid the undesirable stress components, the piezoresistors are located far enough from the fixed ends.

To detect the accelerations, piezoresistors are connected to form Wheatstone full bridges. When the sensor is under ideal conditions, the bridge is balanced and

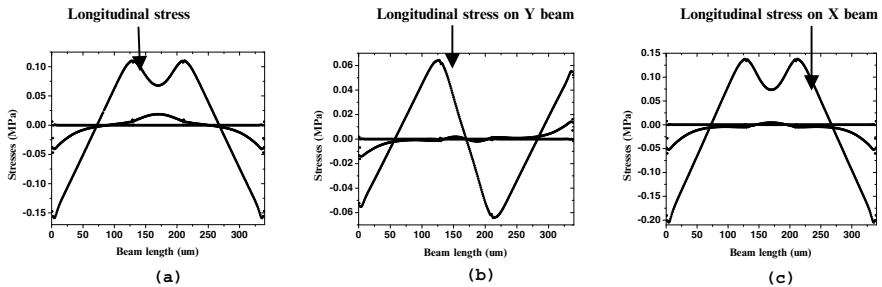


Fig. 3. Stress distribution along sensing beams due to application of a vertical acceleration A_z (a), and a horizontal acceleration A_x (b & c)

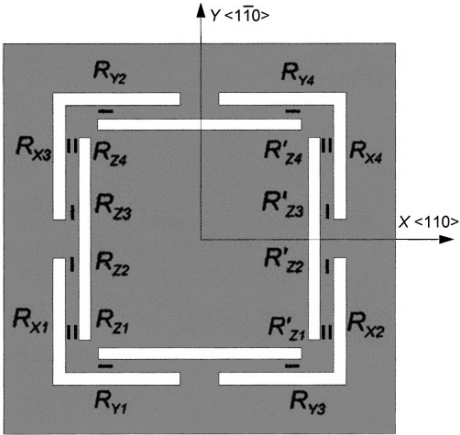


Fig. 4. Arrangement layout of piezoresistors on the beams

the output voltage across the output terminals of the excited Wheatstone bridge is zero. As a result of resistance change in piezoresistors due to the stress, the previously balanced bridge becomes unbalanced. This unbalance causes a voltage to appear across the output terminals of the bridge. This induced voltage can be measured as the output of the sensor.

3. Fabrication of Piezoresistive Acceleration Sensor

The accelerometer was fabricated by the micromachining process based on IC compatible technology and bulk micromachining technology. The fabrication process flow of the accelerometer is shown in figure 5. A double side polished, n-type (100) oriented silicon-on-insulator (SOI) wafer was used as a starting material. The thicknesses of the device layer and handle substrate layer are 10 μm and 450 μm , respectively. First, silicon dioxide (SiO_2) layers were grown on both sides of the SOI wafer by a thermal oxidation process at 1100°C for 30min in $\text{O}_2 + \text{H}_2$. The SiO_2 layer thickness was controlled to be approximately 0.3 μm . Next, photolithography was conducted on the front side of the wafer to pattern the piezoresistors so that their longitudinal axis aligns with the crystal directions $\langle 110 \rangle$ and $\langle 1\bar{1}0 \rangle$ of the

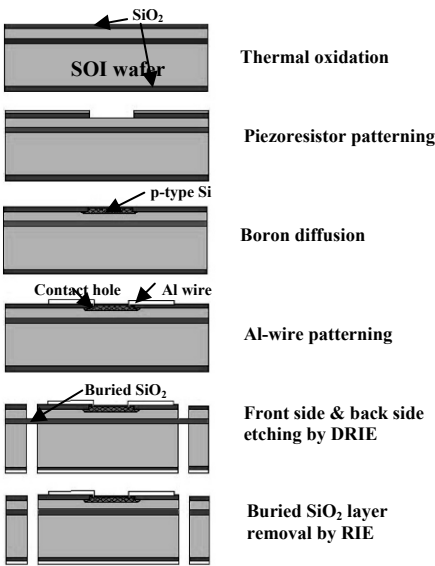


Fig. 5. Fabrication process flow (top to bottom)

silicon (100) plane. Then the p-type piezo-resistors were formed by the boron diffusion process, using a spin-on-dopant source, in N_2 environment at 1000°C for 60 min, and then the drive-in process was carried out in dry O_2 environment at 1100°C for 30 min.

After contact holes were opened by wet etching in the buffered HF solution, the metallization process was conducted to interconnect piezoresistors and to form bonding pads. The aluminum layer with thickness of about $0.5\ \mu\text{m}$ was deposited by sputtering method. Next, the sintering process was performed in N_2 environment at 400°C for 30 min to form an Ohmic contact between electrodes and piezoresistors. After that, beam pattern was defined by photolithography using a double-sided mask aligner on the top side of the wafer. Then, front side deep reactive ion etching (DRIE) process was performed to a buried oxide layer. For the etching process, a mixture of SF_6 and C_4F_8 gases were used. Next, the backside mask was patterned on the aluminum layer and the DRIE process was carried out on the backside of the wafer to form the beams and seismic mass of sensor. Finally, the buried SiO_2 layer was removed by using the reactive ion process (RIE).

The micrographs of the fabricated acceleration sensor are shown in Fig. 6.

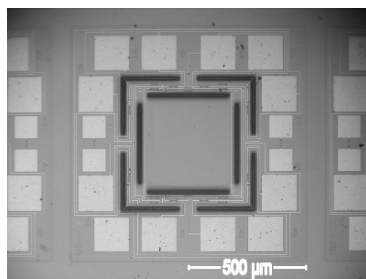


Fig. 6. Microphotograph of fabricated accelerometer

4. Characterization of Acceleration Sensor

The acceleration sensitivities of the device were determined. The measurements were carried out on an electromagnetic exciter. For testing the fabricated acceleration sensors, the dynamic characterization has been performed at 50Hz. Figures 7 and 8 show the output voltage of the accelerometer as a function of acceleration for the components A_x and A_z , respectively. Gain factor of the amplifier used in this measurement was 1000. The voltage source applied to the sensor is 5 V. The net sensitivities for acceleration components A_x (A_y) and A_z without amplifier are $30.5\ \mu\text{V/g}$, and $22.9\ \mu\text{V/g}$, respectively.

One of the most important characteristics of an accelerometer is its frequency performance. An accelerometer should have a uniform sensitivity for a large frequency bandwidth. Figures 9 and 10 show the relation between output voltage and frequency of the accelerometer for A_x and A_z , respectively. It is shown that the device frequency bandwidth is in the range of 100 Hz. The frequency performance of the acceleration sensor is influenced mainly by squeezed-film air damping [11].

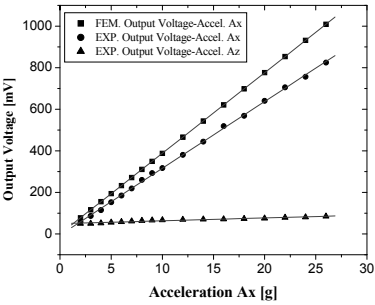


Fig. 7. Output voltage vs. applied acceleration Ax

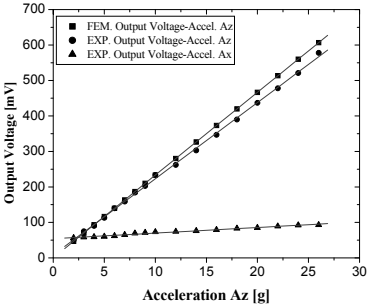


Fig. 8. Output voltage vs. applied acceleration Az

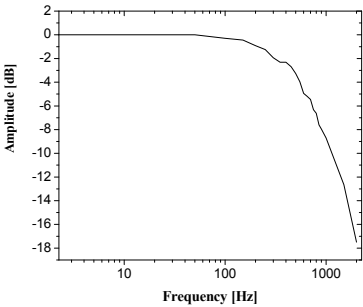


Fig. 9. The amplitude – frequency relation for lateral vibration

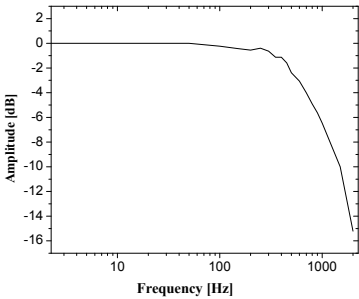


Fig. 10. The amplitude – frequency relation for vertical vibration

5. Conclusions

A miniaturized three-degree-of-freedom acceleration sensor with an overall chip size of $1 \times 1 \times 0.45 \text{ mm}^3$ was developed. The basic structure of the sensor consists of seismic mass suspended on the four surrounding beams, which are fixed to the frame at the middles. The piezoresistive effect was used as a sensing principle of the sensor. Finite element method (FEM) using ANSYS program has been performed to study mechanical and electrical behaviors of the device. The acceleration sensor has been fabricated based on MEMS technology using deep reactive ion etching. The output voltage versus applied acceleration characteristics was carried out based on the dynamic method. The sensitivities for three components of acceleration are linear.

Acknowledgments

This work was supported by the MEMS project funded by NEDO organization, Japan.

References

1. N. Yazdi, F. Ayazi, and K. Najafi, Micromachined Inertial sensors, *Proceeding of the IEEE*, vol. 86, No. 8, 1640-1659, 1998.
2. S. Suzuki, S. Tuchitani, K. Sato, S. Uend, Y. Yokota, M. Sato, M. Esashi, Semiconductor capacitance-type accelerometer with PWM electrostatic servo technique, *Sens. Actuator A21/A23*, 316-319, 1990.
3. W. Kuehnel, S. Sherman, A surface micromachined silicon accelerometer with on-chip detection circuitry, *Sens. Actuators A45*, 7-16, 1994.
4. T. Mineta, S. Kobayashi, Y. Watanabe, S. Kanauchi, I. Nagakawa, E. Suganuma, M. Esashi, Three-axis capacitive accelerometer with uniform axial sensitivities, *Transducer 95*, Stockholm, Sweden, 544-577, 1995.
5. J.A. Plaza, C. Dominguez, J. Esteve, I. Salinas, J. Garcia and J. Berganzo, BESOI-based integrated optical silicon accelerometer *J. Microelectromech. Syst.* **13**, 355-364, 2004.
6. J.H. Sim, D.K. Kim, Y.H. Bae, K.H. Nam and J.H. Lee, Six-beam piezoresistive accelerometer with self-cancelling cross-axis sensitivity, *Electron. Lett.* **34**, 497-499, 1998.
7. C. Acar and A.M. Shkel, Experimental evaluation and comparative analysis of commercial variable-capacitance MEMS accelerometers, *J. Micromech. Microeng.* **13**, 634-645, 2003.
8. D.V. Dao, T. Toriyama, Wells J and Sugiyama S, Silicon piezoresistive six-degree of freedom force-moment micro sensor, *Sensors Mater.* **15**, 113-135, 2003.
9. J.C. Lotters, J. Schipper, P.H. Veltink and W. Olthuis, Procedure for in-use calibration of triaxial accelerometers in medical applications, *Sensors Actuators A* **68**, 221-228, 1998.
10. A.Y. Benbasat and J.A. Paradiso, Gesture and sign language in human-computer interaction, *Proc. Int. Gesture Workshop, GW 2001(London)* (Berlin: Springer), 9-20, 2002.
11. S. Middelhoek, *Handbook of sensors and actuators*, Vol. 8, 2000, Elsevier.

Contributors

Aeschlimann M., 61
Allegretti F., 163
Amarasinghe R., 377

Bac L.H., 263
Bauer M., 61
Bäumer M., 103
Baumert T., 327
Bayer D., 61
Bayer T., 327
Bich V.T., 185, 271
Binh N.T., 271
Binh P.T., 363
Broekmann P., 113
Brune H., 123

Cat D.T., 41
Cham T.T., 363
Chandola S., 247
Chien N.D., 95
Chinh V.D., 79
Cong T.Q., 337
Cong L.T., 257
Cuong L.C., 141

Dao D.V., 377
Duc T.T., 185
Dung N.D., 185
Dung N.V., 141
Duy N.H., 295

Esser N., 247

Felder T., 235
Fleischer K., 247

Fleming A., 163
Friebel D., 113

Gerlach G., 287
Gessner T., 371

Hai L.B., 79
Hanh N., 257
Hien D.T., 11
Hietschold M., 371
Hieu H.N., 141
Hieu T.K., 345
Hoai T.X., 185
Hoai Nam M., 87
Hoang C.M., 377
Hoang H.S., 345
Hoang T.N., 171, 177
Hoi P.V., 363
Hong L.V., 133
Huong N.T.M., 185, 271
Hung P.K., 225
Hung V.N., 377
Hung N.H., 377
Huu Tinh N., 141
Huyen D.N., 279

Jouan M., 171, 177

Khiem N.V., 133
Khuong O.P., 41
Kim Anh T., 87
Kien V.T., 345
Kieu Giang L.T., 87
Klevenz M., 321

- Klumpp A., 327
 Kochmann W., 305
 Kossev I., 235

 Lam T.D., 87, 263
 Lange J., 61
 Lan Anh L.T., 193
 Leitner M., 163
 Levin A.A., 201, 305
 Lien T.T.N., 263
 Linh P.T., 79
 Loc D.X., 87
 Luong T.T., 271

 Mattheis R., 151
 McGilp J., 247
 Meng F., 321
 Meyer D.C., 201, 305
 Mien V.D., 337
 Minh D.L., 257
 Minh L.Q., 87
 Minh N.V., 31, 377
 Müller F., 371
 Müller A.-D., 371
 Minh L.V., 377

 Netzer F.P., 163
 Neubrech F., 321
 Neumann R., 311
 Nghi N.H., 141
 Nghia N.X., 79
 Nghiem V.T., 337
 Ngoc Ha N.T., 345
 Nhan N.T., 225
 Nowitzki T., 103

 Parteder G., 163
 Pätzke N., 305
 Paufler P., 305
 Pfnür H., 69
 Phi H.P., 171, 177
 Pho P.Q., 95, 263
 Phong P.T., 133
 Phong T.C., 23
 Phuc N.X., 133
 Phuong T.T.B., 225
 Phuong Phong N.T., 295
 Pucci A., 321

 Quang D.N., 11
 Quang N.V., 355
 Quynh Anh N.T., 295

 Ramsey M.G., 163
 Reibold M., 305
 Rohmer M., 61

 Schalley C.A., 235
 Schlaup C., 113
 Schreiber M., 1
 Sokolowski M., 235
 Son Tho V.D., 193
 Sorber J., 287
 Steenbeck K., 151
 Sugiyama S., 377
 Surnev S., 163
 Sarpe-Tudoran C., 327

 Thach S.V., 171, 177
 Thanh Nga. T.T., 141
 Thanh Tam P., 345

Thanh Tung B., 377
Thanh Tung M., 141
Thi Thuy N., 271
Thu Nga P., 79
Thuy N.T., 271
Thuy N.T.L., 23
Trong Tinh N., 185, 209
Tram D.T.N., 95
Trang N.T.T., 79
Trinh T.T.N., 141
Trinh T.Q., 287
Trung N.N., 193
Truong P.V., 337
Tsuji T., 209
Tuan P.H., 219
Tuan Tai L., 257
Tung B.T., 377
Tung L.V., 23
Tung M.T., 141
Tung N.H., 11
Tung N.P., 295

Van Tri N., 51
Vögtle F., 235
Vinh H.X., 363
Vinh L.T., 225
Vu L.H., 345
Vu N., 87
Vuong D.D., 95

Wandelt K., 113
Wiemann C., 61
Wollenhaupt M., 327

Xu B., 163
Xuan S.N., 171, 177

Yen P.N.D., 271
Yi G.-C., 87

Zielasek V., 103