Conference Organizers wish to thank the **SPONSORS** listed below for their contribution to the success of the conference.

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14th International Conference on II-VI Compounds

St. Petersburg, Russia, August 23-28, 2009

PROGRAM AND ABSTRACTS
Preface

Welcome at the 14th International Conference on II-VI Compounds (II-VI-2009) which is held this 2009 year, in Saint-Petersburg, Russia, for the first time. The meeting continues a series of biennial conferences, which was started in Durham, UK, in 1983. The latest conferences were held in Niagara Falls (2003), Warsaw (2005), and Jeju Island (2007). The Conference is organized by the Ioffe Physical Technical Institute of RAS, one of the leading research centers in the world in the field of semiconductor physics and technology. It is famous for numerous discoveries in the field, including pioneering studies of excitonic properties of II-VI compounds.

The purpose of the current II-VI compound Conference is to bring together scientists from all over the world, which are active in the fields of basic and applied research of II-VI structures. The Conference Program reflects a revival of interest in the recent years to this group of materials due to the emergence of many fascinating ideas and prospects as well as the development of new technologies. In particular, the wide band gap semiconductors like ZnO, (Zn,Cd)Te, (Zn,Cd)Se provide unique opportunities to exploit the ideas of photonic-band engineering in specially designed quantum nanostructures. This intense activity has yet resulted in the observation of numerous original effects and emergence of new device concepts, including Bose condensation of exciton polaritons ("polariton laser"), triggered single-photon sources for quantum cryptography, optical switches and memories. Important areas that take advantage of the specific properties of II-VI compounds are quantum information processing and spintronics, since II-VI non-magnetic and diluted magnetic semiconductors and quantum dots are ideal objects for experimental modeling of the devices employing the spin degree of freedom. Among other prospective practical applications of the II-VI compounds which will be presented are yellow-to-blue lasers with different pumping types, infrared detectors, terahertz emitters, inter-subband devices like quantum cascade lasers, and nanoscale sensors. A special feature of the 14th Conference is organizing the Session of Review Lectures delivered by most prominent scientists in the field.

The attendance of the present conference is relatively high and world wide: approximately 300 scientists from 26 countries. Beside the Review lecturers, we have 21 invited talks, 60 oral and ~200 poster presentations. The Conference proceedings will be published in a special issue of the Physica Status Solidi (c) not later than early spring 2010.

We would like to thank on behalf of the Organizing Committee all the sponsors listed subsequently for their substantial support. Without their help it would have been impossible to hold the registration fee low for young physicists, which has allowed many of them to participate in this meeting.

We wish all participants an enjoyable and successful meeting.

S.A. Permogorov  S.V. Ivanov  A.A. Toropov

Saint-Petersburg, July 10, 2009
Prof. Dr. rer. nat. Dr. h.c. mult. Gottfried LANDWEHR was born on 22.08.1929 in Osnabrück, Germany. After studying physics at Technical University Karlsruhe, he joined the German National Bureau of Standards Physikalisch Technische Bundesanstalt (PTB), Braunschweig, starting to work on semiconductors and investigating defect-induced electrons in germanium. After his Dissertation (Ph.D.), Gottfried LANDWEHR went to the University of Illinois, Urbana, where he collaborated e.g. with Prof. John BARDEEN (1959-1961), in 1961 he became Assistant Professor there. Back in Germany he became the Head of the President’s Laboratory at the PTB and a member of faculty of Technical University Braunschweig. In 1968, he accepted a position at Würzburg University, Germany, as the chairholder for Experimentelle Physik III and initiated his fundamental research on semiconductors in high magnetic fields peaking up later in the investigations of Q2D-semiconductor systems. In those days he also initiated the famous conference series “Semiconductors in High Magnetic Fields”. Between 1978 and 1983, Gottfried LANDWEHR was director of the Hochfeldmagnetlabor des Max Planck-Institutes für Festkörperforschung in Grenoble, France. Under his directorship there Klaus von KLITZING made his famous measurements on the Quantum Hall Effect, later awarded by the Nobel Prize.

Back at Würzburg University, Gottfried LANDWEHR started working on II-VI semiconductor layered structures grown by molecular beam epitaxy, with substantial contributions especially in the field of semimagnetic semiconductors, but also narrow gap HgCdTe as well as ZnSe based laser diodes. His overall achievements and worldwide scientific interactions made Gottfried LANDWEHR an internationally well renowned scientist with tremendous reputation. He is a member of the Bavarian Academy of Sciences. Prof. LANDWEHR made a considerable contribution to the development of collaboration between German and Russian scientists, in particular from the Ioffe Institute. This his activity was highly evaluated by electing him as External Member of the Russian Academy of Sciences and Honorary Member of the Ioffe Institute, St. Petersburg. During the II-VI-2009 Conference a Complimentary Session will be held to mark the 80th birthday of Prof. Gottfried LANDWEHR, the Honorary Chair of the Conference.
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Contact Information

Prof. S.V. Ivanov,
Ioffe Physical Technical Institute, Polytekhnicheskaya 26,
194021 St.Petersburg, Russia.
Phone: +7 (812) 292-7124
Fax: +7 (812) 297-1017
E-mail: II-VI-2009@mail.ioffe.ru
CALENDAR OF EVENTS

Sunday, August 23
10.00 – 18.00 Registration
10.30 – 12.30 Su1: Review Lectures I
12.30 – 14.00 Lunch
14.00 – 17.00 Su2: Review Lectures II
19.00 – 22.00 Welcome Party

Monday, August 24
8.00 – 18.00 Registration
8.50 – 9.15 Mo0: Opening Session
9.15 – 10.45 Mo1: Microcavities
10.45 – 11.15 Coffee Break
11.15 – 13.00 Mo2: Nanostructures I
13.00 – 14.30 Lunch
14.30 – 16.15 Mo3: Diluted Magnetic Semiconductors I
16.15 – 16.45 Coffee Break
16.45 – 18.15 Mo4: Devices I
18.15 – 20.00 Mo5p: Poster session I

Tuesday, August 25
8.00 – 18.00 Registration
9.00 – 10.45 Tu1: Spin Physics
10.45 – 11.15 Coffee Break
11.15 – 12.45 Tu2: ZnO Nanostructures
12.45 – 14.15 Lunch
14.15 – 15.45 Tu3: Diluted Magnetic Semiconductors II
15.45 – 16.15 Coffee Break
16.15 – 17.00 Tu4: Diluted Magnetic Semiconductors III
17.00 – 18.00 Tu5: Gottfried Landwehr’s Birthday Session
18.00 – 20.00 Tu6p: Poster Session II

Wednesday, August 26
8.00 – 13.00 Registration
9.00 – 10.45 We1: ZnO Growth and Properties
10.45 – 11.15 Coffee Break
11.15 – 12.30 We2: Single Quantum Dots
13.00 – 20.00 Conference Excursion
Thursday, August 27

9.00 – 10.45  Th1: Excitonic and Spin Effects
10.45 – 11.15 Coffee Break
11.15 – 13.00 Th2: Nanostructures II
13.00 – 14.30 Lunch
14.30 – 16.00 Th3: Phonons and Defects
16.00 – 16.30 Coffee Break
16.30 – 17.45 Th4: Devices II
17.45 – 19.15 Th5p: Poster Session III
20.00 – 23.00 Conference Dinner

Friday, August 28

9.00 – 10.45  Fr1: Devices III
10.45 – 11.15 Coffee Break
11.15 – 13.00 Fr2: Microcavities and photonic crystals
13.00 – 14.30 Lunch
14.30 – 15.30 Fr3: New Experimental Approaches
15.30 – 15.50 Fr4: Closing Remarks
## ORAL SESSIONS

### Sunday, August 23

<table>
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<tr>
<th>Time</th>
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<tbody>
<tr>
<td>Su1</td>
<td>Review Lectures I</td>
<td>10:30 - 12:30</td>
</tr>
</tbody>
</table>
| Su1-1      | 40 years of ZnO research – old and very recent results | C. Klingshirn, J. Fallert, J. Sartor, and H. Kalt
|            |                                             | Institut für Angewandte Physik, Universität Karlsruhe; Karlsruhe Institute of Technology, Germany |
| Su1-2      | Physics and prospective applications of quantum dots | A. Ekimov
|            |                                             | Nanocrystals Technology, New York, USA                               |
| Lunch Break|                                            | 12:30 - 14:00                                                         |
| Su2        | Review Lectures II                         | 14:00 - 17:00                                                         |
| Su2-1      | II-VI-based DMSs from discovery to spintronics | J.K. Furdyna
|            |                                             | Dept. of Physics, University of Notre Dame, Notre Dame, USA           |
| Su2-2      | From polariton quantization in thin films to polariton BEC in microcavities | Maxime Richard and Le Si Dang
|            |                                             | Institute Néel, Grenoble, France                                     |
| Su2-3      | Role of II-VI compounds in basic semiconductor research | S. Permogorov
|            |                                             | Ioffe Institute, St.Petersburg, Russia                               |
| Welcome Party|                                            | 19:00 - 22:00                                                        |
Monday, August 24

Mo0  Opening Remarks  08:50 - 09:15
(Chair: S. Ivanov)

Mo1  Microcavities  09:15 - 10:45
(Chair: H. Mariette)

Mo1-1  09:15 - 10:00
Bose-Einstein condensates of exciton-polaritons in CdTe based microcavities (invited)
B. Deveaud-Plédran, K. Lagoudakis, G. Nardin, M. Richard, B. Pietka, Y. Léger, R. André, Le Si Dang
Ecole Polytechnique Fédérale de Lausanne, Switzerland; Institut Louis Néel, Grenoble, France

Mo1-2  10:00 - 10:15
Bose-Einstein condensation of exciton-polaritons: what is the criterion?
A.V. Kavokin
School of Physics and Astronomy, University of Southampton, Southampton, UK

Mo1-3  10:15 - 10:30
Stimulated polariton emission from a ZnSe-based microcavity
C. Kruse, D. Hommel, A. Trichet, M. Richard, and Le Si Dang
Institute of Solid State Physics, Bremen, Germany; Institut Louis Néel, Grenoble, France

Mo1-4  10:30 - 10:45
ZnTe-based microcavities and micropillars containing CdTe quantum dots
Institute of Solid State Physics, University of Bremen, Germany; Institute of Experimental Physics, University of Warsaw, Poland; Institute of Physical Chemistry, "Ilie Murgulescu" of the Romanian Academy, Bucharest, Romania

Coffee Break  10:45 - 11:15
<table>
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<th>Session</th>
<th>Title</th>
<th>Authors</th>
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<tr>
<td>Mo2-1</td>
<td>Magnetic dopants and charge carriers in colloidal II-VI quantum dots (invited)</td>
<td>Daniel R. Gamelin</td>
<td>University of Washington, Seattle, USA</td>
</tr>
<tr>
<td>Mo2-2</td>
<td>MBE overgrowth of ex-situ prepared CdSe colloidal nanocrystals</td>
<td>M. Rashad, Erick M. Larramendi, A. Pawlis, K. Lischka, D. Schikora, M.V. Artemyev, and U. Woggon</td>
<td>Universität Paderborn, Germany; Physics Faculty, University of Havana, Cuba; Technische Universität Berlin, Germany</td>
</tr>
<tr>
<td>Mo2-3</td>
<td>Near-field photoluminescence spectroscopy and imaging of solution synthesized CdSe nanowires</td>
<td>A.M. Mintairov, J. Herzog, K. Kuno, V. Protasenko, and J.L. Merz</td>
<td>University of Notre Dame, USA</td>
</tr>
<tr>
<td>Mo2-5</td>
<td>Hybrid resonant organic-inorganic nanostructures for novel light emitting devices and solar cells</td>
<td>V.M. Agranovich</td>
<td>Russian Academy of Science, Troitsk, Russia; The University of Texas at Dallas, USA</td>
</tr>
<tr>
<td>Mo2-6</td>
<td>ZnO/organic/ZnO sandwich-type semiconductor hybrid structures for photonic applications</td>
<td>S. Blumstengel, S. Sadofev, J. Puls, and F. Henneberger</td>
<td>Humboldt-Universität zu Berlin, Institut für Physik, Germany</td>
</tr>
</tbody>
</table>

**Lunch Break**

13:00 - 14:30
Mo3  Diluted Magnetic Semiconductors I  14:30 - 16:15  
(Chair: J. Furdyna)
Mo3-1  14:30 - 15:00
Ferromagnetism in uniform and non-uniform magnetically doped II-VI compounds  (invited)
Tomasz Dietl
Institute of Physics, Polish Academy of Sciences, Warsaw; Institute of Theoretical Physics, University of Warsaw, Poland

Mo3-2  15:00 - 15:15
Formation of Cr-rich nano-clusters and nano-columns in ferromagnetic semiconductor (Zn,Cr)Te
Y. Nishio, K. Zhang, K. Ishikawa, S. Kuroda, M. Mitome, and Y. Bando
Institute of Materials Science, University of Tsukuba; National Institute for Materials Science, Tsukuba, Japan

Mo3-3  15:15 - 15:45
Collective spin excitations in doped CdMnTe quantum wells  (invited)
D. Scalbert, M. Vladimirova, S. Cronenberger, P. Barate
Group d’Etude des Semiconducteurs, CNRS - Université Montpellier 2, Montpellier, France

Mo3-4  15:45 - 16:00
Intrinsic resonances in Mn$^{2+}$ ion spin clusters in ZnMnSe/ZnBeSe quantum wells
Institute of Physics PAS, Warsaw, Poland; Experimentelle Physik II, TU Dortmund, Germany; Ioffe Physico-Technical Institute, St. Petersburg; Institute of Solid State Physics, Chernogolovka, Russia; Institute of Physics NAS of Ukraine, Kiev, Ukraine; North Caroline State University, USA; Dept. Mathematics and Natural Sciences College of Science, Cardinal S. Wyszyński University, Warsaw, Poland; Institute of Semiconductor Technology, Braunschweig Technical University, Germany

Mo3-5  16:00 - 16:15
Interlayer exchange coupling in MnTe/ZnTe superlattices: magnetic order, magnon confinement and propagation
B. Hennion, W. Szuszkiewicz, S. Petit, E. Dynowska, E.Janik, G.Karczewski, and T. Wojtowicz
Laboratoire Léon Brillouin, France; Institute of Physics PAS, Warszawa, Poland

Coffee Break  16:15 - 16:45
Mo4 Devices I 16:45 - 18:15
(Chair: D. Hommel)

Mo4-1 16:45 - 17:15
Wide-Band-Gap II-VI semiconductor intersubband devices for telecom wavelength applications (invited)
R. Akimoto, K. Akita, G.W. Guangwei, T. Hasama, and H. Ishikawa
Network Photonics Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan

Mo4-2 17:15 - 17:45
Wide bandgap II-VI compounds for quantum cascade lasers operating in the mid- and near-IR wavelength range (invited)
Maria C. Tamargo, William O. Charles, Kale J. Franz, Aidong Shen, and Claire Gmachl
The City College of CUNY, New York; Princeton University, USA

Mo4-3 17:45 - 18:00
Room-temperature tunable mid-infrared lasers on transition-metal doped II-VI compound crystals grown from vapour phase
Lebedev Physical Institute of RAS; Moscow Institute of Physics and Technology (State University), Russia

Mo4-4 18:00 - 18:15
Design and characterization of ZnO-based MESFET devices
Universität Leipzig, Institute for Experimental Physics II, Germany

Mo5p Poster Session I 18:15 - 20:00
## Tuesday, August 25

**Tu1**  
**Spin Physics**  
(Chair: M. Glasov)  
09:00 - 10:45

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Title</th>
<th>Speakers</th>
<th>Location</th>
</tr>
</thead>
</table>
| 09:00 - 09:30 | **Tu1-1**  
Quantum spin Hall effect *(invited)* | H. Buhmann  
Physikalisches Institut, Universität Würzburg, Germany |  |  |
| 09:30 - 09:45 | **Tu1-2**  
Spin splittings in the $n$-HgTe/Cd$_x$Hg$_{1-x}$Te quantum well  
with inverted band structure | M.V. Yakunin, S.M. Podgornykh, N.N. Mikhailov, and S.A. Dvoretsky  
Institute of Metal Physics, Ekaterinburg, Russia; Institute of  
Semiconductor Physics, Novosibirsk, Russia |  |  |
| 09:45 - 10:00 | **Tu1-3**  
Optical manipulation of electron spin coherence in  
CdTe/CdMgTe quantum wells | E.A. Zhukov, M.M. Glazov, E.L. Ivchenko, D.R. Yakovlev, E. Fokina, G. Karczewski, T. Wojtowicz, J. Kossut, and M. Bayer  
Experimentelle Physik II, Technische Universität Dortmund, Germany; Lomonosov Moscow State University, Russia; Ioffe  
Physical Technical Institute, St. Petersburg, Russia; Institute of  
Physics, Polish Academy of Sciences, Warsaw, Poland |  |  |
| 10:00 - 10:15 | **Tu1-4**  
Coherence-mediated optical control of spins of excitons  
Radboud University Nijmegen; Ioffe Physical Technical Institute,  
St. Petersburg, Russia; Experimentelle Physik II, University  
Dortmund, Germany; Institute of Physics, Polish Academy of  
Sciences, Warsaw, Poland |  |  |
| 10:15 - 10:30 | **Tu1-5**  
Control of the resident electron spin in CdSe quantum  
dots by electrical current pulses though micro-coils | J. Puls, Y.S. Chen, V. Gapon, G. Bacher, and F. Henneberger  
Humboldt-Universität, Institut für Physik, Berlin, Germany; Werkstoffe der Elektrotechnik and CeNIDE, Universität Duisburg-Essen, Germany |  |  |
Dynamic nuclear polarization and confinement effects in ZnO quantum dots

P.G. Baranov, S.B. Orlinskii, C. de Mello Donegá, A. Meijerink, and J. Schmidt
Ioffe Physical-Technical Institute, St. Petersburg, Russia; Federal Center of Shared Facilities of Kazan State University, Kazan, Russia; Debye Institute for Nanomaterials Science, Utrecht University, The Netherlands

Coffee Break

ZnO Nanostructures

(Chair: A. Waag)

Random lasing in nanocrystalline ZnO powders (invited)
H. Kalt, J. Fallert, R.J.B. Dietz, J. Sartor, D. Schneider, and C. Klingshirn
Institut für Angewandte Physik, Universität Karlsruhe, Germany

Visible-wavelength random lasing of (Zn,Cd)O/(Zn,Mg)O multiple quantum well structures
S. Kalusniak, S. Sadofev, J. Puls, H.J. Wünsche, and F. Henneberger
Institut für Physik, Humboldt-Universität zu Berlin, Germany

Growth of Zn-polarity MgZnO/ZnO MQWs on bulk ZnO by RF-MBE
S. Morita, S. Jung, T. Honma, Y. Kaifuchi, Y. Ishitani, and A. Yoshikawa
Graduate School of Electrical and Electronics Engineering, Chiba University; Optics and Electronics Laboratory, Fujikura Ltd, Chiba; Venture Business Laboratory, Chiba University, Japan

Residual strain in non-polar a-plane Zn_{1-x}Mg_{x}O \,(0<x<0.55) and its effect on the band structure of (Zn,Mg)O/ZnO quantum wells
J-M. Chauveau, M. Teisseire, J. Zuniga-Perez, C. Deparis, C. Morhain, B. Vinter
Centre de Recherche sur l’Hétéro-Epitaxie et ses Applications, Centre National de la Recherche Scientifique, Valbonne, France; University Nice Sophia Antipolis, Nice, France
Growth and characterization of periodically polarity inverted ZnO structures grown on Cr-compound buffer layers
Center for Interdisciplinary Research, Tohoku University, Sendai, Japan; Dept of Materials Science and Engineering, Chungnam National University, Daejeon, Korea; Dept of Materials Science and Engineering, KAIST, Daejeon, Korea; Major of Nano Semiconductor, Korea Martine University, Yeongo-ku, Pusan, Korea

Lunch Break

Diluted Magnetic Semiconductors II 14:15 - 15:45
(Chair: J. Kossut)

Spin currents in diluted magnetic semiconductors (invited)
S.D. Ganichev
Terahertz Center, University of Regensburg, Germany

Semimagnetic II-VI resonant tunneling diodes – spin filtering by tunneling through 0d states and growth control by XRD
Physikalisches Institut, Universität Würzburg, Germany

Spin dynamics of Mn ions and photoexcited carriers in DMS heterostructures: Spin diffusion in magnetic ion system (invited)
A.A. Maksimov
Institute of Solid State Physics RAS, Chernogolovka, Russia

Mn spin dynamics probed using the combination of high magnetic field pulses and static field
T. Clément, D. Ferrand, M. Bonfim, L. Besombes, H. Boukari, H. Mariette, and J. Cibert
CNRS-UJF-CEA Joint group, Institut Néel, Grenoble, France; Universidade Federal do Paraná Centro Politécnico, Curitiba, Brasil
Coffee Break

Tu4  Diluted Magnetic Semiconductors III 16:15 - 17:00
(Chair: D. Yakovlev)

Tu4-1  16:15 - 16:45
Spin manipulation in magnetic and non-magnetic quantum dots (invited)
Alexander O. Govorov
Department of Physics and Astronomy, Ohio University, USA

Tu4-2  16:45 - 17:00
Optical spin orientation of a single manganese atom in a quantum dot
C. Le Gall, L. Besombes, R. Kolodka, H. Boukari, J. Cibert, H. Mariette
CEA CNRS team "Nanophysique et semiconducteurs", Institut Néel, CNRS & Université Joseph Fourier, Grenoble, France

Tu5  Gottfried Landwehr’s Birthday Session 17:00 - 18:00
(Chair: R. Suris)

Tu5-1  17:00 - 17:20
Gottfried Landwehr – the vertex of high magnetic fields in semiconductor physics
Michael von Ortenberg

Tu5-2  17:20 - 17:40
II-VI Technology at Würzburg: from novel materials to novel functionality
Andreas Waag

Tu5-3  17:40 - 18:00
Semiconductor research at the University of Würzburg
Gottfried Landwehr

Tu6p  Poster Session II 18:00 - 20:00
Wednesday, August 26

We1  ZnO Growth and Properties  09:00 - 10:45
(Chair: A. Yoshikawa)

We1-1  09:00 - 09:15
Overcoming the doping limit in wide gap semiconductors: p-type doping in ZnO
Su-Huai Wei
National Renewable Energy Laboratory, Golden, Colorado, USA

We1-2  09:15 - 09:30
Structural - instability of N-acceptors in homo- and hetero-epitaxially grown ZnO by MBE
Information and Electronic Dept, Graduate School of Engineering, Tottori Univ., Japan

We1-3  09:30 - 09:45
Time resolved and magneto-optical studies of bound exciton complexes in homoepitaxial ZnO
Institute of Solid State Physics, Technische Universität Berlin, Germany; Justus Liebig Universität Giessen, Germany; Ioffe Physico-Technical Institute, St.-Petersburg, Russia

We1-4  09:45 - 10:00
Band-structure and optical parameters for wurtzite MgO, ZnO, and CdO – an ab-initio prediction
A. Schleife, C. Rödl, F. Fuchs, and F. Bechstedt
Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena and European Theoretical Spectroscopy Facility, Jena, Germany

We1-5  10:00 - 10:15
Band profile of ZnMgO/ZnO heterostructures confirmed by Kelvin probe force microscopy
National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan; Tokyo University of Science, Noda, Chiba, Japan
We1-6 10:15 - 10:30

Stoichiometry dependent incorporation and electrical activity of Zn interstitials in homoepitaxial ZnO thin films
Universität Leipzig, Institut für Experimentelle Physik II, Germany

We1-7 10:30 - 10:45

Growth characteristics of poly-crystalline and single-crystalline ZnO layers by ultrasonic spray assisted mist-CVD technique
H. Nishinaka, Y. Kamada, N. Kameyama, K. Kaneko, and S. Fujita
Graduate School of Engineering, Kyoto University, Japan

Coffee Break 10:45 - 11:15

We2 Single Quantum Dots 11:15 - 12:30
(Chair: A. Mintairov)

We2-1 11:15 - 11:45

CdSe/ZnSe nanowire quantum dot: a high temperature single photon source (invited)
K. Kheng, A. Tribu, G. Sallen, T. Aichele, C. Bougerol, R. André, J. P. Poizat, S. Tatarenko
CEA/CNRS/University J. Fourier, Grenoble, France

We2-2 11:45 - 12:00

Electrically driven room temperature emission from a single self-assembled CdSe quantum dot
R. Arians, T. Kümmell, G. Bacher, A. Gust, C. Kruse, D. Hommel
Werkstoffe der Elektrotechnik and CeNIDE, Universität Duisburg-Essen, Germany; Universität Bremen, Germany

We2-3 12:00 - 12:15

Nanofabrication of telluride based sub-micron pillars
S.P. Agnihotri, H. Boukari, H. Haas, L. Besombes, M. Richard, and H. Mariette
Institut Néel, CNRS&Université Joseph Fourier, Grenoble, France

We2-4 12:15 - 12:30

Fluorine-doped ZnSe for applications in quantum information processing
T.D. Ladd, K. Sanaka, Y. Yamamoto, A. Pawlis, and K. Lischka
National Institute of Informatics, Tokyo, Japan; Stanford University, USA; University of Paderborn, Germany

Excursion 13:00 - 20:00
Thursday, August 27

Th1  Excitonic and Spin Effects  09:00 - 10:45
(Chair: C. Klingshirn)

Th1-1  09:00 - 09:30
Excitons in motion in II-VI semiconductors (invited)
J.J. Davies, L.C. Smith, D. Wolverson, V.P. Kochereshko,
H. Boukari, J. Cibert, H. Mariette, M. Wiater, G. Karczewski,
T. Wojtowicz
University of Bath, UK; Ioffe Physico-Technical Institute RAS,
St.Petersburg, Russia; Institut Néel, CNRS, Grenoble, France;
Institute of Physics PAS, Warsaw, Poland

Th1-2  09:30 - 09:45
Spin properties of trions in a dense 2DEG
V. Kochereshko, L. Besombes, R.T. Cox, H. Mariette,
T. Wojtowicz, G. Karczewski, J. Kossut
Ioffe Physico-Technical Institute RAS, St. Petersburg, Russia;
Institut Neel, CNRS, Grenoble, France; Institute of Physics, Polish
Academy of Sciences, Warsaw, Poland

Th1-3  09:45 - 10:00
Optical spin pumping of CdTe quantum wells
G.V. Astakhov, M.M. Glazov, D.R. Yakovlev, E.A. Zhukov,
W. Ossau, L.W. Molenkamp, and M. Bayer
Universität Würzburg, Germany; Ioffe Physical Technical Institute
RAS, St. Petersburg, Russia; Technische Universität Dortmund,
Germany; Lomonosov Moscow State University, Russia

Th1-4  10:00 - 10:15
Fine structure of emission lines from charged
CdSe/ZnSe/ZnMnSe quantum dots
E.A. Chekhovich, A.S. Brichkin, V.D. Kulakovskii,
S.V. Ivanov, A.A. Toropov, and M.M. Glazov
Institute of Solid State Physics RAS, Chernogolovka, Russia; Ioffe
Physical Technical Institute RAS, St. Petersburg, Russia

Th1-5  10:15 - 10:30
Fine structure of two electrons energy levels in a
quantum dot
M.M. Glazov, V.D. Kulakovskii
Institute of Solid State Physics RAS, Chernogolovka, Russia; Ioffe
Physical Technical Institute RAS, St. Petersburg, Russia

Th1-6  10:30 - 10:45
Fine structure of biexcitons in II-VI semiconductor
nanocrystals
A.V. Rodina and Al.L. Efros
Ioffe Physical Technical Institute RAS, St. Petersburg, Russia
Naval Research Laboratory, Washington, DC, USA
Coffee Break 10:45 - 11:15

**Th2** Nanostructures II 11:15 - 13:00
(Chair: E. Oh)

Th2-1 11:15 - 11:45

**Optical properties of single CdS nanosheets and nanowires (invited)**
Howard E. Jackson
Department of Physics, University of Cincinnati, Cincinnati, Ohio, USA

Th2-2 11:45 - 12:00

**Insertion of CdSe quantum dots in ZnSe Nanowires: MBE growth and microstructure analysis**
E. Bellet-Amalric, C. Bougerol, R. André, Y. Genuist, K. Kheng, and S. Tatarenko
Institut Néel, University Joseph Fourier, Grenoble, France

Th2-3 12:00 - 12:15

**Optical study of clustering in a self-assembled CdTe/ZnTe quantum dot plane**
T. Kazimierczuk, A. Golnik, J. A. Gaj, P. Kossacki, P. Wojnar
Institute of Experimental Physics, University of Warsaw; Institute of Physics, Polish Academy of Sciences, Warsaw, Poland

Th2-4 12:15 - 12:30

**ZnTe-based core-shell nanowires grown by molecular beam epitaxy**
Institute of Physics, Polish Academy of Sciences, Warsaw; High Pressure Institute, Polish Academy of Sciences, Warsaw, Poland

Th2-5 12:30 - 12:45

**Scanning spreading resistance microscopy of undoped CdS/ZnSSe multiple quantum well heterostructure**
D.E. Sviridov, V.I. Kozlovsky, D.A. Sannikov
Lebedev Physical Institute of RAS, Moscow, Russia

Th2-6 12:45 - 13:00

**Colloidal ZnO/CdS type II core-shell quantum dots: synthesis and characterization**
Vyacheslav Volkov, Igor L. Kuskovskiy, Nikesh V. Valappil, Fen Xu Hanying Bai, Xueyun Gao, and Hiroshi Matsui
Brookhaven National Lab, Upton, USA; The City University of New York, Department of Chemistry, Hunter College and Graduate Center; Department of Physics, Queens College, USA

Lunch Break 13:00 - 14:30
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<th>Th3</th>
<th>Phonons and Defects</th>
<th>14:30 - 16:00</th>
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<td>Th3-1</td>
<td>14:30 - 14:45</td>
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<td></td>
<td><strong>Inverted optical phonons in II-VI semiconductor compounds</strong></td>
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<td>E.A. Vinogradov, B.N. Mavrin, N.N. Novikova, V.A. Yakovlev</td>
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<tr>
<td></td>
<td>Institute for Spectroscopy of RAS, Troitsk, Russia</td>
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<td>Th3-2</td>
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<td><strong>Unification of the phonon mode behavior of semiconductor alloys within a basic percolation scheme</strong></td>
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<td>J. Souhabi, O. Pagès, A. Chafi, A. V. Postnikov, A. Nassour, S. Doyen, and J. Hugel</td>
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<td>LPMD, Université Paul Verlaine, Metz, France</td>
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<td>Th3-3</td>
<td>15:00 - 15:15</td>
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<td><strong>Resonant Raman scattering in spherical QDs: II-VI versus III-V semiconductor nanocrystals</strong></td>
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<td>M.I. Vasilevskiy, R.P. Miranda, A.G. Rolo, and C. Trallero-Giner</td>
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<td></td>
<td>Centro de Física, Universidade do Minho, Braga, Portugal; University College London, UK; Universidad de La Habana, Cuba</td>
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<td>Th3-4</td>
<td>15:15 - 15:30</td>
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<td><strong>Is the enigma of the anomalous curvature of LO phonon branches for some binary semiconductor compounds finally solved?</strong></td>
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<td>W. Szuszkiewicz, J. Lazewski, B. Hennion, and B. Witkowska</td>
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<td></td>
<td>Institute of Physics PAS, Warszawa; Institute of Nuclear Physics PAS, Kraków, Poland; Laboratoire Léon Brillouin, CEA-CNRS, Gif-sur-Yvette, France</td>
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<td>Th3-5</td>
<td>15:30 - 15:45</td>
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<td><strong>Pre-requisites for the formation of unusual diffusion profiles in II-VI semiconductors</strong></td>
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<td>H. Wolf, J. Kronenberg, F. Wagner, Th. Wichert, and ISOLDE Collaboration</td>
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<td></td>
<td>Technische Physik, Universität des Saarlandes, Saarbrücken, Germany; CERN, PH Department, Geneva, Switzerland</td>
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<td>Th3-6</td>
<td>15:45 - 16:00</td>
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<td><strong>The role of stacking faults and their associated 0.13 eV acceptor state in doped and undoped ZnO layers and nanostructures</strong></td>
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<td></td>
<td>Institut für Halbleiterphysik, Universität Ulm; Materialwissenschaftliche Elektronenmikroskopie, Universität Ulm, Germany</td>
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</table>
Coffee Break 16:00 - 16:30

Th4 Devices II 16:30 - 17:45
(Chair: M. Tamargo)

Th4-1 16:30 - 17:00
E-beam pumped lasers based on II-VI compound nanostructures from the visible to UVA (invited)
M.D. Tiberi, V.I. Kozlovsky, P.I. Kuznetsov
Principia LightWorks Inc., US; Lebedev Physical Institute, Russia; Kotel’nikov Institute of Radio Engineering and Electronics, Fryzino, Russia

Th4-2 17:00 - 17:30
Surface plasmon-enhanced light-emitting diodes (invited)
Min-Ki Kwon, Chu-Young Cho, Baek-Hyun Kim, Seong-Ju Park
Department of Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, Republic of Korea

Th4-3 17:30 - 17:45
Threshold behaviour of green vertical-cavity surface-emitting lasers containing quantum dots or quantum wells
Semiconductor Epitaxy and Semiconductor Optics, Institute of Solid State Physic; Institute of Theoretical Physics, University of Bremen, Germany; Institute of Theoretical Physics, University of Magdeburg, Germany

Th5p Poster Session III 17:45 - 19:15

Conference Dinner 20:00 - 23:00
### Friday, August 28

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<td>Fr1-1</td>
<td>Green to yellow light emitters with II-VI semiconductors (invited)</td>
<td>09:00 - 09:30</td>
<td>K. Kishino and I. Nomura, Department of Engineering and Applied Sciences, Sophia University, Tokyo, Japan</td>
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<td>Fr1-2</td>
<td>MBE grown HgCdTe as a material for megapixel infrared devices (invited)</td>
<td>09:30 - 10:00</td>
<td>Yu.G. Sidorov, V.S. Varavin, S.A. Dvoretsky, N.N. Mikhailov, I.V. Sabinina, M.V. Yakushev, A.L. Aseev, Institute of Semiconductor Physics of the Siberian Branch of RAS, Novosibirsk, Russia</td>
</tr>
<tr>
<td>Fr1-3</td>
<td>Potential applications of ZnO/GaN hybrid heterostructures for cost efficient LED technology</td>
<td>10:00 - 10:15</td>
<td>A. Bakin, A. Behrends, A. Waag, H.-J. Lugauer, A. Laubsch, K. Streubel, Institute of Semiconductor Technology, TU Braunschweig; OSRAM Opto Semiconductors, Regensburg, Germany</td>
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<td>Fr1-4</td>
<td>Hybrid solar cells and LEDs based on ZnO-nanowire arrays</td>
<td>10:15 - 10:30</td>
<td>Apurba Dev, Jan-Peter Richters, Abdelhamid Elshaer, Siegfried R. Waldvogel, Julia Waltermann, Wolfgang Schade, and Tobias Voss, Institute of Solid State Physics, University of Bremen; Kekulé-Institute for Organic Chemistry and Biochemistry, University of Bonn; Institute for Physics and Physical Technologies, Clausthal University of Technology, Germany</td>
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**Coffee Break**

09:00 - 10:00

10:45 - 11:15
**Fr2**  
**Microcavities and photonic crystals 11:15 - 13:00**  
*(Chair : A. Kavokin)*

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<th>Affiliations</th>
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<td>11:15 - 11:45</td>
<td>Polaritons in a ZnO tapered microcavity <em>(invited)</em></td>
<td>Zhanghai Chen, Liaoxin Sun, Hongxing Dong, Yanjing Ling, Qijun Ren, Lihui Bai, Weihang Zhou, and Xuechu Shen</td>
<td>Surface Physics Laboratory, Department of Physics, Fudan University, Shanghai, China</td>
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<tr>
<td>11:45 - 12:00</td>
<td>Novel ZnO nanotaper lasers</td>
<td>S.H. Lee, T. Goto, H. Miyazaki, J. H. Chang, and T. Yao</td>
<td>Center for Interdisciplinary Research, Tohoku University; Department of Applied Physics, Tohoku University, Sendai, Japan; Major of Semiconductor Physics, Korea Maritime University, Pusan, Korea</td>
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<tr>
<td>12:00 - 12:15</td>
<td>Room temperature whispering-gallery exciton-polaritons in ZnO microwires</td>
<td>A. Trichet, S. Xiaoxin, G. Pavlovic, N.A. Gippius, G. Malpuech, Z. Chen, M. Richard, and L.S. Dang</td>
<td>Inst. Néel, Grenoble, France; Surface Physics Laboratory, Fudan University, Shanghai, China; LASMEA, CNRS/University Blaise Pascal, Aubière, France; A.M. Prokhorov General Physics Institute RAS, Moscow, Russia</td>
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<td>12:30 - 12:45</td>
<td>Methods to spectrally tune CdSe/ZnSSe quantum-dot monolithic microcavities</td>
<td>K. Sebald, M. Seyfried, J. Kalden, J. Gutowski, C. Kruse, A. Gust, D. Hommel</td>
<td>Institute of Solid State Physics, University of Bremen, Germany</td>
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<td>12:45 - 13:00</td>
<td>Electromagnetic response of thin layers of metamaterials</td>
<td>S.G. Tikhodeev and N.A. Gippius</td>
<td>A. M. Prokhorov General Physics Institute RAS, Moscow, Russia; LASMEA, Université Blaise Pascal, Aubière, France</td>
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</table>
Lunch Break 13:00 - 14:30

**Fr3** New Experimental Approaches 14:30 - 15:30  
(*Chair: V. Kochereshko*)

Fr3-1  14:30 - 15:00
**Novel mechanisms of optical second harmonic generation in semiconductors (invited)**  
R.V. Pisarev  
*Ioffe Physical Technical Institute, St. Petersburg, Russia*

Fr3-2  15:00 - 15:30
**Ultrafast coherent spectroscopy with strain pulses in semiconductor nanostructures (invited)**  
A.V. Akimov  
*Ioffe Physical Technical Institute, St. Petersburg, Russia*

**Fr4** Closing Remarks 15:30 - 15:50  
(*Chair: T. Shubina*)
POSTER SESSIONS

Monday, August 24

Mo5p  Poster Session I  18:15 - 20:00

Mo5p-1  High-reflectivity distributed Bragg reflectors lattice-matched to ZnTe
W. Pacuski, C. Kruse, S. Figge, and D. Hommel
Institute of Solid State Physics, University of Bremen, Germany;
Institute of Experimental Physics, University of Warsaw, Poland

Mo5p-2  Manipulating emission of CdTeSe quantum dots embedded in synthetic opals
C. Vion, C. Barthou, P. Benalloul, C. Schwob, L. Coolen,
A.N. Gruzintsev, G.A. Emelchenko, W.M. Masalov,
J.-M. Frigerio, A. Maitre
Institut des NanoSciences de Paris; Universites Pierre et Marie Curie, Paris, France;
Institute of Microelectronics Technology and High Purity Materials of RAS, Chernogolovka, Russia;
Institute of Solid State Physics of RAS, Chernogolovka, Russia

Mo5p-3  Investigations of strain distribution in ZnMgSe/ZnSe micro-structures
M. Panfilova, A. Pawlis, S. Michaelis de Vasconcellos,
A. Shchekin, S. Lemeshko, A. Zrenner, and K. Lischka
University of Paderborn, Germany; NT-MDT Co, Zelenograd, Moscow, Russia

Mo5p-4  Synthesis of Indium Oxide Hexagonal Microcavity and Identification of its Whispering Gallery Modes
Hongxing Dong, Zhanghai Chen, Xiaomin Sun, Jian Lu, Wei Xie, H. Hoe Tan, Chennupati Jagadish, and Xuechu Shen
Fudan University, Shanghai, China; Australian National University, Canberra, Australia

Mo5p-5  Picosecond kinetics of the electron-hole layers formation in wide-bandgap II-VI type-II heterostructures
I.I. Tartakovskii, A.A. Maksimov, E.V. Filatov, S.V. Zaitsev,
D.R. Yakovlev, and A. Waag
Institute of Solid State Physics, Russian Academy of Sciences,
Chernogolovka, Moscow region, Russia; Experimentelle Physik II,
University of Dortmund, Dortmund, Germany;
Ioffe Physico-Technical Institute, Russian Academy of Sciences, St. Petersburg, Russia;
Institute of Semiconductor Technology, Braunschweig Technical University, Braunschweig, Germany
Excitonic polaritons in transverse magnetic fields
St. Petersburg State University; Ioffe Physico-Technical Institute RAS, St. Petersburg, Russia; Université Joseph Fourier de Grenoble, France; University of Bath, UK

Surprising stability of trion in relation to free carrier screening
A.A. Klochikhin, V.P. Kochereshko
Ioffe Physical-Technical Institute, St.-Petersburg, Russia; Konstantinov Nuclear Physics Institute, St.-Petersburg, Russia

Competition between above- and below-barrier excitation in the photo-modulation of quantum well optical spectra
University of Bath, Bath, UK; Ioffe Physico-Technical Institute RAS, St. Petersburg, Russia; Institute of Physics PAS, Warsaw, Poland

Interface phonons and polaron effect in II-VI quantum wells
A.Yu. Maslov, O.V. Proshina
Ioffe Physical Technical Institute, St. Petersburg, Russia

Dipolar vibrational modes confined in ZnSe nanocrystals
A. Belogorokhov, L. Belogorokhova, S. Gavrilov
Institute of Rare Metals, Moscow; Moscow State University; Moscow Institute of Electronic Engineering, Zelenograd, Russia

Terahertz photoconductivity of a two-dimensional electron gas in HgTe quantum wells
Yu.B. Vasilyev, F. Gouider, M. Bugar, G. Nachtwei, J. Königmann, C. Brüne, and H. Buhmann
Ioffe Physical Technical Institute, St. Petersburg, Russia; Institut für Angewandte Physik, Braunschweig, Germany; Physikalisch-Technische Bundesanstalt, Braunschweig, Germany; Fakultät für Physik und Astronomie, Julius-Maximilians-Universität Würzburg, Germany

Growth and characterization of ZnMgTe/ZnTe layered structures grown by molecular beam epitaxy
S. Imada, T. Baba, S. Sakurasawa, and M. Kobayashi

Determination of the band-gap of MgS and MgS-rich ZnMgSSe alloys from optical transmission measurements
I. Davidson, R.T. Moug, F. Izdebski, C. Bradford, K.A. Prior
School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, UK
Local measurement of band offset for ZnCdS/ZnSSe nanostructure by Laplace current DLTS cooperated with AFM technique
V.G. Litvinov, V.I. Kozlovsky, D.A. Sannikov, D.E. Sviridov, O.A. Milovanova, and N.B. Rybin
P.N. Lebedev Physical Institute, Moscow, Russia; Ryazan State Radioengineering University, Ryazan, Russia

Growth and characterization of Zn$_{1-x}$Be$_x$Mg$_y$Se solid solutions with luminescence and photoacoustic methods
F. Firszt, J. Zakrzewski, K. Strzałkowski, M. Maliński, S. Lęgowski, H. Męczyńska, A. Marasek, Y.S. Huang, and D.O. Dumcenco
N. Copernicus University, Toruń, Poland; Technical University Koszalin, Poland; National Taiwan University of Science and Technology, Taipei, Taiwan

Determination of the etching mechanism in MgS and ZnMgSSe epitaxial lift off layers
A. Curran, S. Brown, K.A. Prior, R.J. Warburton
School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, UK

Photoluminescence in ZnSe-based diluted magnetic semiconductor quantum well wire structures formed by wet chemical etching
T. Muranaka, S. Iizuka, K. Kodama, K. Ohmori, Y. Nabetani, and T. Matsumoto
University of Yamanashi, Takeda, Japan

Optically detected magnetic resonance in CdMnSe/ZnSe submonolayer quantum wells
Ioffe Physical-Technical Institute of RAS, St. Petersburg, Russia; University of Notre Dame, USA

Optical and magnetic properties of zinc blende MnS in case of 3D-2D transition
Philipps University, Marburg, Germany; Heriot-Watt University, Edinburgh, UK; Center for Electronic Correlation and Magnetism, University Augsburg, Germany

Growth and magneto-optical properties of ZnTe/ZnMnSe quantum dots
Wu-Ching Chou, Wen-Chung Fan, and K.F. Chien
National Chiao Tung University, HsinChu, Taiwan
Mo5p-21 3d Impurities in semimagnetic semiconductors based on wide gap ZnSe, ZnS, and ZnO compounds: X-ray, optical, and magnetic research
Tatiana P. Surkova, Vadim R. Galakhov, Ernst Z. Kurmaev
Institute of Metal Physics, Ural Division of the Russian Academy of Sciences, Ekaterinburg, Russia

Mo5p-22 Enhancement of intra-Mn²⁺ ion transition via Te-isoelectronic center in ZnMnSeTe multiple quantum wells
Graduate Institute of Electro-Optical Engineering, Tatung University, Taipei; Chung Yuan Christian University, Chung-Li; National Chiao Tung University, Hsin-Chu; I-Shou University, Kaohsiung; Chungha Picture Tubes, Ltd., Taoyuan, Taiwan

Mo5p-23 Electron spin relaxation time in CdMnTe quantum well
P. Barate, S. Cronenberger, M. Vladimirova, D. Scalbert, A.P. Dmitriev, F. Perez, H. Boukari
Université Montpellier, France; Ioffe Institute RAS, St-Petersburg, Russia; Institut des Nanosciences de Paris, CNRS/Université Paris, France; CEA-CNRS group “Nanophysique et Semiconducteurs” Institut Néel, CNRS, Grenoble, France

Mo5p-24 The Mn assisted recombination of trions in semimagnetic CdSe/ZnSe/ZnMnSe quantum dots
A.V. Chernenko, A.S. Brichkin, S.V. Sorokin, and S.V. Ivanov
Institute of Solid State Physics RAS, Chernogolovka, Russia; Ioffe Physico-Technical Institute, RAS, St. Petersburg, Russia

Mo5p-25 Enhancement of nonlinear light-spin excitations coupling in diluted magnetic semiconductor
S. Cronenberger, P. Barate, M. Vladimirova, D. Scalbert, F. Perez, H. Boukari
Université Montpellier, France; Institut des Nanosciences de Paris, Université Paris, France; Institut Néel, Grenoble, France

Mo5p-26 Colloidal Mn²⁺-doped CdSe quantum dots
Rémi Beaulac, Paul I. Archer, Stefan T. Ochsenbein, and Daniel R. Gamelin
Department of Chemistry, University of Washington, Seattle, USA

Mo5p-27 Zn₁₋ₓMnₓTe-ZnO core-shell nanowire structures grown by combination of MBE and low temperature ALD techniques
Institute of Physics PAS, Warsaw, Poland; Cardinal Stefan Wyszyński University, Warsaw, Poland; High Pressure Institute PAS, Warsaw, Poland
Mo5p-28  New insights in the formation of self assembled CdTe/ZnTe quantum dots  
P. Wojnar, H. Boukari, and H. Mariette  
Institute Néel, Université J. Fourier, Grenoble, France

Mo5p-29  Synthesis and properties of polymethylmethacrylate/CdS nanocomposites  
A. Biryukov, T. Izaak, E. Gotovtseva, V. Svetlichnyi  
Tomsk State University, Tomsk, Russia

Mo5p-30  Effect of the barrier width on the cathodoluminescence spectra in the strained CdTe/ZnTe superlattices with the quantum dot layers  
I.V. Kucherenko, V.S. Vinogradov, A.S. Trushin, G. Karczewski  
Lebedev Physical Institute RAS, Moscow, Russia; Institute of Physic PAS, Warsaw, Poland

Mo5p-31  Synthesis of ZnSe semiconductor nanostructures by a method of thermal evaporation of a material on porous Al₂O₃ matrixes  
Physical-Technical Institute of UB RAS, Izhevsk, Russia; Udmurt State University, Izhevsk, Russia; Material Science Faculty of Lomonosov’s Moscow State University, Moscow, Russia; Boreskov’s Institute of Catalysis of SB RAS, Novosibirsk, Russia

Mo5p-32  Comparison of optical properties for organically capped and silica coated CdSe quantum dots  
Byoung Woo Lee, Tae Soo Kim, Eunsoon Oh, Ch. Kiran Kumar, Eui-Tae Kim  
Chungnam National University, Daejeon, Korea

Mo5p-33  Influence of 2D precursors on optical properties of self assembled CdSe quantum dots  
Tae Soo Kim, Byoung Woo Lee, Eunsoon Oh, S. Lee, J.K. Furdyna  
Chungnam National University, Daejeon, Korea; Korea University, Seoul, Korea;University of Notre Dame, Notre Dame, USA

Mo5p-34  Physical and chemical cross analyses of II-VI semiconductor nanomaterials  
S. Dalmasso, D. Arl, J.-J. Gaumet, Y. Zhang, and J.-P. Laurenti  
Université Paul Verlaine Metz, Metz, France

Mo5p-35  Cascade upconversion of photoluminescence in ensembles of II-VI semiconductor nanocrystals  
E. Malainho, J.R. Santos, M.I. Vasilevskiy, S.A. Filonovich, Y.P. Rakovich, J.F. Donegan, and A. Rogach  
Universidade do Minho, Braga, Portugal; Universidade Nova de Lisboa, Caparica, Portugal; Trinity College Dublin, Ireland; Ludwig-Maximilians-Universität München, Germany
Mo5p-36  Evolution of CdS:Mn nanoparticle properties caused by pH of colloid solution and ultrasound irradiation  
Chernivtsi National University, Chernivtsi, Ukraine; Lashkaryev Institute of Semiconductor Physics NASU, Kyiv, Ukraine  

Mo5p-37  Radiative recombination dynamics of CdSe/Zn(S,Se)/MgS quantum dots up to room temperature  
S. Zaitsev, R. Arians, T. Kümmler, G. Bacher, A. Gust, C. Kruse, and D. Hommel  
Universität Duisburg-Essen, Duisburg, Germany; Universität Bremen, Germany  

Mo5p-38  EXAFS studies of CdSe/ZnSe/MgS quantum dots performed for single photon emitters  
E. Piskorska-Hommel, A. Wolska, J.I. Flege, R. Hildebrand, J. Falta, A. Gust, C. Kruse, D. Hommel, and F. d’Acapito  
University of Bremen, Germany; Institute of Physics PAS, Warsaw, Poland; European Synchrotron Radiation Facility, Grenoble, France  

Mo5p-39  Interfacial Properties of ultrathin CdSe Quantum Wells  
A. Alfaro-Martínez and I. Hernández-Calderón  
Physics Department, CINVESTAV, Mexico City, Mexico  

Mo5p-40  MBE growth and luminescence spectra of double CdSe/ZnSe quantum dot sheets  
I.V. Sedova, A.N. Reznitsky, S.V. Sorokin, A.A. Klochikhin, V.V. Korenev, S.A. Permogorov, A.A. Sitnikova, and S.V. Ivanov  
Ioffe Physical Technical Institute, St. Petersburg, Russia; B.P. Konstantinov Nuclear Physics Institute RAN, St.-Petersburg, Russia  

Mo5p-41  Thermally activated carrier transfer processes in self-assembled CdTe Stranski-Krastanow quantum dots grown on ZnSe by molecular beam epitaxy  
National Chiao Tung University, Hsin-Chu; Tatung University, Taipei; Chung Yuan Christian University, Chung-Li; National Changhua University of Education, Chang-hua; Chungha Picture Tubes, Ltd., Taoyuan, Taiwan  

Mo5p-42  Synthesis and characterization of CdTe quantum dots for in-vivo imaging  
A. Folk, J. Morales, and M. Sohel  
CUNY-City College of New York, USA; CUNY - Hostos College, Bronx, USA
| Mo5p-43 | **Beryllium chalcogenide alloys for visible light emitting and laser diodes**  
M. Sohel, O. Maksimov, F. Fernandez, and M.C. Tamargo  
The City University of New York, New York, USA; Electro-Optics Center, Pennsylvania State University, Freeport, USA |
| Mo5p-44 | **Formation of Tamm-like interface states in ZnSe/BeTe heterostructures: experiment and theory**  
A.S. Gurevich, M.O. Nestoklon, V.P. Kocgereshko, A. Waag  
Ioffe Physical Technical Institute, St. Petersburg, Russia; Institute für Halbleitertechnik, Braunschweig, Germany |
| Mo5p-45 | **Optical characterization of intersubband transitions in ZnxCd1-xSe/ ZnxCd1-xMg1-x-ySe asymmetric coupled quantum well structures by contactless electroreflectance**  
J.D. Wu, C.T. Huang, Y.S. Huang, W.O. Charles, A. Shen, Q. Zhang, and M.C. Tamargo  
National Taiwan University of Science and Technology, Taipei, Taiwan; The City College and The Graduate Center of CUNY, New York, USA |
| Mo5p-46 | **Optically pumped green lasers with active region composed of multi-sheet electronically-coupled CdSe quantum dots**  
Stepanov Institute of Physics of NASB, Minsk, Belarus; Ioffe Physical Technical Institute of RAS, St. Petersburg, Russia |
| Mo5p-47 | **Photopumped lasing characteristics of yellow-green BeZnSeTe double-heterostructures grown on InP substrates**  
Y. Sawafuji, I. Nomura, T. Ebisawa, S. Kushida, and K. Kishino  
Sophia University, Tokyo, Japan |
| Mo5p-48 | **ZnSe-based laser structures for electron-beam pumping with graded index superlattice waveguide**  
S.V. Gronin, S.V. Sorokin, I.V. Sedova, S.V. Ivanov, N.A. Gamov, V.B. Studionov, D.V. Peregoudov, M.M. Zverev, and P.S. Kop’ev  
Ioffe Physical Technical Institute, St. Petersburg, Russia; Moscow State Institute of Radio Engineering, Moscow, Russia |
| Mo5p-49 | **Green electron-beam-pumped laser arrays based on II-VI nanostructures**  
M.M. Zverev, N.A. Gamov, E.V. Zdanova, V.B. Studionov, D.V. Peregoudov, I.V. Sedova, S.V. Gronin, S.V. Sorokin, P.S. Kop’ev, I.M. Olikhin, and S.V. Ivanov  
Moscow State Institute of Radio Engineering, Russia; Ioffe Physical Technical Institute of RAS, St. Petersburg, Russia; “Gamma” Co Ltd., SRC “Platan”, Fryazino, Moscow region, Russia |
Mo5p-50  The impact of front contact ZnO:Al/Zn$_{1-x}$Mg$_x$O layer on Cu(In,Ga)Se$_2$ thin film solar cells
Xiaonan Li, Ingridre Repins, Brian Egaas, Jian V. Li, Ana Kanevce
National Renewable Energy Laboratory, Golden, CO

Mo5p-51  Ultra-violet ZnSSe, ZnMgS epilayers and MQW structures grown by MOVPE on GaP substrates
Kotel’nikov Institute of Radioengineering and Electronics of RAS, Fryazino, Russia; P.N. Lebedev Physical Institute of RAS, Moscow, Russia; Principia LightWork Inc., CA, USA

Mo5p-52  High sensitive ultraviolet organic-inorganic hybrid photodetectors of ZnSSe grown on p-GaAs with transparent conducting polymer window-layer
Tottori University, Japan

Mo5p-53  Cr$^{2+}$:CdS crystal as a new material for room-temperature tunable mid-infrared lasing
P.N. Lebedev Physical Institute of RAS, Moscow; Moscow Institute of Physics and Technology, Dolgoprudny, Russia

Mo5p-54  ZnSe:Fe crystal – high-gain medium for tunable mid-infrared lasers
N.N. Il’ichev, V.P. Danilov, V.P. Kalinushkin, M.I. Studenikin, P.V. Shapkin, A.S. Nasibov
A.M. Prokhorov General Physics Institute RAS, Moscow, Russia; P.N. Lebedev Physics Institute RAS, Moscow, Russia

Mo5p-55  Simulation design and fabrication of cylindrical capacitive Frisch grid CdZnTe detectors
Dongni Hu, Jiahua Min, Zhaoli Xu, Linjun Wang, Wenbin Sang
Shanghai University, China

Mo5p-56  Analysis of In and Al doped high resistivity CdZnTe crystal
Changjun Wang, Jiahua Min, Chenying Zhou, Xiaoyan Liang, Yue Zhao, Linjun Wang, Yiben Xia
Shanghai University, China

Mo5p-57  Control of vapor pressure of cadmium at growth and annealing of CdZnTe:Cl crystals with the variable content of zinc for nuclear detectors
E.V. Beregulin, N.K. Zelenina, V.P. Karpenko, O.A. Matveev, V.E. Sedov, A.I. Terentyev, A.A. Tomasov
Ioffe Physical Technical Institute, St. Petersburg, Russia
Se-Se isoelectronic centers in high purity CdTe
Rita Najjar, Andrzej Golnik, Régis André, Piotr Kossacki, Henri Mariette, and Jan Gaj
Institut NEEL-CNRS, Grenoble, France; Institute of Experimental Physics, University of Warsaw, Warszawa, Poland

Effect of variable crucible dropping rate on solid-liquid interface in CdZnTe crystal growth
Chenyang Zhou, Jiahua Min, Changjun Wang, Xiaoyan Liang, Jianyong Teng, Linjun Wang, Weiming Shi
Shanghai University, China

Chemical diffusion and defect reactions in CdTe<In>
Charles University, Institute of Physics, Prague, Czech Republic; Chernivtsi National Academy, Chernivtsi, Ukraine

Special features of conductivity of semi-intrinsic CdTe and CdZnTe single crystals used in X- and γ-ray detectors
Chernivtsi National University, Chernivtsi, Ukraine; Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, Kyiv, Ukraine; Research Institute of Electronics, Shizuoka University, Hamamatsu, Japan; Technological Educational Institute of Chalkida, Psahna-Evia, Greece

ZnS:N and ZnS:N,Ag grown by molecular beam epitaxy
A. Kotani, H. Tanaka, T. Kawai, and K. Ichino
Department of Information and Electronics, Tottori University, Tottori, Japan

Self-activated luminescence spectra of CdS(O) in the context of the band anticrossing model
N.K. Morozova, N.D. Danilevich, A.A. Kanakhin
Moscow Power Engineering Institute (Technical University), Moscow, Russia

Point and nanoscale defects in Cd(S, Se,Te) crystals induced by plastic deformation
V. Babentsov, V. Boiko, J. Franc, and G.A. Shepelskii
Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, Kiev, Ukraine; Institute of Physics, Charles University, Prague, Czech Republic
Tuesday, August 25

Tu6p  Poster Session II  18:00 - 20:00

Tu6p-1  Energy transfer processes in ZnSe/ZnMnSe double quantum well structures
S. Jankowski, W. Heimbrodt, S. Horst, A. Chernikov, and S. Chatterjee
Philipps-Universität Marburg, Department of Physics and Material Science Center, Marburg, Germany

Tu6p-2  Tunneling of spin polarized excitons in ZnCdSe and ZnCdMnSe coupled double quantum wells
K. Ohmori, K. Kodama, T. Muranaka, Y. Nabetani, and T. Matsumoto
University of Yamanashi, Kofu, Japan

Tu6p-3  Dynamics of exciton magnetic polaron formation in CdMnSe/CdMgSe quantum wells
Tillmann Godde, Irina I. Reshina, Sergey V. Ivanov, Ilya A. Akimov, Dmitri R. Yakovlev, and Manfred Bayer
Technische Universität Dortmund, Germany; Ioffe Physical-Technical Institute RAS, St. Petersburg, Russia

Tu6p-4  Photoinduced magnetization of magnetic polarons in Cd$_{0.8}$Mn$_{0.2}$Te under high-density resonant excitation of free exciton
K. Katayama
Department of Physics, Tokyo Institute of Technology, Japan

Tu6p-5  Kinetics of exciton magnetic polaron emission in type-II ZnMnSe/ZnSSe QWs
A.S. Brichkin, A.V. Chernenko, V.D. Kulakovskii, S.V. Sorokin, and S.V. Ivanov
Institute of Solid State Physics of RAS, Chernogolovka, Russia; Ioffe Physico-Technical Institute, St. Petersburg, Russia

Tu6p-6  Influence of photo-generated carriers on the Mn-spins in CdMnTe quantum wells studied by spin-flip-Raman spectroscopy in a two-colour experiment
Universität Würzburg, Germany; Ioffe Physico-Technical Institute RAS, St. Petersburg, Russia; Institute of Physics PAS, Warsaw, Poland

Tu6p-7  Relaxation of magnetization controlled by spin diffusion in CdMnTe quantum wells
J. Debus, D.R. Yakovlev, A.A. Maksimov, M.K. Kneip, G. Karczewski, T. Wojtowicz, J. Kossut, and M. Bayer
Technische Universität Dortmund, Germany; Ioffe Physical Technical Institute, St. Petersburg; Institute of Solid State Physics, Chernogolovka, Russia; Institute of Physics, PAS, Warsaw, Poland
Electrical control of spin polarization in a CdMnTe/CdMgTe quantum well on a micrometer scale
Y. S. Chen, T. Kümmell, G. Bacher, M. Wiater, G. Karczewski, T. Wojtowicz
Universität Duisburg-Essen, Duisburg, Germany; Institute of Physic PAS, Warsaw, Poland

Optical and photothermal investigations of Zn$_{1-x}$yBe$_x$Mn$_y$Se solid solutions
N. Copernicus University, Toruń; Technical University Koszalin, Poland; National Taiwan University of Science and Technology, Taipei, Taiwan

Temperature-dependent photoluminescence and contactless electroreflectance characterization of Zn$_{1-x}$yBe$_x$Mn$_y$Se mixed crystals
D.O. Dumcenco, C.T. Huang, Y.S. Huang, F. Firszt, S. Łęgowski, H. Męczyńska, J. Zakrzewski, and K.K. Tiong
National Taiwan University of Science and Technology, Taipei, Taiwan; N. Copernicus University, Toruń, Poland; National Taiwan Ocean University, Keelung, Taiwan

Exchange coupling and crystal field investigations of Eu doped narrow gap semiconductors
S. Isber, X. Gratens
American University of Beirut, Lebanon; Universidade de São Paulo, Brazil

Influence of light on the edge state transport in HgTe/HgCdTe quantum wells
E.G. Novik, M.J. Schmidt, M. Kindermann, and B. Trauzettel
Universität Würzburg, Germany; University of Basel, Switzerland; Georgia Institute of Technology, Atlanta, USA

(100) and (111)CdTe epitaxial layers grown by molecular beam epitaxy for investigation of electron spin relaxation lifetimes
Qiang Zhang, William Charles, Aidong Shen, Carlos A. Meriles, and Maria C. Tamargo
The City College of CUNY, New York; The Graduate Center of CUNY, New York, USA

Photo-EPR and magneto-optical spectroscopy of the iron centers in ZnO
D.V. Azamat, J. Debus, D. R.Yakovlev, V. Yu. Ivanov, M. Godlewski, M.Fanciulli, M.Bayer
Technische Universität Dortmund, Germany; Ioffe Physico-Technical Institute RAS, St. Petersburg, Russia; Institute of Physics PAS, Warsaw, Poland; Cardinal S. Wyszyński University, Warsaw, Poland; Universita degli studi di Milano-Bicocca, Milano, Italy
Raman scattering from ZnO doped with Fe, Mn and Co nanoparticles
B. Hadžić, N. Romčević, M. Romčević, R. Kostić, I. Kuryliszyn-Kudelska, W. Dobrowolski, U. Narkiewicz, and D. Sibera
Institute of Physics, Belgrade, Serbia; Institute of Physics PAS, Warsaw; Szczecin University of Technology, Institute of Chemical and Environment Engineering, Poland

Raman scattering studies of ZnO containing Co:bulk crystals, tetrapodes, and nanowires
Institute of Physics PAS, Warszawa, Poland; Institut des Nanosciences de Paris, France

Annealing effects and generation of secondary phases in ZnO after high-dose transition metal implantation
Universität Würzburg; Universität Göttingen; Universität Jena, Germany; Institute of Physics PAS, Warszawa, Poland

Optical studies on the Zn_{1-x}Co_{x}O films and ion-implanted wires with x \leq 10%
L. Chen, S. Jankowski, S. Ye, A. Ney, S. Müller, C. Ronning, and W. Heimbrodt
University of Marburg; University of Duisburg-Essen; University of Jena, Germany

Structural and optical studies of Zn_{1-x}Mn_{x}O nanopowders prepared via sol gel technique
M. Ebrahimizadeh Abrishami, S. M. Hosseini, E. Attaran Kakahi, and A. Kompani
Ferdowsi University of Mashhad, Iran

Optical properties of ZnO and Zn_{0.95}Mn_{0.05}O nanopowders
V. Sokolov, A. Yermakov, M.Uimin, A. Mysik, V. Pustovarov, and N. Gruzdev
Institute of Metal Physics UD RAS, Yekaterinburg, Russia; Ural State Technical University, Yekaterinburg, Russia

Structural properties of Zn_{0.95}Mn_{0.05}O/Al_{2}O_{3} multilayer structures grown by pulsed laser deposition
A. Khodorov, S. Levechev, A. Chahboun, A.G. Rolo, and M.J.M. Gomes
University of Minho, Braga, Portugal; Dhar Mehraz Sciences Faculty, Fès, Morocco
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Tu6p-29  Controlling the surface-related photoluminescence of ZnO nanowires
Apurba Dev, Jan-Peter Richters, and Tobias Voss
Institute of Solid State Physics, University of Bremen, Germany

Tu6p-30  Modifying growth conditions of ZnO nanorods for solar cell applications
Institut für angewandte Physik, Universität Karlsruhe; Laboratorium für Elektronenmikroskopie, Universität Karlsruhe, Germany

Tu6p-31  Improvement of chemical stability of aqueous solution grown ZnO nanorods by aminosilane modification
K. Ogata, H. Dobashi, K. Koike, S. Sasa, M. Inoue, and M. Yano
Osaka Institute of Technology, Osaka, Japan

Tu6p-32  ZnO nanorods growth on sapphire substrates using aqueous solutions with microwave heating and their photoluminescence properties
K. Ogata, H. Dobashi, S. Sasa, M. Inoue, and M. Yano
Osaka Institute of Technology, Osaka, Japan

Tu6p-33  Optical properties of ZnO nanocrystal-based composites
G.N. Panin, A.N. Baranov, and T.W. Kang
Dongguk University, Seoul, South Korea; Institute of Microelectronics Technology, RAS, Chernogolovka, Russia; Department of Chemistry, Moscow State University, Moscow, Russia

Tu6p-34  Epitaxial growth and characterization of ZnSTeO quaternary alloys
Y. Nabetani, K. Gemma, T. Muranaka, T. Kato, and T. Matsumoto
University of Yamanashi, Kofu, Japan

Tu6p-35  Radical-source MBE of ZnO-related hetero- and quantum well structures for optoelectronic applications
S. Sadofev, S. Kalusniak, J. Puls, Y.-H. Fan, P. Schäfer, and F. Henneberger
Department of Physics, Humboldt University of Berlin, Germany

Tu6p-36  Blue-green PL emission from ZnCdO-based multiple quantum wells grown by RPE-MOCVD
Shizuoka University, Hamamatsu, Japan; NTT Basic Research Laboratories, NTT Corporation, Atsugi, Japan
Tu6p-37  MOVPE growth and study of ZnO, ZnMgO epilayers and ZnO/ZnMgO MQW structures  
P. Kuznetsov, V. Luzanov, G. Yakushcheva, V. Jitov, L. Zakharov, I. Kotelyanskii, V. Kozlovsky  
Kotel’nikov Institute of Radioengineering and Electronics of RAS, Fryazino, Russia; P.N. Lebedev Physical Institute of RAS, Moscow, Russia  

Tu6p-38  Controlled growth of high-quality ZnO-based films and heterostructures for application in optoelectronic devices  
Xiaolong Du, Zengxia Mei, Yang Guo, and Qikun Xue  
Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, China  

Tu6p-39  Non polar ZnO-based heterostructures: a comparison between $a$ and $m$ orientations  
J-M. Chauveau, M. Teisseire, J. Zuniga-Perez, P. Vennegués, H. Kim-Chauveau, C. Deparis, C. Morhain, B. Vinter  
Centre de Recherche sur l’Hétéro-Épitaxie et ses Applications, Centre National de la Recherche Scientifique (CRHEA-CNRS), Valbonne, France; University Nice Sophia Antipolis, Nice, France  

Tu6p-40  Optical in-plane anisotropy of ZnO/(Zn,Mg)O quantum wells  
Y. Fan, J. Puls, G.V. Michailov, S. Sadofev, and F. Henneberger  
Humboldt-University, Institute of Physics, Berlin, Germany; Ioffe Physical Technical Institute, St. Petersburg, Russia  

Tu6p-41  Anisotropy of the dielectric function of ZnO including exciton-polariton formation obtained from ellipsometry  
Munise Cobet, Christoph Werner, Christoph Cobet, Markus R. Wagner, Norbert Esser, Axel Hoffmann, and Christian Thomsen  
Institut für Festkörperphysik, Technische Universität Berlin, Germany; ISAS-Institute for Analytical Sciences, Berlin, Germany  

Tu6p-42  Multi-band theory of magnetoexcitons in ZnO/ZnMnO quantum wells  
W. Bardyszewski  
University of Warsaw, Poland  

Tu6p-43  Optical properties of MgO, ZnO, and CdO in a wide spectral range from first principles  
A. Schleife, C. Rödl, F. Fuchs, and F. Bechstedt  
Friedrich-Schiller-Universität Jena and European Theoretical Spectroscopy Facility, Jena, Germany  

Tu6p-44  Ab initio charge transition levels of transition metals in ZnO – a comparative study of gap corrections  
Marc A. Gluba and N.H. Nickel  
Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany
Two-dimensional polaron mass in ZnO quantum Hall systems
Yasutaka Imanaka, Tadashi Takamasu, Hitoshi Tampo, Hajime Shibata, and Shigeru Niki
National Institute for Materials Science, Tsukuba, Ibaraki; National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan

Solar-blind 4.55 eV band gap Mg$_{0.55}$Zn$_{0.45}$O components fabricated using quasi-homo buffers
Institute of Physics, Chinese Academy of Sciences, Beijing, China; Ion Technology Center, Uppsala University, Sweden; Department of Physics, University of Oslo, Norway

The effect of MgO layer on suppression of visible light photoresponse in n-ZnO/MgO/p-Si UV detector
Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, China

Impact of acceptor states in Mg$_x$Zn$_{1-x}$O Schottky photodiodes
Universidad Politécnica de Madrid, Spain; Research Institute of Electronics, Shizuoka University, Japan

Characteristics of ZnO thin film transistor prepared by two different methods
K. Haga, M. Sakuma, Y. Takizawa, S. Seki
Sendai National College of Technology, Sendai, Japan

Humidity detection measurement ZnO nanodots using quartz crystal microbalance (QCM) method
A. Erol, B. Comba, S. Okur, N. Üzar, N. Tekgüzèl
Istanbul University, Turkey; Izmir Institute of Technology, Turkey

SHG enhancement from one-dimensional polarity inverted structures in ZnO films
T. Minegishi, S. Park, J. Park, T. Yao, and K. Domen
University of Tokyo; Tohoku University, Sendai, Japan

Electroluminescence from a n-ZnO/p-GaN Hybrid LED
A. Behrends, A. Bakin, A. Waag, Ho-Sang Kwack, Le Si Dang
Institute of Semiconductor Technology, Braunschweig, Germany; Institut Néel, CNRS-UJF, Grenoble, France

Sodium doped room temperature ZnO ultraviolet-blue light-emitting diodes employing ZnO/ZnMgO multi-quantum wells on silicon substrate
Z.Z. Ye, S.S. Lin, H.P. He, X.Q. Gu, L.P. Zhu
Zhejiang University, People’s Republic of China
Tu6p-54  
**Nitrogen doping of ZnO**  
Institute of Solid State Physics, Technische Universität Berlin; Justus Liebig Universität Giessen, I. Physics Institute, Germany  

Tu6p-55  
**Effect of annealing on nitrogen-doped ZnO grown by MOVPE with a high-speed rotating disk reactor**  
N. Nishimoto, Y. Matsuo, Y. Fujita  
Innovation Plaza Hiroshima, Japan Science and Technology Agency, Higashihiroshima, Japan; Interdisciplinary Faculty of Science and Engineering, Shimane University, Matsue, Japan  

Tu6p-56  
**Effectiveness of using a ZnO substrate with an off-axis angle for growth of nitrogen-doped ZnO films**  
Iwate University, Morioka, Japan; Iwate Industrial Research Institute, Japan; Sendai National College of Technology, Japan  

Tu6p-57  
**Depth-resolved photoluminescence studies of Na+H co-doped ZnO grown by MBE**  
University of Oslo, Norway; Institute of Physics, Chinese Academy of Sciences, Beijing, China  

Tu6p-58  
**High quality p-type ZnO film grown on ZnO substrate by nitrogen and tellurium codoping**  
Tohoku University, Sendai, Japan; Korea Maritime University, Pusan, Korea; Hoseo University, Korea; Chungnam National Univ., Daejeon, Korea  

Tu6p-59  
**Thermal activation of nitrogen acceptors in ZnO thin films grown by MOCVD**  
J.K. Dangbégnon, K. Talla, J.R. Botha  
Department of physics, Nelson Mandela Metropolitan University, Port Elizabeth, South Africa  

Tu6p-60  
**The role of hydrogen in p-type conductivity conversion of in-situ Na-H codoped ZnO films by MBE**  
Institute of Physics, Chinese Academy of Sciences, Beijing, China; Department of Physics, University of Oslo, Norway  

Tu6p-61  
**On the electrical characteristics of Pd Schottky contacts deposited on the O-polar and Zn-polar faces of bulk ZnO crystals**  
W. Mtangi, J.M. Nel, F.D. Auret, A. Chawanda, C. Nyamhere, and P.J. Janse van Rensburg  
Department of Physics, University of Pretoria, South Africa
| Tu6p-62 | Effects of a high humidity environment and air anneal treatments on the electrical resistivity of transparent conducting ZnO-based thin films | A. Abduev, A. Akhmedov, A. Asvarov, A. Abdullaev, and A. Murtazaliev |
| Tu6p-63 | Mechanism of resistive memory effect in Ga doped ZnO thin films | K. Kinoshita, T. Hinoki, K. Yazawa, K. Ohmi, and S. Kishida |
| Tu6p-64 | Schottky barrier contacts formed on polar-, nonpolar- Mg$_x$Zn$_{1-x}$O film grown by remote-plasma-enhanced MOCVD | A. Nakamura, T. Hayashi, J. Temmyo, A. Hierro, G. Tabares, J.M. Ulloa, E. Muñoz |
| Tu6p-65 | RPE-MOCVD grown ZnCuO films for green light emitting structures | B. Hu, K. Yamamoto, A. Nakamura, and J. Temmyo |
| Tu6p-66 | A novel chrysanthemum-like ZnO nanostructure synthesized by the ultrasonic spray pyrolysis method | Yun Guo, Xiaoyin Wei, Bin Wang, Yue Zhao, Jiahua Min, Wenbin Sang |
| Tu6p-67 | X-ray multiple diffraction – a new method of structural characterization of wurtzite type epitaxial layers | R. Kyutt |
| Tu6p-68 | X-ray analysis of stress and crystal quality of epitaxial RS-MBE ZnO films | R. Kyutt, V. Ratnikov, S. Ivanov, and A. Waag |
| Tu6p-69 | Spin selector by ferroelectric triple barrier resonant tunnel diode | M. K. Li, N. M. Kim, S. J. Lee, and T. W. Kang |
| Tu6p-70 | New tendencies of deposition high quality ZnO films for designing of UV photodetectors on their basis | A. Ievtushenko, G. Lashkarev, V. Lazorenko, V. Khranovskyy, V. Karpyna, O. Kutsay, V. Baturin, A. Karpenko, M. Lunika, L. Kosyachenko, V. Sklyarchuk, O. Sklyarchuk |

Institute of Physics RAS, Makhachkala, Russia |
Tottori University, Japan; Oike & Co., Ltd., Kyoto, Japan |
Shizuoka University, Japan; ISOM and Departamento de Ingeniería Electrónica, Universidad Politécnica de Madrid, Spain |
Shizuoka University, Japan |
Shanghai University, China |
Ioffe Physical-Technical Institute of RAS, St. Petersburg, Russia |
Ioffe Physical-Technical Institute of RAS, St. Petersburg, Russia; Technical University Braunschweig, Germany |
Dongguk University, Seoul; Soongsil University, Seoul, Korea |
Institute for Problems of Material Science, Kiev; V. Bakul Institute for Superhard Materials, Kiev; Institute of Applied Physics, Sumy; Chernivtsi National University, Chernivtsi, Ukraine |
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<td>Institute of Physics, Dagestan Scientific Center of RAS, Makhachkala, Russia</td>
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<td>Institute of Physics, PAS, Warsaw, Poland; College of Science, Cardinal Stefan Wyszyński University, Warsaw, Poland</td>
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<td>Physikalisches Institut, Justus-Liebig-Universität Giessen, Giessen, Germany</td>
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Institute of Semiconductor Physics of the Siberian Branch of the RAS, Novosibirsk, Russia

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U.M. Pysklynets, I.V. Gorichok

Ivano-Frankivsk National Medical University, Ivano-Frankivsk, Ukraine; Precarpathian National University, Ivano-Frankivsk, Ukraine

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M. S. Hammer, C. Deibel, V. Dyakonov

Julius-Maximilians-University of Würzburg, Germany

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Young Soo No, Dong Yeol Yun, Su Youn Kim, Dong Ick Son, and Tae Whan Kim

Hanyang University, Seoul, Korea

Ab initio calculation and Curie temperature of acceptor and donor defects in (Ga,Fe)N and (Zn,Mn)O


Laboratoire de Magnétisme et de Physique des Hautes Energies Département de physique, Faculté des sciences, Rabat, Morocco; Laboratoire de Physique des Hautes Energies Département de physique, Faculté des sciences, Rabat, Morocco; The Institute for Nanomaterials and Nanotechnology, INANOTECH, Rabat, Morocco; Hassan II Academy of Sciences and Technology, Rabat, Morocco; Institut Néel, CNRS-UJF, Grenoble, France
Abstracts
40 years of ZnO research – old and very recent results

C. Klingshirn, J. Fallert, J. Sartor, and H. Kalt
Institut für Angewandte Physik, Universität Karlsruhe (TH), Karlsruhe Institute of Technology (KIT), 76128 Karlsruhe, Germany

ZnO is a wide gap semiconductor which has been investigated since several decades. The material has come into focus again recently, mainly because one expects various possibilities of applications. Most prominent among these are applications in blue/UV opto-electronics. [1,2]

We review in this contribution various topics, stressing both: long known results and very recent achievements. The topics of this review lecture include:

- exciton physics and bandstructure
- laser processes and lasing in bulk, epilayers, nano-rods and powders
- electronic transport properties including n- and p-type doping
- applications e.g. in field effect transistors, LEDs, gas sensors, etc.

Su1-2

Physics and Prospective Applications of Quantum Dots

A. Ekimov
Nanocrystals Technology
235 Elm Road, Briarcliff Manor, NY 10510
USA

Amazing progress in physics and technology of Quantum Dots (QDs) has stimulated incredible activity on search of practical applications of nano-sized materials in various fields from optoelectronics to pharmaceutical industry and biotechnology.

The talk is aimed at reviewing of major breakthroughs in studies of fundamental properties of QDs since their first appearance in early 80’s. Confinement of free and localized electronic excitations in semiconductor QDs, providing highly controllable variation of their optical properties, will be discussed alongside with their prospective applications for “white” LEDs. Then, some attention will be given to confinement of vibronic modes and its impact on energy relaxation and dissipation in semiconductor QDs.
We review the evolution of II-VI-based diluted magnetic semiconductors (DMSs) from their discovery to the present, with special attention on how this work led to current activities in spintronics. The first steps can be traced to the creation of materials themselves: high-quality HgMnTe crystals in the United Kingdom in the mid-1960’s, with further development a decade later of other II-Mn-VI ternary alloys, including wide-gap materials (e.g., CdMnTe), in the Soviet Union and in Poland. These advances were quickly followed by discoveries of a host of spin effects arising from the presence of Mn in the II-VI lattice, in a variety of independent investigations: helicon-excited spin resonance; unsuccessful but well justified attempts at realizing negative refraction in HgMnTe; the observation of dramatic effects due to spin in magneto-transport (e.g., spin splitting of Shubnikov-de Haas oscillations), magneto-optics (e.g., the giant Faraday effect), and such unexpected phenomena as the magnetically-induced metal-insulator transition. A milestone that led to much progress in this area was the theoretical formulation in mid-1970’s of the sp-d interaction between transition metal ions and band electrons of the II-VI host. This intense activity was accompanied by the discovery of new magnetic phenomena in II-Mn-VI materials – the spin glass transition, new types of antiferromagnetic order, discovery of the bound magnetic polaron – that succeeded in “educating” a large body of semiconductor physicists in the area of magnetism.

A giant leap forward in this field occurred in mid-1980’s when it was shown that DMSs can be grown in the form of thin films and multilayers by molecular beam epitaxy (MBE). This resulted in increasing the miscibility of transition metals in the II-VI lattice; in fabrication of DMS-based quantum wells, superlattices, and eventually quantum dots and wires, with a host of new effects achievable by the ability to “tune” band offsets in these structures via spin splitting of the band edges; and in modulation doping of the DMSs. While this ability to grown DMSs in the form of “designer materials” led to a truly new era in this field, it also constituted another milestone of special relevance to this talk: it laid the foundation for concepts that are currently at the heart of spintronics. Seminal femtosecond measurements of spin dynamics and spin polarization that laid the groundwork for later investigations of spin coherence in semiconductors were carried out on II-Mn-VI multilayers. The ability to epitaxially interface ZnMnSe with GaAs-based structures resulted in prototype spin-injection devices such as spin aligners and spin diodes. And, by enabling modulation doping, epitaxy allowed the realization of ferromagnetism in II-Mn-VI quantum wells – an achievement that had major impact on forming the theoretical picture of ferromagnetism in semiconductors generally, including the now very active field of III-Mn-V materials such as GaMnAs. But – because of the rich interplay between spin and electronic phenomena that occur in II-VI DMSs – perhaps the most important long-range impact of these materials can be traced to the fact that research in II-VI DMSs has brought the semiconductor and magnetism communities – communities that had little contact prior to that time – much closer together. It is this interface of semiconductor physics and magnetism that is the foundation of spintronics.
Excitonic polaritons are bosonic quasi-particles, which result from the strong interaction between exciton and photon modes. The concept of polaritons, mixtures of excitons and photons with same momenta, first introduced by Hopfield about 50 years ago, has proved to be very successful in describing optical properties of either bulk or confined semiconductor systems. In this presentation, we will review some past and recent polariton issues: signature of polaritons in bulk and confined systems (Fig.1), relevance of polariton concept in ensemble of quantum dots, Bose-Einstein condensation (Fig.2), and polariton lasing (Fig.3).
Role of II-VI compounds in basic semiconductor research

S. Permogorov
A.F. Ioffe Physical-Technical Institute RAS, St.Petersburg, Russia

The bulk II-VI compounds grown by conventional methods seem to be not very promising materials for electronic applications. First of all, they have a rather high concentration of self-activated defects (about $10^{16}$ cm$^{-3}$) and predominantly the $n$-type of conductivity. The controllable doping of many II-VI compounds by acceptor impurities is almost impossible. However, these compounds are excellent objects for the study of optical properties. The optical transitions in all II-VI compounds are direct, and their band-gap energies cover a wide range of a visible spectrum where the highly sensitive optical detectors are available. The native defects in II-VI compounds are usually self-compensated, which results in low concentration of free carriers and weak screening of exciton states. The exciton optical transitions, due to relatively small dielectric constants, have high oscillator strength, and the exciton binding energies are relatively large. This provides excellent conditions for the study of exciton states from which a vast information on the fundamental properties of near-edge optically accessible electronic states had been gained and many physical processes had been discovered and studied. This information is valid not only for II-VI compounds, but also for other classes of semiconductors. Besides of that, many II-VI compounds crystallize in uniaxial wurtzite structure with the split valence subbands, which in some cases strongly simplifies the theoretical analysis of the results and strongly enlarges the possibilities for the study of electron-phonon interaction. The crystal lattices of II-VI compounds have a large ionicity which strongly enhances the processes of polar electron-phonon scattering. Due to all these properties the II-VI compounds for many decades had served as a model objects for the study of most fundamental properties and physical processes in semiconductors. The classical studies of the fine structure of exciton states, the bound exciton complexes, the studies of resonant Raman and Brillouin scattering, the study of free exciton motion and polariton nature of the exciton resonances, the biexciton states, the study of the multiphonon scattering of hot excitons have been performed for II-VI compounds. Many new methods for the optical study of most basic characteristics of semiconductors had been developed. Later, these methods were successfully applied for the study of other classes of semiconductors.

Presently, the optical studies of II-VI compounds have gained a new momentum due to the development of new epitaxial technologies allowing one to grow the low dimensional heterostructures with nanoscale sizes of particular layers. Of special interest are the studies of the heterostructures involving the layers of semiconductor solid solutions tending to the formation of self-organized quantum dots. Such structures show great perspectives for the optoelectronic applications. However, the prime time of the study of bulk II-VI compounds when most of the fundamental methods for the study of basic semiconductor properties were developed should be always remembered.
Bose-Einstein condensates of exciton-polaritons in CdTe based microcavities


Ecole Polytechnique Fédérale de Lausanne (EPFL), IPEQ, CH1015 Lausanne
Institut Louis Neel, CNRS, Université J. Fourier, 38042 Grenoble

In this talk, we will give an overview of the properties that have been observed for Bose Einstein condensates of polaritons in II-VI microcavities.

In a first part, we will review the basic properties, such as the appearance of long-range order, allowing to claim for Bose Einstein condensation of polaritons. [1] We will detail the similarities and differences between a VCSEL, a polariton laser and a Bose Einstein condensate of polaritons. [2]

In a second part of the talk, we will present detailed experiments allowing to provide in depth information on the specific properties of such condensates. For example, how does the condensate overcome the inherent disorder in a solid state environment? [3] What is the influence of the short lifetime of the polaritons, and of their strongly interacting character?

In the last part of the talk, we will describe more recent experiments such as the observation of vortices[4] and the measurement of the dynamics of the condensation process. Perspectives for further studies will be given in the final part of the talk.[5]

Bose-Einstein condensation (BEC) of exciton polaritons has been recently reported in CdTe- and GaAs-based microcavities with embedded quantum wells at temperatures lower than 40K [1,2]. The existence of BEC has been proved by angle-resolved photoluminescence (PL) measurements showing polariton relaxation to the thermal equilibrium, observation of polariton lasing, and build-up of the 1st order spatial coherence of the ensemble of the polaritons above threshold. This latter observation has been put forward by the authors of Ref. 1 as a decisive evidence for the BEC which directly confirms that the well-known Onsager criterion of BEC \( \frac{\langle \psi^*(\vec{r}) \psi(\vec{r}) \rangle}{\langle \psi(\vec{r}) \psi(\vec{r}) \rangle} \rightarrow 1 \) is verified in their system (\( \psi(\vec{r}) \) being the macroscopic condensate wave-function). Ref. 3 proposes a different criterion for BEC: the build-up of spontaneous vector polarisation of the emission. The argument is that the total polarisation degree is proportional to the order parameter of the condensate, and that the observation of spontaneous polarisation randomly changing from one experiment to another manifests the spontaneous symmetry breaking in the system, which is the smoking gun for BEC. From the point of view of the fluctuation theory we analyze the spatial coherence and vector polarisation in localised polariton condensates and show that the polarisation criterion is more rigorous than the coherence criterion, in general. This is because, in a localised system the coherence length achieves the size of the system below the threshold for BEC, namely, in the fluctuation dominated regime. On the other hand, the spontaneous polarisation remains within the limits of a thermal noise in this regime and only builds up above the threshold for BEC.

References

We report on the observation of stimulated polariton emission from a ZnSe-based microcavity containing 16 ZnCdSSe quantum wells (QWs) located at the antinode position of a 2λ cavity surrounded by a 9.5-fold bottom distributed Bragg reflector (DBR) and a 8-fold top DBR. The DBRs are made of ZnSSe as the high refractive index material and MgS/ZnCdSe superlattices as the low index material. The sample has been grown without rotation on a GaAs (100) substrate using molecular beam epitaxy in order to achieve a spatial detuning of the cavity mode along the wafer plane due to a thickness gradient.

The strong coupling regime between cavity photon modes and quantum well excitons is evidenced by their anticrossing behaviour when the cavity-exciton detuning is varied by moving the observation spot over the sample plane. A Rabi splitting exceeding 40 meV is determined at a detuning of ΔE=0 meV (measured at 5 K), which corresponds to a value of more than 10 meV per QW. This value is significantly higher compared to 4 and 7 meV for GaAs and CdTe, respectively.

Stimulated emission in the strong coupling regime at T = 5 K can be obtained non resonantly under pulsed excitation at around 3.1 eV. This excitation is far from ideal since most of the pumping beam was absorbed in the top DBR and in the barrier, which results in a non uniform distribution of excited carriers in the 16 quantum wells of the microcavity. The distribution of the polariton population in momentum (k) and energy (E) space for a slightly positive detuning (+7 meV) has been measured using angle-resolved measurements of the far-field emission. Below threshold, the population is broadly distributed on the lower polariton branch around the ground state at k_\parallel=0 and E=2.508 eV. When the excitation density is raised above threshold, the ground state becomes massively occupied, and displays a blue shift of 7 meV. This is significantly smaller than the Rabi splitting, indicating that the system is still in the strong coupling regime. The physical mechanism of this stimulated polariton emission, i.e. Bose-Einstein condensation or polariton lasing, and its temperature dependence will be discussed also in this presentation.

*E-mail: ckruse@ifp.uni-bremen.de
We report on the realization and a detailed characterization of photonic structures based on II-VI compounds and designed for ZnTe substrates. Our motivation is to enhance quantum dots (QDs) emission using cavity effects. Distributed Bragg reflectors (DBRs) are used in order to create a microcavity and to confine light in direction perpendicular to the sample plane. Micropillars were etched using a focused ion beam (FIB) in order to confine light in the sample plane by internal reflection. Inside the microcavity, a sheet of CdTe QDs was introduced. The maximum of photoluminescence peak of the QDs ensemble was chosen to spectrally fit to the microcavity.

Our structures were grown using molecular beam epitaxy (MBE) on GaAs substrate followed by a 1 µm thick fully relaxed ZnTe buffer layer, a 20 period bottom DBR, a λ cavity, and a 15 period top DBR. CdTe QDs were deposited in the middle of the cavity. The formation of QDs results from a Zn-induced reorganization process during overgrowth of CdTe using migration enhanced epitaxy (MEE).

The reflectivity spectrum of thus obtained structure reveals a large width of the stopband (about 60 nm), which is a consequence of the comparatively high refractive index step of Δn = 0.5. The cavity mode is observed at 620 nm. Ellipsometry studies were performed separately for all materials used in the structure in order determine both real and imaginary part of refractive indices. The determined parameters are used for simulations of optical properties such as the reflectivity spectrum.

A scanning transmission electron microscopy (STEM) is used for imaging of the main components of the structure, i.e. cavity, QDs, DBR pairs, and internal structure of the low refractive index layer, which is a complex short period superlattice. Using STEM we determined also the exact layer thicknesses.

In order to protect the surface of the structure, a 150nm thick Al₂O₃ layer was deposited on top. Next, a focused ion beam (FIB) was used to etch circularly shaped pillars with diameters ranging from 0.5 to 5 µm. Images of pillars were obtained by scanning electron microscopy (SEM).

Microphotoluminescence spectra of the micropillars contain sharp lines of individual QDs, strongly enhanced at the spectral position of the cavity mode. A possible damage, introduced by the FIB processing, is restricted to a very thin zone, as witnessed by the emission of single QD lines even by the pillars with the smallest diameter of 0.5 µm. Transversal micropillar modes are observed in PL spectrum, revealing a quality factor Q up to 600, in agreement with reflectivity measurements.
The generation, manipulation, and detection of electron spins in semiconductor nanostructures is a central theme in the emerging field of spintronics. This talk will describe the synthesis and physical properties of colloidal diluted magnetic semiconductor nanocrystals such as transition-metal-doped CdSe, ZnO, and ZnSe quantum dots. The talk will describe the use of photochemical carrier generation, magneto-optical spectroscopies, and magnetic resonance spectroscopies to probe carrier spin relaxation dynamics and carrier-dopant magnetic exchange interactions in these colloidal quantum dots. Such effects underlie many important magneto-electronic phenomena in magnetic semiconductor nanostructures, including carrier-mediated ferromagnetism, magnetic polaron nucleation, and proposed spin-based quantum information processing schemes. Basic aspects of doped quantum dot electronic structures will be discussed in this context.

Related references:


MBE overgrowth of ex-situ prepared CdSe colloidal nanocrystals

M. Rashad¹, Erick M. Larramendi², A. Pawlis¹, K. Lischka¹, D. Schikora¹, M. V. Artemyev³ and U. Woggon³

¹Department Physik, Universität Paderborn, Warburger Str. 100, 33098 Paderborn, Germany
²Physics Faculty, University of Havana, Colina Universitaria, C.P. 10400 La Habana, Cuba
³Technische Universität Berlin, Institut für Optik und Atomare Physik, Straße des 17. Juni 135, D-10623 Berlin, Germany

Colloidal NCs exhibit an enormous potential regarding the tunability of their optical and structural properties. As free parameters, the size, shape, material composition and QD density of the NC can be varied and therefore exactly matched to the requirements of specific optoelectronic devices. Alternatively, different types of NC which emit light at several wavelengths can be combined in the same device to achieve multi-color or white light emission from a single chip. In this context the key issue of all applications based on colloidal NC is the integration of the QDs in a semiconductor matrix to stabilize their optical properties and to facilitate the fabrication of micro-resonators and nanostructures with colloidal QDs.

In this work we present a new method, which combines molecular beam epitaxy (MBE) of ZnSe and externally wet-chemically prepared, colloidal NCs of CdSe to achieve fully integrated monolithic epitaxial heterostructures. This technique allows several degrees of freedom for choosing the NCs density, shape and size. We used CdSe(ZnSe) core-shell nanodots with a core radius 2.5 nm and a thin ZnSe shell of 1 to 2 monolayers. The NCs were prepared in solution with a nominal volume concentration of $10^{12}$ NCs/l and $10^{16}$ NCs/l, respectively. Using a spray-coating technique, the NCs were deposited on several substrates (GaAs, Si) and the surface morphology was studied with Atomic Force Microscopy (AFM). From the AFM investigations the resulting density of NCs on the sample surface was estimated for the different substrates.

For investigation of the NCs overgrowth process, ZnSe layers with a thickness of 50 nm were prepared by MBE on GaAs substrates and subsequently spray-coated with CdSe(ZnSe) NCs. Directly after the deposition, the NCs were overgrown with a ZnSe cap layer of varying thickness, again by using MBE. The overgrowth was in-situ monitored by Reflection High Energy Electron Diffraction (RHEED), indicating a two dimensional layer-by-layer formation of the ZnSe cap layer. Ex-situ, the crystallographic properties of the ZnSe buffer and cap layer were investigated with High Resolution X-Ray Diffraction (HRXRD), showing that the ZnSe cap layer on top of the NCs is of high crystalline quality. High-resolution transmission electron microscope (HRTEM) images from the cross-section of the ZnSe/CdSe/ZnSe heterostructures demonstrate that the NCs are embedded in the surrounding ZnSe matrix, maintaining their original size and crystal structure.

Strong photoluminescence (PL) was observed from these hybrid colloidal epitaxial heterostructures. The line shape and energy of the luminescence from the (NCs) embedded in the ZnSe matrix was investigated as a function of the NCs density and the ZnSe cap layer thickness. Results of PL of NCs in micro-resonators are also reported. Our experiments reveal the successful integration of wet chemically prepared colloidal NCs in ZnSe layer stacks grown by MBE.
Near-field photoluminescence spectroscopy and imaging of solution synthesised CdSe nanowires

A. M. Mintairov, J. Herzog, K. Kuno, V. Protasenko, and J. L. Merz,
Department of Electrical Engineering and Department of Chemistry and Biochemistry,
University of Notre Dame, IN, 46556.

The effect of quantum confinement in semiconductor nanostructures results in size- and shape-dependence of optical and electrical properties. Most of the work during the past two decades has focused on zero-dimensional structures - quantum dots (QDs), having discrete atomic-like energy spectrum. One-dimensional systems - nanowires (NWs) - have recently attracted considerable attention due to their unique properties, including strong polarization sensitivity, low lasing thresholds, enhanced carrier mobilities and potential ballistic transport capabilities. Here we report measurements of emission spectra of ultrathin CdSe NWs using low-temperature near-field optical scanning microscope (NSOM) with spatial resolution below the light diffraction limit.

CdSe NWs with mean diameter 7 nm and length exceeding 1 μm were synthesized following a recently developed solid-liquid-solid growth [1]. Samples for NSOM experiments were drop cast onto a SiO/Si substrate. The density of NWs was ~0.5 μm⁻². NSOM measurements were performed using uncoated fiber probes in collection-illumination mode, providing spatial resolution up to 100 nm. Near-field photoluminescence spectra (NPL) were excited by the 488 nm line of an Ar ion laser. The spectra and monochromatic images were measured using a 270 mm focal length spectrometer with a CCD detector and GaAs photomultiplier.

Room temperature NPL spectra of single NWs reveal multiple band structure consisting of a few overlapping bands centered near 1.92 eV (~630 nm). The bands have halfwidth 100 meV and separation ~60 meV. Multiple band structure is related to fluctuations of wire thickness and zinc blende/wurtzite-structure phase admixtures [2]. For most of the NWs we observed time dependent fluctuations of the peak intensity manifesting the blinking effect [2]. The imaging reveals emission inhomogenity along the NWs having a spatial scale ~200 nm.

At low temperature a slight blue shift (~30 meV) of the center of the spectra was observed, along with a narrowing of the band width (to 30 meV) and fine structure consisting of a few sharp lines (halfwidth ~10 meV) superimposed on broad bands. The appearance of the sharp lines indicates carrier localization on QD-like imperfections. The sharp lines show power law blinking behavior with exponential factors for on (off) times 1.6 (1.2).

The work was supported by NSF NIRT grant ECS 0609249.

Colloidal semiconductor nanocrystals are fabricated relatively easy in a variety of shapes, ranging from spherical quantum dots (NQDs) to rod-like nanocrystals (NQRs) with aspect ratios up to 10 [1]. Their properties are strongly shape-dependent due to the electron-hole exchange interaction and the intrinsic crystal/shape anisotropy [2]. This shape-dependence gives the attractive possibility to tune the exciton fine-structure of such nanocrystals [3] and thereby their optical properties [5], provided the relationship between the shape and the fine-structure is understood.

Here we report a shape-induced anomalous behavior of the magneto-photoluminescence (PL) of one-dimensional (1D) NQRs. We find that the circularly polarized components of the NQR PL are split 10 meV at 8 T (which would correspond to a $g$-factor of -20). Above 8 T the splitting decreases monotonously up to 33 T. Furthermore, the degree of circular polarization is opposed to that of spherical NQDs [4]. We explain this behavior by a strong magnetic-field induced mixing of the exciton levels, which we have measured directly with fluorescence line narrowing (FLN) experiments.

We have used core/shell CdSe/CdS NQDs and NQRs. The NQDs have a 3.7 nm diameter, whereas the NQRs have a 3.7 diameter and a length of 10.7 nm (aspect ratio 2.9). Drop-casted samples were mounted in Faraday geometry inside a liquid helium bath-cryostat in a 33 T Bitter-type electromagnet and cooled to 1.2K. Polarized fluorescence line narrowing (FLN) experiments in high magnetic fields allow the characterization of the lowest exciton states in terms of the spin projection $F$ along the nanocrystal $c$-axis [6]. We found that the lowest exciton levels of the NQDs are dipole-forbidden (dark) $F = \pm 2$ excitons, ~5 meV below dipole-allowed (bright) $F = \pm 1$ levels. In contrast, the NQRs exhibit a dark $F = 0$ ground state below bright $F = \pm 1$ levels with a large dark-bright splitting $\Delta_{db} \sim 4.5$ meV.

In contrast to NQDs, where the non-resonant PL is governed by the dark $F = \pm 2$ ground state excitons, in NQRs the ground state plays only a minor role and the PL is dominated by a mixture of higher lying exciton states. At low magnetic fields the bright $F=0^+$ is the main component, at higher magnetic fields the $F=+1$ and $F=-2$ exciton states dominate, causing the anomalous PL behavior. Our measurements demonstrate that the symmetry of the exciton fine-structure of CdSe nanocrystals can be manipulated by their shape can lead to unexpected optical properties. These results suggest that the spin properties of semiconductor nanocrystals can be tuned in a wide range, which is highly desirable for future applications of nanocrystals.

Hybrid Resonant Organic-Inorganic Nanostructures for Novel Light Emitting Devices and Solar Cells

V.M. Agranovich

Institute of Spectroscopy, Russian Academy of Science, Troitsk, Russia
The University of Texas at Dallas, USA

The strategy of integration of organic and inorganic semiconductors in a single nanostructure may lead to many novel devices which take advantage of the good properties of both classes of materials, overcoming the basic limitations of each individual class. Following this idea we discuss properties of hetero-nanostructures based on combination of organic materials and inorganic semiconductors, having respectively Frenkel excitons and Wannier-Mott excitons with nearly equal energies. The resonant coupling between Frenkel and Wannier-Mott excitons in quantum wells (or quantum wires or dots) may lead to striking novel effects: (i) strong enhancement of the resonant all-optical nonlinearity in the strong coupling regime and (ii) highly efficient energy transfer from inorganic quantum well to organic or inorganic material in the weak coupling regime. The latter effect may be especially important for applications: the electrical pumping of excitations in the semiconductor quantum well can be used to efficiently turn on the organic material luminescence. We propose a new concept for light-emitting devices based on this effect. The efficient energy transfer in opposite direction, namely from organic overlayer to quantum well or semiconductor nanocrystals can be used for creation of new generation of solar cells. I have no enough time to discuss analogous processes in a microcavity configuration where predicted and observed giant polariton Rabi splitting drastically changes kinetics of luminescence and conditions of the polariton condensation.

Main time of talk will be used for demonstration the most typical recently published experimental results obtained in Germany (Berlin), UK (London) and in USA (MIT, Brown, An Arbor). These results indeed confirm that combining organic and inorganic semiconductors leads to novel nanoscale design for light-emitting, photovoltaic and sensor applications.
ZnO/organic/ZnO sandwich-type semiconductor hybrid structures for photonic applications

S. Blumstengel, S. Sadofev, J. Puls, and F. Henneberger
Humboldt-Universität zu Berlin, Institut für Physik, Newtonstr. 15, 12489 Berlin, Germany

ZnO and its ternaries ZnMgO and ZnCdO are remarkable exemptions in inorganic semiconductor epitaxy as these materials can be grown with high quality at temperatures as low as room temperatures. Such conditions are compatible with organic thin film growth. Exploiting this unique feature, epitaxial organic/inorganic semiconductor sandwich-type hybrid structures or even superlattices can be prepared. These hybrid structures unite complimentary properties of the two material systems and offer thus functionalities that can not be achieved by the individual components alone. As a precondition, electronic coupling across the inorganic/organic interface is required.

We will report on the growth of sandwich-type hybrid structures composed of a ZnO epilayer or ZnO/ZnMgO quantum well covered by a thin organic layer and capped by ZnO. The entire structure is prepared by molecular beam epitaxy ensuring well-defined interfaces free of extrinsic defects. As organic component serves either a spiro-bifluorene derivative or 2,2’-p-phenylenebis(5-phenyloxazol). Both compounds are excellent emitter materials. Despite the harsh environment during ZnO epitaxy, the molecules survive overgrowth without degradation of their electronic structure and optical properties.

Electronic coupling across the organic/inorganic interface is demonstrated in two different settings: In sandwich-type hybrid structures where the QW is located in close proximity to the organic layer, we observe electronic coupling between “inorganic” QW Wannier excitons and “organic” Frenkel excitons. The coupling is incoherent and mediated via dipole-dipole interaction. A coupling strength of ca. 2 meV is deduced which is already beyond the radiative decay rate. In (Zn,Mg)O/organic hybrid structures with type II energy level alignment, charge separation across the organic/inorganic interface takes place. Moreover, ZnO/organic/ZnO sandwich-type hybrid structures form planar waveguides. In optimized geometries, optical amplification in the enclosed organic layer can be observed at low threshold supported by the waveguide properties of the sandwich as well as by energy transfer.
Ferromagnetism in uniform and non-uniform magnetically doped II-VI compounds

Tomasz Dietl
Laboratory for Cryogenic and Spintronic Research, Institute of Physics, Polish Academy of Sciences, 02 668 Warsaw, Poland
Institute of Theoretical Physics, University of Warsaw, Poland

The demonstrated and foreseen functionalities of ferromagnetic semiconductors such as (Ga,Mn)As and p-(Cd,Mn)Te [1], have stimulated a considerable effort to develop semiconductor systems in which spontaneous magnetization would persist to above room temperature. Indeed, high-temperature ferromagnetic features have been found in a number of semiconductors and oxides doped with various transition metals and rare earth elements or even in materials nominally undoped with magnetic elements. At the same time, it is becoming clear that the adequate characterization of these systems requires the application of advanced space-resolved and element-specific tools [2-4]. On the theoretical side, it has been appreciated that conceptual difficulties of charge transfer insulators and strongly correlated disordered metals are combined in these materials with intricate aspects of heavily doped semiconductors and semiconductor alloys, such as Anderson-Mott localization, defect formation by self-compensation mechanisms, spinodal decomposition, and the breakdown of the virtual crystal approximation [5].

In this talk, after presenting the p-d Zener model that describes successfully p-(Zn,Mn)Te, (Ga,Mn)As, and related systems, the progress in the understanding of the origin of high apparent Curie temperatures in diluted magnetic semiconductors and oxides will be described [2,6-9], paying particular attention to the case of (Zn,Cr)Te [3] and (Zn,Co)O [8]. It will be shown that doping above the solubility limit allows one to fabricate a variety of magnetic nanocrystals embedded coherently into the semiconductor host. Importantly, shape and dimension, and thus blocking temperature of the magnetic particles, can be controlled by co-doping with shallow dopants and through growth parameters. Appealing functionalities of these multicomponent systems will be presented together with prospects for their applications in spintronics but also in electronics, photonics, and thermoelectricity [7,9].

Formation of Cr-rich nano-clusters and nano-columns in ferromagnetic semiconductor (Zn,Cr)Te

Y. Nishio1, K. Zhang1, K. Ishikawa1, S. Kuroda1, M. Mitome2 and Y. Bando2

1Institute of Materials Science, University of Tsukuba, Tsukuba 305-8573, Japan
2National Institute for Materials Science, Tsukuba 305-0044, Japan

In the search for novel ferromagnetic semiconductors with high transition temperatures, the distribution of magnetic elements in the crystal has become realized as a key which dominates magnetic properties of diluted magnetic semiconductors (DMSs)[1]. Indeed, the formation of nano-scale regions containing high-content magnetic elements and according enhancement of ferromagnetic properties have been observed in various DMSs[2-4]. In our recent study on (Zn,Cr)Te[5], it has been demonstrated that the Cr distribution can be controlled in a systematic way by co-doping of donor or acceptor impurities or by the ratio of flux supplies during the MBE growth; the distribution of Cr ions becomes inhomogeneous in the crystals co-doped with iodine (I) as a donor impurity or grown with a surplus supply of Zn flux. As an origin of different uniformities of the Cr distribution, it has been proposed[6] that the aggregation energy between Cr ions can be manipulated through the shift of Fermi energy due to the co-doping of donor or acceptor impurities or the deviation from stoichiometry under different Zn/Te flux supply ratio.

In the present study, we have investigated the structural and magnetic properties of I-doped (Zn,Cr)Te films grown under systematic variations of growth conditions such as substrate temperature during the growth, the growth rate, and the crystallographic orientation. The nano-scale probing of Cr distribution using spatially resolved energy-dispersive X-ray spectroscopy (EDS) reveals that the crystallinity and the shape of Cr-rich regions depend on the substrate temperature during the growth. With the increase of the substrate temperature $T_S$, the crystal quality is improved with the reduction of stacking faults. In addition, at a relatively high average Cr content around $x \approx 0.2$, the shape of Cr-rich regions changes with the increase of $T_S$; Cr-rich regions are formed as isolated clusters at a standard substrate temperature of $T_S = 300^\circ C$, while one-dimensional columnal regions are formed at a higher substrate temperature $T_S = 360^\circ C$. In addition, the Cr-rich nanocolumns are formed in different directions between the crystals grown on the (001) and (111) surfaces. From these directions, it is suggested that Cr ions have the tendency of aggregating along the (111) surface of zinc-blende structure. In the magnetization measurement, the blocking temperature, which appears as a maximum in the magnetization vs. temperature ($M-T$) curve, is increased with the formation of 1D nanocolumns. In addition, the anisotropic magnetization is observed under magnetic fields parallel and perpendicular to the film plane; the blocking temperature and the coercive field become larger with magnetic fields perpendicular to the film plane. This magnetic anisotropy is considered to originate from a difference in the demagnetization field when the magnetic field is applied along the axial or radial direction of the columns.

References
We show that strong carrier-carrier and carrier-Mn couplings in dilute CdMnTe quantum wells lead to a range of new collective spin excitations. We have studied the dynamics of these excitations using time-resolved Kerr rotation in a pump-probe configuration. Experimental results support the existence of a soft precession mode in p-doped quantum wells at temperatures close to the ferromagnetic ordering transition. This mode is a result of coupling between Mn and holes with strongly anisotropic g-factor. In n-doped quantum wells, back and forth oscillation between electron and Mn spins reveals strong coupling between electron and Mn spin excitations. In addition to these mixed electron-Mn modes with short lifetime, a longliving Mn precession decoupled from the 2D electron gas can be excited by the light pulses. Finally, we show that the ferromagnetic electron-Mn spin coupling may lead to a spontaneous patterning of the magnetization under resonant optical excitation. The stability of the system is controlled by both optical excitation power and magnetic field.
Intrinsic resonances in Mn$^{2+}$ ion spin clusters in ZnMnSe/ZnBeSe quantum wells

V. Yu. Ivanov¹, J. Debus², D. R. Yakovlev²,³, A. Maksimov⁴, S. M. Ryabchenko⁵, Yu. G. Semenov⁶, M. Godlewski¹,⁷, M. Bayer², and A. Waag⁸

¹ Institute of Physics, Polish Academy of Sciences, Warsaw 02-668, Poland
² Experimentelle Physik II, TU Dortmund, D–44221 Dortmund, Germany
³ Ioffe Physico-Technical Institute, RAS, St. Petersburg, 194021, Russia
⁴ Institute of Solid State Physics, RAS, Chernogolovka, 142432, Russia
⁵ Institute of Physics NAS of Ukraine, 680028 Kiev, Ukraine
⁶ North Caroline State University, Raleigh, 27695 NC, USA
⁷ Dept. Mathematics and Natural Sciences College of Science, Cardinal S. Wyszyński University, Warsaw, Poland
⁸ Institute of Semiconductor Technology, Braunschweig Technical University, 38106 Braunschweig, Germany

It is known that spin-lattice relaxation of magnetic Mn$^{2+}$ ions in diluted magnetic semiconductors (DMS) has accelerated with increase of Mn concentration due to energy transfer between single Mn$^{2+}$ ions and exchange coupled Mn$^{2+}$ pairs. If Mn$^{2+}$ concentration is low enough, and multiplets of spin states of pairs create a quasi-discontinuous spectrum, this transfer realised by cross-relaxation mechanism in discrete domains of magnetic field where spin levels of single Mn$^{2+}$ ions and pairs multiplets has anti-crossings. Thus, in spin system of magnetic single and exchange coupled magnetic ions an intrinsic resonance exists.

We report on the first observation of such intrinsic resonances in Mn$^{2+}$ spin clusters in ZnMnSe/ZnBeSe DMS quantum wells with Mn concentration $x$ varied in the range 0.004<$x$<0.02. We perform photoluminescence measurements in external magnetic fields up to 10 T and at a low temperature of 1.8 K. Both stationary and time-resolved (with nanosecond time resolution) spectra were measured. It allows measuring directly the spin-lattice relaxation dynamics and evaluating its rate as a function of magnetic fields.

In the magnetic field dependence of the energy position of the emission line a number of discrete minima in the fields around 2.07, 2.56, 3.35, 4.91 and 9.32 T has been observed. At the same fields the spin lattice relaxation dynamics is accelerated as we also detect experimentally. These resonance fields well match with anti-crossings fields of spin multiplets of Mn spin clusters, calculated under consideration of anisotropic dipole-dipole interaction of Mn$^{2+}$ ions and cubic crystal field. At this field the energy transfer from the single Mn to the Mn cluster does not required energy dissipation to e.g. phonon system. As a result spin transfer between them is resonantly enhanced. This technique seems to be a powerful tool for investigation of intrinsic structure of magnetic clusters in DMS nanostructures.
Interlayer exchange coupling in MnTe/ZnTe superlattices:
magnetic order, magnon confinement and propagation

B. Hennion1, W. Szuszkiewicz2*, S. Petit1, E. Dynowska3, E. Janik2, G. Karczewski2, and T. Wojtowicz2

1 Laboratoire Léon Brillouin, CEA-CNRS, CE Saclay, 91191 Gif-sur-Yvette, France
2 Institute of Physics PAS, Al. Lotników 32/46, 02-668 Warszawa, Poland

MnTe-based diluted magnetic semiconductors have been intensively investigated in the past, but pure MnTe in the zinc-blende (ZB) phase could only more recently be obtained with the use of MBE non-equilibrium growth technique. Progress in technology opened new areas of both basic research and possible applications of this material, which seems to be very useful for selected spintronic and optoelectronic devices due to its magnetic properties and an energy gap value of ~3.5 eV at low temperatures. Thick layers of ZB MnTe exhibit an antiferromagnetic (AF) order of type-III at low temperatures (Néel temperature of about 65 K). Such an order persists for MnTe layers in MnTe/ZnTe superlattices (SL). Because of the distortion of the fcc lattice an energy-minimizing magnetic configuration corresponds to the only orientation of magnetic unit cells with their long axis along the SL growth direction. An interlayer exchange coupling has been reported for MnTe/ZnTe SLs [1,2] but its physical origin and an anomalous temperature behavior of observed diffraction structures were not understood.

In this paper several high quality MBE-grown, MnTe/ZnTe short period SLs with various numbers of monolayers (from 3 to 20) in magnetic and non-magnetic slabs were studied by elastic and inelastic neutron scattering. The first method demonstrated a magnetic coherence in selected SLs for a distance as large as 900 Å at low temperatures. The temperature evolution of spectra, quite different from that previously reported in the literature, was found. Possible physical mechanisms responsible for observed phenomena are discussed, an important role of strain and of a magnetoelastic mechanism in interlayer exchange coupling is pointed out. A few years ago we have determined the collective magnetic excitations (magnons) dispersion in quasi-bulk ZB-MnTe slab by inelastic neutron scattering [3]. At present, long range coherency between AF layers observed for ZnTe spacer thickness up to ~25 Å made possible the propagation of magnons along the SL-stacking direction in short-period SLs. For large enough ZnTe spacers the AF MnTe layers are no longer correlated and size quantization effects for magnons in SL take place, leading to magnons confinement. An experimental evidence of both effects was found by inelastic neutron scattering measurements. A simulation with a four-dimensional integration of the convolution between the resolution function and the predicted magnetic scattering cross-section demonstrated a similarity of theoretically predicted and observed spectra. To our knowledge both magnon propagation and magnon confinement are the first such observations for a magnetic multilayer with the use of neutron scattering technique.

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* Corresponding author. E-mail address: szusz@ifpan.edu.pl.

High-speed all-optical switches (>~100Gbps) are fundamental components in all-optical signal processing devices for next-generation fiber communication networks. Such ultrafast nature can be realized by use of the intersubband transition (ISBT) in semiconductor quantum wells (QWs) due to its fast carrier relaxation time of sub-ps—a few ps. QWs with sufficiently large conduction band offsets have to be used, thereby the ISBT wavelength can be shortened to the telecom wavelength of \(\lambda=1.3\text{–}1.55\ \mu m\). In fact, sub-ps all-optical gate switching based on intersubband absorption saturation and its ultrafast recovery has been demonstrated in ISBT waveguide devices based on several material systems \([1]\) such as InGaAs/AlAsSb, GaN/AlGaN and (CdS/ZnSe)/BeTe. A huge CBO up to 3.1eV in wide-band-gap II-VI material system enables tuning of intersubband transitions over a wide range to realize absorption at a telecom wavelength.

In this contribution, we will report ultrafast all-optical switches based on ISBT in wide-band-gap II-VI QWs. The high ionicity in II-VI compounds speeds up carrier relaxation by enhancing the interaction of electrons and LO phonons. We have proposed material system, ZnSe/BeTe for achieving telecom wavelength ISBT. This heterostructure has a large CBO of 2.3 eV for electrons in ZnSe layers, by which we actually demonstrated the ISB absorption as short as 1.6 \(\mu m\) covering the 1.55 \(\mu m\) wavelength\([2]\). We have also developed CdS/BeTe heterostructures, which has a huge CBO of 3.1eV to avoid a slow carrier relaxation process of \(\Gamma(\text{ZnSe})\)-\(\chi(\text{BeTe})\) transfer observed in ZnSe/BeTe\([3]\). These heterostructures have been grown by molecular beam epitaxy. For device applications, confinement of the infrared light into active layers using waveguide structure is important point for enhancing interaction length and reducing an optical gate switching power in the device. As a material of cladding layer, ZnMgBeSe can be employed, since the band gap of this material can be tuned from 2.7 to 4.5 eV with matching a lattice constant to GaAs substrate \([4]\). In order to increase the light intensity in the waveguide for efficient absorption saturation, the mesa width is reduced to the sub-\(\mu m\) range, where the narrowest mesa width is limited by the cut-off property of the waveguide. A separate confinement heterostructure (SCH) is also employed to reduce the switching energy. A Zn\(_{0.4}\)Be\(_{0.6}\)Se ternary \([5]\) or ZnSe/BeTe QWs \([6]\) for optical confinement layer are used to form the SCH in the waveguide device. More recently, strong light confinement by use of high-index contrast waveguide has been fabricated, where MQW channel waveguide (n=2.5) is buried into SiO\(_2\) (n=1.46) cladding layer by employing wafer bonding technology \([7]\). We have demonstrated sub-ps switching response with 20dB on/off extinction ratio in this waveguide device.

References:

Wide Bandgap II-VI Compounds for Quantum Cascade Lasers Operating in the Mid- and Near-IR Wavelength Range

Maria C. Tamargo,1 William O. Charles,1 Kale J. Franz,2 Aidong Shen,1 and Claire Gmachl2
1) The City College of CUNY, New York, NY 10031
2) Princeton University, Princeton, New Jersey 08544, USA

Intersubband (ISB) devices have been the subject of intensive research over the past few years. These devices rely on electronic transitions between the energy levels of a quantum well (QW) within a single band (conduction band or valence band). They are particularly appealing because they promise a large degree of freedom from materials constraints, achieving their performance through bandstructure engineering. Some attractive properties are their fast temporal response and their unipolar nature. An ISB device that is receiving much attention is the Quantum Cascade (QC) laser.

Currently, QC lasers operating in the 4-8μm range have been demonstrated. In view of their success, it is of interest to extend their operation further into the near-IR range. The short wavelength cut-off of QC lasers is determined by the conduction band offset (CBO) of the constituent QW materials. Thus, materials with larger CBO are needed to extend the operation wavelength of QC lasers to shorter wavelength.

Our group has investigated the application of ZnCdMgSe/ZnCdSe heterostructures for the design and fabrication of QC lasers by MBE. Using the method of contactless electroreflectance (CER) we have measured the CBO for these materials to be as large as 1.12 eV, larger than the CBO of materials currently used for these devices. We have grown multi-quantum well structures with excellent crystalline quality and measured their intersubband absorption using FT-IR spectroscopy, demonstrating the ability to obtain transitions at wavelengths below 3μm. We have also grown and fabricated QC structures and observed electroluminescence in the mid-IR range. We are currently exploring the design of structures that incorporate waveguide layers in order to achieve lasing.

Other experiments, such as the use of quantum dots for ISB devices, and the use of other II-VI heterostructures with larger CBO will also be presented.
Room-temperature tunable mid-infrared lasers on transition-metal doped II-VI compound crystals grown from vapour phase

V.I. Kozlovsky,1 V.A. Akimov,2 M.P. Frolov,1,2 Yu.V. Korostelin,1 A.I. Landman,1 Yu.P. Podmar'kov,1,2 Ya.K. Skasyrsky,1 A.A. Voronov2

1P.N.Lebedev Physical Institute of RAS, Leninsky prosp. 53, 119991, Moscow, Russia
2Moscow Institute of Physics and Technology (State University), Institutskii per. 9, 141700 Dolgoprudny, Moscow region, Russia

Market needs in effective solid-state broadly tunable mid-infrared lasers for 2-5 μm spectral range is well known. This range stays difficult for quantum cascade lasers though last great results. The most popular laser now is optical parametric oscillator. However it works only in pulse periodic mode because it bases on nonlinear effect. Therefore II-VI compounds doped by transition metals are certainly interesting as active material for mid-infrared lasers. The advantages of such lasers include broad tuning of lasing wavelength, working at room temperature, high efficiency and possibility to achieve 1-10 W in output power at high quality of laser beam.

Most of transition-metal doped II-VI compounds crystals were grown either by Bridgman method or a solid-state diffusion method. The latter includes the growth of a pure crystal preferably from vapor phase and doping of it by thermal diffusion from the solid metal layer previously coated on the crystal surface. The crystals obtained in such ways are characterized by great intrinsic losses due to high concentration of background defects. Therefore they need to use high doped crystals that is an obstacle to achieve continuous wave (CW) lasing with low threshold and high output power. New growth technique was developed in P.N. Lebedev Physical Institute for last several years [1]. It bases on seeded free growth method with physical transport and allows obtaining of large-size II-VI single crystals uniformly doped by transition metals directly during the growth. Obtained crystals possess small intrinsic losses.

Based on these crystals we achieved a set of new results in development of IR lasers of such a type. CW lasing in a CdSe:Cr crystal was obtained for the first time. The CdSe:Cr crystal pumped by a 1.908-μm thulium fibre laser generated 1.07 W at 2.623 μm at room temperature (RT) with the quantum slope efficiency with respect to the absorbed power equal to 60%. At Cr content of 10¹⁸ cm⁻³, intrinsic laser losses in the crystal were less than 0.045 cm⁻¹. The CW Cr⁺²:CdSe laser was used for pumping the Fe⁺²:ZnSe laser. At cooling ZnSe:Fe crystal to 80 K we achieved CW lasing with output power higher 0.2 W at wavelength of 4.1 μm. Possibility of achieving RT lasing is discussed. Broad spectral tuning from 2.26 to 3.61 μm for Cr⁺²:CdSe laser and from 3.77 to 5.05 μm for Fe⁺²:ZnSe laser was demonstrated at RT in pulse operating.

New active crystals as CdS:Cr, CdSe:Fe and ZnSeTe:Fe were grown. The results of their studied will be present also.

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Design and characterization of ZnO-based MESFET devices


Universität Leipzig, Faculty of Physics and Earth Sciences, Institute for Experimental Physics II, Linnéstr. 5, 04103 Leipzig, Germany

We report on the fabrication of n-type ZnO metal-semiconductor field-effect transistors (MESFETs) by reactive dc-sputtering of Ag, Pd, Pt or Au Schottky gate-contacts on ZnO thin-film channels grown by pulsed-laser deposition (PLD) on sapphire or glass substrates. The devices with Ag-gates on sapphire show excellent electric properties with on/off ratios of up to $10^8$ and very low off currents in the picoampere range [1]. Since p-type doping and realization of highly rectifying Schottky contacts are still a challenge, recent investigations of ZnO-based transistors mostly considered n-type metal-insulator-semiconductor field-effect transistors (MISFETs) suffering from low field-effect mobility and high switching voltages. In this study, however, we use high-quality Schottky gate-contacts [2] to fabricate MESFETs with channel mobilities in the range of 20 to 30 cm²/Vs on sapphire substrates yielding to faster switching speeds. Furthermore typical MESFET switching voltages of ±1V are about one order of magnitude smaller than for MISFETs. Normally-on and normally-off devices have been achieved by tailoring the channel thickness and doping concentration. Reliability tests under the influence of light and elevated temperatures have been performed.

With the values named above, ZnO-based MESFETs fit the requirements for industrial applications specified by Wager [3].

For large area applications (e.g. active-matrix liquid crystal displays), the use of cheap glass substrates is mandatory. However, the non-epitaxial growth leads to a higher density of structural defects. The 20 – 30 nm thin ZnO channels on glass are highly textured. They are $c$-axis-oriented but exhibit twists and tilts of the grains in plane. Nevertheless, the on/off-ratio is still $10^6$ and the mobility is >1 cm²/Vs.

As basic device for logic circuits, we fabricate inverter structures using ZnO Schottky diodes and MESFETs applying Schottky-diode FET logic as known from GaAs technology [4]. The electrical properties including on-off ratio, steepness and transfer characteristic are investigated.

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The increasing understanding of topological phases in condensed matter physics, which was initiated by the quantum Hall effect, has inspired the search for other topological states, especially, in the absence of magnetic fields. As one example the quantum spin Hall (QSH) effect has been proposed for systems with time reversal symmetry and spin-orbit interactions.\textsuperscript{1,2)} In a two-dimensional system this new state is characterized by an insulating bulk and two counter-propagating helical edge states. These Kramers pairs fulfill time reversal symmetry and account for a quantized conductance. It turned out that HgTe-based quantum well (QW) structures are most suitable candidates for a successful experimental realization.\textsuperscript{3)}

In this presentation, the HgTe QW band structure properties and experimental requirements are discussed which lead to the observation of quantized spin polarized edge channel transport, one of the main signatures of the QSH effect.\textsuperscript{4,5)} Experiments will be presented that demonstrate the stability of the quantized conductance and its non-local character. Furthermore, it is possible to show evidence for the spin polarization of the QSH edge channels in an all-electrical measurement which demonstrates the potential of the QSH effect for possible spin injection and detection application in spintronics devices.

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Spin splittings in the $n$-HgTe/Cd$_x$Hg$_{1-x}$Te quantum well with inverted band structure

M.V. Yakunin$^1$, S.M. Podgornykh$^1$, N.N. Mikhailov$^2$ and S.A. Dvoretsky$^2$

$^1$Institute of Metal Physics, S. Kovalevskaya 18, Ekaterinburg 620041, Russia
$^2$Institute of Semiconductor Physics, Lavrentyev ave13, Novosibirsk 630090, Russia

A property of the Cd$_x$Hg$_{1-x}$Te solid solution to transform its band diagram from the gapless to a gapped one with growing $x$ causes a unique energy structure of the quantum well created in the HgTe/Cd$_x$Hg$_{1-x}$Te heterosystem: it is inverted when the HgTe well width $d_w$ is greater than the critical value of $\sim 6.3$ nm so that the conduction band is formed of the $p$-like wave function. Its properties are expected and found to differ from the ones of a traditional conduction band formed by functions of $s$-like character.

We study the quantum Hall effect (QHE) in the HgTe/Cd$_x$Hg$_{1-x}$Te (113) oriented quantum well with $x = 0.6 \pm 0.73$, $d_w = 20.3$ nm, symmetrically doped on both sides with $\sim 10$ nm spacers, electron gas density $1.5 \times 10^{15}$ m$^{-2}$ and mobility $20$ m$^2$/V s, at temperature $\sim 2$ K. Along with the study of magnetoresistivities $\rho_{xx,xy}$ under perpendicular field configuration, $B = B_A$, our specific technique of sample rotation [1] is used to get the most detailed picture on the influence of field component $B_{\parallel}$ parallel to the layers, either in the form of $\rho_{xx,xy}(B_A, B_{\parallel})$ surface functions of two variables or of their maps projected onto the $(B_A, B_{\parallel})$ plane. This allows (i) to get the full picture of magnetic level coincidences within the whole $(B_A, B_{\parallel})$ segment of reachable field values; (ii) to trace the evolution with $B_{\parallel}$ of the spin and cyclotron gaps in the magnetic level spectrum.

As obtained from the $\rho_{xx,xy}(B_A, B_{\parallel})$ maps measured, the positions of points for the locally closed gaps are well described in the frames of a traditional coincidence method [2] for the spin/cyclotron gaps relation $r = 1$ and 2. But it yields the effective $g$-factor value, $g = 33$, that doesn’t allow to describe correctly the QHE structure under the pure perpendicular field with odd-numbered features prevailing over the even-numbered ones. For that purpose, in the frames of a traditional conduction band model, the $g$-factor should fall within the range of $42 < g < 83$, so that the product on the effective mass should be within $1 < m^*/m_0 < 2$ (we use $m^*/m_0 = 0.024$ [3]). The higher value, $g = 58$, is obtained under perpendicular field from comparison of the magnetic field values corresponding to onsets of oscillations and of their splittings. On the other hand, much lower value, $g \approx 8$, is obtained from the observed evolution with $B_{\parallel}$ of the gaps between levels.

To resolve the discrepancies found the following things should be taken into account: (i) zero field spin splittings that might be considerable in the band of $p$-states [4]; (ii) quasi-two-dimensional character of spin splittings in the band of $p$-type character [4,5]; (iii) the level widths influence the obtained absolute values of the gaps [6].

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Optical manipulation of electron spin coherence in CdTe/CdMgTe quantum wells

E. A. Zhukov\textsuperscript{1,2}, M. M. Glazov\textsuperscript{3}, E. L. Ivchenko\textsuperscript{3}, D. R. Yakovlev\textsuperscript{1,3}, L. Fokina\textsuperscript{1}, G. Karczewski\textsuperscript{4}, T. Wojtowicz\textsuperscript{4}, J. Kossut\textsuperscript{4}, and M. Bayer\textsuperscript{1}

\textsuperscript{1}Experimentelle Physik II, Technische Universitaet Dortmund, D-44221 Dortmund, Germany
\textsuperscript{2}Faculty of Physics, Lomonosov Moscow State University, 119992 Moscow, Russia
\textsuperscript{3}Ioffe Physical Technical Institute, Russian Academy of Sciences, St. Petersburg 194021, Russia
\textsuperscript{4}Institute of Physics, Polish Academy of Sciences, PL-02668 Warsaw, Poland

We study experimentally and theoretically the spin coherence of resident electrons in weakly n-doped CdTe/(Cd,Mg)Te quantum wells. Spin dynamics has been examined by a pump-probe time-resolved Kerr rotation technique with a picosecond time resolution under trion resonant excitation. Experiments have been performed at a temperature of 1.9 K and in external magnetic fields up to 3 T applied in the Voigt geometry. Additionally to the commonly used pump-probe technique we apply control pulses to manipulate the generated electron spin coherence. The effects of intensity and polarization of the control pulses and their delay to the pump pulses are studied in detail.

Amplification either suppression of the amplitude of electron spin beats (caused by precession of electron spins in magnetic field) after the arrival of control pulse has been found for different polarizations ($\sigma^+$, $\sigma^-$) and time delay of the control pulse. We have also observed suppression of the beats for linearly polarized control pulses. Additive and nonadditive contributions of the control pulses to the spin coherence generated by the pump pulses have been separated by a proper choice of modulation technique. Both contributions are valuable in the studied structures. By this means the amplitude and the phase of the electron spin coherence have been manipulated optically. The developed theoretical model accounts well for all experimental results.
The interaction of circularly polarized light with electronic states provides a mechanism for spin manipulation in non-magnetic and magnetic solids. Since modern laser sources are able to generate optical pulses with duration of 100 fs and even shorter, such an optical control offers a unique approach for spin manipulation at unprecedentedly fast time-scales. This approach may provide a solution to increase operation speeds in spin-based quantum computing, and magnetic recording. Over the past 10 years considerable progress has been achieved in the understanding of relatively slow laser induced precessional spin dynamics. However, for coherent control of spins, it is essential to understand the laser induced processes in the spin system on a time scale of the optical decoherence (from 20 fs in metals up to 2 ps in semiconductors). The latter is poorly understood because of effects of optical coherence and quantum interference. In particular, in semiconductor quantum wells, these effects are significant in optical experiments with subpicosecond temporal resolution.

We employ both coherent control and pulse shaping techniques to investigate how quantum interference affects ultrafast optical orientation of trion and exciton spins in CdMgTe/CdTe semiconductor quantum wells. (1) Employing coherent control, we demonstrate the observation and control of quantum beatings between exciton and trion spin states on an attosecond time scale by tuning the delay of two-orthogonally polarized pump pulses. (2) Using pulse shaping, it is shown that even "off-resonant" excitation may result in a spin-polarization in an excited state. Such an "off-resonantly" excited spin polarization is characterized by ultrafast dynamics being present only during the action of the laser pulse. Due to quantum interference between the "off-resonant" and "on-resonant" components, the laser-induced spin-polarization may even exhibit oscillations with frequency and amplitude determined by the shape of the pump pulse. We also demonstrate that if the pulse duration is shorter than the time of optical decoherence, one can suppress the spin density oscillations and selectively spin-polarize either the exciton or trion with spectral and temporal resolution beyond the Fourier limit. The experimental results from both the coherent control and pulse shaping techniques are in good agreement with a theoretical model based on optical Bloch equations.
Control of the resident electron spin in CdSe quantum dots by electrical current pulses through micro-coils

J. Puls, Y.S. Chen, V. Gapon, G. Bacher, and F. Henneberger

a) Humboldt-Universität, Institut für Physik, 12489 Berlin, Germany
b) Werkstoffe der Elektrotechnik and CeNIDE, Universität Duisburg-Essen, 47057 Duisburg, Germany

Currently, resident electrons in charged quantum dots (QDs) are being extensively investigated in the context of quantum information processing. All-optical spin pumping as well as read-out can be accomplished via quasi-resonant excitation of the trion feature with circularly polarized photons [1]. Low natural abundance and small size make self-assembled II-VI QDs like CdSe/ZnSe interesting candidates as the hyperfine interaction with the nuclear spins can be strongly modulated with magnetic fields of only some mT [2].

In this talk, we report on our efforts to generate the external fields by electrical currents through µm-sized coils. They consist of a 250 nm thick Au layer made directly on top of a CdSe QD structure by a two-step electron beam lithography and lift-off technique. The distance between coil and QD is given by the thickness of the ZnSe cap layer which is in the order of 50 nm. In contrast to large-scale external Helmholtz coils, micro-coils exhibit much less inductivities and, therefore, are capable of transient magnetic pulses down to the nanosecond regime with sufficiently strong amplitudes of 10 mT and beyond. This allows us to control and manipulate the electron spin as well as the nuclear spins by an appropriate combination of optical and current pulses. Switching between strong and weak hyperfine interaction has been realized by 2 µs long current pulses with an amplitude of 100 mA and rise and fall times of 5 ns combined with a synchronized switching of the circular polarization of the exciting laser light. The photoluminescence transient proves unambiguously that the non-equilibrium electron spin alignment achieved by optical pumping during the active phase of the electrical current cycle is practically instantaneously erased by switching off the current through the micro-coil. The observed time constant of about 20 ns is presently limited by the resolution of the experimental setup.

Dynamic nuclear polarization and confinement effects in ZnO quantum dots

P. G. Baranov1, S. B. Orlinskii2, C. de Mello Donegá3, A. Meijerink3 and J. Schmidt4

1 Ioffe Physical-Technical Institute of the Russian Academy of Sciences, 194021 St. Petersburg, Russia
2 Federal Center of Shared Facilities of Kazan State University, 42008 Kazan, Russia
3 Debye Institute for Nanomaterials Science, Utrecht University, The Netherlands
4 Huygens Laboratory, Leiden University, Leiden, The Netherlands

Dynamic nuclear polarization (DNP) effects have been observed in ZnO quantum dots (QD's) with using high-frequency (95 GHz) pulse electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) at the temperatures of 1.3-2 K. Free standing ZnO nanocrystals with diameters of 2.2, 2.8, 3.4, 4.0 and 4.2 nm were prepared via a wet chemical method and the QD's consist of a ZnO/Zn(OH)2 core-shell structure. The polarization of the nuclear spins is achieved by saturating the EPR transition of the shallow donor present in the ZnO nanoparticles and this polarization manifests itself via the creation of a hole and an antihole in the EPR absorption line of the shallow donor. The polarized nuclear spins create an internal magnetic field and as a result the resonance line of the electron spins, subjected to the microwave irradiation, shifts to a lower external field value resulting a shift of the hole (antihole) in the inhomogeneously broadened EPR line.

DNP effect, is shown, to arise not only from an almost complete polarization of the 67Zn nuclear spins in the ZnO QD's but also of the 1H nuclear spins in the Zn(OH)2 capping layer. To check whether a polarization of the 1H nuclear spins affects the resonance line of the electron spin ENDOR experiments on the protons have been carried out. The strong ENDOR signals around the Zeeman frequency of the 1H nuclear spins indicated that the wave function of the shallow donor (shallow donor Bohr radius of ~1.5 nm) extends into the capping layer. The observation of the resonance frequency of the 1H nuclear spins shifts caused by DNP was explained by the polarization of the 1H nuclear spins, which produce an internal field and thus shift their resonance frequency.

The shift of holes (antiholes) in magnetic field due to DNP increases considerably when performing the experiments on QD's with smaller diameters. The arguments to explain the increase of this shift by DNP of the 67Zn nuclear spins and of the 1H nuclear spins in the Zn(OH)2 capping layer, in combination with the effect of confinement of the electronic wave function of the shallow donor are presented.

The DNP is produced by a spontaneous-emission type, one phonon, cross-relaxation that is mediated by the zero-point fluctuations of the phonon system in the ensemble of QD's. To explain the relatively fast spin-lattice relaxation of the shallow donor in the ZnO QD's we propose that in the dry powder, used in the experiments, the QD's are in physical contact with each other and that the phonons are not confined to one particle.

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Random lasing in nanocrystalline ZnO powders

H.Kalt, J.Fallert, R.J.B.Dietz, J.Sartor, D.Schneider, and C.Klingshirn
Institut für Angewandte Physik, Universität Karlsruhe (TH), Karlsruhe Institute of Technology (KIT), 76128 Karlsruhe, Germany

The phenomenon of random lasing has recently been discovered in various random media and has a large prospect of application in photonics. The basic components of a random laser are in principle identical to the ones of a conventional laser: an active material providing optical gain and a cavity keeping the light in the amplifying medium. In the random laser, light is confined within a disordered medium due to permanent scattering on a microscopic length scale. The light is thus retarded from leaving the active region up to the limit of localized light [1]. The latter results from constructive interference due to the fact that the elastic scattering of light is a completely coherent process.

Scattering media in random lasers are typically dispersed microspheres, nanocrystalline semiconductor powders or porous crystals and glasses. A laser dye can then be added to provide optical gain, or one uses scattering media that deliver optical gain on their own, if excited. One of these bifunctional (scattering and amplifying) random media is nanocrystalline ZnO powder [2]. ZnO powders are ideally suited for the application in random lasers since they have a relatively high refractive index leading to strong light scattering in combination with a high optical gain [3]. Attractive for optoelectronic applications is further the fact that nanocrystalline ZnO powders are cheap and commercially available in large amounts.

The onset of random lasing is evidenced typically by a threshold-like behavior of the optical emission but only under certain conditions narrow laser lines, similar to conventional lasers, occur. Such random lasing spikes have been observed in powders of zinc oxide (ZnO) nanoparticles for the first time [2], but up to now the possible degrees of localization of such laser modes is still an open issue [4]. Recent theoretical work on random lasing predicts that the occurrence of lasing spikes can be caused by both, localized and extended modes of the light [5].

We report here on experiments which are able to directly extract the area of localization of random lasing modes. We investigate microstructured fields of ZnO powder, reducing the number of observed modes and allowing direct correlation to the local structural properties of the ensemble of sub-wavelength particles by SEM. We find that lasing from both kinds of modes (localized and extended) can be observed simultaneously. Our observation also corroborates the prediction that localized modes show a lower loss rate than the extended ones [4].

Semiconductor lasers operating in the visible wavelength range have been a subject of extensive research during the past years. Ternary ZnCdO is a material with considerable potential in this regard, as it can cover in principle band-gaps from the ultraviolet to the near infrared spectral range.

We have systematically fabricated (Zn,Cd)O/ZnO single and multiple quantum well structures and elucidated their optical properties. In the low-density excitation regime, huge polarization-induced electric fields of some $10^8$ V/m are signified by a strong red shift of the photoluminescence band with increasing well width as well as an increase of the lifetime from the ps- to the µs-time scale. Effective screening of these fields occurs already at moderate optical excitation in the 10 kW/cm² range and recovers practically the bare quantum-confined transition energies and short lifetimes. In the same excitation range laser action of specially designed multiple quantum well structures is observed. The low-temperature lasing threshold is only 25 kW/cm² and increases moderately up to room temperature (150 kW/cm²). The emission wavelength is systematically tuneable by structure design. The longest lasing wavelength achieved so far is 510 nm at room temperature.

The laser action can be achieved without preparation of an optical cavity. Both spectral position and separation of the lasing modes are determined by the geometrical shape of excitation area and vary with the excitation power. A theoretical model assuming weak scattering reproduces the experimental finding reasonably well. For specially prepared micro-resonators, narrowing of the mode band and mode selection is demonstrated.
Growth of Zn-polarity MgZnO/ZnO MQWs on bulk ZnO by RF-MBE

S. Morita¹, S. Jeong¹, T. Honma¹, Y. Kaifuchi², Y. Ishitani¹,³, and A. Yoshikawa¹,³
¹Graduate School of Electrical and Electronics Engineering, Chiba University
1-33 Yayoi-cho, Inage-ku, Chiba, 263-8522 Japan
²Optics and Electronics Laboratory, Fujikura Ltd
1440 Mutsuzaki, Sakura, Chiba, 285-8550, Japan
³Venture Business Laboratory, Chiba University
1-33 Yayoi-cho, Inage-ku, Chiba, 263-8522 Japan

ZnO-based heterostructures such as MgZnO/ZnO MQWs have attracted considerable attention as a potential materials-system for high brightness UV light emitters owing to remarkably larger exciton binding energy of ZnO (~60meV) than that of GaN (~24meV). In order to develop such photonic devices, achievement of successful p-type doping of ZnO is one of the most important necessities. Concerning the establishment of their “successfully repeatable” p-type doping, Zn and/or +C polarity growth regime is considered preferable from an efficient nitrogen-acceptor incorporation point of view compared to the case under O-polarity growth. However, fabrication of the high structural quality ZnO-based MQWs under +C polarity growth regime is difficult, because it easily leads to three dimensional growth-mode resulting in rough surface morphology. Then there are a few reports on fabrication and characterization of Zn-polarity MQWs structures.

In this paper, we have studied the growth of +C polarity MgZnO/ZnO MQWs on bulk ZnO substrate at such high temperatures as around 700 °C. First, we have modified the substrate-heating system in our RF-MBE to high-power laser-heating method so that the high temperature growth under keeping high vacuum is possible[1]. Further we have already confirmed that the high temperature growth is effective to improve the surface morphology of +C polarity-grown ZnO smoother[1]. 20 periods of Mg0.2Zn0.8O/ZnO MQWs were grown on Zn-polar bulk ZnO substrates. The energy bandgap of Mg0.2Zn0.8O was found to be 3.76eV from the optical reflectance spectrum. The thickness of ZnO well was 5nm. The structural quality and optical properties of the MQWs were characterized by high-resolution X-ray diffraction (HR-XRD), cathode-luminescence (CL), and photoluminescence (PL) measurements at low temperature.

XRD 20-ω scans showed clear satellite peaks up to 2⁰ orders. This indicates that fine periodic-structure MQWs were formed even under Zn-polarity growth. The PL emission peak of MgZnO barrier layers was 3.66eV at 17K, and the PL spectra from the MQWs showed that the main emission peak shifted to 3.38eV, which was larger than that of homo epitaxial ZnO thin films. In order to identify the main PL peaks are originating from the MQWs, CL spectra at 82K were measured for different acceleration voltages and/or different electron-beam penetration depths from the surface. CL spectra were clearly classified into two peaks, one was from the MQWs and the other was from the bulk ZnO substrate. When the acceleration voltage was lower than 10kV, i.e. corresponding penetration depth was below 300nm, the emission peak was 3.39eV which was almost the same as the PL main peak. With increasing the voltage up to 15 - 20kV, the emission peak was shifted down to 3.32eV, which was corresponding to the emission peak from the bulk ZnO substrate.

Thus we have confirmed that high-quality Zn-polarity MgZnO/ZnO MQWs were grown at high temperatures on bulk ZnO substrate.

Residual strain in non-polar a-plane Zn$_{1-x}$Mg$_x$O (0<x<0.55) and its effect on the band structure of (Zn,Mg)O/ZnO quantum wells

J.-M. Chauveau$^{1,2}$*, M. Teisseire$^1$, J. Zuniga-Perez$^1$, C. Deparis$^1$, C. Morhain$^1$, B. Vinter$^{1,2}$

$^1$Centre de Recherche sur l’Hétéro-Epitaxie et ses Applications, Centre National de la Recherche Scientifique (CRHEA-CNRS), Rue B. Gregory, F-06560 Valbonne, France

$^2$University Nice Sophia Antipolis, Physics Dept., Parc Valrose, F-06102 Nice France

ZnO-based quantum wells have attracted much attention in the last few years due to their opportunity of combining band gap engineering, along with large excitonic binding energies. Indeed theoretical works suggest that the 60meV-binding energy of excitons in ZnO, could be further doubled in quantum wells (QWs). So far studies on ZnO have mainly focused on films grown in (0001) orientation. In this configuration, the wurtzite ZnO layers exhibit built-in electric fields (both piezo and spontaneous components) along the c-axis, i.e. the growth direction. Non-polar surfaces are therefore of a particular interest since the c-axis of the layer lies within the growth plane in this case. As a result it is expected that quantum well structures can be grown without any screening of the exciton binding energies.

In this communication, we report on the growth, structural and photoluminescence properties of a-oriented (non-polar) (Zn,Mg)O/ZnO QWs and multiple quantum wells (MQW) heterostructures grown by plasma assisted Molecular Beam Epitaxy (MBE). The samples were grown on 2” R-plane sapphire by molecular beam epitaxy. A series of QWs with different widths and different Mg content were grown, showing absence of Quantum Confined Stark Effect [1].

The in-plane and out of plane lattice parameters were measured by high resolution X-ray diffraction for Mg content up to 55%. The residual strain is strongly anisotropic. We will show that it is due to an anisotropic strain relaxation process [2]. If we determine the deformation in the growth direction from the assumption of no stress in that direction, we can apply the model of Langer et al. [3] using the recent parameters from Wrzesinski and Fröhlich [4] to estimate the bulk exciton energies. We have found that one expects an exciton energy of 3.41 eV for ZnO strained under our experimental conditions. The photoluminescence excitation energies of the QWs are then satisfactorily simulated when taking into account the variation of the exciton binding energy with the QW width [5]. Although the best overall agreement with the experimental results would be obtained with a bulk exciton energy of 3.42 eV, we already find the results very convincing [6].

References


* jmc@crhea.cnrs.fr, phone: +33493957822
Growth and characterization of periodically polarity inverted ZnO structures grown on Cr-compound buffer layers

J. S. Park, 1 T. Goto, 1 S. K. Hong, 2 J. W. Lee, 3 S. H. Lee, 1 T. Minegishi, 1 S. H. Park, 1 J. H. Chang, 4 J. Y. Lee, 3 and T. Yao 1

1 Center for Interdisciplinary Research, Tohoku University, Sendai, 980-8578, Japan
2 Dept of Materials Science and Engineering, Chungnam National University, Daejeon 305-764, Korea
3 Dept of Materials Science and Engineering, KAIST, Daejeon 305-701, Korea
4 Major of Nano Semiconductor, Korea Martine University, Yeoungdo-ku, Pusan 606-791, Korea

We report on the structural and optical properties of periodically polarity inverted (PPI) ZnO structures on (0001) Al2O3 substrates. In order to realize the PPI ZnO structures, patterning and re-growth methods are used by employing the in-situ polarity controlling method. For the selection of polarity of ZnO films on sapphire substrates, Cr-compound buffer layers are used.1,2 The region with the CrN intermediate layer and the region with the Cr2O3 and Al2O3 substrate were used to grow the Zn- and O-polar ZnO films, respectively. The growth behaviors with anisotropic properties of PPI ZnO heterostructures are investigated. The periodical polarity inversion is evaluated by contrast images of piezo-response microscopy. Structural and optical interface properties of PPI ZnO are investigated by the transmission electron microcopy (TEM) and micro photoluminescence (µ-PL). The inversion domain boundaries (IDBs) between the Zn and the O-polar ZnO regions were clearly observed by TEM. Moreover, the investigations of spatially resolved local photoluminescence characteristics of PPI ZnO revealed much stronger PL at the interfacial region with the IDBs comparing to the Zn-polar or the O-polar ZnO region. The possible mechanisms will be discussed with the consideration of the atomic configuration, carrier life time, and gating effect. Finally, based on the suggested PPI ZnO structures, the scale-down of periodicity of PPI structures was achieved by using laser holographic lithography technique to about 500 nm periodicity. The successful realization of PPI structures with nanometer scale period indicates the possibility for the application to the photonic band-gap structures or waveguide fabrication.

References
Spin currents in diluted magnetic semiconductors

S.D. Ganichev
Terahertz Center, University of Regensburg, 93040 Regensburg, Germany

Spin currents and zero-bias spin separation generated by homogeneous optical excitation with terahertz radiation in (Cd,Mn)Te/(Cd,Mg)Te diluted magnetic semiconductor structures are reviewed. We discuss microscopic and phenomenological theory of this effect and give an overview of experimental data. Microscopic mechanisms of spin currents and zero-bias spin separation excited by terahertz radiation are based on the spin-orbit coupling which provides a versatile tool to generate and to manipulate the spin degree of freedom in low-dimensional semiconductor structures. In gyrotropic semiconductor structures spin-dependent asymmetry of electron scattering induces a pure spin current which results in a spin separation [1-4]. We consider the relaxation mechanism yielding the spin current due to the energy relaxation of a heated electron gas and the excitation mechanism caused by the scattering assisted free carrier absorption. An experimental access to these phenomena provides the application of an external magnetic field converting the pure spin current into a measurable net electric current. We show experimentally and theoretically that the carriers exchange interaction with localized magnetic spins in DMS vastly amplifies this conversion. Two mechanisms are responsible for that: Giant Zeeman splitting of the conduction band states and spin-dependent carrier scattering from localized Mn$^{2+}$ spins polarized by an external magnetic field. We show that in a degenerated electron gas at weak magnetic fields the scattering mechanism dominates the current conversion.

Semimagnetic II-VI resonant tunneling diodes – spin filtering by tunneling through 0d states and growth control by XRD


Physikalisches Institut (EP3), Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Semimagnetic resonant tunnelling diodes (RTDs) based on wide gap II-VI semiconductors can be used as voltage controlled spin-filters, as shown in [Gould et al. Phys. Rev. Lett., 97, 017202, (2006)] or in [Fang et al Appl. Phys. Lett., 91, 022101, (2007)]. The tunnel current and resonance voltage of such structures depend critically on the thickness and composition of the tunnel barriers and the embedded semimagnetic quantum well or quantum dots.

We show that by analysis of x-ray diffraction (XRD) patterns of (Zn,Be,Mn,Cd)Se based RTDs accurate structural information can be obtained, even though the tunnel barriers are typically only ~6 nm thick and are embedded in a complex layer structure which includes the needed contacts and buffer layers. The technique makes use of the high tensile strain of (Zn,Be)Se tunnel barriers with respect to the GaAs substrate, which clearly distinguishes the diffraction patterns originating from the double barrier structure from those coming from all other layers.

Using these XRD optimization techniques several series of II-VI RTDs have been fabricated by molecular beam epitaxy, with current-voltage characteristics showing up to five resonance peaks and a peak to valley ratio of up to 2.5 in measurements at 4.2 K. Gradual increases in the barrier thickness from 4.8 to 7.0 nm, as determined by XRD, lead to a monotonic decrease of the resonant tunneling current by six orders of magnitude, confirming the correlation of XRD results with electrical transport data.

For experiments on nanostructured RTDs that may allow the formation of a zero dimensional resonant tunneling state and control of the resonance by a lateral gate voltage, it is important to fabricate RTDs with the first resonance as close as possible to the injector Fermi level. This has been achieved by lowering the bandgap in the semimagnetic (Zn,Mn)Se quantum well by alloying with Cd. The resonance shifts from 170 mV for a Zn$_{0.92}$Mn$_{0.08}$Se quantum well down to 60 mV for a Zn$_{0.82}$Mn$_{0.08}$Cd$_{0.1}$Se quantum well, and effectively to zero for higher Cd contents.

RTDs with electrons tunneling through zero dimensional states in a single self assembled CdSe quantum dot have also been fabricated, showing clear dot resonances at a few mV applied bias with few pA peak current at 4.2 K. To optimize such structures the electronic and optical properties of CdSe quantum dots embedded in Zn$_{0.8}$Be$_{0.2}$Se tunnel barriers have been studied systematically by photoluminescence, atomic force microscopy and XRD. When the dots are placed in a semimagnetic RTD they show clear spin splitting of the resonance peak by several mV in a magnetic field of 6 T and a remanent splitting of less than a mV at zero field. The resonance behaviour, peak splitting, magnetic and spin injection properties will be discussed and related to composition, layer thickness, lateral size and dimensionality of the RTD structures.
Spin dynamics of Mn ions and photoexcited carriers in DMS heterostructures: Spin diffusion in magnetic ion system

A.A. Maksimov

Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Russia

The need of controlling the dynamic properties of Mn spins in diluted magnetic semiconductor (DMS) heterostructures, namely spin decoherence and especially spin lattice relaxation (SLR) time $\tau_{SLR}$ is obvious because they can turn out as a bottleneck for the speed of possible spintronic applications. In II-VI DMS dynamics of SLR of the Mn spin system covers a very wide temporal range from milliseconds to nanoseconds being strongly dependent on the Mn content. It is reputed that SLR dynamics in DMS is controlled by the number of Mn ion clusters which increases with increasing of Mn concentration. So, in principle, increasing the Mn concentration gives a possibility to shorten the SLR time over this range. On the other hand, the static magnetic properties of the material are also governed by the Mn concentration. For example, by designing a specific value for the SLR time of the randomly uniformly distributed Mn ions in the sample, also the Zeeman splitting is determined. It is crucial to overcome this correlation to tune a single property without influencing others. This problem can be solved by the concept of “digital alloying” in the samples with non-homogeneous magnetic ion distribution, because static and dynamic properties are governed by different mechanisms.

The recent time-resolved magneto-optical experimental investigations of static and dynamic magnetization properties of different DMS heterostructures with non-uniform Mn spatial distribution are reviewed. The $\tau_{SLR}$ dependencies on magnetic field and on concentration of magnetic ions are discussed. The roles of Mn ion clustering and spin diffusion through the magnetic subsystem are revealed. The comparison of model calculations, which take into account the real distribution of Mn ions in the samples, with the experimental results for “digital” superlattices, “parabolic” and “half parabolic” quantum wells with DMS barriers engineered in digital growth technique, and for type I and II DMS quantum wells allows to estimate the spin-spin diffusion coefficients and their dependencies on Mn concentration. Different regimes of complicated non-exponential magnetization relaxation in DMS heterostructures are discussed.
Mn spin dynamics probed using the combination of high magnetic field pulses and static field

T. Clément\(^1\), D. Ferrand\(^1\), M. Bonfim\(^2\)\(^,\)\(^1\), L. Besombes\(^1\), H. Boukari\(^1\), H. Mariette\(^1\) and J. Cibert\(^1\)

\(^1\) CNRS-UJF-CEA Joint group, Institut Néel, BP 166 38042 Grenoble cedex 9, France
\(^2\) Universidade Federal do Paraná Centro Politécnico CP, 19011 Curitiba, Brasil

Mn based II-VI diluted magnetic semiconductors have been intensively studied in the past for investigating the Mn spin properties in model low dimensionality heterostructures. More recently, optical studies with quantum dots containing a single magnetic ion open up new questions about the zero field Mn spin dynamics \([1]\).

Magneto-optical studies with (Cd,Mn)Te quantum wells have shown recently the particular interest of micro-coils for studying the Mn spin dynamic processes in zero field \([2]\). Following these first results, we developed a micro-photoluminescence set up incorporating a 50 μm single turn micro-coil allowing the application of pulsed magnetic field up to 0.35T with rise and fall times of about 15 ns. The pulse width can be tuned from 75 ns up to 2 μs. The set-up is cooled at 6K and placed in the middle of a solenoid magnet, where a static field can be tuned between ±11T. The samples are excited through the micro-coil using a microscope objective, which focuses the excitation Laser on a few μm spot. The collected photoluminescence is detected and analyzed in both circular polarizations using a 0.46m monochromator, a fast photo-avalanche photodiode and a photon counting device. The overall set-up resolution is limited by the pulse temporal profile.

We will present here experimental results on diluted 10 nm (Cd,Mn)Te/CdMgTe quantum wells with Mn concentrations between 0.2% and 1%. We used 200 ns magnetic field pulses up to 0.35T and static magnetic field between ±0.8T. We fixed the detection wavelength on the low energy side of PL excitonic lines and we recorded the time variation of the PL intensity in both circular polarizations. Thanks to the giant Zeeman effect, we deduce the Mn magnetization temporal profiles from the circular polarization rate.

The combination of different static fields and pulse amplitudes allow us to study in details the Mn spin dynamics around zero field. In a field region of about typically ±0.2T, we observed a fast dynamic with characteristic times of few tens of ns and which is limited by the pulsed field sweeping rate. Outside this region, the dynamic is much slower with characteristic decay times of about 1 μs, in agreement with measurement performed with longer pulses. We attribute the fast dynamic to Landau Zener processes, which occur during the field sweeping between different Mn Zeeman levels coupled by hyperfine interactions and strain. The slower dynamics correspond to the Mn spin lattice relaxation rate under non resonant 532 nm Laser excitation. To investigate the effect of strain, we study a 5 monolayer thick (Cd,Mn)Te/ZnTe with a Mn concentration of 1.5%, where the fast Landau Zener processes can be observed in broader region around zero field.

Spin manipulation in magnetic and non-magnetic quantum dots

Alexander O. Govorov

Department of Physics and Astronomy, Ohio University, Athens, Ohio 45701, USA; Govorov@ohiou.edu

This talk will discuss some of the recent results on semiconductor quantum dots with magnetic impurities. A single Mn impurity incorporated in a quantum dot strongly modifies a spectrum of optical emission from a quantum-dot system [1,2]. Importantly, a character of Mn-carrier interaction is very different for II-VI and III-V quantum dots (QDs) [1-3]. In the II-VI QDs, a Mn impurity influences mostly the spin-structure of an exciton or exciton [1,2]. In the III-V dots, a spatial localization of hole by a Mn impurity is very important, and ultimately yields a totally different spin structure [3,4]. Magnetic and spin-orbital interactions in QDs give rise to the coupling between the kinetic motion and spins of electrons. This coupling allows us to manipulate spins of excitons in magnetic and non-magnetic QDs using optical fields [1,2] or by voltage via the Kondo-type interaction [5].

A Mn-doped QD with a variable number of mobile carriers represents an artificial magnetic atom [6]. Due to the Mn-carrier interaction, the order of filling of electronic shells in a magnetic QD can be very different to the case of the real atoms. The “periodic” table of the artificial magnetic atoms can be realized in voltage-tunable transistor structures. For the electron numbers corresponding to the regime of Hund’s rule, the Mn-carrier coupling is especially strong and the magnetic-polaron states are very robust. QD molecules are also very different to the real molecules. QD molecules with magnetic impurities may demonstrate the effect of spontaneous breaking of symmetry and corresponding phase transitions [6]. Single QDs and QD molecules can be viewed as voltage-tunable nanoscale memory cells where information is stored in the form of robust magnetic-polaron states.

In the contemporary seek for miniaturisation of electronic devices and magnetic memories, information storage on a single magnetic atom remains the ultimate challenge of solid state physics. Among others, a promising spintronic device is a single magnetic atom located in a quantum dot (QD)[1]. In this work, we report observations on the dynamics of a single manganese atom embedded in a II-VI semiconductor QD: we present how a three body interaction involving a hole, an electron and the Mn spin allows us to manipulate the electronic spin of the localised Mn atom without using magnetic fields and we show that the Mn presents a long spin memory, exceeding the ms range at low temperatures (4K) and at zero magnetic field.

MBE growth and optical addressing of individual CdTe/ZnTe QDs doped with a single Mn atom were achieved recently. Now, the static properties of this system are well understood[2]: the photon emitted or absorbed by a Mn-doped QD bears information on the spin state of the Mn atom localized in the dot. This is due to the exchange interaction between an electron-hole (e-h) pair and the Mn atom: from the Mn point of view, the e-h pair acts as an effective field along the growth axis that lifts up the degeneracy between its six spin states. The recombination of the e-h pair causes the emission of a circularly polarized photon with an energy which depends on the spin projection of the Mn. In time averaged photoluminescence measurements, this leads to a six line fine structure of the QD emission. It is possible to probe the spin state of the Mn atom thanks to the intensity of the different lines observed in the emission spectrum.

In this communication, we report on the realization of a high degree of spin polarization for a Mn atom in a QD using quasi-resonant or fully-resonant optical excitation at zero magnetic field. Under excitation on an excited state of the dot (quasi-resonant excitation), we were able to optically inject spin polarized e-h pairs. Time-resolved detection of the intensity of a given line of the QD under alternatively s+ s- trains of light reflects the evolution of the population of the corresponding Mn spin state and shows orientation of the Mn spin in the effective field of the injected e-h pairs. Pump-probe experiments demonstrated that the photo-induced spin orientation was perfectly conserved over a few ms. The dynamics and the magnetic field dependence of the optical orientation mechanism show that the spin lifetime of an isolated Mn atom at zero magnetic field is controlled by the Mn spin magnetic anisotropy induced by the built-in strain in the QDs[3], which scales as $S_z^2$ along the growth axis.

Furthermore, using resonant excitation on a given line of the ground state of the exciton-Mn complex, we were able to achieve optical pumping of the Mn spin. Monitoring the time evolution of the resonant fluorescence observed during the optical pumping allows us to directly observe the initialization of the Mn spin. This technique presents the advantage of performing both initialization and measurement of the Mn spin at the same time. These results can be modelled using a rate equation model valid at low excitation power[4]. These experiments demonstrate the possibility to write, read and store information on the spin of a single magnetic atom in a semiconductor QD.

Overcoming the doping limit in wide gap semiconductors: p-type doping in ZnO

Su-Huai Wei

National Renewable Energy Laboratory, Golden, Colorado, USA

Application of semiconductors as electric and optoelectronic devices depends critically on their dopability [1]. Failure to dope a material, i.e., to produce enough free charge carriers beyond a certain limit at working temperature, is often the single most important bottleneck for advancing semiconductor-based high technology. For example, ZnO has a wide band gap (3.3 eV at room temperature) and large exciton binding energy (60 meV), and thus is suitable for making short-wavelength lasers and light-emitting diodes, as well as solar cells. Furthermore, its low material cost, high crystalline quality, and high radiation resistance make it a promising material to compete with currently very successful GaN-based technologies. Unfortunately, similar to most wide-band-gap (WBG) oxide materials, ZnO experiences the doping asymmetry problem, i.e., it can be easily doped n-type (generating electrons), but is much more difficult to be doped p-type (generating holes). This asymmetry-doping problem has severely hindered the potential applications of ZnO. In this talk, I will discuss the general chemical trends of the defect formation and ionization in semiconductors [1] and the origin of the p-type doping difficulty in ZnO [1-3]. Based on our first-principles band structure calculations, I will discuss approaches [4-9] to overcome the p-type doping difficulties in ZnO. These include (1) how to increase the dopant solubility, (2) how to design shallow p-type dopants and (3) how to modify the host band structures to reduce intrinsic defect-compensation.

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Structural - Instability of N-acceptors in Homo- and Hetero-
Epitaxially grown ZnO by MBE

K. Ando, T. Abe, T. Taya, Y. Ishihara, K. Enomoto, Y. Yamazaki, J. Yoshikawa, 
K. Fujino, H. Nakamura, T. Ohno, and H. Kasada

Information and Electronic Dept, Graduate School of Engineering, Tottori Univ., 
Koyama 4-101, Tottori 680-8550, Japan

ZnO, one of attractive widegap semiconductors, has been widely investigated for 
new ultra-violet photo-electronic devices. Using recently developed techniques on 
controlling n- and p-type conductivities, various kinds of test-devices (light emitting- 
or photo-diodes) are successfully demonstrated. At present, however, we have still 
encountered a big technical issue, “an imperfect p-type conductivity control”, which 
strongly prevent us from real practical device application. Here “imperfect p-type 
conduction control” includes several strange phenomena, such as a lack of reproducible 
p-type control, n-/p-type mixed-conduction, unstable photo-illumination effect, and, etc., 
of which reasons are not fully understood yet. In order to understand true mechanism 
on these problems we have made systematic study on N-acceptor doping into homo- 
and hetero-epitaxially grown ZnO films by MBE, and performed detailed 
characterization of N-acceptors focusing on its structural instabilities.

After MBE growth of N-doped ZnO on c-plane ZnO substrate or a-plane sapphire 
using NO* (or N ) radical source, we carried out post-anneal under high (800-900°C) 
temperature in O2 atmosphere. These annealed samples usually represent p-type 
partially, or n- and p-type mixed conduction, suggesting inhomogeneous N-acceptor 
doping. Detailed properties of N-acceptors or N-related deep centers are investigated 
by micro electrical-proving (on ZnO-surface), Hall-measurement using Hall-bar method, 
Photo-induced Persistent Conduction (PPC), Photo-induced Thermally Stimulated 
Currents (TSC) and DLTS experiments.

Major insights on these experimental studies are summarized as follows:

(1) Direct monitoring of p- and n-type mixed (island) structure using micro electrical- 
proving: (island dimension is 50-100 μm in stripe shape)

(2) Abnormal Hall-measurement under strong Magnetic Field in p-ZnO: due to strain 
induced piezo-electric field effect.

(3) Photo-excitation induced Persistent Carrier-Conduction (PPC) appeared in selected 
p-type ZnO island:

(4) Low temperature Photo-illumination induced negative TSC curves in selected p- 
type ZnO island: there exist more than two meta-stable states around N-acceptor 

Above insights (1) and (2) lead to natural interpretation on some strange experimental 
results we encountered in usual 4-terminal van der Pauw Hall measurements. Complete 
lack in reproducible experimental results is mainly due to inhomogeneous p-type doping 
or island structure. New finding on (3) and (4) insights are not independent, but are 
closely linked each other through marked instability of N-acceptor atomic site. These 
photo-induced PPC and negative TSC curves are not derived from island structure, but 
are originated from N-acceptor structural-instability where photo-excitation has caused 
transformation from shallow (effective-mass) acceptor to deep acceptor states like a 
meta-stable AX center, and these findings are consistent with the photo-induced EPR 
experiments (by N.Y. Garces et.al [1]).

This N-acceptor instability is found to strongly connect with strain induced piezo- 
electric field in ZnO, and thus, a precise strain-control becomes very important to 
develop perfect p-type conduction control in N-doped ZnO toward practical device 
application.

Time Resolved and Magneto-Optical Studies of bound exciton complexes in homoepitaxial ZnO

Institute of Solid State Physics, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

S. Lautenschläger, J. Sann, B. K. Meyer
Justus Liebig Universität Giessen, I. Physics Institute, Heinrich-Buff-Ring 16, 35592 Giessen, Germany

A. Rodina
A. F. Ioffe Physico-Technical Institute, 194021 St.-Petersburg, Russia

Homoepitaxial growth of ZnO has the great potential to provide high quality epilayers without strain or dislocations induced by the mismatch of lattice or thermal expansion coefficients. However, the current understanding of the impact of surface polarity on unintentional impurity incorporation, strain and doping is still on an early stage. We report on the effect of the substrate polarity on the structural and optical properties of homoepitaxially grown ZnO epilayers. Essential for 2D growth is the surface preparation of the bulk substrates. Nominally undoped ZnO layers of approximately 1.2 μm in thickness were grown by chemical vapor deposition on Zn- and O-polar ZnO substrates. The epilayers were grown simultaneously in the same reactor to ensure direct comparability between the samples. The effect of impurities and their correlation to local strain fields in the epilayers and substrates is evaluated. Bound exciton recombinations differ significantly for the two polar surfaces.

Magneto-optical PL spectroscopy is applied to determine the electron- and hole effective g-values of the involved defect bound exciton states. Using temperature dependent and angular resolved magneto PL, additional information concerning the charge state, dopant type and symmetry of the defect states are obtained. In addition, a defect related bound exciton state at 3.333eV is observed. We present a comprehensive analysis of this line under the influence of external magnetic and strain fields. The application of uniaxial pressure along the c-axis leads to a splitting of the 3.333eV emission, which does not correlate with shallow donor bound exciton complexes. Possible models for this line are discussed.

In addition, pico-second time resolved measurements reveal the recombination dynamics of free, shallow bound and deeply bound excitons. These results are compared with the transient behaviour of excitonic lines in high quality ZnO substrates. Finally, first results on optical properties of homoepitaxial grown epilayers on a-plane ZnO will be presented and compared to the properties of the polar samples.
Band-structure and optical parameters for wurtzite MgO, ZnO, and CdO – An \emph{ab-initio} prediction

A. Schleife, C. Rödl, F. Fuchs, and F. Bechstedt

Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena and European Theoretical Spectroscopy Facility, Max-Wien-Platz 1, 07743 Jena, Germany

In the rapidly developing field of semiconductor technology, alloys attract attention due to the possibility of band-gap tailoring for optoelectronic and photovoltaic devices. The fundamental gaps of MgO, ZnO, and CdO spread over an energy range that reaches from infrared to ultraviolet light. In experiments, the gap energy has been tuned from 3.4 eV to 4.4 eV in Mg$_x$Zn$_{1-x}$O systems.

For small concentrations, \( x \), MgO and CdO do not occur in their equilibrium rocksalt (\( rs \)) crystal structure but in the wurtzite (\( wz \)) structure. Unfortunately, many properties of \( wz \)-MgO and \( wz \)-CdO are unknown because bulk crystals cannot be grown. However, recent \emph{ab-initio} methods as an inevitable tool for materials science can close this knowledge gap with their predictive power, as we demonstrate here. Today, parameter-free many-body calculations are able to predict the electronic structure and optical properties including even excitonic effects. Spatially nonlocal functionals in combination with sophisticated GW schemes are available and affordable.

We introduce the theoretical concepts of one of the currently most reliable \emph{ab-initio} approaches to the computation of electronic structures \cite{1}. The nonlocal hybrid HSE03 functional, as an approximation to exchange and correlation, is used to compute the starting point for the solution of the quasiparticle equation using the GW approximation. Spin-orbit coupling is also included. We recently used this concept to explain the band ordering in strained ZnO \cite{2}.

The highly accurate electronic band structures resulting for \( wz \)-MgO, \( wz \)-ZnO, and \( wz \)-CdO are used to derive unknown quantities: fundamental gaps, effective electron/hole masses, crystal-field and spin-orbit splittings, optical matrix elements, and exciton binding energies. We show that the gap of \( wz \)-CdO is direct and that the spin-orbit coupling constants of \( p \) states in \( wz \)-CdO are much smaller than in the \( rs \) polymorph. The excitonic effects are reduced along the row from MgO to ZnO and CdO because the gaps decrease, which is accompanied by a huge increase of the static electronic dielectric constants. Also discussed is the direction-dependency and the chemical trend of significantly decreasing electron and hole masses towards CdO \cite{3}.

Finally, we apply Tersoff’s approach to derive branch-point energies as a universal reference energy level. The resulting band alignments of group-II oxide equilibrium and non-equilibrium polymorphs allow us to predict natural band discontinuities \cite{4}.

The implications of parameter-free calculations provide needed understanding of numerous electronic and optical properties of group-II oxides as well as their alloys and heterostructures.

\begin{itemize}
  \item \cite{2} A. Schleife et al., Appl. Phys. Lett. \textbf{91}, 241015 (2007).
  \item \cite{3} A. Schleife et al., Appl. Phys. Lett. (submitted).
  \item \cite{4} A. Schleife et al., Appl. Phys. Lett. \textbf{94}, 012104 (2009).
\end{itemize}
Band profile of ZnMgO/ZnO heterostructures confirmed by Kelvin probe force microscopy

H. Tampo¹, H. Shibata¹, K. Maejima¹, T. Chiu¹, H. Itoh¹, A. Yamada¹, K. Matsubara¹, P. Fons¹, Y. Chiba², T. Wakamatsu², Y. Takeshita², H. Kanie² and S. Niki¹

¹National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan
²Tokyo University of Science, 2641 Yamazaki, Noda, Chiba, 278-8510 Japan

ZnO-based materials have great potential in wide band gap semiconductors based for high-frequency and high-power devices. To date, however, there have been few reports from the viewpoints. Wide band gap semiconductors, for example, SiC, diamond, and GaN, are also possible candidates for such devices. Among these semiconductors, ZnO material has several advantages, such as a higher saturation velocity, a lower lattice mismatch, a high density two-dimensional electron gas (2DEG), a larger conduction band offset for ZnMgO/ZnO, and the possibility of the use of bulk (ZnO) substrates.

ZnO-based materials are wurtzite structure and are fundamentally different from the conventional cubic semiconductors in which they exhibit strong electric polarization effects along <0001> direction. In the previous study, we have demonstrated the electrical properties of Zn₁₋ₓMgₓO/ZnO heterostructures as a function of Mg composition x, and the 2DEG sheet charge dependence on the Mg compositions was obtained as 0.029x (C/m²) [1]. It was concluded that the 2DEG charge was polarization-induced charge and originate from the ZnMgO surface. However the band profile of the heterostructures not still investigated. In this study, we have investigated the band profile of the heterostructure through surface potential measurements by Kelvin probe force microscopy (KFM).

ZnMgO/ZnO heterostructures were grown on c-plane sapphire substrates by radical source molecular beam epitaxy (RS-MBE) with Zn polarity. Elemental Zn, Mg and rf radical oxygen were used as group II and group VI sources, respectively. The ZnMgO layers in this study had the single phase wurtzite structure with Mg composition up to 60% [2]. The surface potential energy was measured by KFM with a Rh cantilever.

Various band parameters were estimated from the KFM measurements, experimental electrical results, and standard physics theory. From Mg composition x dependence of surface barrier height, it was found that there is large density of states at the ZnMgO surface at 0.8 eV below the conduction band minimum. That is, the density of states is small between 0 and 0.8 eV below the conduction band, and the density of states at 0.8 eV below the conduction band is large enough to screen the polarization charge up to x = 0.4. However, the surface potential was suddenly increased over x = 0.4, this was concluded that the surface states at 0.8 eV were not sufficient to screen the polarization charge. Therefore, the surface density of states for the ZnMgO layer at 0.8 eV was estimated around 8×10¹² cm⁻².

Reference

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Stoichiometry dependent incorporation and electrical activity of Zn interstitials in homoepitaxial ZnO thin films

Universität Leipzig, Fakultät für Physik und Geowissenschaften, Institut für Experimentelle Physik II, Linnéstrasse 5, 04103 Leipzig, Germany

We find that the incorporation and the electrical activity of Zn interstitials in homoepitaxial ZnO thin films depend on the stoichiometry of the film, which is controlled and tuned during growth by the oxygen partial pressure.

Four ZnO thin films (thickness~1μm) were grown by pulsed-laser deposition at 650°C on Crystec (000-1)-ZnO substrates at oxygen partial pressures of 0.1 mbar, 0.016 mbar, 0.002 mbar and 0.0003 mbar, respectively. Atomic force microscopy revealed for all samples a high morphological quality. The surfaces exhibit atomically flat terraces with bi-layer steps of height c/2. X-ray diffraction measurements (XRD) showed that all samples grow lattice matched. However, the c-lattice constant is in tendency larger for lower oxygen partial pressures as indicated in figure 2 by the shift of the ZnO (0002) reflection towards lower angles. Therefore only the two films grown at the highest pressure are unstrained.

Photoluminescence spectra at T = 2 K stem from the thin film and substantiate the trend observed in the XRD measurements. The two thin films grown at the two lowest pressures exhibit a higher band gap than the two unstrained films. This is indicated by a change of the spectral position of the transition I_{6a}. In particular the sample with the highest c-lattice constant shows the largest shift of the band gap. Besides the c-lattice constant and the band gap, the relative intensities of the I_{6a} and the I_{3a} transitions depend on the oxygen partial pressure. This confirms the change of stoichiometry for the different growth conditions; it does, however, not simply follow the trends observed for the c-lattice constant and the band gap. The intensity ratio of the transitions I_{6a} and I_{3a} is maximal for the sample grown at 0.016 mbar. Further the free exciton transition is only observed for this sample. From this we conclude, that for this sample the deviation from the ideal stoichiometric ratio is least.

Generally the separation of the electrical properties of the ZnO substrate and the ZnO thin films is nontrivial. By means of thermal admittance spectroscopy we control the depth of the probing volume by the applied dc bias. The reproducible formation of rectifying contacts on homoepitaxial thin films permitted us to characterize the defect level parameters of the homoepitaxial thin films. In contrast to the photoluminescence result the zinc interstitial is only observed for the films grown at the two lowest pressures. This implies that the Fermi level is below the level of the zinc interstitial for the samples grown at the two highest pressures and is explained by an increased compensation.

In summary we present a comprehensive and consistent study correlating morphological, structural, optical and electrical properties of homoepitaxial zinc oxide thin films.

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Growth characteristics of poly-crystalline and single-crystalline ZnO layers by ultrasonic spray assisted mist-CVD technique

H. Nishinaka, Y. Kamada, N. Kameyama, K. Kaneko, and S. Fujita
Graduate School of Engineering, Kyoto University, Katsura 2, Kyoto 615-8520, Japan

We show the unique and promising potential of ultrasonic spray assisted mist-chemical vapor deposition (CVD) as an inexpensive, safe and environmental-friendly large-area growth method for high-quality poly-crystalline and single-crystalline ZnO thin films. In this technique liquid solutions of source materials are used as precursors. They are ultrasonically atomized and the mist particles formed are transferred to the reaction area with the carrier gas [1,2]. In this way, the mist sources can substitute for vaporized sources of toxic and/or dangerous metalorganics. This technique, therefore, can possess excellent controllability for source supply comparable to metalorganic-CVD (MOCVD). The growth can be done even under the open air, allowing low-cost and large-area growth with applying a linear-source nozzle [2].

Using zinc acetate or acetylacetonato as a precursor for Zn with changing the substrate materials and temperatures, (i) transparent and smooth c-axis oriented poly-crystalline ZnO thin films were grown on glass substrates, (ii) ZnO films were grown at the substrate temperature lower than 200°C, (iii) single-crystalline ZnO on sapphire attained the mobility of 90 cm²/Vs, which was reasonably high compared to various ZnO thin films grown by MOCVD, and (iv) two-dimensional step-flow growth, which had been difficult by MOCVD, was achieved by homoepitaxial single-crystalline ZnO films on ZnO substrates. Doping and alloy layers have been successfully achieved by adding the desirable source precursors in the source solution. The results showed as followed; (i) Al-doped ZnO on glass attained low resistivity of the order of 10⁻⁴ Ωcm, which was a standard for certain applications as a transparent conducting oxide, (ii) single crystalline (0001)-oriented wurtzite Zn₁₋ₓMgₓO thin films were prepared between x=0 and 0.3 without phase segregation of rocksalt structure.

This growth technique has also been applied to other oxide thin films such as Al₂O₃, Ga₂O₃, Fe₂O₃ and their alloys. The mist-CVD is supported by high vapor pressure of oxygen at the substrate region, resulting in sufficient suppression of oxygen vacancies. This is advantageous for the growth of high quality oxide thin films. Together with the safe, cost-effective, and environmental-friendly way of the growth, the mist-CVD can be a superior technology in the future for the growth of oxide thin films.

CdSe/ZnSe nanowire quantum dot: a high temperature single photon source

K. Kheng, A. Tribu, G. Sallen, T. Aichele, C. Bougerol, R. André, J. P. Poizat, S. Tatarenko

Nanophysics and Semiconductors group,
CEA/CNRS/University J. Fourier, 17 rue des Martyrs, Grenoble, France

In the past decades, semiconductor quantum dots have become a manifold tool for the development of new light sources, such as lasers, LEDs and single-photon sources. Application of quantum dots as nano-emitters in quantum optical technologies requires control of the dots density and location as well as high temperature operation. Quantum dots based on nanowire are interesting candidates for the development of such nano-emitters.

In this contribution we will outline the advantages offered by the nanowire growth and present our work on the development of the growth of CdSe/ZnSe nanowire quantum dots and their optical studies. The nanowires are grown by MBE in the vapour-liquid-solid growth mode assisted by gold catalysts. Narrow wires with typical diameter of 10 nm can be obtained [1] so that quantum dot heterostructures can be directly grown on defined position, without the necessity of self-assembly. This is especially important for II-VI materials, where self-assembled island formation occurs only within narrow growth parameter spaces. We will show that high quality structures can be obtained that allowed us to optically study single quantum dots, to identify exciton, biexciton and trion by photon correlation measurements. We will discuss the advantages of such nanowire quantum dots structures as compared to epitaxially grown or colloidal quantum dots and show in particular that single photon emission has been demonstrated up to 220 K [2], the highest reported temperature for non-classical light emission from a (non-blinking) semiconductor quantum dot system.

Electrically driven room temperature emission from a single self-assembled CdSe quantum dot

R. Arians, T. Kümmell, G. Bacher
Werkstoffe der Elektrotechnik and CeNIDE, Universität Duisburg-Essen,
Bismarckstraße 81, 47057 Duisburg, Germany

A. Gust, C. Kruse, D. Hommel
Institut für Festkörperphysik, Universität Bremen,
Otto-Hahn-Allee, 28359 Bremen, Germany

Single self-organized semiconductor quantum dots are regarded as one of the most promising approaches for realizing solid state single photon sources. In recent years a variety of concepts have been developed, most of them optically pumped. Moreover, the widely used Ga(In)As material system seems to be limited to low temperatures. The challenge towards a commercial use of single quantum dots as a non-classical light emitter is thus twofold: operation under ambient conditions and integration into an electrically driven device. For both aims, wide-bandgap II-VI quantum dots should be ideally suited: They inherently provide a much better carrier confinement and higher exciton binding energies than the Ga(In)As system, and robust electrically driven emitters with long device lifetimes based on Zn(Cd)Se quantum dots are available [1].

In our contribution, we present both optically and electrically driven emission from one single quantum dot at room temperature. The devices are based on epitaxially grown CdSe quantum dots embedded between ZnSSe/MgS barriers that are optimized with respect to high quantum efficiency at elevated temperatures. This is confirmed by an overall room temperature photoluminescence (PL) intensity that reaches more than 30 % of the PL intensity at T = 4 K. We attribute this to the extremely high band gap (E_g = 5.4 eV) of MgS suppressing thermal emission into barrier states efficiently. For single quantum dots, spectrally narrow PL signals can be detected that broaden at higher temperatures up to FWHM ~ 26 meV at T=300 K due to the exciton-phonon interaction.

For electrically driven devices, the optimized quantum dot active layer is embedded into a p-i-n-diode with ohmic contacts. Choosing an appropriate thickness of 1-2 nm, the MgS barriers do not hamper an electrically driven operation. Most important, electroluminescence from one single quantum dot is observed up to room temperature at a surprisingly low driving voltage of 2.6 V [2]. The single quantum dot exhibits a stable emission with exactly the same temperature-dependent broadening observed in PL. Because the linewidth at room temperature is comparable with the biexciton binding energy, only little spectral overlap with the biexciton emission is present; this will be an important criterion for efficient single photon emission. Thus, our device represents a major step forward towards the realization of compact and highly integrated non-classical light emitters working under ambient conditions without external cooling.

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Nanofabrication of telluride based sub-micron pillars

S.P. Agnihotri, H. Boukari, H. Haas, L. Besombes, M. Richard, and H. Mariette
CEA-CNRS team « Nanophysique et semiconducteurs »,
Institut Néel, CNRS & Université Joseph Fourier, 38042 Grenoble- France

The variety and fine electronic properties of telluride based heterostructures are usually probed by optical spectroscopy thanks to their very good structural quality. To further investigate these materials, especially to correlate optical studies to transport measurements at the sub micron range, it is necessary to develop a well controlled process for the fabrication at the sub-micron level.

Here we report on a standard top-down approach to fabricate sub-micron pillars in telluride heterostructures grown in a Riber P32 Molecular Beam Epitaxy system. We investigated two kinds of structures. One being CdTe quantum wells (6-12 monolayers) grown by atomic layer epitaxy in Zn$_{0.8}$Mg$_{0.2}$Te and Cd$_{0.7}$Mg$_{0.3}$Te and the second CdTe/ZnTe quantum dots induced by elastic relaxation of the strained CdTe [1]. Arrays of sub micron structures were defined by conventional e-beam lithography in PMMA and lift-off of a 50nm thick aluminum hard mask. The diameters of the pillars were tuned from 1micron down to 50nm and the separation between pillars was 5-10 microns to allow for optical addressing of a single pillar. The pattern transfer was performed by a low energy Argon Ion Beam Etching with an etch rate of 20nm/min. The low energy of Argon ions allows for fine control of the etched thickness and limits the density of defects generated by the Argon bombardment. Finally, Optical access to the structures was given by wet etching the Aluminium hard mask.

The morphology and quality of the etched pillars were first investigated by Scanning Electron Microscopy. These studies revealed a good reproducibility and homogeneity of the process. Pillars with a height of about 120nm were fabricated and neither undercuts nor over etching on the base of the pillars could be seen. Finally, this investigation also revealed that the pillars have steep walls (an angle of about 75°) for all diameters. Preliminary results from Argon based Inductively Coupled Plasma Etching showed that similar results can be obtained.

To investigate the electronic properties of such systems, micro Photoluminescence was performed at low temperature (4-10K). In the structures containing the thin CdTe quantum wells, we could clearly isolate strong and sharp PL peaks that can be attributed to localized states on the fluctuations on the quantum well interfaces. This is particularly striking when looking at 100-150nm pillars. In the structures containing the CdTe dots, single dot spectroscopy could easily be performed when looking at pillars smaller than 400nm. We clearly observe the co-existence of excitons, biexcitons and charged excitons when illuminating the device with photons that have a higher energy than the ZnTe Barrier. On the other hand, the dots are mainly neutral when photon creating the electron-hole pairs directly in the dots. It is worth mentioning that this structure allows for a significant gain in detection signal compared to the same studies performed through sub micron opening in an Aluminium mask.

To conclude, we were able to fabricate sub-micron pillars that allow for single dot spectroscopy in Telluride based heterostructures with a significant gain of signal detection. This know how may also open the road towards transport measurement across a single CdTe dot.

Quantum information technology promises revolutionary new capabilities in efficient computation and absolutely secure communication. However, the development of large-scale quantum computers and quantum communication networks requires new technologies in which scalable devices exhibit pronounced quantum interference effects, long quantum coherence times, and compatibility with optical networks.

Impurities in appropriately engineered II-VI semiconductors show strong promise for providing the needed elements for quantum information processing. The direct bandgap in these materials offers high oscillator strengths for optical transitions related to impurity-bound-excitons, and the larger binding energies in contrast to III-V-based devices allow single impurity isolation by nanofabrication. Impurity-related emission shows far less inhomogeneous broadening than quantum-dot-related emission, which enables scalability to many optically connected devices. Critically, the nuclear spins of II-VI materials may be isotopically depleted, which has led to long spin coherence times in optically-dark silicon but is impossible in III-V devices. Finally, the ability to alloy different II-VI materials and lattice-match to GaAs substrates allows a degree of engineering unavailable in other materials under consideration for quantum computers, such as diamond or rare-earth crystals.

We present several experiments indicating the viability of fluorine donors in ZnSe/ZnMgSe quantum wells for quantum information devices. First, we show that single emitters may be isolated in nanometer-scale structures and that they may efficiently emit one photon at a time; such a single-photon source is a critical ingredient of secure quantum communication protocols and quantum computers based on photonic qubits. Then, we show that two independent $^{19}$F:ZnSe devices emit photons that bunch on a beam-splitter, a quantum interference effect which enables photonic quantum computation schemes and allows the entanglement of distant electron spins bound to fluorine donors. Further, we characterize these single photon-sources via single-impurity optical spectroscopy in high magnetic field, revealing the needed spin structure for quantum information processing protocols. Finally, we show progress in coupling these same impurities to high-$Q$ microdisk optical resonators, demonstrating low-threshold lasing on the donor-bound-exciton transitions [1]. Such cavities will also be critical for providing efficient photonic wiring in potential quantum computers. Finally, we present ongoing experiments on the measurement of electron and nuclear spin coherence times for this important impurity.

Neutral excitons are formed from electron-hole pairs bound together by the Coulomb interaction. In most bulk semiconductors they have energy level structures which are analogous to that of a hydrogen atom. Excitons interact strongly with light, so that much of what is known about them comes from studies of their optical properties, especially in magnetic fields. Because of the need for wave-vector conservation during the interaction between excitons and photons, most magneto-optical studies have concerned excitons with wave-vectors which were comparable with those of the photons and therefore small, so that the excitons were essentially at rest. Relatively little is known, therefore, about how the properties of excitons change when they acquire kinetic energy. It is such changes that form the subject of the present paper.

The essential feature of our study is the use of quantum wells that are very wide in comparison with the exciton Bohr radius and in which the changes in energy which result from quantum confinement of the exciton are smaller than the binding energy due to the Coulomb interaction. The two-particle motion can then be considered within the "adiabatic" approximation, in which the exciton is treated as a (hydrogen-like) composite particle formed by the electron and hole mutually orbiting each other (the internal motion), plus a translational motion of their centre of mass. The translational motion can be considered in terms of a particle in a box model and, if the quantum well is sufficiently deep, the component of the exciton wave-vector perpendicular to the plane of the well (i.e. parallel to the growth direction, taken to be the z-axis) has a magnitude $K_z$ which is quantized according to $K_z = N\pi / L$, where $N$ is a non-zero integer and $L$ is the width of the well. In contrast, the components of the wave-vector in the plane of the layer are small. States with different values of $N$ therefore have distinct and slightly different energies, so that when the electron and hole recombine, the resulting photon energies are functions of $N$ and can be resolved with a high resolution spectrometer. These different emission lines correspond to different values of the kinetic energy of the exciton and the behaviour of each under an applied magnetic field can individually be studied. In this way we have found that the magnetic properties, and hence the electronic structure of the excitons, are strong functions of the kinetic energy.

In the present paper we review our experiments on excitons in CdTe, ZnTe, CdMnTe and ZnSe and show that remarkable motion-induced changes in the exciton magnetic moments and diamagnetic shifts can be accounted for by motion-induced mixing between the 1S hydrogen-like ground state of the exciton and higher lying states such as 2P. The mixing is shown to be a consequence of the nature of the valence band and excellent quantitative agreement with experiment is obtained by using values of the Luttinger parameters close to those previously published.
Spin properties of trions in a dense 2DEG

V. Kochereshko
A.F. Ioffe Physico-Technical Institute RAS, 194021, St. Petersburg, Russia
L. Besombes, R.T. Cox, H. Mariette
Institut Neel, CNRS, Grenoble, France
T. Wojtowicz, G. Karczewski, J. Kossut
Institute of Physics Polish Academy of Sciences, PL-02608 Warsaw, Poland

We studied modulation-doped CdTe/(Cd$_{0.7}$Mg$_{0.3}$)Te quantum well structures with a 2DEG of different densities (from $n_e<10^{10}$ up to $n_e\sim10^{12}$ cm$^{-2}$). The structures contained 100 Å single quantum well (SQW) and were δ-doped in the barriers at 100 Å distance from the QW. A special design of the structures made it possible to control the electron concentration keeping all other parameters constant with high accuracy.

In this study we compare Reflectivity PLE and PL spectra taken from the QWs with different electron densities in magnetic fields from 0 T to 11 T.

In the lightly doped structures an exciton and a singlet trion lines were observed at low magnetic fields. The line positions in Reflectivity and PL spectra are coinciding. The exciton line-width in magnetic fields was found to be dependent on the light polarization that explained by spin dependent exciton – electron exchange scattering.

Essential difference between reflectivity and PL spectra was observed at high 2DEG density. In zero magnetic fields in heavily doped structures broad bands in Reflectivity and PL related to a Fermi edge singularity emerge in the positions of exciton and singlet trion lines. In non-zero magnetic fields these broad bands split into a series of relatively narrow lines that shift linearly towards higher energies with a slope proportional to the electron cyclotron energy ($\hbar \omega_c$) and to low energies with a slope $\hbar \omega_M$. In high enough magnetic fields the positions of the lines in the PL and Reflectivity spectra are coincide.

A very unusual behavior was found for Zeeman splitting of exciton and trion lines in reflectivity and PLE spectra. In heavily doped structures the Zeeman splitting of exciton and trion lines is of opposite signs. The exciton splitting dose not depends on the 2D electron density, at the same time the trion splitting changes essentially with increasing electron density. This phenomenon was observed in reflectivity and PLE only, in PL spectra the exciton and trion Zeeman splittings are absolutely equal.

It is naturally expect that optical spectra in 2D case are determined by exciton-electron scattering processes when the creation/annihilation of the exciton is accompanied by an excitation of one or several additional electrons from the states under the Fermi surface into the vacant positions above it. When an external magnetic field is applied electron spectrum becomes discrete and such scattering processes appear as “combined” resonance processes when the creation/annihilation of the exciton is accompanied by the transitions of the additional electrons between the Landau levels.

The observed PL and Reflectivity spectra were analyzed theoretically in the model of the combined exciton-electron processes. Theoretical analyze has shows that taking into account the Landau level broadening is essential for quantitative result.
Optical spin pumping of CdTe quantum wells

G. V. Astakhov,1,2 M. M. Glazov,2 D. R. Yakovlev,2,3 E. A. Zhukov,3,4 W. Ossau,1 L. W. Molenkamp,1 and M. Bayer3

1 Physikalisches Institut (EP3), Universität Würzburg, 97074 Würzburg, Germany
2 A. F. Ioffe Physical Technical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia
3 Experimentelle Physik 2, Technische Universität Dortmund, 44221 Dortmund, Germany
4 Faculty of Physics, M. V. Lomonosov Moscow State University, 119992 Moscow, Russia

We summarize experimental and theoretical studies of all-optical spin pump and probe of resident electrons in CdTe/(Cd,Mg)Te semiconductor quantum wells [1]. A two-color Hanle-MOKE technique (based on continuous-wave excitation) and time-resolved Kerr rotation in the regime of resonant spin amplification (based on pulsed excitation) provide a complementary measure of electron spin relaxation time. The experimental results are substantiated by a theoretical model based on the classical approach to spins. We analyze various scenarios of spin polarization generation (via the trion and exciton states) and discuss difference between continuous-wave and pulsed excitations.

Polarization of the resident electrons and generation of their spin coherence is provided by the capture of the resident electrons into trions. The trions in turn can be either photogenerated by resonant excitation or formed from the excitons. Variation of pump energy (tuning to resonance with either the trion or the exciton) highlights details of the polarization process. Pump density dependences for the two excitation conditions are nearly the same for low densities (as each absorbed photon participates in spin pumping) and substantially different for high densities (for the trion pump the spin polarization tends to 100% while for the exciton pump the spin polarization decreases to zero). Independent variation of pump and probe energies proves that electron localization provides an increase of the spin relaxation time, as also confirmed by temperature-dependent experiments. The spin relaxation time of localized electrons can achieve 30 ns, as independently found in the continuous wave experiment in the limit of low pump density and in pulsed experiments by means of resonant spin amplification.

Fine Structure of Emission Lines from Charged CdSe/ZnSe/ZnMnSe Quantum Dots

E.A. Chekhovich¹, A.S. Brichkin¹, V.D. Kulakovskii¹,

S.V. Ivanov², A.A. Toropov², and M.M. Glazov²

¹Institute of Solid State Physics RAS, Chernogolovka 142432, Russia
²Ioffe Physical Technical Institute RAS, St. Petersburg 194021, Russia

Excitons in semiconductor quantum dots (QDs) can be considered as artificial atoms. The spin structure of an exciton confined into a QD depends on the exchange interaction between electrons (e) and holes (h) in QDs [1]. In a neutral symmetric QD, the e-h exchange interaction splits the exciton state into the optically active (bright) doubly degenerate state with total spin \( J = 1 \) and optically inactive (dark) \( J = 2 \) doublet. In contrast, no splitting is observed in the ground state of trions forming in the case of the exciton localization in a singly charged QD. This state optically active state containing 3 particles is only doubly degenerate as two electrons (holes) form a spin singlet.

Studies of magnetophotoluminescence from CdSe/ZnSe/ZnMnSe QD structures have revealed in addition to the emission lines of excitons and trions, the lines with emission properties being qualitatively different from those of excitons and trions. These lines demonstrate a quartet fine structure unexpected for trions at zero magnetic field. The structure resembles that of excitons in neutral QDs but is characterized with a markedly smaller splitting (less than 1 meV) and approximately equal intensities of all four lines.

The quartet structure of the ground state is typical for an exciton confined in a neutral or in a doubly charged QD. In the latter case two electrons in the ground 1s-state form the spin singlet and do not contribute in the level splitting. All of states of the exciton in the doubly charged QD are optically active for the recombination of 1s electrons, that is in agreement with an experimental observation at the zero field. However, polarization studies of the QD emission in a wide range of magnetic fields show the sequence of polarized components unexpected for doubly charged exciton in CdSe QDs, namely, the observed sequence demands the lowest state to originate from the \( J = 2 \) rather than \( J = 1 \) state. Taking into account of the exchange splitting of the final state (two electrons, one in the ground and one in excited shells) does not solve the problem.

It is not unlikely that the discussed emission corresponds to the recombination of excitons in singly charged QDs having a closely set charged QD. Indeed, QDs in CdSe/ZnSe/ZnMnSe heterostructures are formed by potential fluctuations having a very high density in these structures. Qualitatively, the effect of an electron in a closely set QD is similar to that of the electron in the excited shell of the same QD, but the level sequence in the ground and final states of the exciton in the case of electron confined to a nearby QD could be modified.

Fine Structure of Two Electrons Energy Levels in Quantum Dot

M.M. Glazov¹, V.D. Kulakovskii²

¹Ioffe Physical Technical Institute RAS, St. Petersburg 194021, Russia
²Institute of Solid State Physics RAS, Chernogolovka 142432, Russia

It is well known that energy levels of a localized exciton demonstrate a fine structure caused by the exchange interaction between an electron and a hole [1]. On the other hand, energy levels of a single electron confined in a quantum dot are two-fold spin-degenerate. Here we address theoretically a fine structure of a pair of electrons confined in a quantum disk.

We assume that two-particle states are formed as products of single electron orbitals. The ground state of two electrons is spin singlet. The lowest in energy excited states are formed of one electron on the ground level (occupying S-orbital) and the second electron on the first excited level (P-orbital). There are two such orbital states which are degenerate in axially symmetric disks (SPₓ or SPᵧ). They can be split due to quantum disk anisotropy. The exchange interaction between the electrons splits each of these orbitals into spin singlet and triplet, the triplets are lower in energy. The singlet-triplet splitting in II-VI quantum dots is about 10 meV, therefore it is possible to address triplet states only. These excited states play role of the final states in the processes of the electron-hole recombination in doubly-charged quantum dots.

The symmetry analysis shows that in anisotropic quantum disks the three-fold spin degeneracy of each triplet orbital (SPₓ or SPᵧ) can be completely lifted. The eigenstates are those with z-component of total spin of two electrons mₛ being 0 and two states being symmetric and antisymmetric linear combinations of states with mₛ=±1 and -1. These two states are similar to the linearly polarized states of an exciton in an anisotropic quantum disk [1]. In axially symmetric quantum disks the states SPₓ and SPᵧ form two two-fold degenerate sublevels with the total momentum (spin and orbital) z-component being ±1 and ±2, and two non-degenerate sublevels with the total momentum component being 0. This situation is similar to that of excited exciton states in quantum disks [2].

The microscopic origin of the fine structure of an electron pair is the spin-orbit interaction. We derive spin-orbit terms in the effective Hamiltonian of two electron interaction within 8-band Kane model. The fine structure of triplet states is calculated as function of quantum disk geometrical parameters. The transition between the cases of axially symmetric and anisotropic disks is analyzed [3].

Nonlinear optical properties of semiconductor nanocrystals (NCs) are completely determined by the transitions between 8 exciton and 6 biexciton band edge states. These states are split by electron-hole, hole-hole, and electron-electron exchange interactions enhanced in NCs, by electron-hole Coulomb interaction, by the NC shape and by the crystal field in hexagonal NCs. Although the exciton fine structure in CdSe NCs was very well understood [1], the fine structure of biexcitons has never been observed experimentally because strong nonradiative Auger processes in NCs completely quench biexciton photoluminescence. The theoretical calculations of the biexciton fine structure were performed only in a simplified model [2]. Recently, the biexciton recombinations were observed in a new type of CdTe/CdSe and CdZnSe/ZnSe core-shell NCs [3]. The analyses of these experimental results require urgently detailed theoretical calculations of the biexciton fine structure.

We present here the results of the first theoretical calculations of the biexciton fine structure in spherical core-shell NCs of cubic and hexagonal II-VI semiconductors. The confining potential in the core-shell NCs was approximated by the smoothened harmonic potential [4]. Specific properties of the NC surface was considered using the general boundary conditions applied for the envelope functions at the NC surface [5]. The six band edge biexcitons are formed from two electrons with spin 1/2 and two holes with spin 3/2 at the lowest quantum size levels. Due to the exchange interaction two biexciton states with total momentum $J=2$ (ground state) and $J=0$ are formed in the spherical cubic NC. The deviation from the spherical shape and the hexagonal crystal field split these two states into three states with projections $J_z = 0$ (ground state), $J_z = \pm 1, \pm 2$ and $J_z = 0$. We calculate the dependence of the biexciton fine structure splitting on the NC size, on the parameters of the confining potential and on the parameters of the general boundary conditions. We found also the strong effect of the surface and of the confining potential on the electron-hole exchange interaction and thus on the exciton fine structure (splitting of the exciton states with $J_z = 0$, $J_z = \pm 1$ and $J_z = \pm 2$ [1]). The energies and the oscillator strengths for the allowed optical transitions between biexciton and exciton states that might be observed in stimulated emission or pump-probe experiments were calculated.

We review our work on the optical properties of single CdS nanosheets and nanowires explored by (1) micro-photoluminescence, (2) time-resolved micro-photoluminescence, (3) spatially-resolved Raman scattering and resonant Raman scattering and, finally, (4) photocurrent transport measurements. At low temperatures we observe high quantum efficiencies and strongly polarized photoluminescence emission which can be correlated with TEM measurements of the orientation of these wurzite structures. For the nanosheets, exciton lifetimes of ~200 ps are observed, a value significantly longer than observed for CdS nanowires whose diameter is the same as the thickness of these nanosheets, but shorter than that observed in bulk samples.[1] Spatially-resolved low temperature photoluminescence measurements reveal exciton states with a distinct spatial distribution, and Raman and photoluminescence measurements at room temperature indicate a pattern of stress across the nanosheet. [2,3] Temperature dependent photoluminescence is also used to study the electronic properties of single CdS nanowires. At low temperatures, both near band edge and spatially localized defect-related photoluminescence are observed in many nanowires with spatially localized emissions at lower energies associated with morphological irregularities in the nanowires. [4,5] Spatially-resolved photocurrent measurements of CdS nanosheets with both above bandgap and below bandgap laser excitation, reflect the different hole and electron mobilities as well as significant two photon absorption, which may have implications for potential sensor applications.[6] 

We have recently shown that a single CdSe quantum dot embedded in a ZnSe nanowire (NW) is an efficient single photon source operating at temperature as high as 220K [1]. However, when grown on an oxidized Si (001) substrate in the VLS growth mode catalyzed by gold particles, the NWs present a random distribution of orientation and density.

In this contribution we report on the epitaxial growth of ZnSe/CdSe NWs deposited on a ZnSe (100) buffer layer epitaxially grown on a GaAs (100) substrate. Scanning electron microscopy (SEM) images confirm the formation of <110> oriented nanotrenches generated by Au dewetting at 530°C [2]. The gold particles are localized at the extremities of the nanotrenches opening the way to a self controlled localization of the NWs difficult to achieve with a Si substrate. We have studied by SEM the first steps of the NWs formation and the effect of the growth temperature. Nanoneedles (300°C) or nanorods (above 400°C) can be obtained, the diameter of the rods being in the 10 nm range (i.e below the Bohr diameter in ZnSe). Moreover the NWs are <111> oriented relatively to the substrate and follow a direction perpendicular to the nanotrenches.

The microstructure of the NWs has been studied in detail by High Resolution Transmission Electron Microscopy (HRTEM). The ZnSe NWs adopt the hexagonal wurtzite-type structure and grow along the c-axis. The CdSe inclusions have been identified by Energy Dispersive X-ray spectroscopy as well as by HRTEM, the images being treated by the Geometrical Phase Analysis (GPA) method in order to get the interplanar spacing variations along the wire axis.

Surprisingly the CdSe inclusions, as small as 1.5 nm high, systematically present a cubic zinc-blende arrangement with [111] as the growth axis. Due to the presence of 4 equivalent [111] directions, the modification in the stacking sequence at the inclusion level can explain the change in the orientation of some NWs as observed on SEM images. It is worth noting that the NWs structure is opposite to the bulk-form case, where ZnSe and CdSe present a cubic and hexagonal arrangement, respectively.

Optical study of clustering in a self-assembled CdTe/ZnTe quantum dot plane

T. Kazimierczuk, A. Golnik, J. A. Gaj and P. Kossacki
Institute of Experimental Physics, University of Warsaw, Hoża 69, 00-681 Warsaw, Poland

P. Wojnar
Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/64, 02-688 Warsaw, Poland

Inter-dot coupling attracts a growing attention in view of possible applications in quantum information technologies. Coupled quantum dot (QD) pairs have been recently detected in a single self-assembled CdTe/ZnTe plane [1]. The objective of the presented study was to establish the scale of the inter-dot coupling phenomenon. As the coupling occurs only for QDs close to each other, the number of coupled pairs may serve as a measure of the clustering in the QD ensemble. Our results indicate a strong clustering tendency.

Three CdTe/ZnTe self-assembled QDs were grown by molecular beam epitaxy using tellurium desorption technique [2]. The structures were grown on (001) GaAs substrates with 3 μm CdTe followed by a 0.7 μm ZnTe barrier. Then 3 mono-layers (ML), 6 ML, or 12 ML of CdTe were deposited to form QDs. After tellurium desorption the QD plane was covered by a 100 nm ZnTe cap. Atomic force microscope (AFM) image obtained on a similar sample showed QDs with an areal density of 5×10^9 cm⁻² [3].

A micro-photoluminescence setup was used with the sample mounted directly on the front surface of a microscope and immersed in superfluid helium at T=1.6K. The spatial resolution of the setup was better than 0.5μm. Photoluminescence excitation (PLE) measurements were performed using a CW Rhodamine 6G dye laser. Excitation energy range was 2.02 to 2.15 eV and photoluminescence (PL) was detected below 2.02 eV, i.e., in low-energy tail of QD ensemble emission spectrum. Data was collected on 49 spots over a 7μm x7μm square.

We distinguished characteristic patterns corresponding to single QD emission throughout each PL spectrum. Sharp resonances were detected for some of the observed QDs, evidencing inter-dot coupling, as reported in [1]. We established a statistics of the observed QDs and resonances. The sample with 6 ML of CdTe exhibited the strongest PL. We estimated the average number of QDs per spot for this sample as 20. The resonances were detected for about 50% of them. This result shows a strong clustering tendency, since in case of a random QD distribution, the expected relative number of closely spaced QD pairs would be much lower. The other samples show a similar regularity, although they exhibit a lower QD areal density.

ZnTe-based core-shell nanowires grown by molecular beam epitaxy

W. Zaleszczyk, E. Janik, T. Wojciechowski, S. Kret, P. Dłużewski, E. Dynowska,
A. Presz, G. Karczewski, and T. Wojtowicz

1) Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46,
02-668 Warsaw, Poland

2) High Pressure Institute, Polish Academy of Sciences, Sokolowska 29/37,
01-142 Warsaw, Poland

The studies of semiconductor nanowires (NWs) have been recently intensified due to
the hope of using these 1D structures as “building blocks” for nanoscale electronic and
photonic devices. Heavily p-type doped ZnTe alloyed with MnTe exhibits at low
temperature the paramagnetic-to-ferromagnetic phase transition [1] thus making the
Zn_{1-x}Mn_xTe NWs [2] potentially attractive for model spintronic nanodevices.
We report on the growth of the ZnTe-Zn_{1-x}Mn_xTe, and Zn_{1-x}Mn_xTe-Zn_{1-x}Mg_yTe core-
shell nanowire heterostructures. One of the applications of the shell is in reducing the
influence of surface states on the luminescence efficiency of NW core material.
Properly doped shell can also serve as a remote source of carriers for the NW core. In
the case of ZnMnTe core this hopefully can lead to the carrier mediated ferromagnetism.
Our radial nanowire heterostructures were obtained by a molecular beam epitaxy (MBE)
on GaAs substrates in the VLS (vapor-liquid-solid) growth mode
induced by Au/Ga eutectic droplets [3, 4]. In order to produce shells after the growth of
ZnTe or Zn_{1-x}Mn_xTe NW cores the substrate temperature was lowered to the value
typical for the growth of epitaxial layers in order to force sidewall growth of
Zn_{1-x}Mg_yTe shells. Both undoped and p-type nitrogen doped shells were produced.
Nitrogen acceptors were provided from nitrogen rf-plasma source. The growth of these
zinc-blende (ZB) nanowire heterostructures, having an average diameter of about 150
nm (core 50 nm) and typical length between 1 and 2 μm, was performed on (001),
(111), and (011)-oriented GaAs substrates.
Properties of the nanowires were studied with scanning electron microscopy, high
resolution transmission electron microscopy, X-rays diffraction and photoluminescence.
It was found that the presence of the shell leads, as aimed, to the strong enhancement of
the low-temperature near-band photoluminescence of NW core [5]. This result
constitutes an important step toward realization of nanowire quantum dot based “single
photon on demand” sources.

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Scanning spreading resistance microscopy (SSRM) is an atomic force microscopy (AFM) based technique, which has been developed for electrical characterization of semiconductor devices. Local surface resistivity $\rho$ and carrier concentration ($10^{15} - 10^{20} \text{ cm}^{-3}$) can be determined with spatial resolution as high as 5-10 nm by measuring current flowing between a conducting AFM probe and sample that is biased relative to it. Spreading resistance $R_s$ constitutes the main part of the measured resistance and can be converted to resistivity of sample $\rho$ using formula $R_s = \rho/4a$ where $a$ is the radius of ideal flat, pure ohmic contact. Carrier concentration can be calculated using $\rho$ value with formula $\rho = 1/(en\mu_e + ep\mu_p)$. At this moment devices based on vast variety of doped low resistivity III-V materials has been investigated with SSRM and as far as we know there were no II-VI undoped materials studies. In this work we applied this technique for profiling carriers in quantum wells (QWs) of undoped heterostructures consisted of CdS QWs sandwiched between ZnSSe barriers.

CdS/ZnSSe multiple quantum well heterostructures were grown by MOVPE on the semi-insulating GaAs substrates misoriented by $10^0$ from (001) to (111)A plane in a custom built horizontal quartz reactor in hydrogen at atmospheric pressure and $T = 425 \, ^\circ C$ using diethylzinc (Et$_2$Zn), dimethylcadmium (CdMe$_2$), diethylsulfide (Et$_2$S) and dimethylselenide (Me$_2$Se) as precursors. Thickness of CdS QW was typically 5 nm while thickness of the ZnSSe barrier was typically 100 nm. SSRM measurements were carried out with an AFM Solver P-47 Pro on freshly cleaved surfaces under ambient conditions. We used N – doped diamond coated probes with tip curvature radius about 35 nm. Back contacts were made by indium evaporation on ZnSSe surface in vacuum.

It has been shown that SSRM is really capable of visualizing different semiconductor layers in undoped heterostructures. All quantum wells were clearly resolved. Visualization becomes possible only under negative voltages applied to the CdS/ZnSSe heterostructure, indicating Schottky barrier formation at tip-cleaved surface interface. We noticed that built-in red laser is able to generate carriers in QWs despite of the fact that the photon energy is smaller then band gap energy of CdS QW. One of the possible explanations of this phenomenon is Franz-Keldysh effect. Some estimations of electron concentration in CdS QWs will be carried out also.

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Colloidal ZnO/CdS Type II Core-Shell Quantum Dots: Synthesis and Characterization

Vyacheslav Volkov,1 Igor L Kuskovsky,2 Nikesh V. Valappil2, Fen Xu3, Hanying Bai3, Xueyun Gao3, and Hiroshi Matsui3

1Brookhaven National Lab, CMP Materials Science Department, Upton, NY 11973
2The City University of New York, Department of Chemistry, Hunter College and Graduate Center, New York, NY 10065
3The City University of New York, Department of Physics, Queens College, Flushing, NY 11367

Majority core-shell semiconductor quantum dots (QDs) form a so-called type-I band alignment, for which material with a smaller band gap is a potential well for both electrons and holes. There, however, exists another class of heterostructures, type-II, for which the bands have a staggered character with one carrier is predominantly confined to the core, while the other is located in the shell. Some properties of type-II heterostructures, useful for many applications, are access to an interband emission at the energies below band gap energies of underlying material, suppression of the Auger recombination, and a relatively long exciton lifetimes. Previously, type-II colloidal semiconductor core-shell quantum QDs with photoluminescence in the near-IR regions have been fabricated and investigated. However, there are only a few type-II core-shell QD systems emitting in the visible. Moreover, to the best of our knowledge, colloidal core-shell heterostructures with ZnO cores that possess the type II characteristic has not been reported yet, although recently ZnO/CdS and ZnO/ZnSe nanowires were grown by chemical vapor deposition.

We present our recent work on fabrication and characterization of type-II ZnO/CdS colloidal core-shell QDs with unusual long excitonic lifetime. The synthesis of the type-II ZnO/CdS was carried out in a two-step process, in which we initially synthesized ZnO core particles and then the step-wise slow growth of CdS shell was applied. We combine the evidences from optical absorption, photoluminescence, high resolution TEM, as well as EDX to show that the formed ZnO/CdS nanoparticles are indeed type II QDs.
Inverted optical phonons in II-VI semiconductor compounds

E.A. Vinogradov, B.N. Mavrin, N.N. Novikova, V.A. Yakovlev

Establishment of the Russian Academy of Sciences Institute for Spectroscopy of RAS, 142190, Troitsk, Moscow region, Fizicheskaya str., 5.

There is rather old problem with understanding and explanation of existence of additional to selection rules optical phonons in IR and Raman spectra with inverted frequencies in all semiconductor crystals of $A^2B^6$ compounds and especially in their solid solutions like $AB_2C_{1-x}$. In $Zn_{1-x}Cd_xS$, $Zn_{1-x}Cd_xSe$ and $Zn_{1-x}Cd_xTe$ crystals additional phonons due to dipole vibrations of $Zn$--$Cd$ ions and $Se$--$S$ dipoles in $ZnSe_{1-x}S_x$ were observed. The oscillator strengths of these additional phonons are proportional to difference in ion charges of the dipoles and about 10 times less than for the main dipoles. Nevertheless these additional dipoles have to generate local electric field which has to interact with free carriers.

We believe that the additional inverted phonons can exist due to the next reason. High degree of ionicity of $A^2B^6$ compounds provides large value of LO-TO phonon splitting in the center of Brillouin zone. This splitting is comparable with dispersion of optical phonons in whole zone. As a result there is a quasi-gap in the density of phonon states where quasi-localized vibrations of impurity ion can appear. In frequency region of the quasi-gap the real part of dielectric function is negative and LO-TO splitting of additional quasi-localized vibrations must be inverted – LO frequency must be less than TO frequency.

The results of the first-principles calculations of both the electron density and the phonon structure in $ZnSe_{1-x}S_x$ crystals are discussed.

References:
Unification of the phonon mode behavior of semiconductor alloys within a basic Percolation scheme

J. Souhabi, O. Pages, A. Chafi, A. V. Postnikov, A. Nassour, S. Doyen and J. Hugel
LPMD, Université Paul Verlaine, 1 Bd. Arago, 57078 Metz, France

The traditional classification of vibration spectra in usual zincblende semiconductor alloys AB\textsubscript{1-x}C\textsubscript{x} (A being an anion or a cation) contains two generic types: - A nominal 1-bond->1-mode type for random alloys, subdivided in fact into three distinct sub-types [(i) pure 1-bond->1-mode, (ii) mixed-mode, (iii) modified 2-mode], as covered by the modified-random-element-isodisplacement (MREI) model [1]. In this model, bonds of like species are equivalent (macroscopic insight), immersed into the same uniform continuum whose physical properties are locally averaged, in the sense of the virtual crystal approximation (VCA).

- An anomalous 1-bond->multi-mode type, the sign of a far-from-random substitution if we refer to the Cluster model [2] that has been accepted through use. This model distinguishes between like bonds depending on their first neighbours (microscopic insight) among four possible tetrahedral arrangements (cluster units), whereby the like cluster units are equivalent, again immersed into the same VCA-type continuum, leading to a (iv) 1-bond->4-mode behaviour.

However, our careful re-examination of the vibration spectra in the literature has revealed that even the leading alloys in each class, i.e. InGaAs (i), ZnTeSe (ii), InGaP (iii) and GaAsP (iv), do not exhibit the prototype behaviours they are supposed to represent [3]. Our view is that the VCA misses the essence of the phonon behaviour of alloys. As phonons relate directly to the bond force constant, that is a local property, thereby dependent on the local neighbourhood, a proper understanding should require a detailed insight into the topologies of the B and C substituting species, which guides to the percolation site theory. In this presentation we show that an unified (hence probably universal) description of the phonon behaviour of the alloys we discuss can be achieved on the basis of random B->C substitution within the so-called Percolation model that views the crystal at the mesoscopic scale as a composite of the AB-like and AC-like regions, both resulting from natural x-fluctuations at the local scale. Each region brings a specific phonon per bond, leading to a 1-bond->2-mode type (mesoscopic insight). The Percolation model was originally developed for Zn\textsubscript{1-x}Be\textsubscript{x}-chalcogenides, that are the only exception to phase separation among the novel alloys with light first row elements in substitution (Be, B, N...). These show a unusually large contrast in their bond physical properties (ionicity, bond length, bond stiffness, ...), and, as such, exhibit model phonon behaviours. Generally the VCA-to-Percolation change of paradigm reveals a specificity of phonons to address the alloy disorder at the unusual mesoscopic scale. We are not aware that other experimental techniques have this capability, and we introduce a terminology that phonons act as a mesoscope into the alloy disorder. This is promising, in particular, for the study of long-range spontaneous ordering in alloys [4].

The discussion is supported by contour modelling of representative Raman and infrared spectra of alloys via the Percolation model, and \textit{ab initio} phonon/bond length calculations at critical alloy compositions (dilute-limits, bond percolation thresholds, stoichiometry).

Resonant Raman Scattering in Spherical QDs: II-VI versus III-V Semiconductor Nanocrystals

M. I. Vasilevskiy\(^1\), R. P. Miranda\(^2\), A. G. Rolo\(^1\), and C. Trallero-Giner\(^3\)

\(^1\)Centro de Física, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal
\(^2\)Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK
\(^3\)Departamento de Física Teórica, Universidad de La Habana, Vedado 10400, La Habana, Cuba

We shall give an overview of our theoretical and experimental results on Raman-active optical phonon modes and exciton-phonon (ex-ph) interaction in nearly spherical nanocrystals (NCs) of polar semiconductor materials with cubic crystal structure. A systematic consideration of the effect of reduced dimensionality on both electrons and phonons in a spherical quantum dot (QD) will be presented within the theoretical approach based on a continuum lattice dynamics model and the effective mass approximation for optical phonons and electronic states, respectively. Resonant Raman scattering (RRS) will be discussed with respect to the underlying mechanisms of the exciton-phonon interaction.

Typical RRS spectra of well characterized NCs of the most commonly studied II-VI semiconductors (such as CdSe, CdS and CdTe), possessing the properties of QDs, are constituted by a single asymmetrically broadened band, which peaks at (or slightly below) the bulk longitudinal-optical (LO) phonon frequency [1]. In contrast, the spectra of nanocrystal InP QDs show two almost equally intense peaks centered approximately at the LO and transverse-optical (TO) phonon frequencies of bulk InP [2]. The “anomalous” TO-type mode was also observed for InAs NCs [1].

In polar semiconductors, there are two different mechanisms for ex-ph coupling, a long-range one known as Fröhlich interaction and a short-range one, due to the optical deformation potential (ODP). The momentum conservation in bulk crystals leads to the first-order Raman selection rule of dipole-forbidden Fröhlich-type scattering while the ODP mechanism is dipole-allowed. Because of the lack of translational symmetry in a QD, both mechanisms have to be taken into account. We will show that: (i) confined phonon modes of mixed longitudinal-transverse-interface nature, with the angular momenta \(l=0,2\) (Fröhlich) and \(l=1,3\) (ODP) contribute to the scattering, (ii) the qualitative difference between the RRS spectra of III-V and II-VI dots is due to the fact that the former materials are less ionic and typically have a larger ODP constant compared to the latter [2]. Among the II-VI, the (usually overlooked) ODP mechanism seems to be of some importance for CdTe QDs. The intensity of the ODP-mediated RRS scales with the QD radius as \(R^{-3}\), while for the Fröhlich-type mechanism the scaling law is \(R^{-1}\). We shall compare calculated one-phonon RRS spectra to experimental data demonstrating the trends outlined above. The exciton-polaron effect, important for the multi-phonon scattering in QDs [3], shall also be discussed.

Is the enigma of the anomalous curvature of LO phonon branches for some binary semiconductor compounds finally solved?

W. Szuszkiewicz1*, J. Lazewski2, B. Hennion3, and B. Witkowska1
1 Institute of Physics PAS, Al. Lotnikow 32/46, 02-668 Warszawa, Poland
2 Institute of Nuclear Physics PAS, Radzikowskiego 152, 31-342 Kraków, Poland
3 Laboratoire Léon Brillouin, CEA-CNRS, CE Saclay, 91191 Gif-sur-Yvette, France

The simplified, one-dimensional model of the optical phonon dispersion has been applied for a long time in the case of binary semiconducting compounds. The typical solution for vibrations of one-dimensional atomic chain, with the maximal value of the optical phonon frequency corresponding to the wavenumber q = 0, is an excellent model of lattice vibrations for many important semiconductors, such as GaAs or ZnTe. Under very particular conditions for selected parameters describing the constituent ions the optical phonon dispersion may be even flat but in one-dimensional model one can never obtain a change of the curvature (when point q = 0 corresponds to the optical phonon frequency minimum).

The “anomalous” behavior of the LO phonon mode have been observed by means of inelastic neutron scattering for a few real binary compounds. Between the oldest known examples of this kind is the lattice dynamics of CuCl, crystallizing in the zinc-blende structure [1]. More recent data concern mercury chalcogenides: HgSe and β-HgS [2, 3], also crystallizing in this structure. The lattice dynamics of all compounds above mentioned has been reproduced previously by the rigid-ion model calculations, in the case of CuCl and HgSe an excellent description of the phonon dispersion has been also achieved by \textit{ab-initio} calculations. However, a simple physical model pointing out the basic factors responsible for the “anomalous” shape of the optical phonon branches has not been previously discussed.

Our paper demonstrated that apart from a typical solution well known from one-dimensional model there exists also another one, possible in two- or three-dimensional situation. It is shown that a particular electron charge distribution around ions in the crystal lattice is responsible for “an anomalous” LO phonon mode dispersion. In order to confirm predictions of our simplified, qualitative model the electron charge distribution has been obtained for HgSe by \textit{ab-initio} calculations using the ultrasoft pseudopotentials for both atoms and taking into consideration the \textit{d} electrons for Hg. The principal physical factors that could result in the anomalous LO phonon curvature were identified and discussed. Finally, the simple recipe to crate a new binary compound that exhibits mentioned above property is given.

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*Corresponding author. E-mail address: szusz@ifpan.edu.pl

Pre-requisites for the formation of unusual diffusion profiles in II-VI semiconductors

H. Wolf1, J. Kronenberg1, F. Wagner1, Th. Wichert1, and ISOLDE Collaboration2

1 Technische Physik, Universität des Saarlandes, 66041 Saarbrücken, Germany
CERN, PH Department, CH-1211 Geneva 23, Switzerland

Radiotracer experiments show that the diffusion of the group I elements Cu, Ag, Au, and Na in CdTe and ZnTe exhibit unusual concentration profiles if the diffusion is performed under external Cd pressure [1,2]. After implantation of the radiotracer into the crystal and subsequent annealing under Cd pressure at temperatures in the range between 700 to 850 K peak shaped concentration profiles are observed that are symmetrical with respect to the center of the typically 800 µm thick crystals. The widths of the adjacent depletion regions towards both surfaces depend on the composition of the host crystal and the annealing temperature. The ratio of maximum (at center) and minimum (depletion region) concentration is between 10 and 1000.

The formation of unusual diffusion profiles in binary II-VI semiconductors MX, as observed for of the group I elements e.g. in CdTe, require the following pre-requisites with regard to host material and dopant: i) The host crystal exhibits a significant deviation from stoichiometry $\Delta C$ enabling both, M- and X-excess, as well. In the simplest case only defects in the M-sublattice contribute yielding $\Delta C = [M_i] - [V_M]$. ii) The intrinsic point defects $M_i$ and $V_M$ are shallow donors and acceptors, respectively. iii) The initial value of $\Delta C$ is negative, i.e. the crystal exhibits X-excess. iv) The value of $\Delta C$ becomes positive upon annealing under external vapor pressure of the M-component. v) At diffusion temperature, the dopant is incorporated as charged impurity at interstitial lattice sites and is highly mobile.

The consequence of conditions i) to iv) is the formation of $p$-$n$-transitions inside of the crystal at depths that depend on the diffusion conditions and the initial value of $\Delta C$. That is why the initially X-excess causes $p$-type and the final M-excess $n$-type conductivity. The consequence of condition v) is the equilibration of the dopant with the crystal within a time typically shorter than the diffusion time. In addition, due to the charge of the dopant its profile maps the difference of the Fermi-level to mid-gap position across the crystal.

The conditions listed above are the result of a model that describes quantitatively the diffusion profiles observed for the group I dopants in CdTe [3,4]. This model will be presented and other unusual diffusion phenomena will be discussed that are observable if metal layers are evaporated onto the surface of the crystal before annealing.

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ZnO layers, bulk crystals and also nanostructures frequently show an emission band at 3.31 eV in low temperature photoluminescence (PL) measurements, which at room temperature often remains as the dominant spectral PL feature. The band is strong especially after p-type doping with group V elements, but also appears in Al-doped ZnO and even in nominally undoped ZnO layers and nanostructures of limited crystal quality. It has alternatively been ascribed to LO- or TO-phonon replicas of free excitons, acceptor-bound excitons, donor-acceptor transitions, as two-electron satellites, or free-to-bound transitions. Annealing leads to drastic changes in its intensity.

Low-temperature cathodoluminescence measurements with very high spatial resolution and high-resolution transmission electron investigations were carried out on the same epitaxial ZnO samples with unusual layer orientation. These allow to correlate this emission unambiguously with c-plane stacking faults. The emission is due to the recombination of a free electron with a hole bound to a relatively shallow acceptor state ≈ 130 meV above the valence band edge. Locally, these acceptor states occur in concentrations of up to some 10^{18} cm^{-3}, and thus lead to strong two-dimensional perturbations of the free carrier concentration. This has severe implications for the conductivity of layers and nanostructures in general, and on the interpretation of Hall and luminescence data in particular.
E-beam pumped lasers based on II-VI compound nanostructures from the visible to UVA

M. D. Tiberi\textsuperscript{1}, V.I. Kozlovsky\textsuperscript{2}, P.I. Kuznetsov\textsuperscript{3}
\textsuperscript{1}Principia LightWorks Inc., CA, US
\textsuperscript{2}P. N. Lebedev Physical Institute, 119991 Moscow, Russia
\textsuperscript{3}Kotel’nikov Institute of Radio Engineering and Electronics, 141120 Fryzino, Russia

To date, visible lasers as light sources for display applications utilize second harmonic generation with infrared semiconductor lasers as a pump source [1,2]. In contrast, electron beam pumped vertical-cavity surface-emitting lasers (eVCSEL) based on wide band gap II-VI compounds are of interest because of their high-power, ease of manufacturing and low costs. Efforts are underway for green, blue and UVA semiconductor lasers. In this work, we present the latest results achieved in these areas.

Veeco metal-organic vapour phase epitaxy (MOVPE) reactors are used as they are suitable for high volume production. Blue laser nanostructures have been demonstrated with up to 8 watts of output power. A typical structure consists of 20-25 ZnSe quantum wells (QW) of 8 nm in thickness with a small addition of Cd, Mg and S. These QWs are separated by ZnMgSSe barriers layer closely lattice matched to the GaAs substrate.

A similar design is used for UVA ZnSSe/ZnMgS MQW devices. Room temperature lasing was achieved with structures containing 30 QWs at 376 nm. Lasing at 365 nm was also demonstrated with a bulk ZnMgSSe epilayer matched to GaP with an output power of 1 watt at room temperature. Optimization of growth conditions are continuing for a goal of 10 watts at 365 nm and further yield improvements in blue and green devices.

Surface Plasmon-Enhanced Light-Emitting Diodes

Min-Ki Kwon, Chu-Young Cho, Baek-Hyun Kim, Seong-Ju Park,
Department of Materials Science and Engineering
Gwangju Institute of Science and Technology
Gwangju 500-712, Republic of Korea

Surface plasmons (SPs) have attracted much attention because optical properties can be greatly enhanced by coupling between SPs and the multiple quantum wells (MQWs) in light-emitting diodes (LEDs). We demonstrate the SP enhanced InGaN/GaN MQW blue LED with an Ag nanoparticle layer located underneath the MQWs. An enhancement of 32.2% of optical output power of the LED was observed at an input current of 100 mA. The time resolved photoluminescence (PL) result showed that the PL decay time of the LED with Ag nanoparticles was significantly decreased compared to that of the LED without Ag nanoparticles, indicating that the spontaneous emission rate was increased by the energy transfer between the QW light emitter and the SP of Ag nanoparticle. This result shows that the Ag nanoparticles can be used to greatly increase the internal quantum efficiency of InGaN/GaN MQW blue LED through the coupling of excitons in MQWs and SPs in Ag nanoparticles.

We also demonstrate the surface plasmon enhanced blue LEDs using Ag nanoparticles above the MQWs, which are embedded in $p$-GaN. A large increase in light output power of 48% was achieved with Ag nanoparticles at an injection current of 20 mA due to the improved internal quantum efficiency of LEDs. The enhancement ratio was dependent on the density of Ag nanoparticles. This improvement was attributed to the coupling between MQWs and SPs at the Ag nanoparticles in $p$-GaN.

It is also demonstrated that the electroluminescence (EL) intensity of Si quantum dot (QD) LEDs with Ag particles can be enhanced by 434% relative to a Si QD LED without an Ag layer. The large EL enhancement was attributed to an increase of internal quantum efficiency as a result of Si QD-SP coupling and increased injection efficiency through improved carrier tunneling into Si QDs.

These results indicate that the internal quantum efficiency of LEDs can be remarkably increased by coupling of excitons in quantum wells and quantum dots with SPs in metal nanoparticles.

1 Present address: Department of Electrical and Computer Engineering, University of California Davis, USA
2 Present address: Department of Material Science Engineering, Carnegie Mellon University, USA
Threshold behaviour of green vertical-cavity surface-emitting lasers containing quantum dots or quantum wells

C. Kruse1,*, R. Retzlaff1, M. Seyfried2, K. Sebald2, J. Kalden2, J. Gutowski2, J. Wiersig4, F. Jahnke3 and D. Hommel1

1Semiconductor Epitaxy and 2Semiconductor Optics, Institute of Solid State Physics, 3Institute of Theoretical Physics, University of Bremen, Otto-Hahn-Allee 1, 28359 Bremen, Germany
4Institute of Theoretical Physics, Condensed Matter I, University of Magdeburg, FNW/ITP PF 4120, 39016 Magdeburg, Germany

Vertical-cavity surface-emitting laser (VCSEL) structures for the blue-green spectral region using distributed Bragg reflectors (DBRs) made of ZnSSe as the high refractive index material and MgS/Zn(Cd)Se superlattices as the low index material have been realized. The threshold behaviour and lasing dynamics of both quantum well (QW) VCSELs and quantum dot (QD) VCSELs will be discussed and compared. They show Q-factors of 3500 when they contain QWs as the active region and values up to 7800 when QDs are embedded. Single-mode stimulated emission at a wavelength of 510 nm in monolithic VCSEL micropillars containing QWs under optical excitation at 280 K has been observed [1]. Calculations reveal the influence of polariton coupling and the dynamic detuning of the gain maximum to the cavity modes on the spectral characteristics of the VCSEL emission. In accordance with theory, we find a systematic decrease in threshold excitation power for decreasing pillar diameter as a combined effect of reduced active area and a reduction of the mode volume in the microcavities.

These findings are compared with threshold measurements of VCSELs containing QD stacks as the active region. In order to optimize the properties of the QD stacks for lasing operation, several reference samples without vertical resonator have been fabricated. The stacks consist of one to five CdSe QD sheets symmetrically sandwiched between ZnSSe barriers and are completed by two thin MgS layers on top and bottom of the stack for an improved carrier confinement at room temperature (RT). Sulfur contents ranging from 23% to 45% for the ZnSSe strain compensating barriers between the compressively strained CdSe QD sheets have been investigated. It turned out that the stacks with the highest S content show the highest integrated photoluminescence intensity at RT (maximum at a wavelength of 545 nm, i.e. 2.275 eV). According to reciprocal space maps measured using high-resolution X-ray diffraction (HRXRD) these structures remain fully strained even at this high S content. When the number of QD sheets within the stack is increased from one to five, a threefold enhancement of the PL intensity at RT is observed, while the full width at half maximum (FWHM) remains almost constant at a value of 150 meV ± 5 meV. This is an indication for the homogeneous growth of the QD sheets throughout the structure. These QD stacks are then integrated into vertical resonators as in case of QWs and structured into micropillars of different diameter using a focused ion beam (FIB).


*e-mail: ckruse@ifp.uni-bremen.de
Green to yellow light emitters with II-VI semiconductors

K. Kishino and I. Nomura
Department of Engineering and Applied Sciences, Sophia University
7-1 Kioi-cho, Chiyoda-ku, Tokyo, 102-8554, Japan

II-VI semiconductors are suitable for realizing middle-visible-range (yellow to green) light emitters [1]. Blue-green ZnCdSe/MgZnSSe II-VI laser diodes on GaAs substrates had been once extensively investigated, but the device lifetime was insufficiently achieved, approximately 400h [2]. To meet this situation, with replacing the substrate from GaAs to InP, other II-VI semiconductors such as MgZnCdSe [3,4], MgZnSeTe [5], BeZnTe [6,1], and BeZnSeTe [7,8] were developed. The bandgap energy of MgSe/Zn0.48Cd0.52Se short-period superlattices (SLs), utilized for n-cladding layers [1,8], is linearly changed with the layer-thickness ratio from 2.1 to 3.8 eV, interpolating between MgSe and ZnCdSe bandgaps; MgSe/Be0.4Zn0.6Te SLs were applied for p-cladding layers [1,8], because of the wide bandgap (2.8 eV) and high p-doping property of BeZnTe [6]. BeZnSeTe lattice-matching to InP substrates, whose bandgap covers from 2.1 to 2.8 eV (i.e. from orange to blue) [7], is successfully utilized for the active layer of yellow-green emitters [7,8], because it includes high-covalency BeSe and BeTe of high bond energy [9] in the components. Beryllium containing II–VI compounds was expected to contribute to lengthening of the device lifetime [10]. In fact yellow/green LEDs with BeZnSeTe active layers have been fabricated, demonstrating a long lifetime of over 5000 h [8]. In this talk, the II-VI semiconductors on InP for green to yellow light emitters are discussed, describing about our recent activities on green BeZnSeTe-based LEDs and photo-pumped green lasing emission of BeZnSeTe/(BeZnTe/MgZnSe) double-hetero (DH) structures.

The BeZnSeTe-based LEDs, which consisted of a 10nm-thick BeZnSeTe QW active layer sandwiched by MgSe/BeZnSeTe superlattice (SL) barrier layers, Cl-doped MgSe/ZnCdSe SL n-cladding, and N-doped MgSe/BeZnSeTe SL p-cladding layers, were fabricated on InP substrates by MBE, emitting a pure green light of around 537 nm in wavelength. Aging tests of the devices under DC biased conditions demonstrated a long lifetime (4800 h) without any rapid or catastrophic degradation, which proved a high reliability of BeZnSeTe-based light emitters. Photo-pumped lasing characteristics of the BeZnSeTe DH structures, which consisted of a 100-nm thick BeZnSeTe active layer sandwiched between upper and lower MgSe/BeZnSeTe SL cladding layers, were investigated. The elemental composition of the BeZnSeTe was controlled for green to yellow lasing emissions (538-570 nm in wavelength) and the threshold excitation power densities (Pth) as low as 25-43 kW/cm² were obtained. The samples were excited using frequency tripled Nd:YAG laser light (355 nm) at room temperature. Temperature characteristics of the Pth were evaluated in the temperature range from 20 to 80 °C, observing increase in Pth from 36 to 56 kW/cm². From the increase, the characteristics temperature of threshold (T₀) was estimated to be 140 K. These experimental results prove possibility of BeZnSeTe as an active layer of green LDs.

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MBE grown HgCdTe as a material for megapixel infrared devices


Institute of Semiconductor Physics of the Siberian Branch of the RAS, Russia, 630090, Novosibirsk, Lavrentiev avenue 13.

HgCdTe (MCT) wafers for manufacturing megapixel infrared devices should have a large area with a given composition and high lateral uniformity of the composition. MBE allows one to create such material. Presence of the built-in test equipment for MCT composition measurement, such as ellipsometer, allows one to control precisely and change an epitaxial film composition during growth that creates the non-limiting possibilities for optimisation of photosensitive structures and fabrication of devices with the complicated architecture, such as two-colour photodetectors. MBE can use substrates from various materials, including low-cost, large-area silicon wafers.

There is a problem of In bumps breaking in megapixel devices working at low temperatures because of difference of thermal expansion coefficients between the silicon read out integrated circuit and substrate used for MCT growth. This sets a limit on the format of multielement photodetectors. This problem may be solved by using silicon substrates. The most radical solution - growing MCT epitaxial islands in the windows on the surface of the read out integrated circuit fabricated on a silicon wafer. The use of the substrates with (013) orientation simplifies epitaxy of A2B6 compounds on silicon due to high step density on this surface.

The low growth temperature reduces the capturing of background impurities. As a result there is low level of background doping and high lifetimes of minority carriers in MBE MCT of n-type conductivity. On the MCT growth surface during MBE there is an adsorbed layer of tellurium. The MCT growth conditions used at MBE lead to p-type conductivity material due to formation of vacancies in a metal sublattice. MCT film maintains p-type conductivity when it is capped with a CdTe layer at the end of the growth. MCT films go to n-type conductivity during cool-down in a mercury vapor flow. The background donor in MBE MCT most likely is antisite tellurium. The donor concentration in MCT films increases as the cracking temperature of tellurium flow is increased. The low growing temperature provides non-equilibrium capture of the tellurium which occurs on MCT growth surface. Doping by indium does not call difficulties even at low growth temperatures at MBE MCT whereas doping by arsenic (acceptor impurity) must be followed by high temperature annealing after growth for carrier activation.

The quality of MCT films grown by MBE has reached the level required for fabrication of high performance infrared detectors. It is proved by observation of quantum effects and high mobility of 2D electrons in MCT nanostructures.
At present the main challenge in the development of a wide range of ZnO based devices, first of all LEDs, is to obtain a reliable and reproducible p-type conductivity of ZnO. In the last time this challenge has promoted attempts to realize hybrid structures comprising n-ZnO and another semiconductor which can be easier converted into p-type. The obvious and easiest approach is to manufacture ZnO with GaN heterostructures aiming at the fabrication of hybrid LEDs. In the present paper we give a critical review on the problems as well as potential benefits from different concepts of a combination of ZnO and GaN in a single device. Our recent results on highly efficient ZnO-InGaN hybrid LEDs using an inverted LED concept are also presented and discussed. These hybrid LEDs are comparable to conventional (p-side up) InGaN LEDs with an external quantum efficiency of more than 35%.
Hybrid Solar Cells and LEDs based on ZnO-Nanowire Arrays

Apurba Dev, 1 Jan-Peter Richters, 1 Abdelhamid Elshaer, 1 Siegfried R. Waldvogel, 2 Julia Waltermann, 3 Wolfgang Schade, 3 and Tobias Voss 1

1 Institute of Solid State Physics, University of Bremen, Germany
2 Kekulé-Institute for Organic Chemistry and Biochemistry, University of Bonn, Germany
3 Institute for Physics and Physical Technologies, Clausthal University of Technology, Germany

Due to their large surface-to-volume ratio and high crystalline quality, ZnO nanowires are promising candidates for applications in nanoscale sensing technology and optoelectronics in the blue-UV spectral region. Especially low-temperature grown ZnO nanowires offer interesting properties for the large-scale and low-cost production of environmentally friendly solar cells and light-emitting diodes [1]. When a p-conductive polymer is used to form a hybrid pn-junction, solar cells with efficiencies of a couple of percent have been reported, and UV emission from such a heterojunction has also been observed.

We have employed a wet-chemical synthesis method to fabricate ZnO nanowire arrays on conductive glass substrates with very good homogeneity for areas as large as 1.5 × 1.5 cm². The typical dimensions of the nanowires are about 100 nm in diameter and 2 μm in length. TEM measurements prove the single-crystalline structure of the wires. Photoluminescence measurements (performed at temperatures between T = 4 and 300K) show clear excitonic emission lines which indicate an overall good optical quality, combined with low visible deep-level luminescence. We fabricated ZnO nanowire / PEDOT:PSS compound structures that act as solar cells or light emitting diodes. For these purposes, the PEDOT formulation was modified. This includes the addition of conductivity enhancers based on dimethylsulfoxide or ionic liquids. The polymer/additive mixture was applied as predominantly aqueous solution by air brush technique.

We studied the IV-characteristics of the devices for different polymers and processing parameters and found rectification factors of up to 10⁵ and currents of up to 50 mA/mm². Especially, the annealing time and layer thickness of the polymer layer were found to need precise adjustment to ensure optimized device characteristics. We found that an additional insulating polymer layer (polystyrene) coated directly onto the nanowires helps to improve the device characteristics. This is in agreement with our previous investigations of n-ZnO nanowire/p-silicon light emitting diodes where an insulating silicon dioxide layer between the n-ZnO and the p-Silicon is needed to allow for tunnel injection of holes into the ZnO valence band [2]. We will discuss the relevant mechanisms of the electron transfer between the ZnO nanowire and the p-polymer that allows us to optimize the hybrid LEDs and solar cells.


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Violet-green laser converter based on MBE grown II-VI green lasers with multiple CdSe quantum dot sheets pumped by InGaN laser diode

E.V. Lutsenko¹, I.V. Sedova², A.G. Vainilovich¹, N.P. Tarasuk¹, V.N. Pavlovskii¹, G.P. Yablonskii¹, S.V. Sorokin², S.V. Gronin², P.S. Kop'ev², S.V. Ivanov²

¹Stepanov Institute of Physics of NASB, Independence ave. 68, 220072 Minsk, Belarus
²Ioffe Physical Technical Institute, Polytekhnicheskaya 26, St. Petersburg 194021, Russia

The CdSe quantum dot laser heterostructures grown by molecular beam epitaxy (MBE) on GaAs(100) substrates and optically pumped by an InGaN violet laser diode (LD), integrated in a single device [1], can serve as compact green lasers for numerous applications such as projection television, short-range optical communication via plastic fibers, lidars etc.

An active region of the green MBE grown laser structure used for the violet-to-green conversion experiments include five 2-nm-ZnSe quantum wells (QW) each centered with CdSe quantum dot (QD) sheet of 2.5 monolayer in a nominal thickness. The QWs are separated by 5-nm-thick Zn(S,Se) barriers. The active region is placed asymmetrically in a 200-nm-thick ZnS₀.₁₅Se₀.₈₅/ZnSe superlattice waveguide to provide its maximum overlap with the fundamental mode of electromagnetic field. The waveguide is embedded between the bottom and top Zn₀.₈₈Mg₀.₁₂S₀.₁₆Se₀.₈₄ cladding layers of 1 μm and 20 nm in a thickness, respectively. The InGaN/GaN violet laser diode (λ=416 nm, τₚ=50 ns, Pₚulseₘₐₓ=2 W) was used for optical pumping of the green laser structure. The emission of the LD was focused into a narrow stripe on the green laser cavity by a system comprising one cylindrical and two spherical lenses.

The green laser chips with various cavity lengths were studied, the laser with the cavity length of 139 nm showing best results. Under the pumping enhancement, transformation of edge photoluminescence (PL) spectrum was observed for this sample. A mode structure appeared at excitation power of 0.45W, evidencing reduction of absorption in the CdSe QDs. At the pumping power Pₚₑₓc=0.6 W, clear threshold behaviour of the II-VI laser heterostructure was detected, which was displayed in the sharp intensity increase and spectrum narrowing with the occurrence of a regular longitudinal mode structure. The laser spectrum had a maximum at λₗₐₛₗ=523 nm, and the laser emission was TE-polarized. A single maximum in the far-field pattern of the laser emission was observed, evidencing laser action on the fundamental transversal mode. Dependence of the green laser pulse power on the excitation power also shows the laser threshold at Pₑₓc exceeding 0.6-0.7 W. The emission power reached the maximum value of 65 mW at Pₑₓc=1.3 W. The laser external efficiency and external quantum efficiency were as large as 5 % and 8 %, respectively, at 1.3 W of pumping at room temperature.

Summarizing, using of the high quality green II-VI laser structure with five electronically-coupled QD sheets in the active region has allowed one to ensure homogeneous pumping of all the CdSe QDs and to enhance optical confinement factor, that finally has resulted in reduction of the laser threshold and enhancement of the quantum efficiency and optical gain. This, in turn, has allowed us to increase the pumping power well above the II-VI laser threshold that yield a 8 times increase in the green emission pulse output power and the conversion quantum efficiency from violet to green in comparison with the results reported in Ref. [1].

Exciton-polariton is a quasi-particle formed by the coupling of photon and exciton in solid-state environment. One of the most important systems for realizing polariton in a strong coupling regime is semiconductor microcavity, in which the optical cavity modes can be tailored or tuned to resonant in energies with excitons. It has been predicted that the effective mass of exciton polariton with boson nature can be $10^4$ times of that of the free electron, thus the spontaneous bose coherence of polaritons are expected to occur at much higher temperature. From the point of view of application, the buildup of spontaneous coherent polariton state would trigger an inversionless lasing of so-called polariton laser. Unlike the conventional laser, the polariton laser has no threshold limited. Significant progresses on the bose coherent condensation and the polariton lasing have been made in 2-dimensional planar cavities [1-3]. One of the most exciting achievements is the realization of room temperature polariton lasing in a GaN planar microcavity [2]. Recently, polariton behavior in cavities with reduced dimensionality is attracting more attention [4, 5], since it is expected that the reduced dimensionality will greatly lift the wave vector conservation selection rules in polariton scattering, and it is an effective way to realize polariton quantum degeneracy under nonresonant pumping [4]. On the other hand, as one of the most commonly adopted cavity types for photon confinement, a whispering gallery (WG) resonator where photons are confined two-dimensionally has in deed its advantage for the light-matter interaction studies [5]. The overlap between exciton and cavity mode is greatly enhanced and can be close to unity due to the body of WG microcavity is itself an active medium for excitonic emission. However, despite the above advantages, polariton behavior in WG cavities is less understood, though it is of fundamental importance [5]. Moreover, tunability in both exciton-photon coupling strength and emission wavelength of a polariton laser out of a planar cavity remains difficult. In this talk, we demonstrate a tunable WG resonator for polaritons basing on a taperd ZnO nano-rod with a hexagonal cross-section. Comprehensive polariton behaviors, including the one-dimensional polariton dispersion, polariton wave-guide and polariton lasing are discussed. Our work demonstrates that ZnO WG microcavity is an excellent system for developing polariton-based devices operated at room temperature.

A new type of laser is realized in ZnO nanotapers, in which the nanotaper acts as a distributed mirror to form a laser cavity. Note that such laser cavity has never been realized so far. This laser is characterized by virtually point light source with nearly omni-directional light emission.

Three-dimensional (3D) / two-dimensional (2D) finite-difference time-domain (FDTD) method is applied to analyze the electromagnetic wave in ZnO nanotapers. The analysis on a traveling wave clearly indicates that the tapered region acts as a distributed mirror and that the maximum reflectance occurs at around the nanotaper region with its diameter of the taper being close to the wavelength of the electromagnetic wave. The analysis also shows the formation of standing wave inside the nanotaper in the case of a continuous wave, thus demonstrating that the nanotaper acts as a laser cavity. The analysis further shows that the nanotaper laser is characterized by virtually point light source with nearly omni-directional light emission, which are experimentally demonstrated as well.

Lasing emissions from optically pumped ZnO nanotaper ensembles and single nanotapers are observed at around the wavelength of 380 nm. The dependence of the emission intensity on pumping intensity shows a threshold behavior. As the pumping intensity exceeds the threshold intensity, the emission spectrum shows multiple peaks due to longitudinal mode. The detailed analysis of the emission spectra suggests that the lasing emission is associated with the exciton-exciton scattering process. Strong lasing emission is observed even in the direction normal to the nanotaper direction, which is consistent with the omni-directional lasing behaviors as predicted in the FDTD simulation.

The novel nanotaper lasers can be used to the various laser devices including optical tweezers, laser probes, and mode converters.
Room Temperature Whispering-Gallery Exciton-Polaritons in ZnO Microwires

A. Trichet\textsuperscript{a}, S. Liaoxin\textsuperscript{b}, G. Pavlović\textsuperscript{c}, N. A. Gippius\textsuperscript{c,d}, G. Malpuech\textsuperscript{c}, Z. Chen\textsuperscript{b}, M. Richard\textsuperscript{d} and L. S. Danga

\textsuperscript{a}NPSC, CEA/CNRS/UJF, Inst. Néel, 25 Avenue des Martyrs, 38042 Grenoble, France.
\textsuperscript{b}Surface Physics Laboratory, Fudan University, 200433 Shanghai, China.
\textsuperscript{c}LASMEA, CNRS/University Blaise Pascal, 24 Av. des Landais, 63177 Aubière, France.
\textsuperscript{d}A.M. Prokhorov General Physics Institute RAS, 119991 Moscow, Russia

Nonlinear phenomena in semiconductor microcavities have shown very rich physics in recent years [1-2]. Novel systems and new geometries are now fabricated in order to study the polariton physics of dimensionality D<2 and at higher temperature. Results obtained in polariton mesas and micropillars in which polaritons behave as a 0D bosonic particles are very promising, featuring a discrete spectrum and bosonic stimulation [3]. Although poorly explored, a very interesting situation is the case of the one-dimensional confinement. A very promising system for room temperature polariton studies are bulk ZnO microwires, which can be obtained by various self-organized growth techniques. These wires have two major advantages over other systems: well confined whispering gallery modes (WGMs) can be sustained by total internal reflection on the wire facets. The second point is the very high oscillator strength and very strong binding energy of the ZnO exciton (60meV), which makes it stable at room temperature and high density. Signatures of a very strong coupling with WGMs at room temperature have been recently reported in this system [6].

In this work, we present experimental results obtained at room temperature showing a strong coupling regime of unprecedented quality in this energy range and temperature, in a single ZnO microrod. We also demonstrate the one-D character of the exciton-polaritons using angle resolved spectroscopy. The detailed theoretical consideration of one-dimensional exciton-polaritons in the zinc oxide (ZnO) ZnO microwires is perfomed as well. We solve Maxwell’s equations taking into account the anisotropy of the background dielectric permittivity and of the excitonic response of the ZnO wire. At $k_z = 0$ the optical modes are purely TE (electric field in the plane of the wire) or TM (electrical field along the axis of the wire). The TE modes couples mainly to A and B excitons whereas the TM mode couples to the C excitons which has the strongest oscillator strength. This differs from the case of a planar cavity and results in huge Rabi Splitting of 250 meV which is a record value for a semiconductor structures. Increasing $k_z$, the optical modes mix and contain both TE and TM polarized components. The complicated polariton dispersions and polarization properties which are measured are well described by these calculations.

References

Nanolasers from ZnO nanorods as natural resonance cavities

G. Visimberga\textsuperscript{1}, E.E. Yakimov\textsuperscript{2}, A.N. Redkin\textsuperscript{2}, A.N. Gruzintsev\textsuperscript{2}, V.T. Volkov\textsuperscript{2}, S. Romanov\textsuperscript{1}, G.A. Emelchenko\textsuperscript{3}

\textsuperscript{1}Tyndall National Institute University College Cork, Ireland
\textsuperscript{2}Institute of Microelectronics Technology, Russian Academy of Sciences, 142432 Chernogolovka, Russia
\textsuperscript{3}Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Russia

Zinc oxide nanowires show remarkable optical properties such as wave guiding and lasing and are promising building blocks for novel miniaturized optical and optoelectronic devices. We studied the effect of metal coating on the optical properties of free-standing ZnO nanowire lasers, which is expected to enhance their performances in terms of a reduced excitation power threshold. Catalyst-free Chemical Vapor Deposition (CVD) was employed to synthesize vertically aligned single crystal ZnO nanowires with fairly developed hexagonal crystal faceting. As suggested by electron microscopy data, the grown ZnO is an ensemble of vertical nanorods of different length (the length varied from 1 to 20 \textmu m, depending on the position of the silicon substrate in the reactor), with mean diameter of individual crystallites of about 0.05-0.5 \textmu m and fairly developed hexagonal crystal faceting. The nanorods were n-type, with a rather low resistivity of 10 \textOmega cm. The nanowire array was coated by an aluminum thin layer (50 nm) by electron beam sputtering, thus forming a high-reflectance mirror facet at one end of each one. After removal from the growth substrate by sonication, a second mirror facet was obtained as an effect of the cleavage along the (0001) crystallographic plane, thus leading to an enhanced axial Fabry-Perot (FP) resonator.

Arrays of hexagonal ZnO nanorods with parallel orientation forming a quasi-two-dimensional structure or radial orientation producing cylindrical microstructures are grown in a controlled manner. Multiple sharp lasing peaks were realized from single nanorods constituting these microstructures. The lasing peaks display successive onset and saturation with increasing excitation power density, and fit well the expected resonance spectrum of guided modes in hexagonal nanorods. Several lasing nanorods with diameter below 150 nm and length 2-40 \textmu m were investigated. Laser thresholds were found to range from 30 to 60 kW/cm\textsuperscript{2}, one order of magnitude lower than in the uncoated nanowires. The spectral distribution of lasing modes differed from the expected Fabry-Perot interference pattern as an effect of the accidental lateral Al\textsubscript{2}O\textsubscript{3} coating. This modifies the optical resonator introducing higher order modes with a reduced overlap with the active region.

Investigations of emission spectra and images at the scanning cathodoluminescence of the ZnO nanorods with two mirrors on the ends were carried out at temperature 10K. The emission peaks, related to the recombination of the bound excitons and of the band-edge emission in the violet spectral region, have been detected. The space picture of the local photon modes intensity of the nanorod has been determined for different wavelengths. The new method of visualization of bound optical modes in the laser nano- and microresonators was proposed. The produced structures are expected to find many applications in integrated nanoscale optoelectronics, photonics, and sensor technologies.
Embedding quantum dots (QDs) into microcavities (MCs) promises to provide efficient single photon sources; the most important enabler for quantum key distribution (quantum cryptography) and quantum information processing. To realize quantum optical devices operating at elevated temperatures, CdSe QDs are utilized because they are known for the high temperature stability of their emission. A major problem for self-organized grown QDs is, however, the random spatial and spectral matching of the individual QD position and emission energy with respect to the electric field maximum and spectral position of the cavity mode, respectively. Currently, strong efforts aim at a full experimental control over the coupling of electronic and photonic states for MCs.

The monolithic II-VI based MC samples were grown by molecular beam epitaxy. A ZnSSe λ-cavity contains either three ZnCdSSe quantum wells or a single sheet of CdSe/ZnSe QDs embedded into additional MgS barriers. Distributed Bragg reflectors (DBRs) made of ZnSSe as high-index and MgS/ZnCdSe short-period superlattices as low-index layers are used as the cavity mirrors. Pillar MCs with diameters between 500nm and 2.5µm have been prepared from the epitaxial samples by use of focused-ion-beam milling. A focused laser beam of a frequency doubled Ti:sapphire laser was used for characterization (at low power) as well as for laser annealing (at high power) of the semiconductor structures which are placed in the cryostat of a microphotoluminescence setup.

The optical confinement in the MCs results in the appearance of discrete modes which are observed in the energy spectra. From the spectral width of the modes quality factors of up to 7860 could be determined. To realize the spectral matching between the QD emission and the resonator mode, different methods were used. On one hand, by increasing the temperature the ultrasharp emission lines of single QDs could be successively tuned on resonance with modes of the cavity, and their photoluminescence intensity is tremendously enhanced (this was possible up to 165K). This points to a considerable increase of the collection efficiency in the case of resonance. On the other hand, the spectral tuning of the modes on QD emission lines has been realized by a targeted fine tuning of the diameters of semiconductor pillar MCs by post-fabrication FIB milling. Due to the very sensitive dependence of the spectral position of the modes on the cavity diameter these are precisely blue shifted (2.3meV) by a reduction of the pillar diameter with an accuracy of well below 100nm. Thus, we could tune the MC modes to match the emission energy of individual QDs at a certain temperature.

To create QD-like carrier confinement centres at the defined region of the MC, the QW-based sample was treated with laser at high excitation powers. This resulted in the appearance of very sharp emission lines in the region of the resonator modes and the simultaneous reduction of the QW related emission intensity. This finding may be explained by local heating of the MC at the field maximum of the resonator mode leading to a thermal reorganisation of the Cd concentration in the QW layer. This laser annealing can be used for either creation or modification of already existing QDs. The presented methods are steps towards the full experimental control over the coupling of electronic and photonic states for QD-based MCs to realize efficient single photon emitters in future.
Electromagnetic response of thin layers of metamaterials

S.G. Tikhodeev 1 and N.A. Gippius 1,2

1 A. M. Prokhorov General Physics Institute RAS, Vavilova 38, 119991, Moscow, Russia
2 LASMEA, UMR 6602 CNRS, Universite Blaise Pascal, Aubiere, France

Recently, the electromagnetic response of short-period metallic-dielectric photonic crystals, metamaterials, and the possibilities they open to control the light have attracted a lot of interest. The problem of correct theoretical description of effective electromagnetic response of metamaterials becomes very important. The generalized retrieval procedure of the effective electromagnetic response (including diamagnetism, chirality and bi-anysotropy) of thin metamaterial layers, based on the scattering matrix method will be discussed and illustrated on examples of several typical metamaterial structures. As a consequence of nonlocality of the metamaterials, especially in the vicinity of the resonances, the retrieved response parameters are not the characteristics of the metamaterial only. For example, they change with the metamaterial layer thickness and depend on the outside dielectric environment.
Novel mechanisms of optical second harmonic generation in semiconductors

R. V. Pisarev
Ioffe Physical Technical Institute, Polytekhnicheskaya 26, St. Petersburg 194021, Russia

One of the most interesting features of nonlinear media is generation of vibrations with frequencies different from the frequency of the fundamental optical pump. Among those, second harmonic generation (SHG) being a very symmetry-sensitive process, plays a particularly important role. In this talk we are going to survey recent studies of magnetic-field-induced SHG in several groups of model semiconductors. Strangely enough, until recently there were no detailed spectroscopic studies of SHG at low temperature in applied magnetic fields. We performed such studies in fields up to 10 T at 2 K and higher temperatures. We found that application of a magnetic field induces optical SHG in GaAs [1]. This phenomenon arises from field-induced symmetry breaking causing new optical nonlinearities. A series of narrow SHG lines was observed in the spectral range from 1.52 to 1.77 eV that we attributed to Landau-level quantization of the band energy spectrum. The rotational anisotropy of the SHG signals distinctly differs from that of electric-dipole approximation. Model calculations revealed that nonlinear magneto-optical spatial dispersion that comes together with the electric-dipole term is the dominant mechanism of this nonlinearity.

Basically different mechanisms of optical SHG induced by an external magnetic field were identified experimentally by studying the diluted magnetic semiconductors (Cd,Mn)Te [2]. For paramagnetic compounds the SHG response is governed by spin quantization of electronic states, in contrast with diamagnetic CdTe with its dominant orbital quantization. The mechanisms can be identified by the distinct magnetic field dependence of the SHG intensity which scales with the spin splitting in the paramagnetic case as compared to the $B^2$ dependence in the diamagnetic case. The third group of materials we discuss in this talk is europium-alkali halides EuSe and EuTe [3]. They are magnetic semiconductors with crystallographic and magnetic structures distinctly different from those of GaAs and CdTe. $4f^7$ states of Eu$^{2+}$ ions lie above the $4p^6$ and $5p^6$ states of Te$^{2-}$ ions in EuSe and EuTe, respectively. The conduction band is formed by the $5d$ states of europium. The fundamental absorption band gap is defined by electric-dipole allowed transitions from $4f^7$ states to $4(5)dt_{2g}$ states. Analysis of the electronic structure and selection rules showed that SHG is forbidden in the electric dipole and electric quadrupole approximations. Nevertheless in EuSe and EuTe we observed SHG signals in the presence of an applied magnetic field in the vicinity of the band gap of 2.2-2.4 eV. A particular feature of these compounds is their ability to vary their magnetic structure from antiferromagnetic to ferromagnetic depending on temperature and magnetic field. Detailed study allowed us to come to conclusion that the SHG signals arise due to the ferromagnetic component of the magnetic structure. On the other hand, we could not detect any SHG signals related to the antiferromagnetic component that most probably is due to destructive interference of SHG signals from two equivalent sublattices with antiparallel spin orientation. In addition we detected for the first time magnetic-field-induced third harmonic generation in europium alkali halides in the vicinity of the band gap.

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Ultrafast coherent spectroscopy with strain pulses in semiconductor nanostructures

A.V. Akimov
Ioffe Physical Technical Institute, Polytekhnicheskaya 26, St. Petersburg 194021, Russia

During last decade the methods for generating ultrafast strain pulses and coherent monochromatic THz acoustic waves have been developed. This has opened a new field in solid state physics which is called Ultrafast Acoustics. The present talk is aimed to show how the experimental methods of the ultrafast acoustics are applied to the optical spectroscopy of semiconductor nanostructures. After the short introduction about the basis of ultrafast acoustics, the talk describes the optical experiments [1-3] where the ultrafast strain pulse induces the picosecond energy shift of the resonant optical transitions. As the model excitation the exciton resonance in the semiconductor single quantum well and microcavity strongly coupled to a quantum well is chosen.

For generating the strain pulse a 100 nm thick metal transducer layer was attached to the substrate. This metal film was hit by intense laser pulse and due to thermoelastic effect a strain pulse with duration ~10 ps and amplitude up to $10^{-3}$ was injected into a substrate. This strain pulse travels strongly directed through the crystal towards the nanostructure generating at each momentary position a "nano-earthquake". When the quantum well is hit by this "earthquake", the exciton resonance is shifted on a value up to 10 meV on a ps time scale, as demonstrated by means of optical spectroscopy. At high excitation power formation of the picosecond acoustic solitons with duration ~1 ps can take place.

The effects of the strain pulses are strongly pronounced in the time resolved reflectivity and luminescence spectra. Coherent effects like chirping of the optical transitions and generation of the spectral sidebands are observed.

High-reflectivity distributed Bragg reflectors lattice-matched to ZnTe

W. Pacuski,1,2 C. Kruse,1 S. Figge,1 and D. Hommel1

1 Institute of Solid State Physics, University of Bremen, Postfach 330 440, D-28334 Bremen, Germany
2 Institute of Experimental Physics, University of Warsaw, Hoża 69, PL-00-681 Warszawa, Poland

A distributed Bragg reflector (DBR) is a high quality mirror based on alternating layers with high and low refractive index. Basically a DBR can be made of any transparent materials but it should be made of semiconductor if one needs to combine it with lattice-matched high quality semiconductor heterostructures in order to create monolithic high quality microcavities, lasers or photonic crystals. Moreover, keeping a high quality of the whole structure requires the use of semiconductors with different values of refractive index but with the same lattice parameter. The requirement of lattice matching makes the design and fabrication of those DBRs quite challenging. Successful creation of lattice matched DBRs based on II-VI compounds has been reported so far for three substrates: Cd0.88Zn0.12Te [1], GaAs [2], and InP [3]. We present the first DBR with both high and low refractive index layers lattice matched to ZnTe.

Our DBRs were grown using molecular beam epitaxy (MBE) on a 1 μm thick fully relaxed ZnTe buffer layer deposited on GaAs substrate. The requirements of the lattice matching and of a high refractive index step are fulfilled using a novel method. Instead of using ternary or quaternary compounds, the low refractive index layer is made of a short period triple superlattice based only on the binary compounds ZnTe, MgTe, and MgSe. This is practical for epitaxy, because controlling a layer thickness in the superlattice is much easier than balancing strain by controlling the content. This approach allows us to obtain excellent optical properties: broad stopband and the reflectivity coefficient exceeding 99% for only 15 Bragg pairs.

Characterization of our structures includes in-situ and post-growth optical reflectivity, cross-section imaging using scanning electron microscope (SEM), and reciprocal space mapping using high resolution X-ray diffraction (HRXRD), which confirms pseudomorphic growth of the DBR on ZnTe buffer.

The results are of high interest concerning the realization of optoelectronic devices covering the green to orange spectral range. Furthermore, the integration of Mn-doped CdTe QDs [4,5] into microcavities formed by two high-reflectivity DBRs might pave the way for applications in quantum information science.

MANIPULATING EMISSION OF CdTeSe QUANTUM DOTS EMBEDDED IN SYNTHETIC OPALS

C. Vion1, C. Barthou1, P. Benalloul1, C. Schwob1, L. Coolen1, A.N. Gruzintsev2, G.A. Emelchenko2, W.M. Masalov3, J.-M. Frigerio1, A. Maitre1

1 Institut des NanoSciences de Paris, UMR-CNRS 7588, Universités Pierre et Marie Curie et Denis Diderot, F-75015 Paris, France
2 Institute of Microelectronics Technology and High Purity Materials, Russian Academy of Science, 142432, Chernogolovka, Moscow District, Russia
3 Institute of Solid State Physics, Russian Academy of Science, 142432, Chernogolovka, Moscow District, Russia

Photonic crystals (PCs) in the visible and near infra-red ranges are characterized by a periodic dielectric constant at wavelength scale. As a consequence, the emission of light sources embedded inside PCs can be strongly affected by the band gap such as its propagation with minimal losses, its emission diagram and its life time. Many approaches have been proposed to fabricate 3D periodically modulated dielectric materials. Some of them come from more or less well established microelectronic industry processes such as semiconductor layer-by-layer nanomachining, layer-by-layer direct laser writing, interference lithography using a single diffraction mask, holographic lithography with at least 4 laser beams or two-beam only but with multi-exposure.

One of the most common approaches to prepare 3D PCs takes advantage of the spontaneous self-organisation of spherical colloidal particles. Various self-assembly techniques such as sedimentation, convective or Langmuir-Blodgett ones have been studied as they provide a low cost and relatively easy protocol to obtain artificial opals. SiO2 opals exhibit a pseudo-band gap. Nevertheless the coupling of II-VI nanocrystal emitters in such PCs allows one to recognize and study some basic problems. Large opals have been prepared by the sedimentation method and the size of the balls has been adjusted so that the pseudo-band gap of those PCs lies in the same region than the emission band of CdSe nanocrystals. Diagrams of radiation and the modification of the spontaneous life time of the embedded nanocrystals will be presented and discussed.

We report experimental and theoretical results on photoluminescence of CdTeSe nanocrystals, embedded in silica opaline structure by infiltration of a diluted solution. In comparison to the emission of nanocrystals in an homogeneous medium, strong modification of emission diagrams has been observed. We compare also the modification of the lifetime of embedded nanocrystals inside two opals, one for which the emission of the nanocrystals lies inside in bandgap, and one reference for which the emission is outside the bandgap. We have observed a variation of 10% of the lifetime. Those experimental results are compared to theoretical models, showing good agreement for the emission diagram. The variation of the lifetime could be explained by the different effective index for both opals (5% of lifetime modification) and for 5% by modification of photonic local density of states due to the photonic band gap With a larger index contrast, the photonic bandgap would be larger, and even complete with an inverse opal. In that case, the photonic bandgap influence on the lifetime is expected to be larger and more significant. The insertion of a defect inside opals and localization of nanocrystals inside the crystal are a promising way to control the lifetime of CdTeSe quantum dots in such 3D photonic crystals.
In this contribution we report on the investigation of the strain distribution in ZnMgSe/ZnSe MDs by micro-photoluminescence (μ-PL) and micro-Raman scattering (μ-RS) methods. PL measurements reveal substantially broadened emission lines with a shift to lower energy at the freestanding part, indicating local relaxation in this area. Spatially resolved RS reveals that the frequency of the ZnSe longitudinal optical phonon shifts towards lower frequencies from the supported part to the freestanding part of the micro-disc. The shift of the phonon modes was modelled as a function of the strain distribution and can be explained by the release of strain from the supported part (ZnSe compressively strained on GaAs) to the freestanding part (ZnSe tensile strained on ZnMgSe). Despite the strain relaxation along the radial direction of the MD, the MD is free of extended defects as demonstrated by the absence of the transverse optical phonon lines. These findings indicate that sufficiently high Q-values can be achieved in such MD cavities to facilitate their application in optoelectronic devices.

While micro-disc cavities are applicable as low-threshold lasers with moderate Purcell-Factors, PC membranes allow further increase of the Purcell-Factor due to a reduction of the mode volume to its minimum. In fact, PC-membranes are appropriate to fabricate single-photon-emitters and waveguide structures for integrated optics. ZnSe/ZnMgSe PC structures are promising for highly efficient nano-photonic devices in the wavelengths from the ultraviolet to the green spectral range.

In this context we fabricated ZnSe/ZnMgSe membrane structures and based on our experience with MD cavities, we present measurements of the strain distribution in such membranes by μ-RS scattering and μ-PL. The findings indicate both, defect free release of strain in the freestanding centre of the membrane and efficient PL emission. These preliminary investigations demonstrate a certain step towards the fabrication of PC membranes for single-photon emitters and integrated optical waveguide systems with II-VI compound semiconductors.

Semiconductor whispering gallery (WG) resonators have attracted much attention due to their microscopic size, high quality factor Q, and low lasing threshold power.\textsuperscript{1,2} In a semiconductor WG resonator, the nanostructure itself functions as both the gain medium and the optical microcavity. Up to now, WG resonators with different geometries, such as rings, microspheres, cylinders, nanonails, and nanowires with hexagonal cross section, have been developed. Among them, nanowire with hexagonal cross section has attracted particular interests due to their better optical properties and wider range potential applications. However, the investigation is so far limited on ZnO hexagonal resonators due to the difficulty in synthesizing high quality microcavities with other materials.\textsuperscript{4-6} In this paper, we report the synthesis of indium oxide nanowire and the WG resonator characteristics of the wires. The single-crystal In\textsubscript{2}O\textsubscript{3} nanowires with a hexagonal cross section were successfully fabricated by an in-situ thermal oxidation method. SEM and TEM studies have demonstrated that the hexagonal single-crystalline In\textsubscript{2}O\textsubscript{3} nanowires with very smooth surfaces and highly uniform morphology can be used as an optical cavity. WG modes (WGMs) were directly observed by measuring micro-photoluminescence in the visible spectral range at room temperature. We find that both TM ($E_{\parallel}$c-axis) and TE ($E_{\perp}$c-axis) polarizations can form WGMs in the hexagonal In\textsubscript{2}O\textsubscript{3} cavities. The WGMs peak positions can be calculated using a simple plane wave interference model. The results indicate that the synthesized In\textsubscript{2}O\textsubscript{3} hexagonal nanowires can be competitive candidate for the application of WG optical microcavity in the visible light spectral region.

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Picosecond kinetics of the electron-hole layers formation in wide-bandgap II-VI type-II heterostructures

I. I. Tartakovskii, A. A. Maksimov, E. V. Filatov, and S. V. Zaitsev,
Institute of Solid State Physics, Russian Academy of Sciences,
Chernogolovka, Moscow region, 142432 Russia

D. R. Yakovlev
Experimentelle Physik II, University of Dortmund, D-44227, Dortmund, Germany

Ioffe Physicotechnical Institute, Russian Academy of Sciences, Politekhnicheskaya ul.
26, St. Petersburg, 194021 Russia

A. Waag
Institute of Semiconductor Technology, Braunschweig Technical University, D-38106,
Braunschweig, Germany

The energy relaxation of photoexcited carriers in type-II heterostructures is accompanied by the fast spatial interlayer separation of electrons and holes. We report the results on a detailed study of the picosecond kinetics of the electron-hole layers formation in type-II ZnSe/BeTe heterostructures used as an example with a high localizing potential for both electrons in the ZnSe layer (~2.2 eV) and holes (~0.8 eV), whose energy minimum is located in the BeTe layer. Due to the great difference in the bandgaps of ZnSe and BeTe electron–hole pairs are generated upon photoexcitation only in the ZnSe layer. Photoexcited carrier relaxation in the course of the formation of spatially separated layers of electrons and holes in type-II ZnSe/BeTe heterostructures has been studied based on a high time resolution investigation of fast photoluminescence kinetics. The existence of photoexcited holes in the lowest above-barrier level results in a spatially direct optical transition (DT) band in the photoluminescence spectrum, that is the radiative recombination of photoexcited electrons and holes in the same ZnSe layer. The decay times \( \tau \) of the DT band have been measured in structures with different ZnSe layer thicknesses \( d \) (\( \tau = 2.5, 7.5, \) and 18 \( \text{ps} \) for \( d = 10, 15, \) and 20 \( \text{nm} \), respectively). It is shown that at low levels of laser pumping the increase in the time \( \tau \) can be explained by the fact that the escape rate of photoexcited holes from the lowest above-barrier level in the ZnSe layer into the BeTe layer decreases as the thickness of the ZnSe layer increases.

A considerable slowing down of the luminescence kinetics of the direct optical transitions has been observed in ZnSe/BeTe type-II heterostructures under high-density optical pumping by femtosecond laser pulses. At the highest photoexcited carrier density \( n \sim 10^{18} \text{cm}^{-2} \) the decay times of the DT band in the photoluminescence spectrum reach the values of \( \tau = 35, 75 \) and 200 \( \text{ps} \) for thicknesses \( d = 10, 15, \) and 20 \( \text{nm} \), respectively. The effect is attributed to the potential barrier that appears due to the strong band bending at high densities of spatially separated photoexcited carriers and forms a metastable above-barrier hole state in the ZnSe layer. This yields a longer energy relaxation time of the holes migrating to the adjacent BeTe layer. In the structures with the ZnSe layer thickness \( d > 15 \text{ nm} \) the additional slowing down of the decay time \( \tau \) is determined by the decrease of the of electrons and holes wave functions overlapping in the ZnSe layer which is due to the band bending as well. The experimental results agree well with the numerical calculations.
Excitonic polaritons in transverse magnetic fields

D.K. Loginov
V.A. Fock Institute of Physics, St. Petersburg State University, St. Petersburg
198904, Russia
V.P. Kohereshko
A.F. Ioffe Physico-Technical Institute RAS, 194021 St. Petersburg, Russia
L. Besombes, H. Mariette
Laboratoire de Spectrométrie Physique, Université Joseph Fourier de Grenoble,
France
Yu. Efimov, S. Eliseev, Yu. Dolgikh
Institute of Physics, St. Petersburg State University, St. Petersburg, Russia.
J.J. Davies, D. Wolverson
Department of Physics, University of Bath, Bath BA2 7AY, UK

Reflectivity spectra in magnetic fields from heterostructures with wide quantum well (QW) CdTe/CdZnTe and GaAs/AlGaAs were studied. The QWs were grown by MBE in [100] direction and have thickness of 66 nm for CdTe and 260 nm for GaAs. Reflectivity spectra were measured at normal incidence in magnetic field in Voigt geometry $B \perp K$ [100].

Bright reflectivity peak corresponds to exciton ground state and oscillations running to high-energy side that correspond to interference of polariton states are observed in reflectivity spectra at zero magnetic fields [1]. The experimental spectra demonstrate that the increase of magnetic fields induced a shift of all spectral lines to high energies due to Zeeman effect and diamagnetic shift. Besides, the magnetic field leads to appearance of additional spectral oscillations, which increase their amplitude with increasing magnetic fields. The additional oscillations have smaller amplitude.

The additional oscillations, as it was shown by theoretical analysis, correspond to the interference of optically inactive exciton waves, which begin to appear in the spectra due to mixing between optically active states and optically forbidden states in transverse magnetic fields.

The exciton effective mass was found to increase proportionally to magnetic fields. This effect is due to existing of negative add to exciton energy which is proportional to square of wave vector and magnetic fields in Voigt configuration $\Delta E_{exc} = -B_K K^2 B^2$. The increasing of translational exciton mass is caused by mixing of the main 1S-state exciton state with 2P-excited states.

Reflectivity spectra for magnetic field $B=0$-11T were calculated in exciton polariton model [1] with taken in consideration mixing of 1s- bright exciton states with 1s-dark and 2p excited exciton states. The spectra calculated in that model describes experimental one with high accuracy.

References

Surprising stability of trion in relation to free carrier screening

A.A. Klochikhin1,2, V.P. Kochereshko1
1 A. F. Ioffe Physical-Technical Institute, St.-Petersburg, Russia
2 B. P. Konstantinov Nuclear Physics Institute, St.-Petersburg, Russia

Experiments demonstrate a puzzling different influence of free carriers on the exciton and trion absorption, reflection (and luminescence) spectra observed at zero magnetic fields in CdTe/CdMgTe and ZnSe/ZnMgSSe quantum wells at low temperatures. We have considered in detail the behavior of exciton and trion absorption bands as function of free electron concentration in CdTe/CdMgTe quantum wells. The exciton band has experienced a drastic broadening transforming into the high energy tail of the trion band within concentration interval from nominally zero to 4x1012 cm⁻². At the same time, the trion band conserves its individuality despite of a noticeable broadening. The dependence of the broadening on the electron concentration allows one to relate the process in both cases with an interaction of exciton or trion with free electrons. Indeed, the excitation of the electron-hole pair with two-dimensional wave-vector \( \mathbf{q} \) near the Fermi level at \( p \approx p_F \) creates the pair with the energy \( \frac{\hbar^2 q^2}{2m} + \frac{\hbar \mathbf{pq}}{2m} \). The threshold energy at \( q = 0 \) of this excitation is zero and, therefore, the boundary of the continuum spectrum of combined excitation consisting of free exciton or free trion plus the pair excitation coincides with energy of the free exciton or trion. As a consequence, the inelastic scattering processes with creation of such excitation can homogeneously broaden the exciton and trion bands. The mechanisms responsible for the creation of the pair excitation can be the Coulomb or exchange interaction of the exciton or trion with free carriers. For the charged trion the Coulomb mechanism seems to be the only important because the exchange interaction transforms the trion into the separated in energy triplet state. In the case of electrically neutral exciton, in principle, both mechanisms could be active. However, in the case of large exciton binding energy \( E_B \) as compared with the Fermi energy \( E_F \) the Coulomb interaction is actual only for the wave-vectors \( q \approx a_s^2 >> p_F \). That means that the exchange interaction mechanism should be considered for the exciton. The calculation of the broadening in the first approximation means that we should find the first self-energy correction to the exciton \( \alpha^{ex} \) and to the trion \( \alpha^{tr} \). Then the shape of the absorption band can be presented as

\[
\alpha(\omega) \propto \frac{\Gamma(\omega)}{\pi (\hbar \omega - E_{\lambda,\lambda} - \Delta(\omega))^2 + \Gamma^2(\omega)}
\]

where \( \Gamma(\omega) \) and \( \Delta(\omega) \) are the imaginary and real parts of the self-energy corrections to the exciton or trion.

In conclusion, the broadening of the exciton and trion absorption bands in CdTe/CdMgTe quantum wells as a function of the free carrier concentration is investigated. It is shown that strong difference between exciton and trion broadening behavior is concerned with different interaction mechanisms of excitons and trions with free carriers. The performed calculation has shown that a good agreement with experimental data can be obtained already in the first Born approximation.
We shall report on striking changes in the optical spectra of CdTe quantum wells (in particular, their reflectivity and photoluminescence spectra) generated by excitation directly into the quantum well simultaneously with excitation above the (Cd,Mg)Te barrier band gap energy.

It is well known that, for instance, the excitonic reflectivity of a quantum well or superlattice (probed with weak, broad-band light) may be modulated by a second beam which is, typically, above the band gap of the barrier layers. This effect is generally interpreted in terms of a modulation of the built-in electric field across the structure via the redistribution of the photo-generated carriers, which can partially screen the field; this mechanism therefore invokes the quantum-confined Stark effect (QCSE).

On the other hand, studies of, for example, charge transport and of charged exciton (trion) formation have both shown that above-barrier illumination can also result in a change of the density of free carriers forming a two-dimensional electron or hole gas (2DEG) within the quantum-confined structure. This change may be either an increase or a decrease, depending on the sample details. Generally, the charge density appears to depend in a simple (though not necessarily linear) way on the total illumination intensity and the photoluminescence and other spectra are also dependent on the illumination intensity through trion formation.

In an extension of such measurements, we have studied the effects of illumination by two beams, one above and one below the barrier band gap, with both varying over a large range of intensities. We find a surprising competition effect in which the very large changes induced by relatively high-intensity, below-barrier illumination in the reflectivity spectra appear to be completely reversed by simultaneous illumination above the barrier band gap. The reflectivity is, as above, probed with relatively very weak, broad-band light filtered to remove wavelengths above the barrier band gap.

The details of this competition effect are not yet fully understood; possible models for it could invoke either 2DEG and QCSE effects, or both. However, the fact that the excitonic reflectivity spectrum does not appear to shift in energy as the illumination intensity increases suggests that the QCSE is not the dominant effect. We shall discuss the effect in terms of changing photo-excited carrier concentrations.
Interface phonons and polaron effect in II-VI quantum wells

A.Yu. Maslov, O.V. Proshina
Ioffe Physical Technical Institute, Polytekhnicheskaya 26, St. Petersburg
194021, Russia

A distinguishing feature of II-VI compounds is strong interaction of charge particles with polar optical phonons. For the most II-VI compounds Frohlich constant has the value from 0.5 to 1. The bounding states of charge particles and optical phonons are defined as large radius (Pekar) polaron and result from this strong interaction. An efficient electron–phonon interaction increases in quantum nanostructures as compared to bulk materials and the polaron effect should be more pronounced [1]. On the other hand, several new branches of phonon spectrum tend to be in quantum nanostructures.

Let us consider the case of single symmetrical quantum well. There are three types of phonons in such system, namely phonons of quantum well, barrier phonons and interface phonons localized within the hetero-boundary. In a general way, one should take account of the charge particles interaction with three various branches of phonon spectra. In the present work the theory of polaron states of charge particles and excitons in a quantum well is developed having regard to the interaction with all types of optical phonons. It is shown that distinctions between the dielectric functions of the well and the barriers give rise to the interface optical phonons. The interaction of charge particles with interface phonons plays an essential role in the calculations of polaron effect influence on the exciton states. The calculation method is supposed in our paper [2].

The polaron effect can modify essentially the exciton spectra of interband transitions in a quantum well. The most interesting situation of essential enhancement of polaron effects can be realized in narrow quantum well where the bulk semiconductor polaron radius is larger than the well width. Here the electron (hole) polaron binding energy exceeds the bulk exciton binding energy and has the form:

\[
E_{\text{pol}} = \frac{0.4 m_e \omega_p^2}{\hbar^2 \left( \frac{\hbar \omega_p}{m_e} \right)}
\]

where \(\omega_p\) is optical dielectric permittivity of the barrier, \(m_e\) is electron (hole) effective mass. We emphasize that the value of exciton shift depends essentially on the polarization properties of barrier material. The reason is that the influence of the interface phonons on the polaron states is quite important. In optical spectra, polaron states creation manifests itself as series of intense phonon replicas of the exciton absorption line. The distribution of phonon replica intensities enables one to obtain the information on the parameters of polaron interaction in quantum wells.

The availability of the surface phonons leads to widening the range of materials in which the strong polaron effect should be expected. The results obtained are most useful for the correct determination of optical transition energy in the semiconductor structures with strong electron-phonon interaction. It means that taking into consideration the interface phonons is necessary when one deals with the electron-phonon interaction in low-dimensional semiconductor structures.

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Dipolar vibrational modes confined in ZnSe nanocrystals

A. Belogorokhov, L. Belogorokhova, S. Gavrilov

1) Institute of Rare Metals, 119017 Moscow, Russia
2) Moscow State University, Physics Department, Moscow 119899, Russia
3) Moscow Institute of Electronic Engineering, MIEE, Zelenograd, Moscow 103498, Russia

Recent years several advanced technologies permit the growth of semiconductor nanocrystals (NCs) with quasi-zero-dimensional properties. While the electronic and optical properties of NCs are well understood based on the effective mass theory and have received considerable attention during the last decade, the vibrational properties (phonons confined in spherical NCs of several nanometers in size) of NCs have received much less attention until the last few years. An accurate description of the vibrational modes of a NC is of fundamental interest and is also required to understand the coupling of vibrational modes to electronic charge. Recently it has been shown theoretically that mechanical confinement becomes important both for infrared and Raman-active phonons in the limit of small QDs size [1].

In this work, a numerical calculation of dipole-active phonon modes in spherical ZnSe NCs is presented, which is based on the approach proposed in [2,3]. From these calculations one can predict the infrared spectra of ZnSe NCs with different radius. We studied a series of ZnSe NCs embedded in free-standing layers of por-Al$_2$O$_3$ with varying pore sizes. The size of the ZnSe NCs ranges from 2.1 to ~20 nm and was determined from AFM study. The luminescence spectra of ZnSe NCs were blue-shifted to the visible spectral region compared with that of the bulk ZnSe. This energy shift allowed us to estimate the average size of NCs. The frequencies of the coupled phonon modes with angular momentum $l_p=1$ are interesting because they represent a more general solution with both longitudinal (LO) and transverse (TO) components including a surface mode contribution. The TO components converge to a value of 207 cm$^{-1}$, and the LO components to 246 cm$^{-1}$ in the limit of large NC radius.

The vibrational modes were studied experimentally using FTIR spectroscopy. It was observed that a broad peak between the bulk TO and LO phonon frequencies dominates the spectrum. We assign the peak in the FTIR spectrum to the coupled LO–TO modes with $l_p=1$ on the basis of theoretical calculations for the frequencies of the coupled phonon modes. We also recorded the Raman spectra (RS) in a backscattering configuration with the 488 nm line of an Ar-ion laser at low power to avoid darkening of the quantum dots. In the RS spectra the LO-phonon peak in ZnSe NCs is shifted to lower frequency relative to the frequency of bulk ZnSe. The FTIR and RS spectra of pure porous Al$_2$O$_3$ free-standing layers were recorded to ensure that the observed features were not due to the host material. Two-peak behavior of the RS spectrum was observed that may be due to the presence of the electrostatic Frohlich mode corresponding to a uniform polarization of the ZnSe nanospheres [4].

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Terahertz photoconductivity of a two-dimensional electron gas in HgTe quantum wells

Yu. B. Vasilyev
Ioffe Physical Technical Institute, Polytekhnicheskaya 26, 194021 St. Petersburg, Russia

F. Gouider, M. Bugar and G. Nachtwei
Institut für Angewandte Physik TU-Braunschweig, Mendelsohnstrasse 2, D-38106 Braunschweig, Germany

J. Königmann
Physikalisch-Technische Bundesanstalt, Bundesallee 100, D-38116 Braunschweig, Germany

C. Brüne and H. Buhmann
Fakultät für Physik und Astronomie, Julius-Maximilians-Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Terahertz (THz) photoconductivity is investigated in HgTe/HgCdTe-quantum wells in Hall bar and Corbino geometries at various wavelengths of excited radiation. The radiation source is a $p$-Ge pulsed cyclotron laser (pulse width about 1 μs, repetition rate 1 Hz) which is tunable in the wavelength range 120 μm < λ < 180 μm by an external magnetic field [1].

It is shown that the photoconductivity is caused predominantly by the heating of two-dimensional electron gas (2DEG). We have found that the photoconductivity signal has a bolometric component. The magnetic-field dependence of the bolometric signal has a maximum near the field position of the cyclotron resonance but no pronounced cyclotron resonance lines were observed in spectrally resolved experiments in contrast to results of publication [2].

Because of the low effective mass (0.026 m₀), this material system is especially interesting for detector applications. Time-resolved terahertz photoconductivity measurements yields an estimate of a response time less than 100 ns.

References
Growth and characterization of ZnMgTe/ZnTe layered structures grown by molecular beam epitaxy

S. Imada, T. Baba, S. Sakurasawa, and M. Kobayashi

The electro-optical effect of ZnTe is recently focused, and various device structures utilizing ZnTe are proposed. In order to take advantage of the characteristic feature of ZnTe, the layer thickness should be carefully controlled and the variety of heterostructures such as ZnMgTe/ZnTe should be considered. Since zincblende MgTe and ZnTe are fairly lattice mismatched system (4.1%), the mole fraction and the layer thickness of the ZnMgTe layer need to be promptly designed so that the structure could be free from the lattice mismatch related defects. In this study, ZnMgTe/ZnTe heterostructures were grown and the lattice mismatch strain associated features and quantized effects were evaluated.

ZnMgTe/ZnTe/ZnMgTe layered structures were grown on (100) ZnTe substrates by molecular beam epitaxy (MBE). The oxide layer of the substrate was removed by the atomic hydrogen. Then ZnTe buffer layers (20 nm to 0.5 um) were grown at 360 °C and the ZnMgTe/ZnTe/ZnMgTe layers were followed. The nominal growth rate of ZnTe and ZnMgTe was about 0.5 um/h. The ZnTe capping layer (20 to 80 nm) was grown on top of the layered structure.

The critical layer thickness of the ZnMgTe layer was calculated using the expression of Matthews and Blakeslee; the critical thickness of Zn_{0.88}Mg_{0.12}Te layer on the ZnTe substrate was estimated to be about 0.2 um. In this experiment, the mole fraction of Mg was varied from 3.9% to 15%. The layer thickness of the ternary alloy was maintained within the theoretically predicted critical layer thickness, but some structure employed the layer whose thickness has exceeded the critical layer thickness. The reflection high-energy electron diffraction (RHEED) pattern was monitored throughout the film growth to check the crystallinity of the structure. The X-ray reciprocal space mapping (RSM) measurement was performed to characterize the strain in the layered structure. The (422) diffraction was used to derive the in-plane and out-plane lattice constants of individual layers. Optical properties were studied by the low temperature (4K) photoluminescence.

The RSM indicated that the coherent layer growth was achieved when the layer thickness of the ZnMgTe layer was within the critical layer thickness. The in-plane lattice constants of ZnMgTe were aligned to that of ZnTe, and the coherent growth was confirmed for the sample whose Mg content was up to 15%. Low temperature PL measurement revealed that intense and sharp peak was observed around 2.384 eV for a sample whose Mg content was about 7%, and the sandwiched ZnTe layer (well layer) thickness was about 8 nm. The peak position change was confirmed for samples whose Mg contents were changed. The shift of the peak position would be related to the quantum confinement effect or the mismatch strain of the layered structure.

In summary, various ZnMgTe/ZnTe/ZnMgTe layered structures were grown. The coherent layer growth was confirmed for the layer whose Mg content was as high as 15%. The ZnMgTe/ZnTe/ZnMgTe structure exhibited the strong photoluminescence. These layered structures could be applied to various device structures.

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Determination of the band-gap of MgS and MgS-rich ZnMgSSe alloys from optical transmission measurements

I. Davidson, R.T. Moug, F. Izdebski, C. Bradford, K.A. Prior
School of Engineering and Physical Sciences, David Brewster Building, Heriot-Watt University, Edinburgh, EH14 4AS, UK

Magnesium sulphide (MgS) is a useful barrier material for II-VI structures; providing excellent confinement and associated high quality optical emission. However no single value for its band-gap (or even whether or not it is a direct bandgap material) is currently agreed upon. A range of band-gap values from approximately 4.5 to 5.4 eV have been suggested [1, 2]. Attempts to directly measure the bandgap, by either PL or CL, have so far not succeeded, and one calculation has suggested that MgS is indirect [3]. Transmission measurements are also difficult as MgS will rapidly oxidise if exposed to the atmosphere without a protective layer.

We have developed an epitaxial lift-off technique that utilises MgS as the release layer [4] and have also demonstrated the growth of MgS-rich quaternary alloys In particular, the alloy Zn0.20Mg0.80S0.64Se0.36 resists both acid attack and oxidation and has been successfully used in lift-off structures [5].

A GaAs/ZnSe (10 nm)/MgS (5 nm)/ZnSe (10 nm)/ Zn0.20Mg0.80S0.64Se0.36 (140 nm) structure has been grown by MBE using the method we have described previously. Using our standard epitaxial lift-off procedure we have removed the top two layers and transferred them to a glass substrate.

Before removal, the composition of the alloy was determined by XRI measurements. The bandedge of the alloy was measured at room temperature using transmission/absorption measurements. A bandgap at room temperature of 4.3±0.05 eV has been determined.

The bandgap of ZnMgSSe alloys can be determined from the four binary compound bandgaps and the four ternary alloy bowing parameters. Using our alloy composition and bandgap we are able to determine an estimated direct bandgap for MgS of 5.1±0.05eV. We discuss the ambiguities in the model introduced by the uncertainties in the values of the bowing parameters.

Local measurement of band offset for ZnCdS/ZnSSe nanostructure by Laplace current DLTS cooperated with AFM technique

V.G. Litvinov¹,² V.I. Kozlovsky¹, D.A. Sannikov¹, D.E. Sviridov¹, O.A. Milovanova², and N.B. Rybin²

¹P.N. Lebedev Physical Institute, Leninsky pr. 53, Moscow 119991, Russia
²Ryazan State Radioengineering University, Gagarina 59/1, Ryazan 390005, Russia

Deep level transient spectroscopy (DLTS) is well known technique for studying band offsets in heterostructures. Typically one uses large area electric contacts to the structure studied. Therefore the structure should be uniform along the contact area. However many interesting structures and electric devices are intentionally nonuniform along the surface. Size of a nonuniformity may be of nanometer scale. Therefore it is interesting to combine Laplace current DLTS (LCDLTS) with scanning probe microscopy such as atomic-force microscopy (AFM). In outlook this combination may allow to measure electronic states and band offset for a quantum dot (QD) structure.

In present work we approbate this technique on ZnCdS/ZnSSe nanostructure. These structures did not show any features of QD structure but were macro nonuniform. The ZnCdS/ZnSSe II-type heterostructures were used due to their high conduction band offset (about 0.8 eV for the CdS/ZnSe). It allows to measure current at room temperature and higher. Moreover two-dimensional electron gas in the QWs may be formed in these structures.

ZnCdS/ZnSSe SQW heterostructures were grown by metal-organic vapor-phase epitaxy (MOVPE) on the n⁺-GaAs substrates misoriented by 10° from (001) to (111)A plane at temperature 400 °C. The ZnSSe buffer and cap layers have thicknesses 600 nm and 100 nm respectively. The S content was equal to 0.06 that provided matching to GaAs. The ZnCdS QW thickness was 5-6 nm. The growth runs were carried out at hydrogen atmospheric pressure in a horizontal quartz reactor with an optical window for in situ reflectometry of layer thickness and roughness control. ZnEt₂, CdMe₂, Et₂S and Me₂Se metal-organic compounds were used as precursors.

For II-type heterostructures, energy distance between emission lines of the barrier and QW layers in low temperature cathodoluminescence (CL) spectra gives independent estimation of the conduction band offset. This fact was used for testing local LCDLTS. For this, In contacts were formed on the back side of the GaAs substrate. The barrier contact to the cap layer was formed by the cantilever of AFM. LCDLTS-spectrometer was switched in the circuit of the cantilever.

Local LCDLTS revealed the differences between electron emission processes from the QW in the different places along the structure surface. The LCDLTS spectra were measured at $T = 290 – 390$ K and contained some peaks with an activation energy correlated with the CL spectrum data. The conduction band offset was estimated at 350 meV for the central part of the structure while it increased by 40 meV to edge parts.

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Growth and characterization of Zn$_{1-x-y}$Be$_x$Mg$_y$Se solid solutions with luminescence and photoacoustic methods

F. Firszt$^1$, J. Zakrzewski$^1$, K. Strzałkowski$^1$, M. Maliński$^2$, S. Łęgowski$^1$, H. Męczyńska$^1$, A. Marasek$^1$, Y. S. Huang$^3$, and D. O. Dumcenco$^3$

$^1$Institute of Physics, N. Copernicus University, Grudziądzka 5/7, 87-100 Toruń, Poland,
$^2$Department of Electronics, Technical University Koszalin, Sniadeckich 2, 75-328 Koszalin, Poland
$^3$Department of Electronic Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

Zn$_{1-x-y}$Be$_x$Mg$_y$Se semiconductor is an interesting material for application in construction of green lasers, and photodetectors operating in blue and UV spectral region. Based on Zn$_{1-x-y}$Be$_x$Mg$_y$Se p-i-n photodiodes characterize very low dark current and high “rejection rate” for visible radiation. For application in multilayer technology, knowing of optical and thermal properties of the used materials is very important. Up to date only a few papers were published concerning growth and properties of Zn$_{1-x-y}$Be$_x$Mg$_y$Se solid solutions. This work deals with photooptical, luminescence and photoacoustic (PA) investigations of bulk Zn$_{1-x-y}$Be$_x$Mg$_y$Se mixed crystals.

Zn$_{1-x-y}$Be$_x$Mg$_y$Se solid solutions were grown from the melt by the modified Bridgman method. Photoluminescence (PL) and photoluminescence-excitation (PLE) spectra were measured in the temperature range from 30 K to room temperature. PA spectra were measured applying the mechanically chopped radiation from the xenon lamp after passing through monochromator. The PA signal was detected using an open PA cell with piezoelectric transducer and lock-in technique. Measurements of photoconductivity and transmission spectra were carried out at room temperature.

Photoluminescence spectra at low temperatures of Zn$_{1-x-y}$Be$_x$Mg$_y$Se samples consist of exciton line, an “edge emission” due to recombination of shallow donor-acceptor pairs and the main green luminescence band positioned at the energy 2.2-2.5 eV, depending on composition. As the temperature increases, the edge emission is thermally quenched but the exciton line and green emission were observed up to room temperature. PLE spectra at low temperatures exhibit two distinct features indicating existence of two (shallow and deep) acceptor levels. This interpretation is based on results of measurements of spectral distributions of photoconductivity taking into account that investigated Zn$_{1-x-y}$Be$_x$Mg$_y$Se samples were n-type semiconductors.

The piezoelectrically detected photoacoustic amplitude and phase spectra were measured in the energy range from 2.1 eV to 3.3 eV. From these data, using the Jackson and Amer theory, the dependence of energy gap on composition was determined. The influence of surface preparation on the photoacoustic phase and amplitude spectra was investigated. The thermal diffusivity was determined from the dependence of photoacoustic signal on modulation frequency of radiation illuminating the sample applying the theoretical model developed by Blonskij et al.

The photoluminescence and photoluminescence-excitation spectra provide information concerning radiative recombination processes in semiconducting materials, while photoacoustic spectral characteristics are directly related to the nonradiative transition paths. Photoconductivity measurements can provide information on both, radiative and nonradiative recombination processes of excited carriers. Some fundamental parameters characterizing Zn$_{1-x-y}$Be$_x$Mg$_y$Se crystals obtained with the mentioned above different methods were compared and discussed.
Determination of the etching mechanism in MgS and ZnMgSSe epitaxial lift off layers

A. Curran, S. Brown, K.A. Prior, R.J. Warburton
School of Engineering and Physical Sciences, David Brewster Building,
Heriot-Watt University, Edinburgh, EH14 4AS, UK

Recently, we have developed a technique for removing MBE grown II-VI semiconductor multilayers from a GaAs substrate by including a sacrificial layer of MgS underneath the structure of interest [1]. This epitaxial lift-off technique follows the procedure originally described [2] which was designed for GaAs/AlGaAs structures containing a sacrificial AlAs layer. Although we have applied the same method to II-VI heterostructures, it was not clear if the underlying lift-off mechanism was the same in both cases. Here, we show that MgS etching can be described by the same model as that originally proposed. In addition we propose a model to explain why alloys of both ZnMgX (X = S, or Se) and AlGaAs the etch rate is a sensitive function of the composition.

A series of epitaxial ZnSe/ZnCdSe structures were grown with MgS lift off layers of thicknesses \(L = 2, 5, 20\) and \(30\) nm. These were cleaved into \(3\) mm x \(3\) mm squares which were coated with apiezon wax and etched in \(30\%\) HCl, following our standard lift off procedure. The time required to completely detach the layer allows an estimate of the etch rate, \(v\). In agreement with the model [2], the etching speed for the three largest \(L\) varies according to \(v \propto 1/\sqrt{L}\). The maximum etching speed for MgS is \(3\) mm hr\(^{-1}\), which is far greater than that of AlAs under the same conditions. The maximum etching speed is predicted to be dependant on the solubility of the gaseous etching products which for MgS and AlAs are \(H_2S\) and \(H_2\) respectively. The observed ratio of the etching speeds is correct, given the solubilities of these two compounds.

The surface tension of the wax bends the epitaxial layer upwards, allowing the etchant to access the sacrificial layer. Without the wax, the layers will not etch, and for very small thicknesses of MgS \((L = 2\) nm) the etch rate is also zero. We suggest that if the adhesion forces between two layers can be made large enough, then they will overcome the surface tension of the wax which bends the layer and inhibit the etching. This occurs in two situations: first when the interlayer separation is small enough for the interlayer attractive forces to dominate, and second when the layer contains a significant mole fraction of an insoluble component. We have modelled AlGaAs or ZnMgS alloy layers as a network of atoms which can be removed (Al or Mg) or not (Ga or Zn) from between two fixed boundaries, representing the surrounding GaAs or ZnSe layers. As the concentration of the non-removable species rises, chains of atoms form which eventually bridge the gap between the two layers and provide adhesion. We have modelled this for the whole concentration range, and for a range of layer thicknesses. Over a wide range we find that the numbers of chains formed, and hence adhesion, decreases only slowly with increasing layer thickness, but changes very rapidly over a relatively small composition range. We demonstrate that this behaviour can explain the observed transition from a soluble binary to an insoluble ternary alloy even with low concentrations of the insoluble component.

Photoluminescence in ZnSe-based Diluted Magnetic Semiconductor Quantum Well Wire Structures Formed by Wet Chemical Etching

T. Muranaka, S. Iizuka, K. Kodama, K. Ohmori, Y. Nabetani, and T. Matsumoto

Department of Electronic Engineering, University of Yamanashi, Takeda 4-3-11, Kofu 400-8511, Japan

II-VI based diluted magnetic semiconductor (DMS) heterostructures have been attracted a lot of attention because of their unique properties such as giant Zeeman splitting due to the strong exchange interaction between the carriers and the localized magnetic ion spins. For device application, it is essential to understand their optical and magnetic properties, as well as to form nanostructures at will. In this paper, we describe the optical and magnetic properties in ZnSe-based DMS quantum well (QW) structures and quantum well wire (QWW) structures formed by wet chemical etching process.

The ZnMnSe/ZnCdSe QW structures were grown on ZnSe buffer layers on GaAs(001) substrates by using molecular beam epitaxy. Line-and-space patterns with pitches from 3 to 5 μm were photolithographically patterned onto the QW structures. The lines were oriented along the [110] and [1-10] directions, respectively. The patterns were transferred to the QW structures by using wet chemical etching with a solution of H3PO4:H2O2:H2O and, finally, the mesa-shaped QWW structures were prepared. The wire widths were varied from 200 to 800 nm.

Photoluminescence (PL) and magneto-PL measurements for the ZnMnSe/ZnCdSe DMS planar QW and QWW structures were performed by using a non-polarized He-Cd laser (325 nm) as an excitation source. The polarization dependence of the ZnMnSe/ZnCdSe DMS QW and QWW structures was observed at 14 K by using a linear polarizer placed before a CCD/monochromator. The magneto-PL measurements for the QWW structures were carried out at 4 K in a superconducting split-coil magnet. An external magnetic field up to 8 T was applied along the [110] or [1-10] direction of the samples in the Voigt configuration.

Under no magnetic field, the intensity of the PL spectrum from the planar QW structure was slightly polarized when the angle of the polarizer, \( \theta \), was parallel to the [110] direction. The linear polarization degree, defined as \( P(\theta) = (I(\theta_{\text{max}}) - I(\theta_{\text{min}})) / (I(\theta_{\text{max}}) + I(\theta_{\text{min}})) \), was 5%. On the other hand, the intensities of the PL spectra from the QWW structures were strongly polarized when \( \theta \) was parallel to the wire direction. The linear polarization degrees of 41 - 44% and 30 - 36% were obtained from the QWW structures along the [110] and [1-10] directions, respectively, and those values showed the wire-size dependence.

Under external magnetic field perpendicular to and parallel to the wire directions, the PL spectra were taken from the QWW structure with 800 nm width. The degree of polarization dependent on magnetic field was not clearly observed, but a slight PL peak energy shift dependent on magnetic field was observed in spite of its large scale. This shift was larger when magnetic field was perpendicular to the wire. Such behavior was observed in the nm-scale ZnMnSe/ZnCdSe DMS wire embedded in the step-and-terrace structure on vicinal substrate [1], indicating of anisotropic Zeeman shift in the present structure.

Optically detected magnetic resonance in CdMnSe/ZnSe submonolayer quantum wells

D. O. Tolmachev1, R. A. Babunts1, N.G. Romanov1, P. G. Baranov1, B.R. Namozov1, Yu.G. Kusrayev1, S. Lee2, M. Dobrowolska2 and J. K. Furdyna2

1 Ioffe Physical-Technical Institute of the Russian Academy of Sciences, 194021 St. Petersburg, Russia
2 Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556, USA

The most extensively studied semimagnetic semiconductors are II-VI compounds in which a fraction of the group II sublattice is replaced at random by Mn. Incorporation of Mn atoms into II-VI semiconductors modified their optical and magnetic properties [1]. In this communication, fine structure of isolated Mn$^{2+}$ ions, which is ascribed to low symmetry effects caused by low dimensionality and spin-dependent energy transfer from excitons to Mn$^{2+}$ ions were revealed in CdMnSe/ZnSe sub-monolayer quantum wells by optically detected magnetic resonance (ODMR).

The structures under study were grown by MBE on GaAs(001) substrate and consisted from ZnSe buffer layer and 7 periods including 0.3 monolayers (ML) of CdMnSe (20% of Mn) and 10 ML of ZnSe. 35 GHz ODMR was recorded by monitoring the intensity of both exciton emission and internal Mn$^{2+}$ luminescence. A decrease of the photoluminescence intensity of excitons in quantum wells and an increase of the photoluminescence intensity of Mn$^{2+}$ under EPR conditions were observed. The spectral dependence of ODMR detected via luminescence in the red corresponds to $^4T_1 \rightarrow ^4A_1$ transition of Mn$^{2+}$. The spin-dependent energy transfer from excitons to an intra-Mn excitation was suggested to occur.

ODMR spectra of Mn were found to be anisotropic around [001] growth direction. We believe that the fine structure splitting of Mn EPR lines, which appear due to low dimensionality of quantum wells is the reason of the observed anisotropy of the ODMR spectra. Since in high magnetic fields and at low temperatures the lowest fine structure levels of Mn$^{2+}$ are more populated because of Boltzmann distribution the $M_s=-5/2 \leftrightarrow M_s=-3/2$ EPR transition dominates the spectrum. The observed anisotropy of ODMR is consistent with the positive sign the fine structure parameter which is estimated as being about 50x10$^{-4}$ cm$^{-1}$, much smaller than $D=-200x10^{-4}$ cm$^{-1}$ for CdMnSe quantum dots reported in our recent publication [2].

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Optical and magnetic properties of zinc blende MnS in case of 3D-2D transition

M. Demper\(^1\), L. Chen\(^1\), C. Bradford\(^2\), H.-A. Krug von Nidda\(^3\), K. A. Prior\(^2\), A. Loidl\(^3\) and W. Heimbrodt\(^1\)

\(^1\)Department of Physics and Material Science Center, Philipps University, Marburg -
\(^2\)School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh -
\(^3\)Center for Electronic Correlation and Magnetism, University Augsburg

The continuous decrease of magnetic structures meets fundamental limits. Hence the essential question is: How much can the size of such materials be reduced before the macroscopic properties disappear? Regarding electronic correlations and magnetism, this question is still open, despite the fact that these days structure sizes can be reached, where quantum effects dominate.

Manganese sulfide in its metastable zinc blende structure is a highly isotropic antiferromagnet with a type III spin arrangement which can be well described by the isotropic Heisenberg-operator. It is known from the Mermin-Wagner theorem that an ideal 2D-Heisenberg material cannot develop any kind of long range magnetic order even at lowest temperatures. Real two dimensional materials do never fulfill the preconditions of the theorem, e.g. due to the broken symmetry at the interface. Nevertheless, the question remains what happens at the 3D-2D transition. Thus, we studied the influence of the magnetic-nonmagnetic interface of MnS/ZnSe heterostructures in case of different thicknesses of the antiferromagnetic MnS layers. The metastable zinc blende MnS-layers have been grown by MBE with thicknesses between 1 ML and 10 nm between ZnSe cladding layers. This structures have been studied by photoluminescence, time-resolved spectroscopy and SQUID-measurements in external magnetic fields and a wide temperature range between 2K and room temperature in order to reveal the influence of the interfaces on the magnetic and optical properties.

The PL spectra of the MnS layers exhibit a strong yellow emission band corresponding to the internal \(^{4}\!T_1\rightarrow^{6}\!A_1\) transition of the manganese 3d-states which offers an optical access to the antiferromagnetic phase transition of MnS as a function of the applied external magnetic fields. SQUID and the optical measurements reveal a pronounced metamagnetism of MnS. In Addition to the antiferromagnetic phase transition at about 100 K in zero magnetic field for all layers, a ferromagnetic phase transition occurs for the thinnest MnS films in weak external magnetic fields. The detailed study of the metamagnetic behavior reveals the influence of the interface in dependence on layer thickness, magnetic field strengths and temperature. The metamagnetism is explained by a significantly modified exchange coupling at the interface. Two critical temperatures have been found: (i) The bulk-Neél temperature is unchanged but can be tuned by strain. (ii) The ferromagnetic phase transition temperature is about 150 K.

The time resolved measurements of the \(^{4}\!T_1\rightarrow^{6}\!A_1\) Mn internal transitions exhibit a strong non-exponential decay which is also influenced by the metamagnetism. The radiationless energy transfer inside the Mn subsystem as well as the transfer to acceptor states and the respective temperature and field dependence will be described in a spin dependent kinetic model calculation.
Growth and magneto-optical properties of ZnTe/ZnMnSe quantum dots
Wu-Ching Chou, Wen-Chung Fan, and K.F. Chien
Department of Electrophysics, National Chiao Tung University, HsinChu 30010, Taiwan

ZnTe/ZnMnSe quantum dots were grown on GaAs substrate by molecular beam epitaxy. The time integrated and time resolved photoluminescence measurements were analyzed by the $\sigma_+$ and $\sigma_-$ circular polarization. The magnetic field dependence of the circular polarization rate $P = (I_+ - I_-)/(I_+ + I_-)$ follows the Brillouin function. Circular polarization $P$ is 48% at 1 Tesla and reaches maximum value of 78% above 4 Tesla. The Kohlrausch’s stretching exponential function well correlates both the $\sigma_+$ and $\sigma_-$ decay profiles. For the faster decay curve, the stretching parameter $\beta$ drops from 0.50 to 0.45 and the decay time $\tau$ decreases from 120 ns to 70 ns as the magnetic field was increased from 0 to 6 Tesla. On the other hand, for the slower decay profile, $\beta$ remains at constant value of 0.50 and $\tau$ shrinks from 120 ns to 100 ns.
3d Impurities in Semimagnetic Semiconductors Based on Wide Gap ZnSe, ZnS, and ZnO Compounds: X-Ray, Optical, and Magnetic Research

Tatiana P. Surkova, Vadim R. Galakhov, Ernst Z. Kurmaev
Institute of Metal Physics, Ural Division of the Russian Academy of Sciences, 620041 Ekaterinburg GSP-170, Russia

Interest in the study of the electronic structure of wide-gap II-VI semimagnetic semiconductors is motivated both by the construction of ZnSe- and ZnO-based semiconductor lasers operating in the green-blue-ultraviolet region of the spectrum and due to ferromagnetism with high Curie temperature. Doping with 3d elements changes the optical properties of these compounds and gives rise to magnetic effects depending on the energetic position of the 3d ion states and their interaction with the host bands.

In this work we will show an influence of synthesis conditions on the local structure of impurity atoms of 3d elements in semiconducting compounds. For this aim we have used X-ray absorption and X-ray emission spectroscopies. X-ray spectra were measured at Beamline 8.0.1 of the Advanced Light Source (Lawrence Berkeley National Laboratory, USA) and at Beamline I511 at MAX II (Sweden).

We have found that at the synthesis of bulk samples, 3d impurity ions substitute cation positions, and superexchange, as a rule, does not lead to ferromagnetism. In bulk samples during the equilibrium growing process 3d metal ions substitutionally occupy Zn cation sites, and their superexchange interactions (through an anion) do not cause ferromagnetic ordering, usually. However, if nonequilibrium growth methods are used, for example, for thin films, impurity atoms along with cation substituent can take interstitial positions, and their superexchange interaction can lead to ferromagnetic properties at room temperature.

Investigations of Mn L\(_{2,3}\) emission spectra and electronic structure of Zn\(_{0.8}\)Mn\(_{0.2}\)O epitaxial films annealed at different temperatures (see figure) showed that the reason of the observed suppression of ferromagnetism at T > 600 °C is segregation of Mn atoms. In this case Mn atoms occupy both substitutionally Zn positions, and interstitial positions, causing strong antiferromagnetic Mn-Mn exchange interactions. Mn L\(_{2,3}\) emission spectra of Zn\(_{1-x}\)Mn\(_x\)S (x = 0.14-0.3) show that the Mn impurities do not form clusters in the host ZnS lattice. A shift in the position of Mn L\(_3\) XES feature suggests a change in the nature of the hybridization between the Mn 3d\(_{3/2}\) and S 3p states as a function of x.

We have applied resonant inelastic X-ray scattering for detection of d-d transition between the filled and empty states of Zn\(_{0.95}\)Cr\(_{0.05}\)S. We have found that Cr-impurity ions are in the 2+ valence states. At the first time, we have observed in the X-ray spectra two bands centered at 2.4 and 1.1 eV. One can believe that they are related to 2+ → 1+ photoionization of chromium and Cr\(^{2+}\) intra-shell transition, respectively.

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Enhancement of intra-Mn$^{2+}$ ion transition via Te-isoelectronic center in ZnMnSeTe multiple quantum wells

C. S. Wu¹, C. S. Yang¹*, J. S. Wang², K. F. Chien³, W. C. Chou³, C. W. Luo³, S. R. Jian⁴, M. T. Chiang⁵, and C. N. Mo⁵

¹Graduate Institute of Electro-Optical Engineering, Tatung University, Taipei, Taiwan
²Department of Physics and Center for Nano-Technology, Chung Yuan Christian University, Chung-Li, Taiwan
³Department of Electrophysics, National Chiao Tung University, Hsin-Chu, Taiwan
⁴Department of Materials Science and Engineering, I-Shou University, Kaohsiung, Taiwan
⁵Chungha Picture Tubes, Ltd., Taoyuan, Taiwan

Abstract

In this study, Zn$_{1-x}$Mn$_x$Se$_{1-y}$Te$_y$/ZnSe multiple quantum wells (MQWs) was grown using molecular beam epitaxy. The Mn ($x$) and Te ($y$) concentration were controlled at around 2 % and 3 %, respectively, to reduce the lattice mismatch between the ZnMnSeTe and ZnSe. The well width was varied from 0.5 nm to 2 nm. The thickness of space layer, ZnSe, was fixed at 2 nm to avoid the influence upon each well. The power-, temperature-dependent and time resolved photoluminescence are employed to character the optical properties of the ZnMnSeTe/ZnSe MQWs. The magnitude of intra-Mn$^{2+}$ ion transition would be influence by Mn and Te concentration in ZnMnSeTe epilayers. The excited carriers would be tapped by Te-isoelectronic center rather than be excitons. Additionally, the trapped carriers transfer to intra-Mn$^{2+}$ and recombine. In ZnMnSeTe/ZnSe MQWs, the carriers transfer channel is significant enhanced due to the quantum size effect to localize the free carriers. The emission of intra-Mn$^{2+}$ has a potential to be the red-light source for II-VI white light emitting diodes.

*Corresponding author’s e-mail: csyang@ttu.edu.tw
We have studied electron spin relaxation in diluted magnetic semiconductor (DMS) CdMnTe quantum wells (QW). Our samples are n-type modulation-doped quantum wells with electron concentration between $7 \times 10^{10}$ cm$^{-2}$ and $4.4 \times 10^{11}$ cm$^{-2}$ and very low Mn concentration about 0.2%. This system is a good model for polarized 2D electron gas due to the presence of the giant Zeeman effect with an external magnetic field.

In non-magnetic semiconductors electron spin relaxation is usually dominated by the Dyakonov-Perel mechanism. In DMS the s-d exchange interaction provides a more efficient spin relaxation mechanism, due to mutual electron-Mn spin-flips [1],[2]. Y.G. Semenov has proposed a model of electron spin relaxation mechanism in CdMnTe quantum wells based on quantum kinetic equations, which predicts the magnetic field dependence of both longitudinal and transverse spin relaxation times [3]. We have extended this model to the case of the degenerate electron gas. We have measured the transverse electron spin relaxation time by time-resolved Kerr rotation technique as a function of magnetic field and electron concentration. We found that the measured relaxation times are much shorter than that predicted by the theory.

We examine the possible reasons for this disagreement, such as inhomogeneous heating of the sample within the laser spot [4] or the influence of photocreated holes on the electron spin relaxation.

The Mn assisted recombination of trions in semimagnetic CdSe/ZnSe/ZnMnSe quantum dots

A.V. Chernenko, A.S. Brichkin,
Institute of Solid State Physics of RAS, 142432, Chernogolovka, Russia
S.V. Sorokin and S.V. Ivanov
Ioffe Physico-Technical Institute, RAS, 194021 St. Petersburg, Russia

The photoluminescence and time-resolved spectra on an ensemble and single CdSe/ZnSe/ZnMnSe quantum dots (QDs) are measured in both Faraday and Voigt geometries. The presence of intermediate barrier allowed to avoid fluctuation broadening of photoluminescence lines and substantially reduce the Mn assisted non-radiative recombination, which allows to observe negatively charged X trions and study their dynamics in the magnetic field. It was found that PL spectra of trions strongly depend on the non-radiative recombination. For instance, the intensity of the lower energy $\sigma^-$ polarized trion line slightly changes with B whereas the intensity of the $\sigma^+$ polarized line visibly increases in the magnetic field. This fact is related with spin dependent selection rules of the non-radiative energy transfer from photoexcited QDs to Mn ions. It is well known that this process effectively suppress radiative recombination in semimagnetic materials as soon as the optical transition energy exceeds the energy of the Mn internal transition. This condition is usually satisfied in Cd(Mn)Se/Zn(Mn)Se QDs, which makes their PL studies at high Mn content impossible. The model of such a process based on Anderson Hamiltonian is proposed. It is shown that the dominant mechanism of the spin-dependent energy transfer is specific for transition and rare-earth metals incorporated into semiconductor matrix (covalent effects) and not related with the dipole-dipole energy transfer (Dexter-Foerster-like mechanism). Characteristic times of both mechanisms are estimated and confirm the above conclusion. The same mechanism is responsible for the highly effective electric pumping of Mn ions incorporated into II-VI semiconductor matrix. The phonon-assisted non-radiative energy transfer is also considered and the effectiveness of this process is compared with the direct process.

It is shown that the observed peculiarities of PL spectra of trions is a result of interplay between the non-radiative energy transfer and the spin relaxation of trion states. The spin relaxation time seems to be slow enough, hundreds ps, because of large lh-hh splitting in QDs due to strain and size quantization.
Enhancement of nonlinear light-spin excitations coupling in diluted magnetic semiconductor

S. Cronenberger, P. Barate, M. Vladimirova, and D. Scalbert
Groupe d’Etude des Semi-conducteurs, UMR 5650, CNRS, Université Montpellier 2,
Place Eugène Bataillon, Montpellier Cedex 34095, France

F. Perez
Institut des Nanosciences de Paris, UMR 7588, CNRS/Université Paris VI et VII,
Campus Boucicaut, 140 rue de Lourmel, 75015 Paris, France

H. Boukari
CEA-CNRS group « Nanophysique et Semi-conducteurs », institut Néel, CNRS, 23
Avenue des Martyrs, 38042 Grenoble, France

Frequency- and phase-shaped femtosecond pulses are used to create and probe, through stimulated resonant raman scattering (SRS), collective spin-flip excitations of a two dimensional electron gas in Cd$_{1-x}$Mn$_x$Te quantum wells ($x$~0.002).

In the Raman scattering process, photons are absorbed at one frequency and emitted at another (Stokes shift), creating a spin excitation in the medium [1,2]. When exciting the system with spectrally broad pulses there are destructive interferences between resonant and nonresonant photons similar to interferences in a two photon absorption process [3]. By appropriately shaping the pulse it is possible to eliminate these interferences or to rotate the phase of the photons so that all photon pairs interfere constructively.

The experimental method we use to generate and probe the spin excitations is time resolved Kerr rotation technique [4]. A pump pulse generates, through SRS process, the spin excitations while the efficiency of the generation process is determined by measuring the Faraday rotation of a linearly polarized probe pulse. In the setup used the spin dynamics can be studied by changing the delay between pump and probe pulses [5].

We demonstrate how, by shaping the amplitude and phase of the pump pulse, it is possible to enhance the generation of collective spin-flip excitations. We are able to enhance the light-spin excitations coupling by one order of magnitude.

Advances in doping of colloidal semiconductor nanocrystals have led to new materials showing fascinating physical properties of potential technological importance. This presentation will summarize the major new physical properties that have emerged following successful synthesis of one of the most widely studied colloidal semiconductor nanocrystal systems, CdSe quantum dots, doped with one of the most widely studied transition metal dopant ions, Mn$^{2+}$. These properties include spin-polarizable excitonic photoluminescence, magnetic circular dichroism, exciton storage, sensitized photoluminescence, and excitonic magnetic polaron formation. The physical properties of these colloidal doped quantum dots are shown to compare favorably with those of analogous self-assembled quantum dots. The rich variety of physical properties displayed by colloidal Mn$^{2+}$-doped CdSe quantum dots, combined with their processability and ease of handling, highlights their attractiveness for future fundamental and applied research.

Related publications:
Zn$_{1-x}$Mn$_x$Te-ZnO core-shell nanowire structures grown by combination of MBE and low temperature ALD techniques

E. Janik$^1$, A. Wachnicka$^1$, L. Wachnicki$^1$, E. Guziewicz$^1$, M. Godlewski$^{1,2}$, W. Zaleszczyk$^1$, A. Presz$^1$, S. Kret$^1$, P. Dłuzewski$^1$, G. Karczewski$^1$ and T. Wojtowicz$^1$

1) Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland
2) Department of Mathematics and Natural Sciences, College of Science, Cardinal Stefan Wyszyński University, ul. Dewajtis 5, 01-815 Warsaw, Poland
3) High Pressure Institute, Polish Academy of Sciences, Sokolowska 29/37, 01-142 Warsaw, Poland

We report on the two step growth of nanowires (NWs) forming core-shell structures. The Zn$_{1-x}$Mn$_x$Te nanowires constituting the core (x ranging from 0 to 0.15), were obtained by molecular beam epitaxy (MBE) with the use of vapour-liquid-solid (VLS) mechanism proposed by Wagner and Ellis [1]. The epitaxial growth of NWs was performed on GaAs substrates covered with Au/Ga droplets, acting as catalysts [2,3]. The nanowires length to diameter aspect ratio was about 20. As a next step the NWs were transferred to a separate atomic layer deposition (ALD) system and coated by thin ZnO layer. We used diethylozinc (DEZn) as an organic zinc precursor and deionized water as oxygen precursor [4]. In the ALD process doses of precursors were separated by purging the growth chamber with a neutral gas. Thus, precursors met only at surface of a growing film, enabling perfect conformity of the obtained films. This is why we could uniformly coat the Zn$_{1-x}$Mn$_x$Te core with a thin layer of ZnO forming the shell. The Zn$_{1-x}$Mn$_x$Te-ZnO core-shell structures were extensively studied by scanning electron microscopy, high resolution transmission electron microscopy, X-rays diffraction and photoluminescence. The impact of ALD process parameters (including precursors’ doses and substrate temperature) on morphology and photoluminescence properties of our structures were studied.

We believe that our results are important because ZnO is a semiconductor with a vast variety of possible practical applications, notably in the area of ultraviolet/visible emitting devices and detectors, gas sensors, solar cells, piezoelectric transducers, transparent electronics and spintronics. For some of these applications the structures with large surface to volume ratio and/or in the form of free standing NWs are required or preferable. We hope that Zn$_{1-x}$Mn$_x$Te-ZnO core-shell structures could be useful for many of those applications, especially in the area of sensors.

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References

New insights in the formation of self assembled CdTe/ZnTe quantum dots

P. Wojnar, H. Boukari, and H. Mariette
CEA-CNRS Group “Nanophysique et Semiconducteurs”. Institute Néel, Université J. Fourier, 25 Avenue des Martyrs, F-38054 Grenoble, France

Despite of an intensive study of the optical properties of Te-based quantum dots (QDs), there is still some lack of understanding of the formation process of these structures. The aim of the present study is to find parameters which are responsible for the formation of CdTe/ZnTe self assembled QDs and to propose mechanisms which may lead to this process.

The QDs made of II-VI semiconductors do not form spontaneously despite of a lattice mismatch between the dots and the barrier material of 6.2%. The QDs formation process takes place only after an additional treatment, i.e., the covering of the surface with an amorphous tellurium layer at 20°C and its thermal desorption [1]. The formation of self assembled QDs is monitored in situ by means of the Reflectivity of High Energy Electron Diffraction (RHEED). The streaky two dimensional (2D) RHEED pattern disappears completely after covering with a tellurium layer and reappears after the thermal desorption of this layer in form of a spotty, three dimensional (3D) image. This 2D-3D phase transition is an in-situ sign of the formation of self assembled QDs.

In the present study, we investigate a similar method of the QDs formation. The most striking difference is the temperature of the tellurium deposition, which is considerably higher, in the range of 140°C-210°C, than previously. Surprisingly, the RHEED pattern of the tellurium deposited at elevated temperatures exhibit a spotty character suggesting a crystalline structure of this material. While increasing the temperature, we observe a clear desorption of the tellurium layer, which is manifested as a disappearance of the spotty pattern and the appearance of the pattern related to the CdTe surface. A systematical study has been performed, in which we have varied the deposition temperature and the deposition time of the tellurium layer. It has been found that a certain Te deposition time, corresponding to a certain thickness of the tellurium, is required at a given deposition temperature for the formation of QDs. Below this Te-thickness the 2D-3D transition does not occur, despite of a clear sticking of the tellurium to the surface. The 2D-3D transition may appear in the whole temperature range under investigation after a sufficiently long Te-deposition time, even at relatively high temperatures (~200°C), where the sticking of the tellurium is relatively slow. On the other hand, the desorption temperature of the tellurium layer does not have any great impact on the process of QDs and has been varied from 250°C to 280°C. Small temperature changes used in the present approach strongly suggest that the temperature is not the driving force for the QDs formation.

An important advantage of the deposition of tellurium at elevated temperatures is a considerable reduction of the time required for the formation of one QDs plane, and therefore, the reduction of any possibly contaminations, which opens a way to fabricate multilayer structures of quantum dots of high quality.

Semiconductor nanoparticles A2B6 group are of particular interest because of their size-dependent photophysical, photochemical and non-linear optical properties. CdS nanoparticles immobilized into the optical polymers have or will have great potential applications in lighting technology. We worked out of one-stage technique for synthesis of CdS/polymethylmethacrylate (PMMA) nanocomposite which allows to control of particles size during process of synthesis.

Reaction mixture contains monomer – methylmethacrylate (MMA) and cadmium salt. CdS nanoparticles formation takes place when H2S dissolved in MMA is added to this mixture with slow rate. Size control was realized when CdS deposition passes under irradiation. Irradiation of reaction mixtures is carried out by means of powerful lamp supplied of narrow-band filters. After the deposition of CdS solutions are held on UV light for the termination of polymerization process.

The possibility of monomer radicals generation with the participation of CdS conduction band electrons may apparently serve as a reason for the advanced photocatalytic activity of cadmium sulfide nanoparticles in polymerization. Photogenerated electrons and H⁺ ions obtained in CdS deposition reaction take part in polymerization:

\[
\text{CdS} + h\nu \rightarrow h^+ + e^- \\
e^- + M \rightarrow M^- \\
M^- + H^+ \rightarrow HM^+ \\
HM^+ + M \rightarrow MM^+
\]

Here M is monomer molecule.

We suggest that the polymerization of MMA takes place on the surface of growing CdS nanoparticles at the moment when they begin to absorb of irradiation light. This moment connects with the manifestation of quantum confinement effects, i.e. with the difference in the absorption of CdS nanoparticles with different size. After polymer formation grow of particles stops and their agglomeration becomes impossible. Thus size-controlled synthesis of CdS nanoparticles is carried out.

It is noticeably that location of absorption band depended on wavelength of irradiation light. The first exciton peak position depends on wavelength irradiation light too. Particle size increases from 2 to 6 nm when wavelength of irradiated light growing from 365 to 450 nm. Luminescent properties of obtained nanocomposites were investigated. The wide peak of a surface luminescence located in long-wave area was observed on luminescence spectra. The peak of a bulk luminescence of cadmium sulphide had small intensity and was not display in all spectra. Position of luminescence band also depended on wave length of radiation and on the size of particles that is well known size effect for the nanoparticles.

The intensive surface luminescence indicates high defect of CdS nanoparticles. We assumed, that defects are vacancies of sulphur, or not completely replaced trifluoracetate ions. After addition of solvents with high permittivity intensity of bulk luminescence increases. Surface luminescence disappears almost completely.

This work was partly supported by the ADTP «Development of high school potential on 2009-2013» project 2.1.1/2161 «Photoprocesses in monodisperse systems with A2B6 semiconductor nanoparticles under high power laser excitation».
The influence of the ZnTe barrier width on the cathodoluminescence (CL) spectra of the CdTe/ZnTe superlattices (SL) with CdTe quantum dots (QD) is studied. Self-assembled QD’s were formed by depositing 3 CdTe monolayers (ml) on ZnTe surface. The ZnTe barrier width varied in the range of 5 – 100 ml in these SL’s. As estimated by transmission electron microscopy the average lateral size of QD’s is about 3 nm while their density approaches $10^{12}$ cm$^{-2}$. Cathodoluminescence spectra were measured in the range of 200 – 900 nm at 80 and 300 K. The accelerating voltage equal 15.1 and 3 kV and current $\mu$A. For the samples with the barrier width of 100, 50 and 25 ml CL spectra consist only of a single band with maximum at $E = 2.03 – 2.01$ eV at 80 K and the full width at half maximum $\Delta E = 50$ meV. We assign this band to the emission from the QD ensemble. For the samples with 10 ml barrier width the emission band splits into two lines of different intensity with maxima at $E = 2.01$ and 1.95 eV. However the emission spectrum of SL with 5 ml barrier width consists also of only one band with maximum at $E = 1.92$ eV.

We explain these results by the influence of biaxial strain, resulting from the lattice mismatch, on the ground state of the heavy-hole and light-hole subbands. The strain effect is sensitive not only to atomic misfit but also to layer thickness. The strain splitting, being comparable to zero-strain valence-band offset ($\Delta E_v \approx 55$ meV), completely reorganizes the whole pattern. The heavy-hole ground state is pushed above the light-hole one for biaxial compression and below for biaxial dilation [1, 2].

According to the calculations [1, 2] we suggest that quantum wells for electrons and heavy holes are located in the CdTe layers for the samples with thick barriers, and we observe $E_{hh}(\text{CdTe}) – E_{gh}(\text{CdTe})$ transitions. These SL’s belong to the type-I configuration. Strain-induced deformation of SL with 10 ml ZnTe layer (compressed CdTe and dilated ZnTe layers) give rise to the case when both heavy-hole ground state in the CdTe layers and light-hole subband in the ZnTe layers are overlapped and we observe $E_{hh}(\text{CdTe}) – E_{lh}(\text{CdTe})$ and $E_{gh}(\text{CdTe}) – E_{lh}(\text{CdTe})$ transitions. For the most thin ZnTe layer (5 ml) the hole ground state is the light-hole one located in ZnTe layer. It is important to note that due to different spatial localization of electrons and holes the magnitude of CL signal is much less for this sample in comparison with the samples with thick barriers. Thus it is possible to assign this SL to type-II configuration.

Raman scattering studies showed decrease in the ZnTe LO phonon frequencies with decrease of the barrier width due to the effects of dilation and quantum confinement as well as increase in CdTe LO-phonon frequency in the SL with thick barriers due to the compression effect [3].

For the CdTe/ZnTe SL with the deposited CdTe layer thickness of 1.5 ml we observed equidistant lines separated by 42 meV in QD and wetting layer emission bands. Taking into account that the longitudinal optical phonon (LO) energy equal to 21 meV in the bulk CdTe we attributed this fact to enhanced luminescence caused by 2LO-assisted relaxation. The strength of exciton-LO-phonon hybridization is especially high near the resonance when the splitting between the ground and excited states is multiple to LO-phonon energy.

Synthesis of ZnSe semiconductor nanostructures by a method of thermal evaporation of a material on porous Al₂O₃ matrixes

R. Valeev¹,², E. Romanov², A. Deev¹, A. Eliseev³ and P. Krylov², V. Kriventsov⁴

¹ Physical-Technical Institute of UB RAS, Kirova st. 132, Izhevsk 426000, Russia
² Udmurt State University, Universitetskaya st. 1, Izhevsk 426034, Russia
³ Material Science Faculty of Lomonosov’s Moscow State University, Leninskiye Gory, Moscow 119992, Russia
⁴ Boreskov’s Institute of Catalysis of SB RAS, Lavrent’ev st.5, Novosibirsk 630090, Russia

A special place in nanoelectronics development allocated to the nanostructures on the basis of the quantum dots massives isolated from each other by dielectric layers or the semiconductor with the big gap width. The correlated massives of quantum dots today are the most perspective candidates for manufacturing of devices of quantum logic and quantum computers, and owing to effective issue and a high quantum emission - high effective display units. Massives of quantum dots of wide gap semiconductors are perspective for creation of sources of radiation of visible area, solar sells or fluorescent labels [1].

In work essentially new approach to creation semiconductor nanostructures a method of thermal evaporation of a material on matrixes porous aluminium oxide is offered. The essence of a method consists in evaporation of a material on substrates through a porous aluminium oxide film received by a method of two-phase anode oxidation in dissolving electrolits [1]. Selection of conditions of oxidation (density of a current, time of oxidation, a chemical compound of electrolit) allows to vary diameter and length of holes over a wide range (diameter from 5 up to 200 nanometers; thickness of a film from 0,2 microns up to 200 microns), that makes a porous aluminium oxide matrix rather perspective for use as a mask or a pattern for formation spatially-ordered semiconductor nanocomposites. At evaporation a material through film’s porous part settles on walls of holes at which filling and after the matrixes etching are formed nanowires, and after removal of a matrix from a substrate on it remain nanodots of a material.

Nanostructures of ZnSe with various diameter and length nanowires depending on diameter of holes and thickness of a porous aluminium oxide matrix have been received. Microscopic and ACM researches of the received structures was performed. Interatomic distances, coordination numbers, mean-square deviations of atoms have been calculated from EXAFS spectra. Comparison with data for continuous ZnSe films was also performed.

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Comparison of optical properties for organically capped and silica coated CdSe quantum dots

Byoung Woo Lee, Tae Soo Kim, Eunsoon Oh*
Department of Physics, Chungnam National University, Daejeon 305-764, Korea

Ch. Kiran Kumar, Eui-Tae Kim
Department of Materials Science & Engineering, Chungnam National University, Daejeon 305-764, Korea

Colloidal semiconductor nanocrystals (quantum dots) and their core/shell structures have been attracting a great deal of attention in light-emitting diodes, photovoltaic cells, fluorescent biological imaging and biolabelling applications. It was reported earlier that the operation voltage of n-TiO₂/CdSe QDs/p-Si LEDs was drastically changed with the surface ligands of the colloidal QDs, which was explained by the fact that the ligands may act as a current blocking layer [1]. It is crucial to understand the influence of the ligands in colloidal QDs in order to develop devices with these nanostructures. In this work, we studied the influence of the ligands on optical properties such as photoluminescence (PL) intensity and carrier lifetime by cw- and time-resolved PL measurements.

The colloidal core-shell CdSe/ZnS quantum dots (QDs) with trioctylphosphine oxide (TOPO) ligand were synthesized via pyrolysis. Then the TOPO ligands were replaced with 3-mercaptopropionic acid (MPA) under Ar environment. Also, the TOPO QDs were coated with silica shell via a microemulsion method. In case of TOPO QDs, both the PL intensities and the lifetimes were increased with increasing temperatures above 220 K, which was not observed for the MPA QDs (see Fig. 1). This may be due to the subtle displacements of the semiconductor surface atoms induced by a phase transition in the capping layer. For MPA and silica coated QDs, the PL peak was observed at longer wavelength than that of the TOPO QDs (see Fig. 2), which may indicate the influence of the strain.

Influence of 2D precursors on optical properties of self assembled CdSe quantum dots

Tae Soo Kim, Byoung Woo Lee, Eunsoon Oh*
Department of Physics, Chungnam National University, Daejeon 305-764, Korea

S. Lee
Department of Physics, Korea University, Seoul 136-701, Korea

J. K. Furdyna
Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556

Optical properties of self assembled CdSe quantum dots (QDs) embedded in ZnSe matrix are investigated on a series of samples grown by molecular beam epitaxy, with CdSe coverage varying from 0.5 to 2.6 monolayers. It was reported earlier that the formation of the 2D precursors was evidenced in the cross-sectional scanning transmission electron microscopy (STEM) image for the 1.5 ML coverage sample [1]. In this paper, we investigated the optical properties of these samples by the cw- and the time resolved photoluminescence (PL) measurements, and discussed the influence of the 2D precursors.

Figure 1 shows the PL spectra taken with various excitation powers and the energy-dependent PL lifetimes for the 1.5 ML coverage sample. As seen in Fig. 1, the two PL peaks corresponding to the 2D precursors and the QDs are well resolved at 160 K. With increasing the excitation density, the relative intensity of the 2D precursors with respect to that of the QDs was increased. This suggests the saturation of the carriers in the QDs for relatively high excitation density.

The PL lifetimes of the 2D precursors were also found to increase with increasing excitation power, whereas those of the QDs were not strongly power dependent (see Fig. 1). The relatively short carrier lifetime of the 2D precursors at a lower excitation density is probably due to the carrier transfer from 2D precursors to the QDs. For higher excitation density, we suggest that such carrier transfer process is limited due to the saturation of the carriers in the QDs, resulting in the increase of the PL lifetime of the 2D precursors. This model can explain the excitation density dependence of the spectra and the PL lifetime.

Colloidal II-VI highly luminescent nanocrystals (NC) are important in fundamental studies and in technological applications such as light emitting diodes, low-threshold lasers, single photon emission sources and photovoltaic cells. Indeed, the control of the size of II-VI semiconductor nanomaterials (CdX with X = S or Se) has allowed the luminescence properties to be tailored to any wavelength across the visible spectrum, by monitoring excitonic transition energies through confinement of the electron hole wave functions.

We report herein physical and chemical cross analyses on II-VI CdSe NC obtained by using a chemical route, alternative to the widely prevalent epitaxial growths. II-VI NC are grown, either via the single source precursor methodology based on the thermal growth of a cadmium chalcogenide precursor in an alkylamine solvent, or via the microwave assisted growth of cadmium stearate. Growth temperature and reaction time are monitored in order to control the transition energies of the samples via the NC sizes. Joint physical and chemical techniques are used to surround the correlation between the NC optical properties and size distribution.

Room temperature photoluminescence and absorption spectroscopies allow the analysis of quantum size effects. We measured emission energies ranging from ~ 2.5 eV (green) down to 2.1 eV (orange) with good feature regarding previous results in field of high quality NC. The average size of NC and their size distributions are measured by transmission electronic microscopy (TEM). The joint optical and TEM data on the overall agree with most previous results from literature. Mass spectrometry techniques provide additional data about composition, size, surface and stability when analyzing NC by access (i) to pseudo-molecular ion with the ratio mass over charge (m/z) and (ii) to the structure information by the MS/MS fragmentation process.
Cascade Upconversion of Photoluminescence in Ensembles of II-VI Semiconductor Nanocrystals

E. Malainho¹, J. R. Santos¹, M. I. Vasilevskiy¹, S. A. Filonovich², Y. P. Rakovich³, J. F. Donegan³, and A. Rogach⁴

¹Centro de Física, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal
²CENIMAT/I3N – CEMOP, Universidade Nova de Lisboa, Caparica 2829-516, Portugal
³School of Physics and CRANN Research Centre, Trinity College Dublin, College Green, Dublin 2, Ireland
⁴Photonics and Optoelectronics Group, Department of Physics and CeNS, Ludwig-Maximilians-Universität München, Germany

Highly luminescent semiconductor nanocrystals (NCs) possess a number of interesting and important properties that are tunable thanks to their size-dependent discrete electronic spectra characteristic of quantum dots (QDs). One of such properties is the up-converted photoluminescence (PL), i.e. the emission of photons with energy higher than that of the exciting photons. It is of great interest for applications in multi-colour displays, bio-imaging systems, unconventional lasers and solid-state optical refrigeration devices.

In this work, we consider the thermally activated photoluminescence up-conversion, also known as anti-Stokes photoluminescence (ASPL), where the additional energy comes from the phonon bath. ASPL has been observed in a variety of systems including ensembles of NCs of several semiconductor materials, such as CdSe, CdTe and CdSe/ZnS core/shell nanoparticles [1]. In order to observe the PL up-conversion, the sample must be excited at the lower limit of its absorption spectrum [1]. The anti-Stokes shift can reach 0.2-0.3 eV and the ASPL intensity increases strongly with temperature. We will present the theory of this effect, based on the QD polaron effect and explaining, for the first time, all the principal features of the ASPL in colloidal solutions of chemically grown NCs. The proposed ASPL mechanism [2] includes (i) polaron-mediated up-conversion by one optical phonon energy in each QD, and (ii) cascade re-absorption and re-emission processes involving several NCs of successively smaller sizes within the sample, leading to the experimentally observed large anti-Stokes spectral shifts. The results obtained by our Monte-Carlo simulations based on the model outlined above, reproduce all the experimentally observed ASPL trends in NC's solutions and are being extended to layers of closely packed NCs. The agreement with the experimental data [1] confirms the validity of the proposed mechanism and provides predictive power for the ASPL applications. We shall discuss one of such applications, consisting in the use of semiconductor QDs for optical cooling.

Evolution of CdS:Mn nanoparticle properties caused by pH of colloid solution and ultrasound irradiation

A.I. Savchuk\textsuperscript{1}, G.Yu. Rudko\textsuperscript{2}, V.I. Fediv\textsuperscript{1}, A.G. Voloshehuk\textsuperscript{1}, E.G. Gule\textsuperscript{2}, S.A. Ivanchak\textsuperscript{1}, V.V. Makoviy\textsuperscript{1}

\textsuperscript{1}Department of Physics of Semiconductors and Nanostructures, Chernivtsi National University, Chernivtsi 58012, Ukraine
\textsuperscript{2}V.E. Lashkaryev Institute of Semiconductor Physics NASU, Kyiv 03028, Ukraine

In recent years II-VI semiconductor nanoparticles doped with transition metal ions have attracted much attention. Among this kind of nanomaterials, the semiconductor nanocrystals embedded in a transparent matrix such as polymers are investigated because of their stability, dopant-host interactions, improved luminescent properties and exhibition of the quantum confinement effect, which allows “band gap engineering”. It is essential to systematically address these issues not only for understanding the electronic processes, but also for realizing their full potential applications.

Although recent achievements in methods of colloid chemistry have made a large variety of colloidal nanoparticles available, fabrication of nanocomposites with the adjusted parameters is still a difficult task. One of the possible ways to solve this problem is using different external fields and factors in order to vary nanoparticle properties. In this work we report on the role of external factors such as ultrasound irradiation and pH of colloid solution in preparation of CdS:Mn nanocomposite films.

A series of CdS:Mn nanoparticles-polyvinylalcohol (PVA) composite films have been prepared by means of in situ synthesis method via the reaction of Cd\textsuperscript{2+}, Mn\textsuperscript{2+} - dispersed PVA with sodium sulfide. All steps of the synthesis were performed in the presence of Cd\textsuperscript{2+} ions excess at room temperature. During the preparation process, the effect of such important operating variables as the Na\textsubscript{2}S precursor concentration, pH of the solution, ultrasound irradiation was observed. The as-prepared films were characterized by photoluminescence (PL) spectroscopy method. The PL measurements were performed by using excitation wavelength of 375 nm from LED source. The investigations were carried out in temperature range of (4.2-300) K. It was found, that peak positions of PL bands, their relative intensities and full width at half maximum (FWHM) are sensitive to ultrasound irradiation and pH of solution.

The effects of pH on PL band behavior are the following. One can observe the red shift of the high energy band, decrease of its relative intensity, increase of FWHM when value of pH is increased. Possible mechanisms for this behavior as well as ions surrounding schemes for CdS:Mn nanoparticles are proposed. In addition, the alteration of PL spectra of composites films by means of ultrasound irradiation are studied. The PL spectra remain unchanged for low values of pH and essential changes are revealed for higher values of pH. Enhancement of the band edge luminescence of the films by ultrasound treatment was observed. These results are explained in framework of changes in the nanoparticle adsorption structure. The results on the PL spectra indicated that Na\textsubscript{2}S concentration in range of (10^{-4}-10^{-3} M) do not influence on their behavior caused by pH of solution change, but the effect is significant in case of ultrasound irradiation.

The observed findings are important for the controlled manufacturing of CdS:Mn nanoparticles-PVA composite films with the adjusted properties.
Radiative recombination dynamics of CdSe/Zn(S,Se)/MgS quantum dots up to room temperature

S. Zaitsev*, R. Arians, T. Kümmell, and G. Bacher

Werkstoffe der Elektrotechnik and CeNIDE, Universität Duisburg-Essen, Bismarckstr.
81, 47057 Duisburg, Germany

A. Gust, C. Kruse and D. Hommel

Institut für Festkörperphysik, Halbleiterepitaxie, Universität Bremen, Otto-Hahn-Allee,
28359 Bremen, Germany

The discrete energy level structure of self-assembled semiconductor quantum dots (QD) triggered a variety of innovative optoelectronic applications like single photon source. For device operation under ambient conditions, a detailed understanding of the radiative recombination dynamics of the fine structure split exciton states is required and the zero-dimensional electronic properties have to be conserved until room temperature. However, non-radiative losses as well as thermal emission into excited states, the wetting layer or the barrier prevented the study of the radiative recombination dynamics in self-assembled quantum dots up to room temperature until now.

In this contribution we report on room temperature emission and its dynamics from epitaxially grown CdSe QDs in a Zn(S,Se) matrix that is sandwiched between additional MgS barriers [1]. This design allows us to preserve a very high quantum yield and track the QDs recombination dynamics up to room temperature.

At low temperatures, we observe a fast initial decay (~ 0.6 ns) followed by a quite long decay constant on the order of 80 ns. While the fast component includes both, radiative recombination of bright excitons and bright-dark transfer, the latter is attributed to the recombination lifetime of the dark exciton. With increasing temperature, the fast initial decay disappears and above 100 K, we obtain a decay time of about 1.2 ns, which is independent on temperature up to 300 K. A rate equation model including bright and dark state recombination and a spin flip process for bright-dark conversion is able to qualitatively describe our findings without the need of including non-radiative losses and/or thermal carrier escape into the wetting layer or the barrier. From this we can conclude that the radiative lifetime of the bright exciton is independent on temperature up to room temperature, a clear proof for the zero-dimensionality of the system over the whole temperature range.


*) Permanent address: Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow dist., Russia
EXAFS studies of CdSe/ZnSe/MgS quantum dots performed for single photon emitters

E. Piskorska-Hommel\textsuperscript{1,2}, A. Wolska\textsuperscript{2}, J. I. Flege\textsuperscript{1}, R. Hildebrand\textsuperscript{1}, J. Falta\textsuperscript{1}, A. Gust\textsuperscript{1}, C. Kruse\textsuperscript{1}, D. Hommel\textsuperscript{1} and F. d’Acapito\textsuperscript{3}

\textsuperscript{1}Institute of Solid State Physics, University of Bremen, Otto-Han Allee NW1, 28359 Bremen, Germany
\textsuperscript{2}Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland
\textsuperscript{3}European Synchrotron Radiation Facility, 6 Rue Jules Horowitz Bp 220, 38043 Grenoble Cedex 9, France

CdSe/ZnSe dots are promising materials for single photon emitters at room temperature [1]. The chemical compositions and ordering of atoms in crystal lattices of semiconductor nanostructures (quantum wells, wires and dots) are important parameters influencing substantially their electrical and optical performance. Therefore it is important to find a method that provides a comprehensive knowledge of the chemical compositions and of the local structure of such semiconductor nanostructures. The CdSe/ZnSe system exhibits about 7\% lattice mismatch that causes the formation of zero-dimensional islands. For the CdSe/ZnSe system, CdSe islands are only observed when a special capping procedure is applied or when migration enhanced epitaxy for the cap is used to enhance the Cd surface segregation [2, 3]. It is therefore essential for the CdSe dot formation that they are embedded in a ZnSe matrix.

In order to clarify the influence of the overgrowth parameters on the structure of the formed CdSe quantum dots extended x-ray absorption fine structure (EXAFS) was used. Due to its selectivity for a chosen element, EXAFS is well situated for characterization of the atomic ordering present in the CdSe/ZnMgSSe system. The studied samples were grown by molecular beam epitaxy on (100) GaAs substrate covered with a GaAs buffer layer and 50 nm ZnSe. The quantum dots were embedded in 1 nm MgS and 1.4 nm ZnSSe surrounding the 3 monolayers CdSe active quantum dot region. Finally a ZnSe cap of 25 nm was deposited. The enhanced vertical and lateral confinement was successfully realized by this ZnSSe/MgS barrier combination. Using the EXAFS technique the local structure around Cd atoms and the nominal concentration of Cd atoms in CdSe quantum dots was resolved. Strong intermixing between the ZnSe cap layer and the CdSe QD layer was observed. The quantitative results of the data analysis showed that the CdSe quantum dots contain about 50 \% of Cd atoms on cation sites. The bond lengths and atomic ordering within strained CdSe/ZnMgSSe alloys is determined by EXAFS and is discussed in detail.

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References
CdSe/ZnSe ultrathin quantum wells (UTQWs) presenting a single and intense excitonic emission peak can be produced under appropriate growth conditions by atomic layer epitaxy (ALE) [1]. This feature is achieved even when the ultrathin CdSe film that constitutes the well is finished with fractional monolayers. This single peak excitonic emission, very narrow in the case of subnanometric UTQWs, indicates the absence of thickness fluctuations, which would be clearly detected because of the large differences in excitonic emission produced by monolayer fluctuations in the UTQWs. For each CdSe UTQW there are two interfaces: i) ZnSe/CdSe closer to the substrate, and ii) CdSe/ZnSe closer to the surface sample. The first one is abrupt; Cd atoms do not diffuse into the lower ZnSe barrier. The second one is an interface produced by a nearly homogeneous mixing of Cd and Zn atoms that results in a uniform QW thickness with only small interfacial composition fluctuations [2] The homogeneous mixing is due to a thermally activated process that produces the removal of Cd atoms by impinging Zn atoms during the ZnSe barrier growth; this process can be controlled to tune the emission. The self-smoothing process at the second interface is demonstrated by the analysis of the photoluminescence spectra of UTQWs with thickness of 2, 2.5, 3 and 3.5 CdSe ML. The study of the evolution of the excitonic peak with temperature in the 14 to 300 K range allows us to estimate that the maximum composition fluctuations in the well are around 2%, evidenced by the S-shaped curve in the curve describing the behavior of the excitonic peak energy as a function of temperature. This type of curve is observed due to potential fluctuations within the QW and will be explained in terms of exciton migration within regions of the QW with slightly different composition.

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MBE Growth and Luminescence Spectra of Double CdSe/ZnSe Quantum Dot Sheets

I.V. Sedova¹, A.N. Reznitsky¹, S.V. Sorokin¹, A.A. Klochikhin¹,², V.V. Korenev¹,
S.A. Peremogorov¹, A.A. Sitnikova¹, and S.V. Ivanov¹
¹Ioffe Physical Technical Institute, St. Petersburg 194021, Russia
²B.P. Konstantinov Nuclear Physics Institute RAN, St.-Petersburg, Russia

The coherent CdSe/ZnSe insertions with a nominal thickness in the range of 1-3 monolayer (ML) are known to generate arrays of CdSe-enriched islands, or quantum dots (QDs), incorporated into the body of an alloyed ZnCdSe quantum well (see e.g. [1] and references therein). Those QD nanostructures employed in the active region of optically and electron-beam pumped lasers have been shown to improve dramatically laser performance [2,3]. Using of several QD sheets in the laser active region may enhance optical confinement factor, increase quantum efficiency and decrease threshold of the optically pumped lasers, if they are electronically coupled [4].

In this paper, photoluminescence (PL) and structural properties of double CdSe QD sheet structures have been studied to elucidate mechanisms of the electronic and strain field interaction between the QD planes. Two sets of the CdSe/ZnSe nanostructures (called A and B in the following) have been grown by molecular beam epitaxy (MBE) pseudomorphically on (001) GaAs substrates at a temperature of 280°C. The structures of each set have a similar design and comprise two CdSe QD sheets of different nominal thickness, placed in a different sequence from the 60-nm-thick bottom ZnSe layer to the 20-nm-thick ZnSe cap: 1.5 ML and 2.5 ML in A series, but 2.4 ML and 1.5 ML in B series. CdSe insertions were formed in a conventional MBE mode and separated by a ZnSe barrier of different thickness of 8-60 ML. Following the barrier thicknesses (tsp) in ML the samples of A series a called A50, A12 and A8, whereas those of B series - B60, B25 and B12.

The QD morphology was observed by using transmission electron microscopy technique, while emission spectra were studied at 2K under the 50 mW/cm² excitation power of 442 nm line of He-Cd laser. PL spectra of samples A50 and B60 with the largest tsp exhibit two bands of the exciton recombination from both self-organized CdSe QD sheets which should be treated as independent [5]. Then two clear trends should be noted in the PL spectra with the tsp reduction (tsp ≤ 25 ML): (i) a dramatic decrease in the PL intensity of the thinner CdSe insertion in the samples of both series presumably due to electronic coupling between the vertically stacked QDs; (ii) the different signs of the PL band maximum shift for thicker QD sheets for series A and B. The samples A12 and A8 demonstrate red shift of the PL band maximum (16 and 22 meV from A50, respectively) in comparison with the blue shift in samples B25 and B12 (34 and 44 meV from B60, respectively). The surface and elastic energies of the double QD sheets, as well as the influence of the lattice deformation in the ZnSe barrier on the CdSe QDs shape and stress should be taken into account to explain the electronic properties of the nanostructures.

4. S.V. Ivanov et al., phys. stat. sol. (a) 204, 251 (2007)
Thermally Activated Carrier Transfer Processes in Self-assembled CdTe Stranski-Krastanow Quantum Dots Grown on ZnSe by Molecular Beam Epitaxy

K.F. Chien¹, W.C. Fan¹, W.C. Chou¹*, C.S. Yang²*, C.S. Wu², J.S. Wang³, Y. T. Shih⁴, M. T. Chiang⁵, and C. N. Mo⁵

¹ Department of Electrophysics, National Chiao Tung University, Hsin-Chu, Taiwan
² Graduate Institute of Electro-Optical Engineering, Tatung University, Taipei, Taiwan
³ Department of Physics and Center for Nano-Technology, Chung Yuan Christian University, Chung-Li, Taiwan
⁴ Department of Physics, National Changhua University of Education, Chang-hua 50058, Taiwan
⁵ Chungha Picture Tubes, Ltd., Taoyuan, Taiwan

Abstract

The thermally activated carrier transfer processes in self-assembled CdTe quantum dots, which were grown on ZnSe matrix in Stranski-Krastanow mode, were studied using temperature-dependent and time-resolved photoluminescence (PL) measurements. At 10 K, the lower energy wind of PL peak, which is attributed to the ground state emission from larger dots, exhibits a single exponential decay profile. Whereas, the emissions from the excited-state of larger dots and ground state of small dots contribute the higher energy portion of the PL spectrum and show multi-exponential exponential decay. The average carrier life time, which was determined from the PL peak decay profile, decreases with increasing temperature due to the phonon assisted recombination at the temperature range from 10 to 50 K. At temperature above 50 K, the carrier transfer from small dots to larger dots was observed. The carrier activation energy is around 10 meV.

*Corresponding author’s e-mail: wuchingchou@mail.nctu.edu.tw, csyang@ttu.edu.tw
Synthesis and Characterization of CdTe Quantum Dots for In-Vivo Imaging

A. Folk\textsuperscript{1}, J. Morales \textsuperscript{2}, and M. Sohel \textsuperscript{3}\textsuperscript{*}

\textsuperscript{1} Department of Chemistry, CUNY-City College of New York, New York, NY 10031
\textsuperscript{2} Department of Biology, CUNY-City College of New York, New York, NY 10031
\textsuperscript{3} Natural Sciences Department, CUNY-Hostos College, Bronx, NY 10451

Abstract: Previous efforts in making quantum dots (QDs) water-soluble to enhance intracellular delivery have involved either the conjugation of the QD with a protein, such as denatured bovine albumin serum or the surface ligand exchange with either mercaptopropionic acid or aminoethanethiol have shown to be cytotoxic. Current methods of synthesis of water-soluble CdTe QDs are unfit for in-vitro imaging. A colloidal synthesis of cadmium telluride QDs was investigated. The QDs, which were synthesized by reacting elemental tellurium dissolved in tributylphosphine with a mixture of cadmium oxide, octadecene, and oleic acid. These QDs, which were characterized by transmission electron microscopy (TEM), ranged from 6 to 10 nm in diameter. The identity of the compound post-synthesis was confirmed by X-Ray diffraction (XRD) patterns. The negligible peak shift in the near-infrared (NIR) region observed in the UV-vis spectra of the aliquots removed at different time intervals indicated fast and controlled growth of the QDs.

*To whom correspondence should be addressed to
Email: msohel@hostos.cuny.edu
Beryllium chalcogenide alloys for visible light emitting and laser diodes

M. Sohel1*, O. Maksimov2, F. Fernandez1, and M. C. Tamargo3

1Hostos College of The City University of New York, Bronx, New York 10451, U.S.A.
2Electro-Optics Center, Pennsylvania State University, Freeport, PA 16229, USA
3The City College of The City University of New York, New York, NY 10031, U.S.A.

Abstract: Beryllium chalcogenide alloys has attracted a lot of attention because of their strong lattice hardness and high degree of covalent bonding. We give a brief overview of the current advances in the development of the green light emitting and laser diodes (LEDs and LDs). We review problem of the rapid degradation of LDs based on II-VI material family. We cover recent advances in this area stressing the development of novel beryllium chalcogenide alloys. We discuss an increase in the lifetime of beryllium - containing LEDs recently reported by several research groups. These results demonstrate that beryllium chalcogenide alloys are attractive for the design of visible light emitters.

* To whom correspondence should be addressed
Email: msohel@hostos.cuny.edu
Formation of Tamm-like interface states in ZnSe/BeTe heterostructures: experiment and theory

A.S. Gurevich, M.O. Nestoklon, V.P. Kochereshko
Ioffe Physical Technical Institute,
Polytekhnicheskaya 26, St. Petersburg 194021, Russia
A. Waag,
Institute für Halbleitertechnik,
Hans-Sommer-Straße 66, D-38106, Braunschweig, Germany

Recent spectroscopic studies reveal an experimental evidence of the Tamm-like interface states (TIS) existence in ZnSe/BeTe heterostructures [1]. A set of periodical undoped ZnSe/BeTe structures with different layer thicknesses, grown by MBE, was studied in wide (all visible) spectral range using low-temperature spectroscopic ellipsometry. Besides the conventional interband optical transitions, a number of optical transitions with energies laying in the heterostructure bandgap was observed. One of important peculiarities is that in contrary with the interband optical transitions (which exhibit high energy shift due to quantum confinement) the energies of these transitions decrease with heterostructure layer thicknesses decreasing.

In the present paper microscopic calculations were performed in order to demonstrate the possibility of TIS formation at ZnSe/BeTe heterointerface. A junction of two different semi-infinite atomic chains was considered in terms of one-dimensional LCAO approximation. Each chain was formed by a sequence of alternating metallic and non-metallic atoms, representing binary semiconducting compounds such as ZnSe and BeTe. It was found that for the single heterojunction with Zn-Te interface atoms formation of a pair interface states is possible: an electron TIS lies a few tens of meV below the conduction band edge of ZnSe, whereas hole TIS lies a few tens of meV above the valence band edge of BeTe. Behavior for the heterojunctions formed by Be-Se bonds is also discussed.

The obtained possibility of simultaneous formation of an electron and a hole TIS localized near the same heterojunction coincide well with the observation of effective photoluminescence (PL) for the above structures in the spectral range of heterostructure bandgap [2]. Due to PL spectral position it was interpreted as a radiative recombination of electrons and holes captured into the corresponding TIS.

Optical characterization of intersubband transitions in Zn$_x$Cd$_{1-x}$Se/Zn$_x$Cd$_y$Mg$_{1-x-y}$Se asymmetric coupled quantum well structures by contactless electroreflectance

J. D. Wu,$^1$ C. T. Huang,$^1$ Y. S. Huang,$^1$,* W. O. Charles,$^2$ A. Shen,$^2$ Q. Zhang,$^3$ and M. C. Tamargo$^4$

$^1$Department of Electronic Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan
$^2$Department of Electrical Engineering, The City College and The Graduate Center of CUNY, New York, New York 10031, USA
$^3$Department of Physics, The City College and The Graduate Center of CUNY, New York, New York 10031, USA
$^4$Department of Chemistry, The City College and The Graduate Center of CUNY, New York, New York 10031, USA

*Author to whom correspondence should be addressed; e-mail: ysh@mail.ntust.edu.tw

Contactless electroreflectance (CER) was used to characterize the possible optical transitions in a Zn$_x$Cd$_{1-x}$Se/Zn$_x$Cd$_y$Mg$_{1-x-y}$Se asymmetric coupled quantum well (ACQW) structure which was used to investigate the active region of an intersubband electroluminescence structure designed for emission at $\lambda = 4.5 \ \mu \text{m}$. Such a structure could comprise the active region of a quantum cascade laser. The ACQW sample was grown by molecular beam epitaxy on (001) semi-insulating InP in a dual chamber Riber 2300P system. One period of the ACQW structure starting from the spacer layer is made up of the following layers in angstroms: 110/34/6/30. The ACQW were repeated 30 times and the wells were doped with chlorine. The multiple ACQW structure was terminated with the growth of a 291 Å ZnCdSe cap layer. The compositions and energy gaps of the well/barrier (or spacer) were determined to be Zn$_{0.43}$Cd$_{0.57}$Se/Zn$_{0.20}$Cd$_{0.19}$Mg$_{0.61}$Se and 2.08/3.03 eV, respectively, at room temperature by photoluminescence (PL) and x-ray diffraction measurements.

The CER spectrum of this ACQW sample was measured at room temperature. The transition energies were obtained using a fit based on the first derivative of a Lorentzian lineshape function due to the bound origin of the transitions. The ground state transition was assigned by comparing with the PL emission signal taken from the same structure. In order to assign the remaining transitions, calculations were performed based on the envelope function approximation, considering that the well was doped. The values for the effective masses were obtained from a linear interpolation of the binary values. A value of the conduction-band band offset $Q_e = \Delta E_c/\Delta E_g = 0.80$ was used. The identified transitions correspond to the symmetry allowed and symmetry forbidden but parity allowed transitions. The calculation agrees well with the measured values. From these data, the intersubband transitions can be estimated. The values of intersubband transitions were further confirmed by Fourier transform infrared absorption measurements. The results show that CER can be used to investigate optical and electronic properties of the complex ACQW structures, including prediction of the intersubband transition energies.
Optically pumped green lasers with active region composed of multi-sheet electronically-coupled CdSe quantum dots

A.G. Vainilovich1, E.V. Lutsenko1, N.P. Tarasuk1, V.N. Pavlovskii1, A.L. Gurskii1, G.P. Yablonskii1, I.V. Sedova2, S.V. Sorokin2, S.V. Gronin2, S.V. Ivanov2, P.S. Kop’ev2

1Stepanov Institute of Physics of NASB, Independence ave. 68, 220072 Minsk, Belarus
2Ioffe Physical Technical Institute of RAS, St. Petersburg 194021, Russia

Green semiconductor lasers are promising for numerous applications such as short-range optical communications, laser location and navigation, projection television etc. Compact ZnMgSSe/CdSe quantum dot (QD) lasers pumped by an e-beam [1] or a violet III-N LD [2] can be employed for such applications as having rather high efficiency and slow degradation in comparison with II-VI LDs. Using of electronically-coupled multiple QD sheets in the active region of such lasers enable one to reduce the laser threshold and to improve various laser characteristics [2]. In this paper we analyze the effect of cavity length on performance of such multi-QD-sheet laser structures.

Laser characteristics of optically-pumped heterostructures with the active region comprising five electronically-coupled stacked CdSe QD sheets, grown by molecular-beam-epitaxy (MBE), have been investigated as a function of cavity length. The 2.5-monolayer-thick CdSe QD planes are separated by the combined tensile-strained barriers, each including a 3-nm-thick ZnS0.15Se0.85 layer surrounded by 1-nm-thick ZnSe spacers, which are intended to compensate partly the strong compressive stress induced by the QD planes. The active region is inserted in the asymmetric 200-nm-thick ZnS0.15Se0.85/ZnSe superlattice waveguide at a distance of 130 nm from the thin (20 nm) cap Zn0.88Mg0.12S0.16Se0.84 cladding layer (Eg=2.97 eV at 300K). A 1-μm-thick bottom cladding layer of the same composition separates the waveguide from a GaAs substrate. The samples were excited by the radiation of a pulsed N2 laser (λ=337 nm, τp=8 ns, P=40 kW) focused by a cylindrical lens for pumping of CdSe QD lasers and a cw HeCd laser (λ=325 nm, P=15 mW). The values of laser threshold and differential quantum efficiency were measured at room temperature as functions of the cavity length.

The samples showed sharp laser threshold, TE polarization of the laser emission and a single-maximum far-field pattern. It was defined from calculations and measurements of the spectral-angular distributions of the output radiation that lasing takes place on the fundamental mode. Minimal laser threshold obtained was as low as 2.2 kW/cm², and maximal external quantum efficiency was of about 50 %. The values of the characteristic gain, the internal quantum efficiency, the transparency threshold and internal losses were estimated as described in [3]. The measurements of laser parameters (differential quantum efficiency and laser threshold) as functions of cavity length allowed us to derive the following internal laser characteristics: characteristic gain G0 = 114 cm⁻¹; internal quantum efficiency ηi = 65.4%; transparency threshold IT = 1.22 kW/cm²; internal losses αi = 2.55 cm⁻¹.

The laser structure with five coupled QD sheets, exhibited such parameters, seems to be very suitable for high-efficiency and low-threshold laser applications.

Photopumped lasing characteristics of yellow-green BeZnSeTe double-heterostructures grown on InP substrates

Y. Sawafuji, I. Nomura, T. Ebisawa, S. Kushida and K. Kishino
Department of Engineering and Applied Sciences, Sophia University
7-1 Kioi-cho, Chiyoda-ku, Tokyo, 102-8554, Japan

Photopumped lasing characteristics of yellow-green BeZnSeTe double-heterostructures (DHs) were investigated. By controlling the elemental composition of the BeZnSeTe active layer, yellow-to-green (538-570 nm in wavelength) lasing emissions were obtained with low threshold excitation power densities (Pth) of 25-43 kW/cm\(^2\). Temperature dependencies of the Pth were investigated for the different wavelength samples; the Pth values at 80 °C were 46-56 kW/cm\(^2\). This experiment proved that BeZnSeTe has high ability as an active layer of yellow-green laser diodes (LDs).

BeZnSeTe, BeZnTe and MgZnCdSe II-VI compound semiconductors on InP substrates are very attractive materials for yellow-green LDs and LEDs. Especially, BeZnSeTe, which possesses direct bandgap energies from 2.1 to 2.8 eV under the lattice matching, is expected as materials of active layer. Inclusion in BeZnSeTe of beryllium chalcogenides (BeSe and BeTe) enhances lattice-hardness of the crystal, contributing to lengthening the device lifetime. So far we fabricated yellow-green LEDs with a BeZnSeTe active layer to achieve long lifetime (>5000h) operations. Recently, we succeeded in photopumped lasing of BeZnSeTe DHs. In this talk, wavelength and temperature dependencies of the Pth of BeZnSeTe DHs were systematically described.

The DH samples consisted of a 100-nm thick BeZnSeTe active layer sandwiched between upper and lower MgSe/BeZnTe superlattice (SL) cladding layers, and ZnCdSe buffer and ZnTe cap layers; these layers were grown on (100) InP substrates by a double-chamber MBE system. In this experiment, three DH samples of the Be(x)Zn(1-x)Se(y)Te(1-y) active layer with different elemental compositions (x/y) were prepared. From X-ray diffraction and photoluminescence (PL) peaks from the active layer, the x/y values were evaluated to be 0.15/0.36 (sample A), 0.12/0.36 (sample B), and 0.077/0.36 (sample C). The DH sample surface was excited with a frequency-tripled Nd:YAG laser (355nm) through a cylindrical lens and then the lasing emission light was detected from the sample facet with a multichannel spectrum analyzer. Room temperature lasing wavelengths of samples A, B, and C were 538, 548, 570 nm, respectively; the corresponding Pth values were 43 (A), 37 (B), 25 kW/cm\(^2\) (C); thus the value slightly decreased with increasing the lasing wavelength. Threshold carrier densities (Nth) corresponding to the Pth values were estimated to be around 1×10\(^{18}\) cm\(^{-3}\) by calculating absorbed photon numbers. Note that these Nth values are quite low, which suggests that the BeZnSeTe can generate a high optical gain sufficient for lasing at a low threshold current density. Temperature dependency of the Pth was evaluated at the temperature range higher than the room temperature. Slight increase in Pth from 36 to 56 kW/cm\(^2\) for sample A was observed with the increased temperature from 20 to 80 °C, which corresponded to the characteristic temperature T\(_0\) of 140K.

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ZnSe-based electron-beam-pumped (EBP) lasers emitting in the green part (520-550 nm) of visible spectrum are of great interest due to the possibility of compact device fabrication. During the last years the extremely low threshold current density ($J_{th}=0.4-0.5\text{A/cm}^2$, $E_e=5-12\text{keV}$) and high efficiency laser structures were grown by MBE [1]. This paper reports on our recent results on fabrication of the II-VI EBP laser heterostructures with graded-index superlattice (SL) waveguide, aimed at improvement of carrier collection in the active region at electron beam energies much below 10keV.

A ZnMgSSe/ZnSSe/Zn(Cd)Se laser heterostructure has been grown by molecular beam epitaxy (MBE) pseudomorphically to GaAs(001) substrate via a GaAs buffer epilayer at a substrate temperature 270-280°C. The structure consist of a 1.6-μm-thick ZnMgSSe bottom cladding and a Zn(Mg)SSe/ZnSe graded index waveguide (GIW) with the total thickness of 290 nm, centered with a ZnCdSe/ZnSe quantum well (QW). The GIW comprises a set of ZnMgSSe/ZnSe and ZnSSe/ZnSe strained short-period SLs with gradually variable layer thicknesses and constant Mg and S compositions, placed symmetrically around the ZnCdSe QW to provide the effective band gap reduction to the QW. Measurements of laser parameters were carried out at 300K in a transverse excitation geometry and a pulse mode at the electron beam energy $E_e=6-16\text{keV}$.

The lasing wavelength is $\lambda=535\text{nm}$, and the threshold current density is $J_{th}=1.2\text{A/cm}^2$ at $E_e=8-12\text{keV}$. One should note, that in spite of twice larger $J_{th}$ in comparison with best results [1], the GIW laser structure demonstrates the highest value of output power ~8.5W per facet ($E_e=16\text{keV}$) among the structures with a single QW active region. This value of output power is comparable with that obtained previously in EBP laser structures with multiple QW active region and extended waveguide [2]. No saturation of the output power has been observed. The GIW EBP laser structure has demonstrated no visible degradation even at rather high values of electron beam current. It can be related to the reduction of stress in the compressively strained ZnMgSSe/ZnSe graded index SLs as the structure is heated by the electron beam during measurements at high currents and superior elastic properties of the alternately strained SLs.

To optimize the structure, calculations of minibands of each SLs within the waveguide have been carried out. The transport properties of laser structures are limited by heavy holes as having the lowest mobility. So, to provide the effective carrier transport the hh-miniband of the neighbor SLs should overlap significantly along with the decrease of an effective hh-miniband bandgap in the QW direction.

Summarizing, the using of GIW seems to be an efficient way to improve degradation stability and increase the output power of EBP laser heterostructures. Improvement in the hole transport to the QW due to proper GIW design is expected to result in reduced threshold current density at low electron beam energy.

Green Electron-Beam-Pumped Laser Arrays based on II-VI Nanostructures

M.M. Zverev1, N.A. Gamov1, E.V. Zdanova1, V.B. Studionov1, D.V. Peregoudov1, I.V. Sedova2, S.V. Gronin2, S.V. Sorokin2, P.S. Kop'ev2, I.M. Olikhov3, and S.V. Ivanov2

1 Moscow State Institute of Radio Engineering, Electronics and Automations, Moscow, 117454 Russia
2 Ioffe Physical Technical Institute of RAS, St. Petersburg, 194021, Russia
3 “Gamma” Co Ltd, SRC “Platan”, Fryazino, Moscow region, 141190, Russia

Electron-beam-pumped (EBP) green semiconductor lasers based on undoped ZnSe-based structures can be used for numerous applications, such as projection television, optical communications, medicine etc. The minimum value of the room-temperature (RT) threshold current density in an electron beam, achieved for II-VI laser structures with single CdSe quantum dot (QD) sheets, has been recently reported to be 0.4-0.5 A/cm² for the electron energy of 8-9 keV at the transverse pumping [1]. Multi-quantum well (MQW) laser structures of similar design demonstrated the efficiency up to 8.5% and the peak pulsed power 12 W per one facet at RT [2]. To increase the peak output power one can use both the larger laser active region, e.g. enhanced MQW waveguide, and the multi-element laser array. This paper reports on design and studies of MQW ZnSe-based laser arrays pumped by a pulsed electron beam.

The MQW laser structures were grown by molecular beam epitaxy pseudomorphically on GaAs (001) substrates via a GaAs buffer layer. The structures consist of a 2.15-μm-thick bottom Zn0.90Mg0.10S0.15Se0.85 cladding layer followed by the extended ZnS0.14Se0.86/ZnSe strained superlattice (SL) waveguide lattice-matched to GaAs as a whole [3]. The structure is capped with a thin (20 nm) Zn0.90Mg0.10Se0.15S0.85 cladding layer. The active region comprise ten 10-nm-thick ZnSe QWs, each being centered with a Zn0.75Cd0.25Se QW, placed equidistantly inside the SL waveguide. The total width of structure exceeds 4 μm.

Rectangular laser bars with the cavity length in the 0.5-2.6 mm range and the bar width up to 5 mm were cleaved from the thinned wafer. To avoid the excitation of transverse intrinsic optical modes in the semiconductor bars, one-dimensional laser arrays were fabricated by scribing the 0.3-0.5-mm-wide cells on the bar surface, using a N2-laser as a cutting tool. The active elements of EBP lasers include 1, 2 or 3 one-dimensional arrays mounted as a staircase on a copper heat sink. The transverse excitation geometry was used. All experiments were performed at RT, employing the electron beam with an energy up to 24 keV and pulse duration ~ 0.5 μs as a pumping source. The detected lasing wavelength was of 535 nm. Maximum achieved value of the output pulse power of 630 W with an efficiency of 5% per one facet was measured at electron beam energy of 24 keV for the laser active element consisted of three one-dimensional arrays - 26 laser cells, each having a width and a cavity length of 0.5 mm and 1.3 mm, respectively. The average pulse power per a single cell was of 24 W. Some degradation of laser cells was observed after irradiation of the maximum output power. The destructions were located near the cavity mirrors and near the structure defects.

The possibilities of further increasing the output power and efficiency without the degradation of II-VI active elements are discussed.

The Cu(In,Ga)Se₂ (CIGS) solar cell is representative of high-efficiency thin-film solar cells. Currently a bi-layer structure of ZnO:Al/ZnO is used as a front contact layer and CdS is used as a window layer in high-efficiency CIGS solar cells. When wide-band gap CIGS is used, the conduct band offset between CIGS and the window layer becomes unfavorable. Our previous study indicated that by alloy with MgO, the energy bandgap of Zn₁₋ₓMgxO and conduction band minimum are increasing. In this work, we studied the impact of using Zn₁₋ₓMgxO to replace the resistive intrinsic ZnO and CdS in the CIGS solar cells. The effects of the Mg content and layer thickness of the Zn₁₋ₓMgxO on the junction formation are investigated. We found that the amount of Mg in the Zn₁₋ₓMgxO layer and the layer thickness alter the cell properties significantly. The series resistivity of CIGS devices increases with Mg content and Zn₁₋ₓMgxO layer thickness, which is due to the high resistivity of the Zn₁₋ₓMgxO and CdS layer. However, the impact of the Mg content is not limited to the front contact layer; it extends to underneath the CIGS layer. The Mg interdiffusion into the CIGS layer could explain the degradation in open-circuit voltage and shunt resistance. Device characterization indicates that the carrier concentration in the CIGS layer is changed by the Zn₁₋ₓMgxO layer, which supports the Mg interdiffusion assumption. As Mg content increase, the conduction band minimum of Zn₁₋ₓMgxO layer is moving up, the positive conduction band off-set between Zn₁₋ₓMgxO layer and CdS acts as the barrier against photogenerated electrons. Therefore, a decrease of short-circuit current is observed. Our observation indicates that the properties of a CIGS solar cell can be seriously altered by the front contact layers. This abstract is subject to US government rights.
Ultra-violet ZnSSe, ZnMgS epilayers and MQW structures grown by MOVPE on GaP substrates

P. Kuznetsov1), G. Yakushcheva1), V. Jitov1), L. Zakharov1), V. Luzanov1), V. Kozlovsky2), M. Tiberi3)

1) Kotel’nikov Institute of Radioengineering and Electronics of RAS, 1 Vvedenskogo sq., 141190 Fryazino, Russia
2) P.N. Lebedev Physical Institute of RAS, 53 Leninsky pr., 119991 Moscow, Russia
3) Principia LightWork Inc., CA, USA

Recently the blue e-beam pumped vertical-cavity surface-emitting laser was fabricated on the base of ZnSSe/ZnMgSSe nanostructures grown on GaAs substrates by MOVPE technique [1]. Similar UV laser may be fabricated using ZnSSe/ZnMgS nanostructures grown on GaP substrates. With that end in view one has to study the growth of thick ZnSSe and ZnMgS epilayers with high surface and crystal quality.

We report about growth of such ZnS-based epilayers and nanostructures on GaP substrates. Atmospheric pressure MOVPE technique and horizontal quartz reactor were used for this purpose. ZnEt₂, (MeCp)₂Mg were tested as II group precursors and various compounds (Et₂S, t-Bu₂S, i-Pro₂Se, Me₂Se, Et₂Se) were tested as S and Se precursors. The growth were carried out at (100) GaP substrates with different misorientation (5, 10 degrees towards [110] and 10, 15 degrees towards [111]A directions). As-grown epilayer and structures were studied by photoreflection (PR), photoluminescence (PL), cathodoluminescence (CL), X-ray diffraction, optical and AFM microscopy techniques.

To determine the uniformity of Mg content over the depth in thick structures, chemical step-etching was performed followed by PL measurements. The thickness of the layer was determined from the PR spectra.

Numerous growth experiments allowed us to determine that good surface and crystal quality of 4-5 µm thick ZnSSe, ZnMgS epilayers and ZnSSe/ZnMgS nanostructures can be achieved at temperatures 500-530 °C on GaP substrates misoriented of 10 or 15 degrees towards [111]A directions. The most suitable VI-group precursors are Et₂S₂ and Et₂Se. We failed to obtain good surface and crystal quality of thick ZnSSe, ZnMgS epilayers using t-Bu₂S, i-Pro₂Se owing to their homogenious reaction with II- group precursors. It is very difficult to obtain stable composition of ZnSSe with small contents of selenium using Me₂Se because of its high partial pressure. We can not obtain thick structures using Et₂S which reacts with (MeCp)₂Mg very slowly.

Low temperature CL spectra show that thick ZnMgS epilayers, grown under constant flow of (MeCp)₂Mg supplied into reactor, do not have stable composition. The depth dependence of Mg content was determined from a series of PL spectra obtained at step-etching of the structure. We used this dependence for correction of Mg supply during the growth of long-period ZnSSe/ZnMgS nanostructures in order to obtain structures with narrower barrier peaks.

The thick ZnSSe/ZnMgS structure containing 30 QWs was used for fabrication of e-beam pumped laser. The structure was coated by dielectric mirror, epoxed to sapphire holder and then GaP substrates was chemically removed. Second dielectric mirror was coated to complete the laser etalon. The UV lasing at 376 nm was achieved under longitudinal pumping by a scanning electron beam at room temperature.

High Sensitive Ultraviolet Organic-Inorganic Hybrid Photodetectors of ZnSSe grown on p-GaAs with Transparent Conducting Polymer Window-layer


Department of Information and Electronic Engineering, Graduate School of Engineering, Tottori University, 4-101 Koyama-Minami, Tottori 680-8552, Japan

The developments of ultraviolet (UV) photodetectors using widegap semiconductors have been explored for application in new optical storage-system, defense, and medical fields. In the development of these UV detectors, a reduction of optical absorption loss in the window layer is the most important key technology. Previously, we demonstrated ultraviolet photodiodes of ZnSSe n+-i-p structure on p-GaAs using extremely thin n+-window layer (150Å), which exhibit quantum efficiency of 45 % in ultraviolet region (300 nm) [1]. In this structure, an optical absorption loss in UV region is about 30 %, and two technical issues arose: (i) severe sensitivity limit in ultraviolet region due to this large optical absorption loss in deep ultraviolet region, and (ii) limitation of donor doping into extremely thin window layer (<100 Å). These technical issues, however, can be overcome by using a new organic-inorganic hybrid structure, present here.

In this study, we have developed organic-inorganic hybrid Shottky-type photodetectors with conducting polymer as a window layer on ZnSSe/p-GaAs wafers. Photo-detector wafers used in this study were grown by molecular beam epitaxy (MBE). The device wafer structure is i-ZnSSe(active layer) / p-ZnSSe / p-ZnSe-p-ZnTe superlattice / p- GaAs substrate. We used poly (3,4-ethylenedioxythiophene) : poly (styrenesulfonate) (PEDOT:PSS) as conducting polymer window layers formed by spin coating technique on the semiconductor ZnSSe layers. The thickness of PEDOT:PSS layer was 150 nm, and transmittance in the optical region of 300–500nm is over 85 %. This high transmittance leads to an extremely low absorption loss in the blue-ultraviolet optical region and high quantum efficiency. The window areas of PEDOT:PSS were formed by lift-off or wet-etching process. Top and bottom electrical contacts are silver and indium, respectively.

We have succeeded in fabrication of new polymer/ZnSSe structure photodiodes on p-GaAs substrates. The present device has exhibited very high blue-ultraviolet external quantum efficiency ηex = 70–90 % without anti-reflection coating. The external quantum efficiencies in the UV region is ηex = 80 % (wavelength : 300 nm), which is higher than commercial Si UV-photodiode of ηex =54 %. Furthermore, the devices exhibit deep UV quantum efficiency ηex = 71 % (wavelength : 250 nm). Another important property of the present photodetector is a low dark current below 10pA/mm² (10V) equipped with Pt guard-ring structure, which is as same as commercial Si photodiodes. These results have proved an excellent potential of a new organic-inorganic hybrid photodiodes for practical high-sensitive ultraviolet photodetectors.

**Cr\textsuperscript{2+}: CdS crystal as a new material for room-temperature tunable mid-infrared lasing**

A.I. Landman,\textsuperscript{1} V.A. Akimov,\textsuperscript{2} M.P. Frolov,\textsuperscript{1,2} Yu.V. Korostelin,\textsuperscript{1} V.I. Kozlovsky,\textsuperscript{1} V.V. Mislavskii,\textsuperscript{2} Yu.P. Podmar'kov,\textsuperscript{1,2} Ya.K. Skasyrsky,\textsuperscript{1} A.A. Voronov\textsuperscript{2}

\textsuperscript{1}P.N.Lebedev Physical Institute, Russian Academy of Sciences, Leninsky prosp. 53, 119991, Moscow, Russia
\textsuperscript{2}Moscow Institute of Physics and Technology (State University), Institutskii per. 9, 141700 Dolgoprudnyi, Moscow region, Russia

Solid-state broadly tunable mid-infrared lasers are of great interest for solving numerous scientific and applied problems. Applications include laser remote sensing of the atmosphere, high-resolution spectroscopy, metrology, trace gas analysis, environmental monitoring, medicine, etc. Transition-metal-doped II-VI compounds are promising laser materials for 2-5 \textmu m spectral region.

In [1] we have reported on the first demonstration of lasing from Cr\textsuperscript{2+}:CdS. The luminescence band of this crystal is shifted to the longer wave-length range as compared with the most studied Cr\textsuperscript{2+}:ZnSe and extends from 1.8 to 3.5 \textmu m. Till recently, Cr\textsuperscript{2+}:CdSe was the only Cr\textsuperscript{2+}-doped II-VI compound which has shown lasing beyond 3.1 \textmu m [2]. Due to the better mechanical properties and the higher thermal conductivity of CdS compared to CdSe the Cr\textsuperscript{2+}:CdS looks promising laser material. In this paper, we report the results of more detailed study of grown crystals and their laser characteristics.

The growth was performed by seeded physical vapor transport in helium from two separated sources with CdS and CrS [3]. CdS:Cr single crystals of 30 mm in diameter and 10 mm in height with doping level up to 2\texttimes10^18 cm\textsuperscript{-3} were obtained.

Photoabsorption and photoluminescence of grown crystals were studied. The measured values of peak absorption and emission cross sections were found to be 1.4\texttimes10\textsuperscript{-18} and 1.1\texttimes10\textsuperscript{-18} cm\textsuperscript{2} respectively. The emission lifetime of the exited state, \textsuperscript{5}E, of Cr\textsuperscript{2+} in CdS host was measured to be 0.93 \mu s at room temperature and 7.3 \mu s at liquid nitrogen temperature.

Room-temperature pulsed-laser operation was obtained under pumping by the 1.94 \textmu m output of a Tm:YAP laser. The output of the free-running Cr\textsuperscript{2+}:CdS laser was centered at \sim 2.6 \textmu m, and an absorbed energy slope efficiency of 38.8 \% was demonstrated. With an intracavity prism, the Cr\textsuperscript{2+}:CdS laser was tuned from 2.2 to 3.3 \textmu m. The laser properties of Cr\textsuperscript{2+}:CdS under CW pumping by Tm:fibre laser were studied also.

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ppland@mail.ru
ZnSe:Fe crystal – high-gain medium for tunable mid-infrared lasers

N.N. Il’ichev1, V.P. Danilov1, V.P. Kalinushkin1, M.I. Studenikin1, P.V. Shapkin2, A.S. Nasibov2

1 A.M. Prokhorov General Physics Institute of RAS, 38 Vavilov St., 119991 Moscow, Russia
2 P.N. Lebedev Physics Institute, RAS, Leninskii Prospect 53, 119991 Moscow, Russia

In the last decade, A2B6 semiconductors doped with transition metal ions (Cr2+, Fe2+) showed a promising potentiality as active media of tunable infrared lasers and became important materials for solid-state infrared photonics [1]. Of special importance is ZnSe:Fe crystal since it shows the unique laser characteristics at room-temperature (wide tuning range 3.9–4.8 μm and high laser gain [2]). Here we report on room temperature superluminescence ZnSe:Fe-laser.

The Fe2+ ions were doped into ZnSe crystal by means of diffusion under conditions of the thermodynamic equilibrium of phases. Thickness of doped layer was about 100 μm. Pump radiation from a 2.94-μm actively Q-switched Er:YAG laser (E ≈ 10 mJ, τ = 100 ns) was focused by a cylindrical lens to a line of length ~ 10 mm and width ~ 100 μm on the ZnSe crystal surface containing the Fe2+ -doped layer. The crystal’s opposite surfaces were cleaved and radiation of ZnSe:Fe-laser (4.6–4.7 μm) passed through these output surfaces in two opposite directions. The output energy of ZnSe:Fe-laser reached E ≈ 2 mJ with efficiency η ≈ 10%.

A detail analysis of the general properties of 4.7-μm laser irradiation has been carried out. Measured value of the divergency of output beam was about 0.04–0.05 rad. The distinct refraction of laser beam on output cleaved surfaces of laser crystal was observed. Because of this, a cavity providing feedback for emission was absent, and emission appeared due to high gain. Our estimations show that if about 30% of active ions are pumped to the upper level the product of the gain by length (1 cm) of the pumped stripe will be ~ 30 at the luminescence band maximum, which is sufficient for obtaining superluminescence. The dependence of the emission pulse energy on the pump energy has a threshold (~ 2.4 mJ) and the emission band is more than an order of magnitude narrower than the luminescence band.

The obtained data suggest that we have observed superluminescence. It is possible that the superluminescence regime is favoured by the system geometry in which Fe2+ ions are contained in a thin (~ 100 μm) near-surface layer at high (~ 10^20 cm^-3) concentrations and emission propagates along this layer perpendicular to the pump beam direction.

From the results it may be stated that Fe : ZnSe crystal doped with Fe2+ ions by means of diffusion technology is an effective active media for tunable mid-infrared solid-state lasers.

References
Simulation design and fabrication of cylindrical capacitive Frisch grid CdZnTe detectors

Dongni Hu, Jiahua Min, Zhaoli Xu, Linjun Wang, Wenbin Sang
School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China

CdZnTe (CZT) nuclear detector have been widely utilized as X,γ ray detectors and imaging instruments for their high detecting efficiency and good energy resolution, and have many applications in the field of national security, nuclear detection, nuclear control, astrophysical research and medical imaging, etc. However, the poor transport of holes will degrade the spectral performance of the conventional metal-semiconductor-metal planar CZT detectors. The capacitive Frisch grid CZT detector can overcome the collection problem of holes and improve the detector performance. In this paper, the design parameters of the cylindrical capacitive Frisch grid CZT detector were optimized through finite element simulation using ANSYS software, based on a 3-dimensional weighting potential analysis for the first time. The weighting potential distributions of the model with different ratio between screen length and device height (L/H), insulator thickness (d), insulator relative permittivity (εr), electrode areas of anode and ratio between diameter of cylindrical model and device height (D/H), were studied. Simulation results indicated that the detector, with a longer screen length, a thinner insulator layer, a bigger relative permittivity value, a smaller electrode area of anode and a smaller diameter value of cylindrical model compared to device height could get a more compressed weighting potential. And finally the optimized parameters with a ratio of L/H=100% and ε/d>20 mm⁻¹ were obtained. However, considered about the very high electric field between the anode and the grid that might be the potential factor producing a leakage current, the design parameters have to be compromised and the optimized parameters should be with a ratio of L/H of about 80%, d/εr<0.1 mm and the anode diameter of about 2 mm.

Based on the simulation results, the cylindrical and cuboid capacitive Frisch grid CZT detectors were fabricated. They were both treated by two-step passivation process, in which the mixed solution of bromine–methanol and lactic acid in ethylene glycol (BMLB) treated CZT wafer was first etched by using a KOH aqueous solution, and then by using a NH₄F/H₂O₂ mixed solution. The leakage current of two different geometrical structure was measured by the current-voltage measurement. The results showed that the cylindrical capacitive Frisch grid CZT detector could get better performance than the cuboid capacitive Frisch grid CZT detector. This indicated that the passivation effect of the cylindrical structure was better than that of the cuboid structure. The cylindrical structure could more effectively reduce leakage current of the CZT detector.

Key words: CdZnTe, Simulation, Frisch grid, cylindrical

* Corresponding author: hhddmn1220@126.com, Tel.: 13564595452
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Analysis of In and Al doped High Resistivity CdZnTe Crystal

Changjun Wang, Jiahua Min, Chenying Zhou, Xiaoyan Liang, Yue Zhao, Linjun Wang, Yiben Xia

School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China

Abstract: CdZnTe is a material, which offers the opportunity to achieve excellent spectral and spatial resolution for compact hard X- and gamma-ray detection systems operating without cryogenics. The performance of detectors is generally dominated by the bulk material properties. Therefore, how to grow high-quality CdZnTe crystals with good microstructure integrity and excellent electrical property has become a popular study for researchers these years. In this paper, the Vertical Bridgman Method was used to grow In-doped, Al-doped and In, Al co-doped CdZnTe crystals, in which the amount of In is $10 \times 10^{17}/\text{cm}^3$, Al is $10 \times 10^{17}/\text{cm}^3$, In-Al is $5 \times 10^{17}/\text{cm}^3$ respectively. The low-temperature photoluminescence (PL), deep level transient spectroscopy (DLTS) and X-ray diffraction (XRD) were applied to study the energy level of chief defect and the possible existence of compensatory mechanisms in CdZnTe crystal.

The XRD results showed that lattice distortion existed in the three samples, and the degree of lattice distortion in Al-doped crystal was obviously higher than that of In-doped crystal. The possible reason was that the stress which caused by the occupation of In and Al atom at Cd vacancy made atoms depart from their equilibrium position and led to the flex and distortion of lattice. At the same time, as the radius of In and Al atom is different, the stress caused by them was also different, which produced different lattice distortion. The DLTS results showed that, in the three samples, the deep level electron traps all existed at the same place which is 0.74eV below the conduction band. This energy level may caused by the antisite defect of [TeCd]. Results of PL test showed that both In and Al atoms occupied the original Cd vacancy in CZT crystal and formed donor defects of shallow substitute [$In_{Cd}^-$][Al_{Cd}^+]. Meanwhile, [$In_{Cd}^-$], [Al_{Cd}^+] and [$V_{Cd}^{2-}$] also combined and became the compound defect of [(Al_{Cd}^+-V_{Cd}^{2-})] and [(In_{Cd}^+-V_{Cd}^{2-})]. Comparing with different doped CZT crystals, the defect concentration of In-doped crystal was higher than that of the Al-doped crystal, which was possibly due to the different compensation amount of Cd vacancy caused by the different concentration of In and Al dope.

Therefore, according to the test results, as the radius of In and Al atom is different, the lattice distortion of Al-doped CZT crystal is larger than that of the other doped CZT crystal, which make the defect concentration become greater.

Key words: In:CdZnTe; Al:CdZnTe; X-ray diffraction; Low-Temperature PL; Deep Level Transient Spectroscopy; Lattice distortion

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Corresponding author: dajiang@shu.edu.cn. Tel.: +86 158 0190 2032.
Control of vapor pressure of cadmium at growth and annealing of CdZnTe:Cl crystals with the variable content of zinc for nuclear detectors

E.V. Beregulin, N.K. Zelenina, V.P. Karpenko, O.A. Matveev, V.E. Sedov, A.I. Terentyev, A.A. Tomasov

Ioffe Physical Technical Institute, Polytekhnicheskaya 26, St. Petersburg 194021, Russia

Compensation of conductance of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}:\text{Cl}$ crystals with variable content of Zn ($x = 0.0002$, $x = 0.005$ $x = 0.01$ and $x = 0.05$) for nuclear detectors both during postgrowth annealing of ingots and at annealings of separate samples at different vapor pressures of Cd was investigated.

Value of minimal concentration of Zn, $x = 0.0002$, since which its effect on a range of vapor pressure of cadmium in which there is an inverse of conductance type is revealed will approximately match to concentration of Cl. Annealing temperature of samples 900°C was chosen, in terms of conditions of formation of the natural point defects concentration comparable to concentration of chlorine in a sample that is necessary for a charge compensation in the semiconductor. It is shown, that in annealed samples a minimum of concentration of electrons (inverse in p-type) is shifted aside major magnitudes of $P_{\text{Cd}}$ at increasing of Zn content in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}:\text{Cl}$. It is established that at a constant value of Cl concentration in samples with the greater concentration of $\text{V}_{\text{Zn}}$ the role of $\text{V}_{\text{Cd}}$ in a charge compensation of point defects decreases and thus it is required also higher $P_{\text{Cd}}$ for inverse of an acceptor state in donor. At the small content of zinc ($x = 0.005$ and $x = 0.01$) point defects of cadmium have a determining effect on compensation of conductance in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}:\text{Cl}$. At the content of zinc $x = 0.05$ compensation of the charged defects is insufficiently controlled by change of a vapor pressure of cadmium, and it is necessary to take into account essential effect of point defects of zinc. Thus, for obtaining the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}:\text{Cl}$ crystals ($x \geq 0.05$) with the best transport performances, it is necessary to control not only a vapor pressure of cadmium, but also a vapor pressure of zinc during growing material.

The made conclusions have been used at $\text{Cd}_{1-x}\text{Zn}_x\text{Te}:\text{Cl}$ crystal growing. On crystals with Zn content $x=0.0002; 0.005; 0.01$ with change of conditions of annealing it was possible to achieve high values of $\mu_{s_1}\tau_1$ and $\mu_{b_1}\tau_1$, comparable with these values for $\text{CdTe}:\text{Cl}$. For crystals with $x=0.05; 0.1$ $\mu_{s_1}\tau_1$ and $\mu_{b_1}\tau_1$ practically did not depend on conditions of postgrowth annealing.

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Se-Se isoelectronic centers in high purity CdTe

Rita Najjar¹, Andrzej Golnik², Régis André¹, Piotr Kossacki², Henri Mariette¹ and Jan Gaj²

¹CEA-CNRS group “Nanophysique et semiconducteurs”, Institut NEEL-CNRS, BP166, 38042 Grenoble cedex 9, France
²Institute of Experimental Physics, University of Warsaw, Hoża 69, 00-681 Warszawa, Poland

We detect zero-dimensional exciton states related to impurity centers based on Se in CdTe semiconductor layers. In very high purity CdTe, doped with Se at low density, sharp discrete lines arising from single emitters are observed in photoluminescence spectra. These lines fall within 40 meV below the CdTe band gap energy. We were able to unveil the in-plane optical anisotropy of these individual centers, identify their particular crystal configuration and map their spatial distribution. The most prominent lines are due to a hole and an electron bound to nearest-neighbor selenium pairs in a tetrahedral CdTe environment. This assignment is confirmed by an ultra low spatial density of the emitters (consistent with the probability of forming pairs) and by a common linear polarization direction of the emitted light, parallel to [110]. Within this framework, a discussion of the nature of isoelectronic traps in semiconductor will be presented.

Time resolved spectroscopy has been used to observe the characteristic lifetimes of excitons bound to the Se pairs. At 2K, the decay time of these localized excitons has been found to be of the order of 8 ns. Also, signature of transfer mechanisms of Se-Se bound exciton in CdTe:Se is observed at higher values of the excitation power. Finally we performed autocorrelation measurements on a spatially isolated center emitting at 1.557 eV (see figure below)

The experimental autocorrelation function exhibits a marked dip at Δt=0 (antibunching) which proves definitely that we address a single photon emitter at E = 1.557 eV due to a Se-Se isoelectronic center.

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Effect of Variable Crucible Dropping Rate on Solid-liquid Interface in CdZnTe Crystal Growth

Chenying Zhou*, Jiahua Min, Changjun Wang, Xiaoyan Liang, Jianyong Teng, Linjun Wang, Weiming Shi
School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China

Abstract: Compound semiconducting cadmium zinc telluride (CZT) could be used as X-ray and γ-ray detecting material and has a wide range of applications. Nowadays, CZT room temperature nuclear radiation detectors also plays an important role in the protection of the environment and prevention of nuclear terrorist attacks. So far vertical and low pressure Bridgman method (VLPB) is regarded as a promising way to grow CZT crystals for its advantages such as equipment requirement achieved easily and process controlled easily.

Process of CdZnTe crystal growth with low pressure and vertical Bridgman method was simulated by the software of Comsol Multiphysics. In this paper, the influence of variable crucible dropping rate on the solid-liquid interface was investigated. The heat exchange processes such as thermal conductivity, convection and radiation as well as phase change process were taken into account during the calculation. Considering the factor that the crucible dropping rate was variable, the function expression of furnace temperature change was particularly defined by using the function of Heaviside. Moreover, the selection and analysis of crucible dropping rate was obtained by the combination of orthogonal experimental design method and regression analysis method, and the value of relative crystal growth rate was defined so that the influence of variable crucible dropping rate on solid-liquid interface could be discussed by comparing this value.

The simulation results showed that if the crucible dropping rate was 3.5mm/h (v1) in the first stage and 0.6mm/h (v2) in the second stage, and the distance (d) between the bottom of crucible and the position of melting point in the temperature field was 0.02m at the time of dropping rate change, the solid-liquid interface was appreciably convex after 211 hours’ growth, while the length of CdZnTe crystal was 5cm and the diameter was 3cm. Meanwhile, according to the result of calculation, the relative crystal growth rate was 0.45%, which made the solid-liquid interface smooth and kept the crystal grow up spontaneously.

Key words: CdZnTe; Solid-liquid interface; Regression analysis; Orthogonal experimental design; Relative crystal growth rate;

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*Biography: Chenying Zhou (1984–), female, Shanghai, China. She received the B.S. degree and now is studying for M.S. degree in the School of Materials Science and Engineering, Shanghai University. Her technical research is mainly about the process of CdZnTe crystal growth.

Corresponding author: zhouchenying1984@yahoo.com.cn. Tel.: +86 139 1794 6156.
Chemical diffusion and defect reactions in CdTe<In>

R. Grill, E. Belas, M. Bugár, B. Nahlovskyy, P. Moravec, and P. Höschl
Charles University, Faculty of Mathematics and Physics, Institute of Physics,
Ke Karlovu 5, Prague 2, CZ-121 16, Czech Republic

Chernivtsi National University, 2, vul. Kotziubinskoho, 58012 Chernivtsi, Ukraine

Recent progress at the understanding of defect structure of CdTe doped by group III and group VII donors including quantitative description of principal defect reactions allows a realistic modeling of electric properties and diffusion. Contrary to the high temperature defect equilibrium studied extensively in the past, the evolution of defect structure occurring during the cooling was much less explored in spite of a big effect it has on electric properties at the room temperature. In this talk we report on the experimental and theoretical study of defect structure, defect relaxation and electric properties of CdTe doped by indium, which is frequently used for a preparation of room temperature X- and gamma-ray semiconductor detectors. Experiments are based on high temperature in-situ galvanomagnetic measurements performed at temperature in the 673-1173K range and at defined Cd pressure $P_{Cd}$. Theoretical modeling of defect structure and diffusion is done within quasichemical formalism and local defect equilibrium.

Both experimental results and theoretical simulations demonstrate the possibility to control the low temperature free carrier density by initial component pressure at which the defect equilibrium is established and by changing the cooling rate. The character of defect reactions is principally given by the initial stoichiometry deviation mediated by Cd vacancies, which compensate substitutional donors In$_{Cd}$ and near maximum $P_{Cd}$ by Cd interstitials. The cooling rate limits the Cd diffusion and defect self-compensation, which proceeds at low temperature. Theoretical fit of experimental results is used for more precise specification of properties of involved point defects and for the determination of chemical diffusion coefficient in CdTe<In>. 
Special Features of Conductivity of Semi-Intrinsic CdTe and CdZnTe Single Crystals Used in X- and γ-ray Detectors

L.A. Kosyachenko¹, O.L. Maslyanchuk¹, O.V. Sklyarchuk¹, O.F. Sklyarchuk¹, V.A. Gnatyuk², T. Aoki³, C.P. Lambropoulos⁴

¹Chernivtsi National University, Kotsybinsky Str. 2, Chernivtsi 58012, Ukraine
²Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, prospekt Nauky 41, Kyiv 03028, Ukraine
³Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Hamamatsu, Japan
⁴Technological Educational Institute of Chalkida, Psahna-Evia 24400, Greece

CdTe and CdZnTe are the basic materials used for the manufacture of semiconductor spectral X- and γ-ray detectors and for imaging devices. The application field of such detectors, operating without cryogenic cooling, has permanently expanded. The main difficulty in fabrication of CdTe and CdZnTe detectors is attributed to the requirement that the electrical conductivity of the semiconductor should be close to the intrinsic one. Only in this case, it is possible to create a strong electrical field in the active region of a device which is sufficient for efficient collection of charges generated by photon absorption.

We have performed the experimental investigations and calculations based on the electroneutrality equation and revealed some features of the electrical conductivity mechanism in semi-insulating CdTe and CdZnTe single crystals which have not been discussed in the literature. These features are associated with the presence even in purest and crystalline perfect single crystals (e.g. made by Acrorad Corporation) residual impurities and accidental defects of both of donor and acceptor types which create shallow and deep levels in the band gap of the semiconductor. As it was possible to expect, the calculations showed that to obtain the material with the electrical conductivity close to intrinsic one was simpler by compensating the impurity with the level located near the midgap. Our calculations allowed us to define also the compensation degree accuracy which was needed to keep the electrical conductivity in the given limits. The results of consideration of electron and hole statistics in the compensating semiconductor with deep levels allowed us to explain the anomalous behavior of the temperature dependence of the electrical conductivity experimentally observed in CdTe and CdZnTe. While the thermal activation energy ΔE of the electrical conductivity of the intrinsic semiconductor should be equal to $E_g/2$ ($E_g$ is the band gap at $T = 0$), our measurement results imply that $\Delta E > E_g/2$ even in the case when the impurity level is considerably shifted from the midgap in $p$-type CdTe and CdZnTe. Such anomaly is due to participation of electrons in the electrical conductivity of a $p$-type semiconductor. The calculation has shown that an excess of $\Delta E$ over $E_g$ increases with rising the compensation degree of the impurity responsible for the electrical conductivity of the semiconductor and can be ~ 0.2 eV and even more. Because the electron mobility of CdTe and CdZnTe single crystals is higher than the hole mobility by more than one order of magnitude, the effect appears significant even in the case when the Fermi level is considerably shifted from the midgap.

The discussed features of the electrical conductivity mechanism strongly affect the operating characteristics of CdTe and CdZnTe detectors in particular the reproducibility and temperature dependence of their parameters.
ZnS is well-known as a host material for efficient phosphors used in cathode-ray tubes, electroluminescence devices, etc. It is also known as a semiconductor that has a wide band-gap of 3.7 eV and hardly shows p-type conduction. Therefore, it is worthwhile achieving p-type control in ZnS as both basic research and applied research for optoelectronic devices operating in visible to UV spectral range. So far, there have been several reports on p-type conduction in ZnS, including our results on ZnS:Li [1]; however, the properties and/or reproducibility have not met requirements for practical use. Although p-type ZnSe:N can be grown by molecular beam epitaxy (MBE) using N plasma source, there were few reports on the application of this technique to ZnS. On the other hand, Kishimoto et al. reported that the incorporation of Ag enhanced p-type conduction in their ZnS:N samples grown by vapor phase epitaxy [2]. Therefore, it is interesting to investigate the effect of Ag addition and its mechanism in MBE-grown samples. In this paper, we report N acceptor doping of ZnS using MBE and RF plasma N source. The effects of Ag co-doping of ZnS:N are also reported.

ZnS:N and ZnS:N,Ag epi-layers were grown on (001) GaP substrates by a MBE system designed for the sulfide growth and equipped with an RF plasma source using N2 gas. The details of the growth conditions were similar to those reported elsewhere [3]. The epi-layers were characterized by using secondary-ion mass spectroscopy (SIMS), X-ray diffraction, low temperature photoluminescence (PL), etc. The capacitance-voltage (C-V) characteristics were also measured using the double Schottky configuration, i.e., two concentric Au electrodes with different areas so that the conduction type was determined by the dependence of the capacity on the polarity of the bias voltage.

The SIMS analysis showed the existence of nitrogen in the ZnS:N epi-layers, and the low temperature PL spectra of the ZnS:N epi-layers exhibited acceptor-related emission lines. While the undoped ZnS epi-layers showed weak n-type behavior in C-V characteristics, most of the ZnS:N layers showed semi-insulating characters. In addition, some of the ZnS:N layers grown under the optimum conditions exhibited p-type behavior. The variation in the capacitance with varying the bias voltage was small and it was difficult to estimate the reliable values of net acceptor concentration, however, the above results indicate the conversion of the conduction type into a p-type. The effects of Ag addition to the ZnS:N layers on the electrical and the other properties are also presented.

Self-activated luminescence spectra of CdS(O) in the Context of the Band Anticrossing Model

N. K. Morozova, N. D. Danilevich, A. A. Kanakhin

Moscow Power Engineering Institute (Technical University),
111250 Moscow, Russia

Interpretation of the spectra of CdS(O) self-luminescence is given by using the band anticrossing theory, which determines a change of the band structure under an action of oxygen isoelectronic impurities [1-2].

The unmasked bands SA and SAL of the CdS(O) luminescence are similar to those earlier investigated in ZnS-ZnSe(O) and define the spectral position of band components in dependence on the dissolved oxygen concentration. Green edge emission of CdS, as it turned out, is analogous to the SAL band in ZnS-ZnSe(O), but its H-component is absent since it corresponds to the area of fundamental absorption. Analysis of SA and SAL complexes in CdS also confirms their analogy to ZnS(ZnSe).

On the basis of the experimentally defined position $E_0$ the dependence $\gamma(O)$ and the band structure model for CdS(O) are proposed. The role of oxygen aggregates in bowing band gap in the luminescence of CdS(O) crystals is explained. These results are described in comparison to earlier investigations of ZnS-ZnSe(O) [1-8].

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Point and nanoscale defects in Cd(S, Se,Te) crystals induced by plastic deformation

V. Babentsov¹, V. Boiko¹, J. Franc², and G.A. Shepelskii¹

¹Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, Kiev 03028, Ukraine
²Institute of Physics, Faculty of Mathematics and Physics, Charles University, Prague CZ 121 16, Czech Republic

The effect of uniaxial plastic deformation, indentation, and scribing along the selected axes on the excitonic and deep level photoluminescence (PL) of CdS, CdSe, CdTe, and ternary CdSeTe compounds was studied. Moving dislocations produce special near band-gap narrow PL lines, and changes in the deep level emission, in particular, a relative intensity increase or appearing of the near midgap 0.8 eV, 1.1 and 1.45 eV bands in CdTe, and corresponding PL bands in CdS, CdSe, and CdSeTe.

The unstable with temperature narrow near bandgap PL lines were accompanied in the uniaxially plastically deformed CdS with the absorption lines. These lines were not found to be related to the stable defects which existed in the crystal prior deformation. These facts, together with a great absorption coefficient, gave the possibility to ascribe these lines to the excitons bound to nanoscale defects.

Further investigations on the defects with deep levels in undoped and doped samples of CdS, CdSe, and CdTe have been performed by increasing the density of defects by mechanical indentation and scribing. By this process extended as well as point defects are introduced in respect with the selected crystal axes, namely, in the cation and anion sublattices. More precisely, the rosette arms and the area between two adjacent scribing, and the direction of scribing were considered in relation with the crystal axes. The same emission bands were also studied corresponding to undeformed and deformed crystals with low and higher deformation (different loads to the indentor).

Measurement of the integrated PL reveals that besides the observed quenching, the deep level relative intensities increase, and some bands appears in the luminescence of plastically deformed crystals. The relative intensities of the deep level PL bands in the spectra depend on the applied load and on the orientation of indentation. The present observations as well as previous works show that plastic deformation causes generation of nonradiative recombination centers, but also generate commonly observed defects of the lattice, that can be attributes to the cation or anion vacancies, respectively, depending on the dislocation nature. During the dislocation movement, also, these point defects may form one dimension nanoscale defects with specific spectroscopic features.

The observed phenomenon of the dislocation interaction with an impurity-defect system may be important for the stabilization of compensation, minimization of trapping, and studying of nano-structures in the crystal environment.
Energy transfer processes in ZnSe/ZnMnSe double quantum well structures

S. Jankowski, W. Heimbrodt, S. Horst, A. Chernikov, and S. Chatterjee

Philipps-Universität Marburg; Department of Physics and Material Science Center, Renthof 5, D-35032 Marburg, Germany

The complicated interplay of energy transfer and tunneling processes in a series of asymmetric ZnSe/ZnMnSe double quantum well (DQW) structures are investigated by steady-state and time resolved photoluminescence at low temperatures and external magnetic fields up to 7 Tesla. The pure quantum mechanical tunneling process is only a minor contribution to the magnetic field dependence of the emission even in case of small barriers and strong QW coupling. The experimental results are supported by quantum well calculations.

All samples are grown on a ZnSe buffer on a (100) GaAs substrates. The inner barrier width was varied between 5 nm and 100 nm and the Mn concentration was set to >30% to avoid a type I – type II transition, which occurs already at small magnetic fields in case of smaller Mn contents. Remarkable differences are found when comparing the optical properties of ZnSe/ZnMnSe DQWs with earlier measurements on supposedly very similar system CdTe/CdMnTe DQW structures. The external magnetic field manipulates the barrier height and splits the states of the quantum wells due to the Giant Zeeman effect of the ZnMnSe barriers in both systems. However, the systems are different in the following two aspects: Firstly, the ZnSe quantum wells are under tensile strain yielding the light-hole (lh) exciton states as the lowest lying states in energy while traditionally, systems with heavy hole (hh) excitons as lowest lying state are investigated. Secondly, the band gap of both ZnSe wells and ZnMnSe barriers are larger than the internal 3d-transition of the Mn$^{2+}$ ions. Thus, the expected tunneling behavior is camouflaged.

The magnetic field dependence of the energy exchange between band states and the internal 3d states of the Mn influences the emission properties. The energy transfer from the exciton bath into the Mn systems obeys spin conservation as the $^6A_1 \rightarrow ^4T_1$ transition involves a spin flip. In this process, both dark excitons and bound excitons are involved. This transfer process is, however, strongly field dependence. The exciton envelope-functions of the quantum wells strongly penetrate the barriers, therefore the exciton - Mn bath interaction is strong even for the ZnSe wells. The intensity and decay time of the QW-PL is influenced by the dwindling of the loss channel to the manganese subsystem.

Additionally, in Faraday geometry, the conduction band splits into the lower and higher energy $|1/2,-1/2>$ and $|1/2, 1/2>$ states and the lh splits into the $|3/2,-1/2>$ and $|3/2, 1/2>$ state, respectively. However, the $|1/2,-1/2>$ to $|3/2,-1/2>$ transition is dipole forbidden in this geometry. Therefore, the PL intensity decreases up with increasing applied external magnetic field until the hh and lh states cross at the critical field $B_c$ where the $|1/2,-1/2>$ to $|3/2,-3/2>$ transition becomes favored due to the stronger Zeeman splitting and is the lowest transition in energy. The tunneling processes are covered by the respective intensity changes.
Spin states in quantum dots have been proposed as candidates of quantum bits in quantum computing. Understanding of the spin-interaction, -tunneling or -transfer phenomena, and controlling and manipulating of the spin state of localized carriers or excitons are crucial for realizing new spin-electronic devices. In this paper we describe interaction between spin-polarized excitons localized in ZnCdSe and ZnCdMnSe coupled double quantum wells (DQWs). The degree of the interaction is expected to depend on the distance between interacting excitons and also on the energy levels of the excitons [1].

ZnSe/ZnCdSe/ZnSe/ZnCdMnSe/ZnSe DQW structures were grown by molecular beam epitaxy on GaAs (100) substrates. A diluted magnetic semiconductor (DMS) well and a non-DMS (NMS) well were separated by a ZnSe NMS spacer layer of thickness $L_S$. The compositions of Cd and Mn were 25 and 3 %, respectively. The DMS well thickness $L_{DMS}$ and NMS well thickness $L_{NMS}$ were so designed as to set the energy level of the DMS well ground state close to the second excited state level of the NMS well. In order to study the degree of interaction by changing the distance and the energy level separately, two series of samples were prepared. The first series includes samples with a fixed $L_{DMS}$ and different $L_S$’s, and the samples in the second series have a fixed $L_S$ and different $L_{DMS}$’s. Circularly polarized magneto-photoluminescence (PL) and -reflectance spectra were measured in the Faraday geometry at 4 K for $B = 0 – 8$ T. PL was excited by using the 325 nm line of a He-Cd laser. The 477 nm line of an Ar + laser was also used to excite carriers only in the NMS well. The degree of circular polarization $P = (I^+ - I^-) / (I^+ + I^-)$ was measured as a function of magnetic field, $L_S$ and $L_{DMS}$, where $I^+$ and $I^-$ are respectively the PL intensities due to down-spin and up-spin exciton recombinations. In addition to the magnetic field, electric field was applied normally to the sample surface in order to shift the energy levels in the DMS and NMS wells.

The ground-state exciton PL in the DMS and NMS wells were observed respectively around 2.7 and 2.5 eV. The DMS wells showed large positive $P$s in magnetic fields and the NMS well showed negative $P$s in case of no interaction, as well as SQW samples. The $P$ of NMS well ($P_{NMS}$) was found to change from -5 % to +4 % at $B = 4$ T according to the degree of interaction between excitons in the two wells. In the first series samples, the $P_{NMS}$ of the sample with $L_S = 50$ and 100 Å was respectively +1.5 and +1.5% at $B = 4$T. The samples with $L_S = 500$ and 1000 Å and NMS SQW showed $P_{NMS} = -4\%$. The data indicate that the number of down spin exciton in the NMS well increased by tunneling from the DMS well with decreasing $L_S$. In the second series samples, where strong coupling is expected with $L_S = 30$ Å, the samples with $L_{DMS} = 20, 15$ and 10 Å showed $P_{NMS} = +4, -2$ and -5\%, respectively. The electric field perpendicular to the sample surface was found to change the $P_{NMS}$. The data indicate that the degree of interaction changed according to the energy levels in the two wells. The calculation of quantum levels of the coupled DQW suggested resonant tunneling from the ground state of the DMS well to the second excited state of the NMS well.

Dynamics of Exciton Magnetic Polaron Formation in CdMnSe/CdMgSe Quantum Wells

Tillmann Godde, Irina I. Reshina, Sergey V. Ivanov, Ilya A. Akimov, Dmitri R. Yakovlev, and Manfred Bayer

Experimentelle Physik II, Technische Universität Dortmund, D-44221 Dortmund, Germany

Ioffe Physical-Technical Institute RAS, 194021 St. Petersburg, Russia

It is known that strong spin-spin exchange interaction between s and p band carriers and d-electrons of Mn$^{2+}$ ions in diluted magnetic semiconductors may result in formation of an exciton magnetic polaron (EMP). The previous studies in bulk as well as in low dimensional structures have been mainly concentrated on CdMgMnTe and ZnMnSe compounds. Formation times on the order of 50 – 100 ps have been reported [1,2]. Here we present the results in the new material system based on CdMnSe/CdMgSe type I quantum well (QW) structure.

Five periods of CdMnSe/CdMgSe layers with quantum well width 38 Å, and barrier thickness 97 Å were grown by molecular beam epitaxy on InAs (001) substrates. The Mn concentration was 6.5 % and that of Mg 17%. Time integrated photoluminescence (PL) measurements allow to determine the energy of EMP $E_{\text{MP}}$. Reflectivity spectra in conjunction with circular polarization dependence on magnetic field yield $E_{\text{MP}} = 15$ meV. Selective excitation technique gives the value of 12 meV. The strong blue shift of PL line (about 10 meV) with temperature increase from 2 to 25 K clearly confirms EMP contribution to PL spectra.

Time resolved PL measurements using streak camera and pulsed excitation have been performed for different magnetic fields $B$ and temperatures $T$ in the range from 0 to 7 T and 2 to 25 K, respectively. At low $T=2$ K and $B=0$ we observed strong red shift of the PL line by 18 meV with the time constant of about 500 ps. Increase of magnetic field or temperature leads to disappearance of the PL shift, which is attributed to EMP suppression. From $B$ and $T$ dependences we distinguish between the non-magnetic and magnetic contributions of the localization. We find $E_{\text{MP}} = 15$ meV, which is in agreement with time integrated measurements. Surprisingly we find a slow EMP formation time of 500 ps, which is significantly longer than the values reported earlier. We propose that such behaviour is related to strong auto-localization of the EMP, accompanied with the compression of the heavy-hole envelope wave-function. This conclusion is supported by decrease of the exciton lifetime from 600 ps to 200 – 400 ps with increase of magnetic field and temperature.


Semimagnetic semiconductors are mixed crystal where the cations of host semiconductor are partially substituted for magnetic ions. Photoexcitation of electron and hole of a semimagnetic semiconductor results in an exciton and the exciton aligns spins of magnetic ions in its area of wave function through $s,p$-$d$ exchange interaction; finally the exciton becomes an exciton magnetic polaron. In these days, we reported discovery of a nonlinear PL band of Cd$_{0.8}$Mn$_{0.2}$Te (hereinafter referred to as high-density exciton magnetic polaron: HD-EMP band) [1] by selective excitation of the localized exciton. As the origin of the HD-EMP band, we suggested the high-spin state of HD-EMP. In the high-spin state, every spin of Mn ions points in the same direction. Recently, we have built up a time-resolved Kerr-rotation measurement system with a view to study the magnetization of the high-spin state of HD-EMP. In this paper, we discuss photoinduced magnetization of Cd$_{0.8}$Mn$_{0.2}$Te under the high-density free exciton resonant excitation, as a first step. Figure 1 shows timer-resolved Kerr-rotation signals of a single bulk crystal of Cd$_{0.8}$Mn$_{0.2}$Te without magnetic field. In the case of band-to-band excitation, no significant signals appear. In contrast, we can observe three peaks in the case of the free-exciton resonance excitation. Every three peak changes its polarity when polarization of pump light is changed from $\sigma^+$ to $\sigma^-$ polarization. The peak at time origin corresponds to coconstantaneous existence of pump and probe pulses. Then, the second peak around 30 picoseconds is originating from the carrier spins transferred from the energy state resonated with the pump light to that of probe energy. Finally, the third peak, arising from 40 picoseconds and having its maximum around 80 picoseconds, corresponds to the magnetization by the exciton magnetic polaron formation. Changing the pump energy from band-to-band to the free-exciton resonance enables us to suppress spin relaxations. This result is consistent and supportive for our suggestion that the selective excitation of localized excitons with energy lower than that of free excitons leads to the high-spin state of HD-EMP. As the next step, experiments under high-density selective excitation of localized excitons will be expected. This work was supported in part by Global Center of Excellence Program "Nanoscience and Quantum Physics", from MEXT, Japan.

References
Kinetics of exciton magnetic polaron emission in type-II ZnMnSe/ZnSSe QWs

A.S. Brichkin, A.V. Chernenko and V.D. Kulakovskii
Institute of Solid State Physics of RAS, 142432, Chernogolovka, Russia
S.V. Sorokin and S.V. Ivanov
Ioffe Physico-Technical Institute, RAS, 194021 St. Petersburg, Russia

Type II semimagnetic QWs are very attractive objects to explore excitonic magnetic polarons because of expectedly long, ns range, excitonic life-time caused by the special separation of electrons and holes.

To study this issue photoluminescence time-integrated and time-resolved spectra of ZnMnSe/ZnSSe QWs are measured at temperatures 2-20 K in magnetic fields up to 10T both perpendicular and parallel to the sample growth plane. Two MBE grown samples containing 10 periods of Zn$_{1-x}$Mn$_x$Se/ZnSSe QWs' with $x_{\text{Mn}}=0.1$ and 0.16 are measured under an above band gap pulsed excitation (pulse duration and pulse repetition are 1.5 ps and 80 MHz, respectively)

Two relatively broad lines with FWHM about 12-15 meV separated by 18-20 meV are observed in PL spectra. Detailed studies allow one to attribute the high and low energy lines to recombination, respectively, of weakly localized excitons (with lifetime $\tau \sim 100$ ps) and excitonic magnetic polarons (EMPs) with $\tau \sim 5$ ns comparable to the distance between the exciting pulses. The EMP emission demonstrates two formation kinetics. The fast one has a characteristic time $\tau_{1}^{\text{EMP}} \sim 30-50$ ps whereas the slow one continues $\tau_{2}^{\text{EMP}} \sim 150-200$ ps. The fast kinetics results in an increase of the EMP emission just at the spectral position of the EMP line whereas the slow one starts from the emission of delocalized excitons and is followed by a monotonic shift of the emission (~ 15 meV) to the EMP position. The slow process is the typical EMP formation process. It starts from a hole localization on potential fluctuations with subsequent gradual alignment of Mn ion spins due to p-d exchange interaction. The fast process demands the holes to be captured by potential fluctuations with spin polarized Mn ions. Such fluctuations appear after the EMP recombination. The relaxation of macroscopic magnetic moment of EMP is quite slow process which provides their living during several ns till the next exciting pulse. Note that this process provides a nearly half of photoexcited EMP at the pulse repetition of 12 ns.

One of important characteristics of EMPs is its effective volume. To estimate the EMP volume and its dependence on magnetic field the magnetic field dependences of the ratio of intensities of LO and no phonon (NP) EMP emission lines have been investigated both in Faraday and Voigt geometries. The localization volume determines the range of allowed k-space for emitting LO phonons. As a consequence the relative intensity of the LO replica or Huang-Rhys factor decreases approximately proportional to the EMP localization radius [1]. The value of EMP localization radius $r = 3-4$ nm have been found for both samples. In the sample with $x_{\text{Mn}}=0.16$ $r$ increases weakly, less than 2 times at the in-plane magnetic field B=10 T, and about 5 times at magnetic field of 10 T normal to the QW’s plane. In the sample with $x_{\text{Mn}}=0.10$ the increase of $r$ is much stronger: about 4 times at B=10 T in the Voigt geometry and nearly ten-fold in the magnetic field of 3-4 T in the Faraday geometry.

Reference:
Influence of photo-generated carriers on the Mn-Spins in CdMnTe Quantum Wells studied by Spin-Flip-Raman Spectroscopy in a Two-Colour Experiment

C. Kehl, G. Astakhov, J. Geurts, W. Ossau
Universitaet Wuerzburg, Physikalisches Institut, Experimentelle Physik III, 97074 Wuerzburg, Germany

Yu. Kusrayev, K. Kavokin
A.F.Ioffe Physico-Technical Institute, RAS, 194021 St. Petersburg, Russia

T. Wojtowicz
Institute of Physics, Polish Academy of Sciences, 02668 Warsaw, Poland

According to theoretical predictions [1], in diluted magnetic II-VI compounds the strong exchange interaction between the magnetic ions (Mn) and a two-dimensional gas of heavy holes (2DHG) should reduce the Zeeman splitting of localized Mn-spins.

We have studied this effect in Cd_{1-x}Mn_xTe quantum wells with a photo-induced 2DHG. By Spin Flip Raman Spectroscopy, we have measured with high accuracy the Raman shift from the paramagnetic resonance transition of the Mn-spins in an in-plane magnetic field as a function of the hole concentration. This concentration was varied by additional optical irradiation with different intensities.

The samples were suited for the optical generation of an excess concentration of holes in the undoped CdMnTe well by the utilization of a CdMgTe barrier (20% Mg, E(Gap) = 1.91eV) as a capping layer. In this capping layer the energy bands are tilted due to the mid-gap pinning of the Fermi-level at the CdMgTe surface. This tilting drives positive charges towards the well, and negative ones towards the surface. The positive carrier diffusion from the barrier into the well was controlled by additional above-barrier illumination (Ar-laser: 2.41eV). For the assessment of the photo-induced hole concentration we utilize the near-band-edge photoluminescence spectrum of the well, in which these carriers manifest themselves by the formation of positively charged excitons (trions). The net carrier density in the well is monitored qualitatively by the trion-to-exciton intensity ratio, and quantitatively by their spectral distance, which includes the carrier-induced shift of the Fermi-energy in the well.

When applying the resonant magneto-Raman spectroscopy for studying the Mn g-factor, we utilized multiple spin flip scattering, which specifically may occur in quantum wells [2]. For external in-plane B fields (Voigt-geometry) up to 4.5 T, Mn spin flips up to the fourth order allowed a high-accuracy g-factor determination.

As the main result a clear decrease of the g-value in the order of 10% with increasing net charge carrier density is observed. While the g-factor is about 2.00 without additional carriers from above barrier illumination, the value decreases to ~1.85 by the influence of these carriers. This result is interpreted in terms of a hole-induced exchange interaction between Mn ions as an indication of magnetic softening with increasing hole concentration according to Ref.[1].

Relaxation of magnetization controlled by spin diffusion in CdMnTe quantum wells

J. Debus, D. R. Yakovlev, A. A. Maksimov, M. K. Kneip, G. Karczewski, T. Wojtowicz, J. Kossut, and M. Bayer

1Experimentelle Physik II, Technische Universitaet Dortmund, D-44221 Dortmund, Germany
2Ioffe Physical Technical Institute, Russian Academy of Sciences, St. Petersburg 194021, Russia
3Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Russia
4Institute of Physics, Polish Academy of Sciences, PL-02668 Warsaw, Poland

Spin dynamics of the magnetic ions system in diluted magnetic semiconductors (DMS) is controlled by spin-lattice relaxation mechanisms. For a Mn-ion in II-VI DMS the spin-lattice relaxation time varies from nanoseconds to milliseconds depending on the Mn concentration [1]. It is long for low Mn contents which would limit high-speed applications.

We suggest a mechanism to accelerate the spin-lattice relaxation. Appearance of this mechanism is possible only in DMS heterostructures with nonuniform concentration of magnetic ions, where the spin diffusion inside the magnetic ion system moves nonequilibrium spins from the parts with low relaxation rate (low Mn content) to the parts with high relaxation rate (high Mn content).

The efficiency of this mechanism has been analyzed theoretically and examined experimentally for (Cd,Mn)Te/(Cd,Mg)Te heterostructures: (i) digital superlattices and (ii) parabolic quantum wells formed by the gradient of the Mn concentration across the well width. Relaxation dynamics was measured by all optical technique, when the Mn spin system was heated by laser pulses and changes in the giant Zeeman splitting of excitons were detected in time domain. Acceleration of spin-lattice relaxation by one-two orders of magnitude has been found. The relaxation dynamics is modeled and a good agreement with experiment is achieved, which allows determination of the spin diffusion coefficient. Also regimes of nonexponential relaxation of magnetizations are found and discussed.

Electrical control of spin polarization in a CdMnTe/CdMgTe quantum well on a micrometer scale

Y. S. Chen, T. Kümmell, G. Bacher

Werkstoffe der Elektrotechnik and CeNIDE, Universität Duisburg-Essen, Bismarckstr. 81, 47057, Duisburg, Germany

M. Wiater, G. Karczewski, T. Wojtowicz

Institute of Physics, Polish Academy of Science, Al. Lotnikow 32/46 02-668 Warsaw, Poland

Gaining control over the spin degree in a semiconductor is a key issue in spintronics. A straightforward approach is the usage of magnetic fields, where, however, high frequency operation is quite challenging. Here, we present an approach based on microscale current loops, where strongly enhanced spatial and temporal resolution are expected as compared to traditional macroscopic Helmholtz coils. This allows us to demonstrate a local control of the spin polarization in a diluted magnetic semiconductor quantum well (DMS QW) on a micrometer length scale and a sub-microsecond time scale.

By electron beam lithography and lift-off technique, gold microscale coils are defined atop a Cd$_{1-x}$Mn$_x$Te/Cd$_{0.7}$Mg$_{0.3}$Te ($x = 0.067$) DMS QW. Introducing a current through the coil, an electrically switchable magnetic field can be induced which aligns the Mn$^{2+}$ ion spins in the DMS QW layer. Due to $sp$-$d$ exchange interaction between Mn$^{2+}$ ions and carriers, the effective g factor of a heavy-hole exciton is quite large at low temperature ($g_{\text{eff}} \approx 200$ at 4.2 K). This leads to a huge Zeeman energy splitting and therefore an efficient carrier spin polarization by the current-induced magnetic field, which can be probed by spatially and temporally resolved photoluminescence spectroscopy.

A pronounced carrier spin polarization of up to 8.5% is obtained by the current-induced field without external magnetic field. The spatial spin distribution directly reflects the locally varying sign and amplitude of the current-induced field. While for small currents a linear relation between current and spin polarization is obtained, the current-induced heating limits the degree of Mn$^{2+}$ ion spin ordering for $I > 60$ mA. To separate the influence of the current-induced field and the current-generated heating on the spin polarization, we analyze the spin polarization at an external field of 100 mT, which generates a spin polarization of about 50% at 4.2 K. Depending on the direction of the current, the total magnetic field will be enhanced or reduced whereas the current-generated spin heating is independent on the current direction. From the difference between the spin polarization in positive ($\rho_+$) and negative ($\rho_-$) direction, the corresponding current-induced magnetic field can be obtained. The evaluated magnetic field increases linearly with the current amplitude, and the spatial distribution and the amplitude (up to > 20 mT) can be well reproduced by Biot-Savart law. By evaluating the averaged value of $\rho_+$ and $\rho_-$, the spatial distribution of the spin temperature of the Mn$^{2+}$ ions can be extracted. Performing time-resolved experiments, the dynamics of both, magnetization and local heating are probed. We extract a phonon lifetime on the order of 1 $\mu$s and a spin-lattice relaxation time < 100 ns, the latter limited by the time resolution of the setup.

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Optical and photothermal investigations of Zn$_{1-x-y}$Be$_x$Mn$_y$Se solid solutions

F. Firszt$^1$, K. Strzałkowski$^1$, J. Zakrzewski$^1$, M. Maliński$^2$, S. Łęgowski$^1$, H. Łęczyńska$^1$, D. O. Dumcenco$^3$, C. T. Huang$^3$, and Y. S. Huang$^3$

$^1$Institute of Physics, N. Copernicus University, Grudziądzka 5/7, 87-100 Toruń, Poland,
$^2$Department of Electronics, Technical University Koszalin, Sniadeckich 2, 75-328 Koszalin, Poland
$^3$Department of Electronic Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

Zn$_{1-x-y}$Be$_x$Mn$_y$Se semiconductor is an interesting magnetic material for spintronics as a spin filter layer with possible applications in memory technology. The energy gap of BeSe is larger but lattice constant is smaller than corresponding values of ZnSe and MnSe. Mixing of these three binaries allows obtaining Zn$_{1-x-y}$Be$_x$Mn$_y$Se material with different energy gap and lattice constant, matched to different substrates. For application in multilayer technology, knowing of optical and thermal properties of such material is very important. Up to date only a few papers were published concerning growth and properties of Zn$_{1-x-y}$Be$_x$Mn$_y$Se solid solutions. This work deals with optical, luminescence and photoacoustic investigations of bulk Zn$_{1-x-y}$Be$_x$Mn$_y$Se mixed crystals.

Photoluminescence spectra at low temperatures of Zn$_{1-x-y}$Be$_x$Mn$_y$Se samples with Be and Mn content not exceed 20% consist of relatively weak exciton line, shallow donor-acceptor band (edge emission) and the main yellow luminescence band positioned at the energy about 2.05 eV associated with internal transition in Mn ions. The exciton line was observed in samples with Mn content up to 0.2. For larger concentration of manganese only yellow emission is observed at temperatures from 35K to room temperature. The photoluminescence-excitation spectra, when the emission is detected at 2.05 eV, exhibit clearly resolved structure interpreted as due to transitions from the ground $^6A_1(^6S)$ state of Mn to different excited states associated with crystal field splitting.

As the temperature increases, the Mn related emission initially shifts towards lower energies followed by the high energy shift with further temperature rise. Applying the crystal field theory, it has been shown in literature that the major influence on the energetic position of Mn-related PL versus temperature is from the bond length in the crystal. The anomalous temperature behaviour of Mn related emission in Zn$_{1-x-y}$Be$_x$Mn$_y$Se can be explained if one supposes the negative thermal expansion at low temperatures (similar effect was observed in ZnMnTe). With increasing temperature from 30K the lattice shrinks, causing increasing the value of the crystal fields seen by Mn ion. This in turn influences the energetic position of the first excited state $^4T_1(^4G)$ reducing the transition energy to the ground state $^6A_1(^6S)$. Interpretations of the piezoelectrically detected photoacoustic spectra were performed using Jackson and Amer theory. From the spectral dependence of the amplitude and phase of photoacoustic signal the variation of energy gap with composition was determined. In the investigated range of compositions the increasing of Mn content does not influence the value of the energy gap significantly but increasing of Be causes noticeable increase of the band gap energy. The thermal diffusivity was determined from the dependence of photoacoustic signal on modulation frequency of radiation illuminating the sample. It was calculated with the method of fitting of experimental data to theoretical model developed by Blonskij et al.
Temperature-dependent photoluminescence and contactless electroreflectance characterization of Zn$_{1-x-y}$Be$_x$Mn$_y$Se mixed crystals

D. O. Dumcenco, C. T. Huang, Y. S. Huang*, F. Firszt, S. Łęgowski, H. Męczyńska, J. Zakrzewski and K. K. Tiong

1Department of Electronic Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan
2Institute of Physics, N. Copernicus University, Grudziądzka 5/7, 87-100 Toruń, Poland
3Department of Electrical Engineering, National Taiwan Ocean University, Keelung 202, Taiwan

*Author to whom correspondence should be addressed; e-mail: ysh@mail.ntust.edu.tw

A detailed optical characterization of a series of Zn$_{1-x-y}$Be$_x$Mn$_y$Se mixed crystals grown by the modified high pressure Bridgman method from the melt has been carried out via temperature-dependent photoluminescence (PL) and contactless electroreflectance (CER) in the temperature range of 10 to 300 K. Room temperature surface photovoltage spectroscopy has been used as a diagnostic technique of checking the surface condition of the sample. For the mechanically polished sample, the surface photovoltage spectrum at room temperature exhibits a broad feature which is most likely related to the surface states induced by mechanical defect. This feature can be eliminated via mechanical polishing and followed by chemical etching, and hence, only the exciton line was observed for the damage-removed sample.

PL spectra at low temperatures consist of an exciton line, an emission due to recombination of donor-acceptor pairs and broad bands related to the Mn$^{2+}$ intra-ionic transitions. Near band-edge transitions have been observed in the CER spectra. For the low temperature CER spectra, well-resolved Rydberg's series with $n = 1$ and 2 can be clearly observed for low Be/Mn ratio in Zn$_{1-x-y}$Be$_x$Mn$_y$Se solid solutions, while only a single feature is observed for samples with higher Be/Mn ratio. The peak positions of the excitonic emission lines in PL spectra correspond quite well to the energies of the fundamental transitions determined from CER measurements. The transition energies and broadening parameters of the band-edge excitonic features were determined from PL and CER spectra. The temperature variation of the band-edge transition energies were analyzed with the Varshni equation and an expression containing the Bose-Einstein occupation factor for phonons. The temperature dependence of the broadening function also has been studied in terms of a Bose-Einstein equation that contains the electron (exciton)-longitudinal optical (LO) phonon-coupling constant. The parameters that describe the temperature dependence of the band-edge excitonic transitions are evaluated and discussed.

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In the present study, we investigate the magnetic and electric properties of Europium doped IV-VI tin chalcogenides (SnSe and SnS). Unlike other studied rare-earth doped IV-VI materials, SnSe and SnS crystallize in a double layer like orthorhombic crystal. The Eu ions have different environment (reflected by the low site symmetry) as well as a different number of nearest neighbors. The investigation is based on low temperature magnetization measurements and theoretical modeling of the experimental results, Electron Paramagnetic Resonance (EPR), and Resistivity Measurements. Q-band (34 GHz) EPR measurements show that the site symmetry of Eu$^{2+}$ at 4.2 K is orthorhombic and the average Landé factor was determined to be $g = 1.99 \pm 0.01$ and $1.97 \pm 0.01$. The crystal field parameters were obtained from the fitting of the angular positions of the EPR Lines. For both samples, the exchange-coupling between nearest-neighbors (NN) Eu$^{2+}$ ions was estimated from magnetization and magnetic susceptibility measurements using a model that takes into account the magnetic contributions of single ions, pairs and triplets.
Influence of light on the edge state transport in HgTe/HgCdTe quantum wells

E. G. Novik, M. J. Schmidt, M. Kindermann, and B. Trauzettel

1 Physikalisches Institut (EP3), Universität Würzburg, 97074 Würzburg, Germany
2 Department of Physics, University of Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland
3 School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332, USA
4 Institut für Theoretische Physik und Astrophysik, Universität Würzburg, 97074 Würzburg, Germany

Type-III HgTe/HgCdTe quantum wells (QWs) attract a lot of interest during the last few years due to their unique low energy properties such as the quantum spin Hall effect and topological quantum phase transition [1]. Here we consider finite HgTe/HgCdTe QWs with the HgTe layer thickness close to the critical value corresponding to the topological phase transition in the presence of an external magnetic field applied along the growth direction. We calculate the band structure and optical transitions in these QWs and study the influence of light on the charge transport in magnetic-field induced edge states.

The comparison of an effective model [1] with a well-established 8-band $k\cdot p$ model [2] for the symmetrically doped HgTe/HgCdTe QWs was carried out for the relevant range of the well thickness and for wide range of carrier density ($\sim 10^{11}\div10^{12}$ cm$^{-2}$). The parameters as well as the range of applicability of the effective model were determined from this comparison. The effective model was then extended to study optical transitions between Landau levels in the bulk as well as between the edge states. The selection rules for these transitions are found and based on them a method for optical manipulation of charge transport in the QW edge states is proposed. It was shown that with properly tuned laser light it is possible to scatter an electron of the hole-like (counterclockwise moving) edge state into the counterpropagating electron-like (clockwise moving) edge state at constant crystal momentum. This process reverses the group velocity of the scattered electrons and can be used to manipulate the charge current [3].

(100) and (111) CdTe epitaxial layers grown by molecular beam epitaxy for investigation of electron spin relaxation lifetimes

Qiang Zhang\textsuperscript{a,b}, William Charles\textsuperscript{b,c}, Aidong Shen\textsuperscript{c}, Carlos A. Meriles\textsuperscript{a,b}, and Maria C. Tamargo\textsuperscript{b,d}

\textsuperscript{a}Department of Physics, The City College of CUNY, New York, New York 10031
\textsuperscript{b}The Graduate Center of CUNY, New York, New York 10016
\textsuperscript{c}Department of Electrical Engineering, The City College of CUNY, New York, New York 10031
\textsuperscript{d}Department of Chemistry, The City College of CUNY, New York, New York 10031

Based on our previous experience with the growth of ZnSe on GaAs, we have improved the substrate on which we deposit CdTe by first depositing a ZnSe buffer on the bulk GaAs crystal. This allows us to control the II-VI/III-V heterovalent epitaxy prior to the CdTe deposition. Depending on the details of the process used in the formation of the interface between ZnSe and CdTe during MBE growth, it was possible to stabilize the growth of either (100) or (111) CdTe epitaxial layers on the (100) ZnSe/GaAs substrate. Reflection high-energy electron diffraction was used to observe the nucleation of the epitaxial layers in situ during the growth, while x-ray diffraction and photoluminescence measurements indicate that the CdTe is of high structural quality despite the large lattice constant mismatch of 14.3\% between CdTe and ZnSe.

To investigate the spin relaxation lifetimes of the CdTe layers, optically pumped and time-resolved Kerr rotation experiments were performed at different temperatures and excitation wavelengths on the CdTe films with different crystal orientation. The longest spin relaxation times observed at room temperature are 33 ps and 57 ps for (111) and (100), respectively, which are consistent with published values [1]. However, although there is no apparent change of the electron spin relaxation times of the (111) CdTe with temperature, that of the (100) CdTe layers increases by as much as a factor of three when the temperature is reduced to about 100K. The different behavior between the samples with different crystal orientation may be related to the strain or strain-related defect structure within the samples. The study of electron spin relaxation times of electrons in semiconductors could contribute the potential applications for spintronic devices and quantum computation.

Photo-EPR and magneto-optical spectroscopy of the iron centers in ZnO

D.V. Azamat\textsuperscript{1,2}, J. Debus\textsuperscript{1}, D. R. Yakovlev\textsuperscript{1,2}, V. Yu. Ivanov\textsuperscript{3}, M. Godlewski\textsuperscript{3,4}, M. Fanciulli\textsuperscript{5,6}, M. Bayer\textsuperscript{1}

\textsuperscript{1}Technische Universitaet Dortmund, Experimentelle Physik II, D–44221 Dortmund, Germany
\textsuperscript{2}Ioffe Physico-Technical Institute, Russian Academy of Sciences, St. Petersburg, 194021 Russia
\textsuperscript{3}Institute of Physics, Polish Academy of Sciences, Warsaw 02-668, Poland
\textsuperscript{4}Dept. Mathematics and Natural Sciences College of Science, Cardinal S. Wyszyński University, Warsaw, Poland
\textsuperscript{5}Laboratorio Nazionale MDM, CNR-INFM, 20041 Agrate Brianza (MI), Italy
\textsuperscript{6}Dipartimento di Scienza dei Materiali, Universita degli studi di Milano-Bicocca, Milano, Italy

ZnO has attracted increasing interest as promising material for optoelectronics and spintronics. Magnetic properties of ZnO can be controlled by the doping with transition metal ions among which Fe$^{3+}$ is one of the interesting candidates. We report on the properties of Fe$^{3+}$ centers in hydrothermally and CVT grown ZnO single crystals investigated by photo-EPR and optical spectroscopy. Detailed magneto-optical studies of Zeeman components of spin-forbidden electric dipole transitions $^4T_1 \rightarrow ^6A_1$ of Fe$^{3+}$ center in ZnO reveal the trigonal symmetry of fine structure of lowest $^8S$ excited state. The studies were performed in external magnetic fields up to 10 T and in the temperature range from 2 to 30 K. The energy positions of the Zeeman components at 8 T were measured as a function of the direction of applied magnetic field in (1120) and (0001) planes. The detailed check of the angular variation of Zeeman lines shows two magnetically non-equivalent Fe$^{3+}$ centers. These special features were accounted by contribution of higher spin Zeeman terms of dimension $S^3B$. The photo-generated EPR spectra of trigonal Fe$^{3+}$ centers were detected in hydrothermally grown ZnO single crystals in addition to three types of charge-compensated iron centers presented in these samples in the dark conditions.
Raman scattering from ZnO doped with Fe, Mn and Co nanoparticles

B. Hadžić, N. Romčević, M. Romčević, R. Kostić, I. Kurylisyn-Kudelska, W. Dobrowolski, U. Narkiewicz and D. Sibera

1 Institute of Physics, Pregrevica 118, 11080 Belgrade, Serbia
2 Institute of Physics Polish Academy of Science, Al. Lotnikow 32/46 02-668 Warsaw, Poland
3 Szczecin University of Technology, Institute of Chemical and Environment Engineering, Pulsaktiego 10, 70-322 Szczecin

The purpose of this work was to study optical properties of nanosized powders of ZnO doped with Fe₂O₃, MnO and CoO. Nanocrystalline samples were synthesized by wet chemical method. Samples were characterized by X-ray diffraction to determine composition of the samples. The mean crystalline size varied from 8-52 nm for ZnO doped with Fe₂O₃, between 9-100 nm for ZnO doped with MnO and between 14-156 nm for ZnO doped with CoO.

In this paper we report the experimental spectra of micro-Raman measurements, at different laser powers. With increases of laser power, the peaks shifts to lower frequencies and broadens. In all samples raman peak at 436 cm⁻¹ is clearly visible. This peak is typical for undoped ZnO nanoparticles [1].

For the samples of ZnO doped with Fe₂O₃ the raman spectrum shows a band at ~ 642 cm⁻¹. The presence of this band is typical for Fe doped ZnO nanoparticles [1]. In these sample, especially in case of high doping level, bands from various crystal structures are identified (Fe₂O₃, ZnFe₂O₄) from about 514 to 660 cm⁻¹.

For the samples of ZnO doped with MnO raman peak at ~ 660 cm⁻¹ is clearly visible. This peak is typical for spinel structure. In these samples especially in case of high doping level, bands from various crystal structures are identified (ZnMnO₃, Mn₃O₄) at about 315 and 525 cm⁻¹.

For the samples of ZnO doped with CoO the raman spectrum shows a band at ~ 691 cm⁻¹. The presence of this band is typical for Co₃O₄. We also observed bands at ~ 194, 482, 521 and 618 cm⁻¹. These bands are typical for Co₃O₄, too.

Raman scattering studies of ZnO containing Co: bulk crystals, tetrapodes, and nanowires


1 Institute of Physics PAS, Al. Lotników 32/46, 02-668 Warszawa, Poland
2 Institut des Nanosciences de Paris, UMR 7588, UPMC, 140 rue de Lourmel, 75015 Paris, France

Diluted magnetic semiconductors (DMSs), which have been studied for more than forty years, have recently attracted a lot of attention because of their potential applications in future spin-based electronics and optoelectronics (spintronics). Among these materials DMSs grown on the basis of ZnO play a prominent role due to the fact that room-temperature ferromagnetism has been predicted for some mixed crystals of this type. Simultaneously, the trend towards nanomaterials has focused a huge experimental effort on the growth and physical properties of these materials in the form of nanowires. Up to now, the observed ferromagnetism has been usually attributed to possible inclusions or clusters of ferromagnetic materials. The Raman spectroscopy can be a perfect tool to detect and to identify such secondary phases in nominally uniform ZnO-based DMSs.

In this paper we analyze, using Raman spectroscopy, the optical properties of ZnO nanowires or tetrapods containing Co and compare them to properties of bulk crystals of Co-doped ZnO. The growth of bulk Zn_{1-x}Co_{x}O mixed crystals with a nominal composition \( x \leq 0.05 \) was achieved using chemical vapor transport (CVT) in Zn rich conditions. The Zn_{1-x}Co_{x}O tetrapod-shaped nanostructures and nanowires (with nominal \( x = 0.08 \)) were grown by rapid thermal evaporation process of mixture of zinc, cobalt acetate and aluminium acetate with a molar ratio 1:0.08:0.01. The growth process took place in a horizontal tube furnace in open quartz tube and under ambient air atmosphere. The Raman spectra of the bulk crystal containing about 1.6% of Co allowed us to observe, besides the phonon related peaks characteristic of the ZnO host lattice, additional structures at low and high frequency. The high frequency features above 100 cm\(^{-1}\) can be attributed to the presence of metallic Co and CoO precipitates in the sample. The line observed at about 5 cm\(^{-1}\) may be interpreted as an evidence of the splitting of the ground state of Co\(^{2+}\) ion in ZnO due to the wurtzite symmetry of the local crystal field. The second line at about 13.5 cm\(^{-1}\) can result from the presence of the second Co\(^{2+}\) ion in the vicinity of the first one and is related to the electronic transition to the lowest excited state of such ion pair. This interpretation is confirmed by \( \text{ab-initio} \) calculations, which demonstrate that both the local lattice deformation and the superexchange interaction between ions can significantly modify the scheme of the lowest Co\(^{2+}\) energy levels. The Raman spectra of various forms of nanostructures did not reveal the presence of both supplementary phases (like, e.g., Co or CoO) or Co\(^{2+}\) ion pairs. However, possible presence of undetectable, small clusters, responsible for ferromagnetism in nanostructures cannot be ruled out.

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* Corresponding author. E-mail address: szusz@ifpan.edu.pl
* E-mail address: Jean-Francois.Morhange@insp.jussieu.fr
Annealing effects and generation of secondary phases in ZnO after high-dose transition metal implantation

M. Schumm, M. Koerdel, C. Ziereis, J. Geurts
Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany
S. Müller
II. Physikalisches Institut, Universität Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany
C. Ronning
Institut für Festkörperphysik, Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany
E. Dynowska, Z. Gołąbek, W. Szuszkiewicz
Institute of Physics, Polish Academy of Sciences, al. Lotników 32/46, 02-668 Warszawa, Poland

For ZnO, the partial substitution of the nonmagnetic Zn ions by magnetic transition metal (TM) ions is predicted to be a viable path towards room temperature ferromagnetism [1]. Still, the required TM concentrations for these systems are high and for some TM they may exceed their solubility limit in ZnO. Therefore, with regard to the desired magnetic properties, key questions are whether the TM ions are uniformly distributed on the Zn atom sites and whether a sufficient crystal quality of the ZnO host material is preserved. In case of a formation of precipitates and secondary phases, a considerable undesired magnetic impact is expected. Technologically, a widely used method for the incorporation of TM elements in ZnO is ion implantation. However, this method also implies the requirement of a thorough post-implantation annealing for recovering the radiation damaged ZnO lattice. For high TM implantation doses, this annealing procedure is expected to enhance the risk of secondary phase formation, especially because it is very often performed in air atmosphere.

For studying such effects, we applied micro-Raman spectroscopy and high-resolution X-ray diffraction (XRD) on ZnO crystals implanted with Mn, Fe, Co, and Ni, respectively. The implantation concentrations were between 4 at.% and 16 at.%. Employing stepwise annealing in air up to 900 °C, we analyzed the impact of the annealing on the ZnO crystal lattice as well as the onset of secondary phases. Micro-Raman surface scans gave access to lateral inhomogeneities. While the 500 °C annealing induces a considerable lattice recovery, secondary phases are observed for TM concentrations ≥ 8 at.% after the treatment at 700 °C. Their microstructure strongly depends on the transition metal (TM) species. Various stoichiometric and non-stoichiometric TM oxide precipitates (e.g. Mn3O4, ZnMn2O4, ZnFe2O4, ZnCo2O4), as well as elemental TM clusters (Co, Ni) are identified by their Raman and XRD signatures. The magnetic characteristics of these secondary phase materials, which in addition may be modified by their occurrence as small clusters, may substantially determine the magnetic behaviour of the high-dose implanted ZnO samples.

Optical studies on the Zn$_{1-x}$Co$_x$O films and ion-implanted wires with $x \leq 10$

L. Chen$^1$, S. Jankowski$^1$, S. Ye$^2$, A. Ney$^2$, S. Müller$^3$, C. Ronning$^3$ and W. Heimbrodt$^1$

$^1$ Department of Physics, University of Marburg, Renthof 5, D-35032 Marburg, Germany
$^2$ Experimental Physics, University of Duisburg-Essen, Lotharstr. 1, D-47057 Duisburg, Germany
$^3$ Institute for Solid State Physics, University of Jena, Max-Wien-Platz 1, D-07743 Jena, Germany

A variation of magnetic behavior as a function of Co content $x$ or with different growth and annealing procedures was found in high quality ZnCoO films obtained by UHV-magnetron reactive sputtering on sapphire substrates and ZnCoO wires obtained by ion implantation technique of single crystalline ZnO wires synthesized by a vapour-liquid-solid process. For example, films with higher Co content are superparamagnetic revealing a blocking behavior of the magnetization whereas those with lower Co content are paramagnetic. Annealing of the samples in vacuum or oxygen modify the magnetic properties differently. Such annealing procedures affect simultaneously the lattice structure, the electronic and the magnetic properties. Annealing at high temperatures leads to segregation and the respective formation of Co/CoO nanoclusters which are found to be responsible for the ferromagnetism in the ZnCoO films.

Magneto-optical spectroscopic studies in fields up to 7 T at low temperatures and temperature-dependent resonant Raman studies on the film and wire samples are used to reveal the correlation between magnetic properties and optical as well as crystallographic properties in dependence on the Co content and the annealing procedure. The Raman spectroscopy has been performed in the temperature range from 100 to 800 K by means of the 325 nm line of a HeCd laser yielding excitation above the band gap transitions of various ZnCoO samples. In situ Raman measurements during annealing in different gas atmospheres and vacuum, in which the lattice structure and magnetic properties are simultaneously modified, clearly give a correlation between Raman spectra and magnetic behaviour.

The photoluminescence of the ZnCoO samples are characterized by three contributions, the excitonic transitions, a green band caused by the Oxygen vacancy, and the Co intra-ionic d-d transitions. Zeeman spectroscopy was possible only in case of the smallest Co concentrations. For higher Co content magnetic circular dichroism measurements have been performed. The magneto-optical results also strongly support the assumption, that, the observed ferromagnetism in our ZnCoO samples is caused by Co/CoO nanoclusters.
Structural and Optical studies of Zn$_{1-x}$Mn$_x$O nano powders prepared via sol gel technique

M. Ebrahimizadeh Abrishami, S. M. Hosseini, E. Attaran Kakhki, and A. Kompani
Department of Physics (Materials and Electroceramics Laboratory), Ferdowsi University of Mashhad, Iran

Zn$_{1-x}$Mn$_x$O ($x=0, 0.02, 0.06, 0.10, 0.15$) nanopowders were synthesized by the sol gel technique. Mn doping and calcination temperature effects on structural properties were investigated by X-ray diffraction analysis. No secondary phases were observed even in the Zn$_{0.85}$Mn$_{0.15}$O nanopowder calcinated at low temperatures. Size and morphology of nanoparticles were observed by SEM images. Optical characterization was studied by means of Fourier transform infrared (FTIR) spectroscopy. Kramers-Kronig’s analysis of mid-IR reflectance spectra was employed to determine the doping effect on optical constants and optical phonon modes frequencies.
Optical properties of ZnO and Zn$_{0.95}$Mn$_{0.05}$O nanopowders

V. Sokolov$^1$, A. Yermakov$^1$, M. Uimin$^1$, A. Mysik$^1$, V. Pustovarov$^2$, and N. Gruzdev$^1$

$^1$ Institute of Metal Physics UD RAS, S.Kovalevskaya Str. 18, 620041, Yekaterinburg, Russia

$^2$ Ural State Technical University, Mira Str. 19, 620002, Yekaterinburg, Russia

Nanocrystals of oxide diluted magnetic materials have recently attracted a great interest to spintronics devices creating. Apart from this, nanopowders may be considered as new effective catalysts and photoluminescence materials. In this report we present luminescent and optical absorption spectra of ZnO and Zn$_{0.95}$Mn$_{0.05}$O nanopowders obtained by gas-phase synthesis in the oxygen contained argon atmosphere.

For ZnO nanocrystals at room temperature a broad absorption peak with the maximum at the light quantum energy of 3.30 eV was observed. With the decrease of the temperature to 77.3 K the peak became narrower and shifted towards the energy of 3.36 eV. The second peak appeared at 3.42 eV as well. For Zn$_{0.95}$Mn$_{0.05}$O nanocrystals at 77.3 K two broad lines were distinctly seen at 3.37 eV and 3.42 eV. The direct observation of exciton lines (inherent in single crystals) in the absorption spectra indicates that the crystal structure of ZnO and Zn$_{0.95}$Mn$_{0.05}$O nanopowders is quite perfect and close to the structure of ZnO and Zn$_{0.95}$Mn$_{0.05}$O single crystals.

Photoluminescence spectrum of Zn$_{0.95}$Mn$_{0.05}$O nanocrystals at the temperature of 90 K consists of two broad peaks at 2.1 eV and 2.9 eV. The first peak arises due to transitions forming the yellow – orange band of the luminescence in ZnO. The appearance of the second peak at 2.9 eV is caused by the presence of Mn impurities due to the generation of the Dangling Bond Hybrid state which is splitting from the top of the valence band. The Zn$_{0.95}$Mn$_{0.05}$O photoluminescence excitation spectrum of the Mn related peak exhibits broad profiles at 3.9 eV, 4.5 eV and 5.3 eV. They are interpreted in terms of the hybridization between the d-states of the Mn$^{2+}$ ions and the deep valence sub-bands.

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Structural properties of Zn$_{0.95}$Mn$_{0.05}$O/Al$_2$O$_3$ multilayer structures grown by pulsed laser deposition

A. Khodorov$^1$, S. Levichev$^1$, A. Chahboun$^2$, A. G. Rolo$^1$, and M.J.M. Gomes$^1$

$^1$Physics Centre, University of Minho, 4710-057, Campus de Gualtar, Braga, Portugal
$^2$Physics Department, Dhar Mehraz Sciences Faculty, BP 1796, Fès, Morocco

The challenge of the nowadays physics and material science is creating the magnetic tunnelling junction (MTJ) structures operating at 300 K, or even higher, and with better spin accumulation and less interface spin scattering effect. There has been growing interest in studying a direct method for magnetization reversal involving spin transfer from spin-polarized current injected into the device. Within this field of research, dilute magnetic semiconductors (DMSs) are especially important materials. In these materials, rare earth or transition metal ions replace a considerable number of the native ions in the semiconductor’s lattice. As an extensively studied DMSs system, transition metal-doped ZnO shows Curie Temperature $T_C$ well above room temperature, and promising magneto-optical and magneto-transport behavior [1].

In this work, Zn$_{0.95}$Mn$_{0.05}$O thin films (with thickness 4 – 20 nm) and multilayered structures Zn$_{0.95}$Mn$_{0.05}$O/Al$_2$O$_3$ were grown by Pulsed Laser Deposition (PLD) deposition techniques. Post growing annealing was performed to promote the formation of Zn$_{0.95}$Mn$_{0.05}$O nanocrystals (NCs) in the dielectric matrix.

The samples were structurally characterized by Raman spectroscopy, Grazing Incidence X-ray Diffraction (GID), Grazing Incidence Small angle X-ray Scattering (GISAXS) techniques. The crystalline structure of Zn$_{0.95}$Mn$_{0.05}$O was proved by Raman and GID techniques. NCs shape, size distribution and spatial arrangement were estimated from GISAXS data using IsGISAXS program [2].

Annealing conditions are observed to influence significantly on the crystallinity, size, shape, and distribution of NCs array. Moreover, GISAXS and GID techniques demonstrate to be powerful tools for characterization of buried NCs arrays.

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Surfactant Effect of Mn in ZnMnO Epilayers Grown by Plasma-assistant Molecular Beam Epitaxy


1Graduate Institute of Electro-Optical Engineering, Tatung University, Taipei 10452, Taiwan
2Department of Physics and Center for Nano-Technology, Chung Yuan Christian University, Chung-Li, Taiwan
3Department of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan.
4Institute of Physics, National Chiao Tung University, Hsinchu, Taiwan.
5Department of Materials Science and Engineering, I-Shou University, Kaohsiung, Taiwan.
6National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan.

The diluted magnetic semiconductors, Zn1-xMnxO, were grown on c-Al2O3 using plasma-assisted molecular beam epitaxy. The few Mn atoms was suggested to act as a surfactant when the Mn concentration is less than 1%. There are several techniques to figure out this phenomenon. The in situ reflection high energy electron diffraction patterns change from a spot pattern of ZnO epilayer, which was grown in Zn-rich condition, to a streaky one of ZnMnO epilayer. It implies a strong smoothing effect raised as Mn deposited. The average surface roughness is around 2.11 nm, as determined by atomic force microscopy. X-ray diffraction exhibits a relaxation of the compressive strain between the ZnMnO film and the sapphire substrate, correspondingly observed in the absorption spectra. Additionally, the X-ray absorption near-edge spectroscopy (XANES), exhibits the characteristics of Mn2+ in formal valence. The total electron yield spectra obviously reveal the full characteristics of Mn2+ around surface. However, the characteristics of Mn2+ totally disappear in the fluorescence yield spectra. This implies that the Mn may just exist close to the surface, indicating the few Mn atoms acting as a surfactant.

*Corresponding author’s e-mail: csyang@ttu.edu.tw
Structural and magnetic properties of Co-Ga co-doped ZnO thin films fabricated by pulsed laser deposition

Liping Zhu, Zhigao Ye, Xuetao Wang, Zhizhen Ye, Binghui Zhao

State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, People’s Republic of China

Co-Ga co-doped ZnO films were fabricated by pulsed laser deposition (PLD) on quartz crystal substrates. The obtained films preserved wurtzite structure with c-axes growth preference with no obvious second phases detected. Optical measurements show the presence of the cobalt ions in a tetrahedral crystal field, which proves that the Co$^{2+}$ substitution of Zn$^{2+}$ in the ZnO lattice act as magnetic cation. Hall measurements indicate that the films are n-type conductivity with the electron concentrations of $\sim 10^{20}$ /cm$^3$ which is much higher than that of the Co-doped films, suggesting the effective incorporation of Ga in the films. Room temperature ferromagnetism is observed for the Ga-Co co-doped thin films.
The specific heat and the high-resolution thermal diffusivity measurements have been used to study the critical parameters of magnetic phase transition in Zn$_{0.95}$Mn$_{0.05}$O doped by nitrogen. Diluted magnetic semiconductor Zn$_{1-x}$Mn$_x$O (x = 0.05) thin films were prepared by using ultrasonic spray pyrolysis. The films were additionally doped with nitrogen in order to obtain a p-type conductivity. Aqueous solutions of zinc acetate, manganese acetate, and ammonium acetate were used as sources of Zn, Mn, and N, respectively. The hole concentration in the nitrogen-doped films was in the range of $10^{15}$ – $10^{18}$ cm$^{-3}$ at room temperature. The dependence of the magnetization on the magnetic field, (M-H) curve, for the nitrogen-doped Zn$_{0.95}$Mn$_{0.05}$O samples showed a hysteresis loop at low temperatures. A Curie temperature of around 75K for the sample with a hole concentration of $10^{18}$ cm$^{-3}$ was determined from the temperature dependence of the magnetization, while the undoped films showed a paramagnetic behavior at all temperatures investigated.

The temperature dependence of the specific heat revealed a pronounced \( \Delta \) shaped peak at 75 K for the highly nitrogen-doped sample [1]. Such dependencies indicate a well defined second-order phase transition in this sample. In order to determine the critical parameters of this magnetic phase transition the high-resolution thermal diffusivity measurements in the vicinity of the Curie temperature have been conducted. The critical parameters of the ferromagnetic-paramagnetic transition have been obtained through the analysis of the inverse of the thermal diffusivity near the Curie temperature. Taking into account that the inverse of the thermal diffusivity has the same critical behavior as the specific heat, the critical exponent \( \alpha \) has been determined. The results are consistent with the 3D Heisenberg model for the magnetic phase transition.

Optical and magneto-optical properties of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$

V. O. Pelenovich$^1$, U. V. Valiev$^2$, Sh. U. Yuldashev$^{1,3}$, and T. W. Kang$^3$

$^1$ Department of Thermophysics, Academy of Sciences, 28 Katartal, Tashkent 700135, Uzbekistan
$^2$ Department of Optics, National University of Uzbekistan, Tashkent, Uzbekistan
$^3$ Quantum-Functional Semiconductor Research Center, Dongguk University, 3-26 Pildong Chungku, Seoul 100-715, Korea

ZnO is a wide-band-gap of 3.37 eV semiconductor and has recently received particular attention because of its promising applications for blue light emitting devices and as a candidate for the fabrication of diluted magnetic semiconductors (DMS) with a Curie temperature above room temperature. The possibility to create spin-optoelectronics devices based on magnetic ZnO films has stimulated interest in study of the optical and magneto-optical properties of these materials. In this work we report the results of investigation of the optical absorption and magnetic circular dichroism (MCD) spectra of the $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ thin films in the temperature range of 77-300K.

The manganese doped ZnO films were deposited on quartz substrates by ultrasonic spray pyrolysis method similar to that described in Ref.1. Aqueous solutions of zinc acetate (0.5 mol/l) and manganese acetate (0.5 mol/l) were used as sources of Zn and Mn, respectively. The substrate temperature was set at 300 – 500 °C and the thickness of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films was about 200nm. The optical absorption and MCD spectra were measured for samples with different concentration of Mn by using a xenon lamp as an excitation source and the MCD spectra have been measured in Faraday configuration using a photoelastic modulator. At low temperature of 78 K the optical absorption spectra of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ exhibited the strong absorption peaks which were attributed to the free excitons. These results indicate a high optical quality of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films grown by ultrasonic spray pyrolysis. With increasing of manganese concentration the exciton peak maxima are shifted to the short-wavelength region which is connected with increasing of the bandgap energy. A significant MCD signal near the band edge of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ at room temperature has been observed. The analysis shows that this MCD signal is due to the Zeeman splitting of the A and B excitons, which is enhanced by the sp-d exchange interaction in the Mn-doped ZnO.

Preparation of ZnO Nanorod on Various Substrates by Aqueous Solution Deposition

Ming-Kwei Lee, Cho-Han Fan, Yu-Lin Tsai, Chen-Lin Ho, Ting-Huang Kuo, Nai-Roug Cheng, Chih-Chen Hsiao, and Jia-Chi Lin
Department of Electrical Engineering, National Sun Yat-sen University, Kaohsiung, 80424, Taiwan, R. O. C.
Tel: 886-7-5252000 ext. 4120
Fax: 886-7-5254199
Electronic mail: mklee@mail.ee.nsysu.edu.tw

ZnO is a promising material for optoelectronic applications due to its wide direct band gap of 3.37 eV and high exciton binding energy of 60 mV at room temperature. ZnO one-dimensional structures exhibit unique physical, chemical and optic characteristics. In this study, the aqueous solutions of zinc nitrate (Zn(NO3)2 6H2O) 0.01 M 80 ml and hexamethylenetetramine (C6H12N4, HMT) 0.1 M 30 ml were used to prepare ZnO nanorod on (a) GaN (b) glass, (c) plastic and (d) ITO/plastic substrates. Moreover, a simple sonication method was used to increase the density of nanorods. ZnO nanorod with diameters range from 119 nm and with an average height 597 nm were successfully grown on GaN substrate at 70 °C for 4 hrs as shown in Fig. 1 (a) and (b). The ZnO nanorod structure is vertically aligned and has single crystalline growth along ZnO [0001]. The X-ray diffraction patterns and the TEM images are shown in Fig. 2 and 3. A great crystalline examined by the SAED pattern is obtained as shown in Fig. 3 (b). The atomic structure of the individual ZnO nanorod was investigated by high-resolution transmission electron microscopy (HRTEM) as shown in Fig. 4 (b) and (c). It clearly shows that the lattice fringes in HRTEM with d-spacing about 0.52 nm match the interspacing of the (0001) planes of wurtzite ZnO.

A sonication method was used to increase the density of nanorod. After sonication, the nuclei were dispersed uniformly in the deposition solution. Higher density and the smaller diameter nanorods were obtained as shown in Fig. 1 (c) and (d). The length and diameter are 363 nm and 88 nm, respectively.

In order to accommodate the lattice mismatch between ZnO rods and other large lattice-mismatched inexpensive substrates, a sputtered ZnO buffer layer was used on different substrates. Figure 5 shows the morphology of ZnO nanorod structure on (a) glass, (b) plastic and (c) ITO/plastic substrate coated with ZnO buffer layer. High density of ZnO nanorod can also be obtained.
There is much interest on nano-structures owing to their great potential for various applications and new scientific aspects. Nano-fabrication requires wavefront technology to produce nano-structures such as nanopoles, nanorods, nanowires, and so on. Templating with ordered structure is widely employed for the controlled production of materials with desired properties. On the other hand, biological systems have complicated hierarchical architecture involving nano-structures inside, and are expected as another candidate for new nano-templates having new functions and applications.

The butterfly-templated ZnO was produced from a butterfly wing at Shanghai Jiao-tong University. The morphologies and microstructures of the specimens have been investigated by using x-ray diffraction and electron microscopy, but there is no report about the electronic structures. It is therefore very interesting to investigate the electronic structures of the butterfly-template ZnO by using photoelectron spectroscopy.

Photoelectron experiments were carried out at Saga university beamline BL13 in Saga Light Source, where synchrotron radiation with the critical energy of 1.9 keV was provided from the 1.4 GeV storage ring. Ultraviolet Photoelectron Spectra (UPS) were obtained with photons in the range of 40 to 80 eV using a plane grating monochromator. The UPS spectra were also measured on the bulk ZnO plate grown by metal organic decomposition in Saga University, for comparison.

The UPS of butterfly templated ZnO shows the valence band and Zn-3d peak that are similar to those of bulk ZnO plate at a glance, indicating that the butterfly-template ZnO has almost the same electronic structures as the bulk ZnO plate. However, it was found that there are differences in the details of the valence band structures. The valence band in the butterfly-template ZnO is widely distributed around 7 eV in binding energy, while that in the bulk ZnO plate has a peak at 5.5 eV. The important parameters such as band bending and electron affinity were also derived, resulting in the different values between the butterfly-template ZnO and the bulk ZnO plate. The structure of the secondary electrons was also different between them. These results indicate that the distribution of O-2p and Zn-3d states consisting the valence band as well as Zn-4p orbitals contributing the conduction band are slightly different between the butterfly-template ZnO and the bulk ZnO plate. It is interesting to consider whether these differences may be due to the nano-structures of butterfly-template.
Defects in ZnO nanoparticles and their optical properties

K. Senthilkumar1, M. Tokunaga1, H. Okamoto1, O. Senthilkumar2, Y. Fujita1
1Interdisciplinary Faculty of Science and Engineering, Shimane University, Matsue 690-8504, Japan
2Research Project Promotion Institute, Shimane University, Matsue 690-8504, Japan

ZnO is known as a versatile material applicable in optoelectronics, solar cells, photocatalysis, varistors, cosmetics and rubber industries. Nowadays, it has more attention for the biomedical application in the ultraviolet-blue range due to its luminescence properties. Multicolor imaging based on ZnO nanoparticles will further be attractive for the application. Especially near infrared imaging is a highly useful tool to study biomolecules because of the possibility of a high penetration depth at this region. Generally the defects play an important role in the emission and absorption properties of the materials and devices. In this study, the defects formed during the preparation of ZnO nanoparticles by a gas evaporation technique were analyzed. A zinc metal source was basically evaporated by discharging the electrode and reacted with oxygen to form ZnO nanoparticles. Air was used as the oxygen source [1]. As prepared nanoparticles were having very good UV-blue emission and considerable green, yellow, orange and near IR emissions depending on the preparation conditions. The probability of multiple common defects such as zinc interstitial (Zni), interstitial oxygen (Oi), zinc vacancy (VZn), oxygen vacancy (VO), substitution of Zn at O position (ZnO), and substitution of O at Zn position (OZn) was studied in detail. The formation of these defects related to the experimental parameters such as chamber pressure, airflow and applied current.

The emission properties of ZnO nanoparticles were examined by using a 325 nm He-Cd laser excitation source. Depending on the experimental conditions, the particles showed an UV emission around 375 nm due to the excitation of free excitons near the band edge, a green emission associated with oxygen deficiency and located around 540 nm due to electronic transition from oxygen vacancy (Vo) to valance band (VB), a yellow emission commonly attributed to the interstitial oxygen defect and located around 580 nm due to electronic transition from zinc interstitial (Zni) to interstitial oxygen (Oi), and a near IR emission associated with zinc anti-sites observed around 760 nm due to electronic transition from zinc interstitial (Zni) to substitution of Zn at O position (ZnO). The absorbance properties were examined using a UV-Visible spectroscopy. The samples showed corresponding UV absorbance around 370 nm and in addition a near IR absorbance started at around 0.9 μm for few of the samples in accordance with the way of their preparation. The Raman spectra were measured using a 514 nm Ar+ ion laser. The common ZnO related fundamental and a set of multi-phonon modes were identified. The formation of these modes depends on the presence of intrinsic lattice defects [2]. The results will be discussed in detail.

References
Controlling the Surface-Related Photoluminescence of ZnO Nanowires

Apurba Dev, Jan-Peter Richters, and Tobias Voss
Institute of Solid State Physics, University of Bremen, Germany

The wide band gap and high exciton binding energy of ZnO have made this material a promising candidate for optoelectronic devices in the blue and near UV spectral region. In addition, one-dimensional ZnO nanostructures like nanowires and nanorods have drawn significant interest due to their potential applications in nanoelectronics and nanophotonics. Because of their increased surface-to-volume ratio when compared to standard bulk crystals, they show pronounced surface-related phenomena. For any practical application these surface effects need to be understood and controlled.

We studied the surface effects of ZnO nanowires with different diameters in low-temperature photoluminescence experiments (both time integrated and time resolved). We found a diameter-dependent emission band located in the near-band-edge region of the ZnO photoluminescence spectrum which saturates at elevated excitation densities and which we therefore attributed to surface effects [1].

We achieved control over the relative intensity of this surface-related emission band by coating the nanowire surface either with dielectric materials (different polymers or amorphous aluminum oxide) or with metals [2,3]. The results demonstrate that any dielectric coating strongly enhances the surface-related emission and suppresses the visible defect luminescence whereas a metallic coating results in the opposite behavior. In order to understand these findings we developed a model of the electronic properties of the surface region of ZnO nanowires which accounts for the band bending due to Fermi-level pinning [3]. Whereas dielectric materials screen the dipolar surface charges of the nanowires and thereby reduce the band bending, the deposition of metallic films onto the nanowires results in the introduction of additional surface states that will be filled with electrons due to the n-type conductivity of the ZnO nanowires. With this model we explain both the changes in the near-band-edge photoluminescence of the bare and coated ZnO nanowires and the modified relative intensity of the green defect luminescence before and after coating.

Strong enhancement of band edge emission and quenching of deep-level emission was also observed (even at room temperature) after treating the nanowires with a relatively mild argon plasma. Investigations at low temperatures revealed a drastic enhancement of the surface emission after plasma treatment which can also be understood in the frame of the above mentioned model.

Our findings can be applied to many ZnO-nanowire-based light-emitting or sensing devices whose performance crucially relies on the electronic structure of the nanowire surface region.

Modifying growth conditions of ZnO nanorods for solar cell applications

J. Sartor\textsuperscript{1}, F. Maier-Flaig\textsuperscript{1}, J. Conradt\textsuperscript{1}, J. Fallert\textsuperscript{1}, H. Kalt\textsuperscript{1}, D. Weissenberger\textsuperscript{2}, D. Gerthsen\textsuperscript{2}

\textsuperscript{1} Institut für angewandte Physik, Universität Karlsruhe (TH), 76128 Karlsruhe, Germany
\textsuperscript{2} Laboratorium für Elektronenmikroskopie, Universität Karlsruhe (TH), 76128 Karlsruhe, Germany

The controlled growth of nanostructures is one of the major goals of current ZnO research. Especially in the form of nanorods ZnO offers a lot of possible applications as sensors, resonators for nanoscaled lasers or as part of solar cells. Under optimized growth conditions well aligned arrays of uniform sized nanorods can be produced with a vapor transport method \cite{1}. But for some particular applications the choice of growth parameters is restricted and deviates from optimum. E.g., solar cell applications require the ability to grow on suitable substrates (typically transparent conducting oxides (TCO)) and thus lower growth temperatures have to be used in the vapor transport growth.

The aim of this work is to improve dye-sensitized solar cells as well as polymer solar cells by introducing appropriate nanorods. Additionally, ZnO might also replace the expensive ITO anode. In a dye-sensitized cell the large surface area of a dense nanorod array is used for efficient charge separation. Electron transport through these nanorods is expected to be improved compared to the one through a layer of nanocrystalline particles. For this application the length of the nanorods should be several ten µm. Polymer solar cells on the contrary require nanorods with a length of 400nm or less which are introduced into the active layer.

The growth behavior on different TCO substrates was examined. Using a pure Zn powder source instead of the usual ZnO + C source material, allowed to reduce the growth temperature from 950°C to 510°C - so even glass substrates can be used. Photoluminescence and TEM measurements show that the good crystalline quality of the nanorods usually found at high growth temperatures was preserved. The growth parameters were successfully modified to control the size of the nanorods within two orders of magnitude. Nanorods fitting the requirements of the two types of solar cell were reproducibly grown.

Improvement of chemical stability of aqueous solution grown ZnO nanorods by aminosilane modification

K. Ogata, H. Dobashi, K. Koike, S. Sasa, M. Inoue and M. Yano
Osaka Institute of Technology, Osaka, 535-8585 Japan

Due to large surface area of ZnO nanorods, novel applications such as high sensitive biosensors are greatly expected. On the other hands, considering the fact that ZnO is dissolved in biofluids with pH values between 4.5 and 9.0 [1], the large surface area itself may enhance the dissolution of nanorods and cause not only degradation of the nanorod-based devices but also the cytotoxicity to living body [2,3]. For the improvement of the chemically unstable property, aminosilane modification onto the surface of ZnO nanorods was conducted.

ZnO nanorods were grown using aqueous solution of zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and hexamethylenetetramine (C₆H₁₂N₄) [4] at 95°C on α-plane sapphire substrates. Concentration of those source materials was set to be equimolar of 100mM. Prior to ZnO nanorod growth, substrates were treated with phosphoric acid based solution. After nanorod growth by heating, samples were thoroughly washed using deionized water and organic solvents to remove unexpected precipitations on the ZnO nanorods. For the aminosilane modification, ZnO nanorods were immersed in a toluene solution containing 1% aminopropylmethoxysilane (H₂NCH₂CH₂CH₂Si(OCH₃)₃, APTMS) at 60ºC [5]. The chemical bonds formed by this silanization process act as anchors to combine biofunctional molecules such as enzymes with the ZnO surface. Characterization by X-ray photoelectron spectroscopy (XPS) revealed that peaks of both N and Si, constituent elements of APTMS, were clearly detected with a slight decrease of Zn peak in intensity compared with that of unmodified ZnO nanorods. This tendency was also observed in the case of flat epitaxial ZnO films. Since the thickness of the APTMS layer on the ZnO films was estimated to be a few monolayers using an angle-resolved XPS technique, it is expected that the surface of the ZnO nanorods was covered with an APTMS layer with similar thickness.

Then, the chemical stability of the nanorods before and after the silanization was studied by immersing in a dilute (10mM) hydrochloric acid (HCl) solution at room temperature. Unmodified bare ZnO nanorods were nealy disappeared after 5min. in agreement with the chemically unstable property of ZnO, while APTMS modified ones remained their original structure. This result indicates improvement of chemical stability by the aminosilane modification, probably due to formation of covalent Si-O bonds on the surface of ZnO nanorods.

ZnO nanorods growth on sapphire substrates using aqueous solutions with microwave heating and their photoluminescence properties

K. Ogata, H. Dobashi, S. Sasa, M. Inoue and M. Yano
Osaka Institute of Technology, Osaka, 535-8585 Japan

ZnO nanostructures such as nanorods and nanotubes are of greatly interest due to original shapes and unique properties. Until now, novel applications based on ZnO nanostructures, biosensors [1,2] and photonic crystal [3] for instance, were demonstrated. In addition to that, availability of aqueous solution process for the fabrication of those nanostructures is one of the prominent advantages in comparison with those of Si and III-V compounds. Although lots of ZnO nanorod growth techniques on polycrystalline Indium Tin Oxide (ITO) and seeded ZnO nanoparticles on glass substrates were conducted, only a few papers on single crystalline oxide were reported [4,5]. In present study, ZnO nanorods were grown on a and c plane sapphire substrates by using aqueous solutions with microwave irradiation heating where high energy-efficiency and rapid heating are available. Their photoluminescence (PL) properties were also investigated.

ZnO nanorods were grown using aqueous solution of zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and hexamethylenetetramine (C₆H₁₂N₄) [5] at 95ºC. Concentration of these source materials were set to be equimolar (30,100mM). Prior to ZnO nanorod growth, substrates were treated with phosphoric acid based solution. After nanorod growth by heating, samples were thoroughly washed using deionized water and organic solvents to remove unexpected precipitations on the ZnO nanorods. SEM images revealed that ZnO nanorods with about 200nm diameter were obtained without significant dependence on the surface planes of sapphire substrates and on the concentration of source materials.

PL spectra were measured at 6K with the excitation of 325nm line of He-Cd laser. From the ZnO nanorods grown with 100mM concentration, sharp emission at 3.3609eV with a peak width of 2.2meV associated with LO phonon replicas at 3.296 and 3.217eV were observed, suggesting that high quality ZnO nanorods were obtained and that major incorporated impurity was Al. On the other hands, dominant broad emission at around 3.31eV was observed from those grown with 30mM concentration. At the moment, the origin of the 3.31eV emission is under discussion, however, considering its broadness and presence of LO phonon replica at 3.26eV, it could be attributed to the transition from free electron to neutral acceptor which is related with defects [6]. This result suggests that growth condition with higher concentration of source materials is of importance for obtaining high quality ZnO nanorods.

Optical Properties of ZnO nanocrystal-based composites

G. N. Panin1,2, A. N. Baranov3, and T. W. Kang1

1. Department of Physics, QSRC, Dongguk University, Seoul, South Korea.
2. Institute of Microelectronics Technology, RAS, Chernogolovka, Moscow distr., Russia.
3. Department of Chemistry, Moscow State University, Moscow, Russia.

Semiconducting zinc oxide nanocrystals (Eg>3.2 eV) are transparent in visible light and can be high conductive due to shallow level native defects or impurity doping. Composites prepared from such nanocrystals in various wide band gap organic or inorganic matrices demonstrate electrical and optical properties which depend strongly on their surface and interface states because of a high nanocrystal surface to volume ratio. Such nanocomposite films are promising for fabrication of novel electronic and optical devices showing multifarious resistance and light modulation [1-3]. Furthermore the ZnO nanocrystals in the form of nanowires were reported to be ferromagnetic at room temperature [4].

In this paper we report on optical properties of ZnO based composites prepared from ZnO nanocrystals such as Al (In)-doped particles or nanorods (tetrapods) distributed in MgO (or polymer) matrices obtained by the chemical solution synthesis and heat treatment as previously described [5, 6]. The nanocrystals characterized by high resolution SEM, TEM and XRD techniques were in the range of 20-150 nm in diameter and 20-5000 nm in length and revealed the single crystal structure. Photoluminescence and cathodeluminescence spectra of the ZnO nanocrystals show the UV near-band edge emission peak at 382 nm and the oxygen vacancy-related green luminescence band around 520 nm. However, the composites consisting of the ZnO nanorods distributed in MgO nanoparticle matrix demonstrate suppression of the green emission and enhancement of their UV emission and transparency in comparison with the pristine ZnO nanocrystals. The mechanisms of the observed quenching of deep luminescence and enhancement of ZnO nanocrystal transparency as well as a possibility to control the optical properties of the ZnO/MgO (polymer) nanocomposite films by an electric field are discussed.

References

O atom in ZnTe forms localized states in the band gap state. Increasing the O concentration up to alloy of ZnTe and ZnO, it is expected that the localized states can be tailored to intermediate band. By using intermediate band of ZnTeO alloy, the photon that has lower energy than the band gap energy can be absorbed. This helps the effective use of solar spectrum and improves the efficiency of semiconductor solar cell. The theoretical efficiency of ZnTeO solar cell is 58% when O concentration is 2%. However, it is hard to grow ZnTeO alloys due to the large lattice-mismatch and crystal structures between ZnTe and ZnO. In this work, we added S to ZnTeO because ZnS has intermediate lattice constant of ZnTe and ZnO, and ZnS forms both crystal structures of zincblende and wurtzite. The properties of ZnS are expected to increase the O concentration and improve the crystalline quality.

ZnSTeO alloys were grown on ZnTe (001) substrates by MBE equipped with a RF radical cell. Growth temperature was 330 °C. We used ZnS as a S source because the evaporation pressure of elemental S is quite high for the control of S concentration. The concentrations of group VI elements were controlled by O2 flow rate, while the supply amount of Te and S sources were fixed. The S composition in ZnSTe reference sample was 7.6%.

The XRD spectra showed that the lattice constant of epitaxial ZnSTeO alloy becomes small with increase of O2 flow rate. Phase separation nor nonuniform concentration distribution was not observed. To estimate the concentrations of group VI elements, EPMA was performed. As a result, O concentration increased and Te concentration decreased when O2 flow rate was increased. S concentration was not changed. The obtained maximum O concentration in this study was 0.41%. It should be emphasized that the O concentration of ZnTeO, which was grown under the same condition as ZnSTeO but without S supply, was 0.18%. Therefore, introduction of S into ZnTeO increases the O concentration. Although the investigation of bonding configuration or such atomic scale characterization has not been done yet, we consider that S atoms may surround O atoms. The intermediate structural properties of ZnS help to suppress strain energy in the crystal.
Radical-source MBE of ZnO-Related Hetero- and Quantum Well Structures for Optoelectronic Applications

S. Sadofev, S. Kalusniak, J. Puls, Y.-H. Fan, P. Schäfer, and F. Henneberger
Department of Physics, Humboldt University of Berlin, Newtonstr. 15, Berlin 12489, Germany

There is still an ongoing search for ZnO-related heterostructures that are suitable for optoelectronic applications. In this talk, we summarize our recent efforts to fabricate well-defined ZnCdO/ZnO and ZnO/ZnMgO quantum well (QW) structures as well as their N doping and resultant electrical properties.

The structures are grown by radical-source molecular beam epitaxy (MBE). Low-temperature growth and an appropriate growth stoichiometry have allowed us to overcome the solid solubility limits and to alloy ZnO with MgO or CdO in strict wurtzite phase up to mole fractions of several 10%. In this way, we can modulate the band-gap from 2.1 to 4.5 eV. For deposition on ZnO substrates, the ternaries exhibit (0002) o-rocking-curve widths as low as as 19 arc sec and, despite the different thermodynamic crystal structure, pseudomorphic growth over several 100 nm, both at alloy compositions up to 25 % (ZnMgO).

Single crystalline layer-by-layer growth is accomplished enabling the fabrication of atomically sharp heterointerfaces and uniform multiple QW structures, where layer thicknesses and alloy composition can be directly controlled by oscillations in reflection high-energy electron diffraction. The quantum structures exhibit prominent band-gap-related emission in the whole composition range and low-threshold room-temperature lasing from ultraviolet to green wavelengths. Based on transmission electron microscopy and X-ray diffraction data, we discuss the role of post-growth annealing, interdiffusion at the heterointerfaces, lattice relaxation, and defect or dislocation formation, all needed to be mastered in order to achieve high radiative yields as well as to tune the wavelength.

We have systematically reinvestigated N doping of ZnO and its ternaries by changing temperature, fluxes, and stoichiometry conditions. The background n-doping level of the starting films is about $4 \times 10^{16}$ cm$^{-3}$ and the mobility 170 cm$^2$/Vs at room temperature. It turned out that the N incorporation in ZnO depends sensitively on the growth temperature. We can change the N concentration from $3 \times 10^{17}$ to $3 \times 10^{20}$ cm$^{-3}$ without degradation of crystal quality in a temperature window of only 75 °C. We present a careful analysis of Hall and van-der-Pauw measurements taking into account the substrate/film interface layer. The Hall data are complemented by diode characteristics of pn-junction from which the electrical activity of the N dopant can be also inferred.
Blue-green PL emission from ZnCdO-based multiple quantum wells grown by RPE-MOCVD

K. Yamamoto1, M. Adachi2, T. Tawara3, H. Gotoh4, A. Nakamura5, and J. Temmyo1,2

1 Graduate School of Science and Technology, Shizuoka University,
3-5-1 Johoku Naka-ku, Hamamatsu, 432-8011, Japan
2 Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Naka-ku,
Hamamatsu, 432-8011, Japan
3 NTT Basic Research Laboratories, NTT Corporation, 3-1 Morinosato-Wakamiya,
Atsugi, 243-0198, Japan

The band gap of Zn1-xCdxO alloy films grown by remote-plasma-enhanced metal organic chemical vapor deposition (RPE-MOCVD) has been controlled from 1.8 to 3.3 eV [1]. We have characterized the photoluminescence (PL) lifetime and potential fluctuation in Zn1-xCdxO films, clarifying that typical PL lifetime in Zn0.8Cd0.2O film is around hundred ps [2]. In this study, we have successfully observed blue-green PL emission from Zn0.85Cd0.15O/ZnO multiple quantum wells (MQWs) grown by RPE-MOCVD, and have realized the enhancement of the exciton recombination in Zn0.85Cd0.15O well layer with the result of shorter PL lifetime in MQWs, while characterization on ZnCdO/ZnO quantum wells grown by radical source molecular beam epitaxy has been recently reported [3].

(0001) Zn0.85Cd0.15O/ZnO MQWs, with 10 periods, were grown on (11-20) sapphire substrates by RPE-MOCVD, starting with a 100 nm thick ZnO buffer layer. The widths (LW) of Zn0.85Cd0.15O well are 2, 4, 8, 11, and 21 nm. The width of ZnO barrier layer is 10 nm. The width of these layers is controlled by growth time, according to growth rate. (0001) Zn0.85Cd0.15O single layer (SL) grown on (11-20) sapphire substrate was used as the reference, and the thickness is 140 nm. The periodicity between Zn0.15Cd0.85O well layer and ZnO barrier layer was confirmed by the satellite peaks of X-ray diffraction pattern. The optical properties at low temperature were characterized by steady-state PL (SSPL) and time-resolved PL (TRPL). He-Cd laser was used as the excitation source for SSPL. In order to characterize PL lifetime, TRPL was performed using a streak camera system with the frequency-doubled beam of mode-locked Ti:sapphire laser.

PL emission energy of Zn0.85Cd0.15O SL at 20 K is 2.77 eV. PL peak energy of MQWs shows a blue-shift from 2.77 to 2.97 eV with decreasing LW from 21 to 2 nm. The energy shift well agrees with the calculation. The conduction/valence band offset ratio of 65/35 and the ZnO masses (m_e = 0.28m_0 and m_h = 0.78m_0) were used. PL lifetime in Zn0.85Cd0.15O/ZnO MQWs gradually shortens from 70 to 55 ps with decreasing LW from 8 to 2 nm, indicating the enhancement of the exciton recombination in Zn0.85Cd0.15O well layer.

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MOVPE growth and study of ZnO, ZnMgO epilayers and ZnO/ZnMgO MQW structures

P.Kuznetsov1), V.Luzanov1), G.Yakushcheva1), V.Jitov1), L.Zakharov1), I.Kotelyanskii1), V.Kozlovsky2)

1) Kotel’nikov Institute of Radioengineering and Electronics of RAS, 1 Vvedenskogo sq., 141190 Fryazino, Russia
2) P.N. Lebedev Physical Institute of RAS, 53 Leninsky pr., 119991 Moscow, Russia

The interest in ZnO-based structures is fueled by its prospect in ultraviolet optoelectronics devices. Some applications of such structures overlap with that of GaN-based, however in case of ZnO-based structures there is advantage connected with large exciton binding energy (60 meV) [1]. MOVPE technology, most adapted to mass production of semiconductor structures, it is not enough developed up to date in respect to ZnO-based materials.

MOVPE growth of ZnO, ZnMgO epilayers and ZnO/ZnMgO MQW structures were carried out at atmospheric pressure of hydrogen in horizontal quartz reactor. We used ZnEt2, (MeCp)2Mg, t-BuOH as precursors and Al2O3, AlGaN/Al2O3 templates as substrates. As-grown structures were studied using photoreflection (PR), photoluminescence (PL), cathodoluminescence (CL), X-ray diffraction and optical microscopy techniques.

Dependences of the ZnO growth rate and crystal quality on the growth temperature and t-BuOH : ZnEt2 ratio in vapour phase were studied. The morphology and crystal quality of the grown layers with wurtzite structure are improved with increasing of t-BuOH : ZnEt2 ratio. It is established, that temperature 430 °C and thirty-fold excess of t-BuOH optimal growth condition. The best films grown on Al2O3 have FWHMs of (002) rocking curve of 0.2 angle degree. Near band edge emission with maxima varied from 374.5 to 377 nm is dominated in PL spectra at 300K. The intensity of the intraband emission with minimum about 500 nm is two orders of magnitude lower.

ZnMgO epilayers were grown at temperature 430°C on the both substrates. According to the diagram of the ZnO-MgO binary system, the solubility MgO in wurtzite ZnO is less than 4 mol%, but in epilayers this value may be much larger [2]. According to PR, PL and X-ray measurements our layers with Mg content of up to 35% have a wurtzite structure. Since MgO has large band edge, including 10 % Δg to the composition of ZnMgO films allows shifting on 200 meV to UV region of spectra.

Good crystal quality of ZnO and ZnMgO layers and large band-gap offset allowed us to realize long period ZnO/ZnMgO MQW structures. The series of MQW structures with different parameters (barrier composition, QW and barrier thicknesses, period number) were grown and studied. In most cases there are effective carrier transport into QWs and the strong ZnO emission dominate in cathodoluminescence spectra.

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Controlled Growth of High-Quality ZnO-Based Films and Heterostructures for Application in Optoelectronic Devices

Xiaolong Du, Zengxia Mei, Yang Guo, and Qikun Xue
Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
E-mail: xldu@aphy.iphy.ac.cn

ZnO is an attractive wide-band gap (3.37 eV at room temperature) oxide semiconductor for its great potential in short-wavelength optoelectronic devices, such as ultraviolet (UV) detectors, UV and blue light emitting devices. Doped with transition metal atoms, ZnO can be used as a ferromagnetic semiconductor for fabrication of spintronic devices. Moreover, rare-earth metal doped ZnO thin films are promising for visible or infrared emitting devices and planar optical waveguide amplifiers. In all these applications, it is essential to prepare high-quality ZnO films and heterostructures. In this work, controlled growth of ZnO-based thin films by molecular beam epitaxy (MBE) has been intensively studied with emphasis on interface and bandgap engineering. The relationship between growth conditions and properties of multilayer structures has been investigated too. Several optoelectronic devices, such as UV detectors and light emitting diodes, have been fabricated from the samples prepared under optimized conditions.

Due to lattice mismatch and chemical dissimilarity between ZnO and substrates available, a delicate control of the interface plays a key role in strain relaxation and polarity selection of the ZnO films. The interface engineering usually begins with an appropriate substrate pretreatment to obtain desired surface structure, on which a transition layer can be grown to compromise the structural and chemical difference. A ZnO buffer layer is then deposited at low temperature to relax misfit strain. One of our strategies is the use of ultra-thin AlN or MgO layers between the ZnO film and substrate to control the interface structure for unipolar ZnO films growth. In this part, we would summarize our recent study on the interface control in ZnO epitaxy on several substrates (sapphire[1], LSAT[2], silicon[3] and spinel[4]), and discuss underlying mechanism.

In the second part, we would discuss the growth of single-phase wurtzite MgxZn1-xO alloys (x=0 to 0.55) on sapphire substrate. We show that the band gap energy Eg could be tuned from 3.3 eV to 4.55 eV, which covers UV-A, UV-B, and solar-blind spectral regions. For the growth of high Mg-content MgZnO films, a low Mg-content Mg0.2Zn0.8O buffer layer is employed as a quasi-homo epitaxy template to accommodate the big bonding configuration difference between Mg-O and Zn-O in wurtzite structure. This way, the phase separation of rock-salt MgO could effectively be suppressed. This bandgap engineering method proves very successful in growth of ZnO/MgZnO heterostructures.

References
Non polar ZnO-based heterostructures: a comparison between \( a \) and \( m \) orientations

J-M. Chauveau\(^1,2\)*, M. Teisseire\(^1\), J. Zuniga-Perez\(^1\), P. Venneguès\(^1\), H. Kim-Chauveau\(^1\), C. Deparis\(^1\), C. Morhain\(^1\), B. Vinter\(^1,2\)

\(^1\) Centre de Recherche sur l’Hétéro-Epitaxie et ses Applications, Centre National de la Recherche Scientifique (CRHEA-CNRS), Rue B. Gregory, F-06560 Valbonne, France
\(^2\) University Nice Sophia Antipolis, Physics Dept., Parc Valrose, F-06102 Nice France

\*jmc@crhea.cnrs.fr, phone: +33493957822

ZnO-based heterostructures have attracted much attention in the last few years due to their opportunity of combining band gap engineering, along with large excitonic binding energies. So far studies on ZnO have mainly focused on films grown in (0001) orientation. In this configuration, the wurtzite ZnO layers exhibit built-in electric fields (both piezo and spontaneous components) along the c-axis, i.e. the growth direction. Non-polar surfaces are therefore of a particular interest since the c-axis of the layer lies within the growth plane in this case. As a result it is expected that quantum well structures can be grown without any screening of the exciton binding energies. Two non-polar orientations can be grown: \( a\)-\( \{1\overline{1}2\overline{0}\} \) or \( m\)-\( \{10\overline{1}0\} \).

In this communication, we compare the growth, structural and photoluminescence properties of \( a\)-oriented and \( m\)-orientated heterostructures grown by plasma assisted Molecular Beam Epitaxy (MBE). The samples were grown on 2” R- and M-plane sapphire by molecular beam epitaxy using the same growth conditions for comparison.

The in-plane and out of plane lattice parameters were measured by high resolution X-ray diffraction in both orientations. The residual strain is strongly anisotropic in \( a\)-oriented layers while \( m\)-oriented layer are nearly fully relaxed. It is due to the different strain relaxation processes, depending on the growth orientations, \( i.e. \) domain matching epitaxy vs lattice matching epitaxy. This was confirmed by high resolution TEM study of the ZnO/Al\(_2\)O\(_3\) interfacial structures. The microstructures are dominated by a high density of basal stacking faults in both orientations. Luminescence properties were studies by means of photoluminescence excitation (PLE) and reflectivity measurements. We present the correlation between strain states, defect densities and optical properties.

Finally series of quantum wells were grown in both orientations with different thickness. The photoluminescence energies of the QWs are satisfactorily simulated by taking into account the residual strain and the variation of the exciton binding energy with the QW width.
Optical in-plane anisotropy of ZnO/(Zn,Mg)O quantum wells

Y. Fan\textsuperscript{*}, J. Puls\textsuperscript{*}, G.V. Michailov\textsuperscript{b}, S. Sadofev\textsuperscript{a}, and F. Henneberger\textsuperscript{a}

\textit{a) Humboldt-University, Institute of Physics, 12489 Berlin, Germany}

\textit{b) Ioffe Physical Technical Institute, St. Petersburg 194021, Russia}

Compared to sulfides and selenides, II-VI oxides exhibit a drastically reduced spin-orbit coupling giving rise to the expectation that, e.g., ZnO represents an ideal material for spintronic applications. In order to explore this potential, we have grown a variety of ZnO/ZnMgO quantum well (QW) structures by radical-source molecular beam epitaxy on a-plane sapphire substrates \cite{1}. Adding Mn during the well growth allowed us to obtain even diluted magnetic QW structures. Measurements related to the exciton spin alignment uncovered some very peculiar properties. In an external magnetic field $B$ along the (0001) growth direction, the excitonic photoluminescence (PL) of diluted magnetic QWs becomes increasingly circularly polarized. The polarization degree saturates at about $B = 2$ T, but surprisingly with a finite value of 0.5 to 0.6. In non-magnetic QWs, an extremely low optical orientation (less than 3 \%) is found under resonant pumping of the exciton ground-state in circularly polarized excitation-detection mode. Repeating the experiment with linear polarization, an optical alignment of about 15 \% is obtained. To clarify the peculiarities concerning the excitonic spin, we have studied the polarization properties of the excitonic PL and PL excitation bands. In all samples, a distinct in-plane optical anisotropy (linear dichroism) of more than 10 \% is found in the PL signal. Such a preferential in-plane axis of linear polarization is, at least qualitatively, in accord with a strongly suppressed excitonic optical orientation, i.e., a lack of exciton spin memory. For a multiple QW sample, this anisotropy could be even demonstrated for the PL excitation efficiency at the lowest exciton state, most likely due to a linearly anisotropic absorption of the QW. The PL of this sample shows two well resolved lines due to localized (X) and charged excitons (X\textsuperscript{-}). Common and different signatures of these two PL features of integer and non-integer total spin will be used to discuss different mechanisms of this anisotropy, e.g., an additional uniaxial strain caused by the different thermal expansion of the sapphire substrate along the two non-equivalent directions in the a-plane, the quantum confined Pockels effect due to a partly screened built-in electric field \cite{1}, or, the long-range electron-hole exchange interaction in conjunction with an anisotropic localization and the quasi-degenerated sub-valence bands.

Anisotropy of the dielectric function of ZnO including exciton-polariton formation obtained from ellipsometry

Munise Cobet, Christoph Werner, Christoph Cobet, Markus R. Wagner, Norbert Esser, Axel Hoffmann and Christian Thomsen

1Institut für Festkörperphysik, Technische Universität Berlin, 10623 Berlin, Germany
2ISAS-Institute for Analytical Sciences, 12489 Berlin, Germany

The dielectric response functions of bulk and layered ZnO for electric field polarizations parallel and perpendicular to the \(c\)-axis are obtained in the spectral range from 2.5 to 32eV by ellipsometry with synchrotron radiation. In such a strongly excitonic material, the formation of exciton-polaritons is significant. As a consequence, additional peaks occur in the spectra, which are seen in ellipsometry for the first time and cannot be explained with a classical Lorentz oscillator. The peaks are reproduced and confirmed by Reflectance Anisotropy Spectroscopy (RAS), too. We believe these additional features to match the longitudinal frequencies \(Z_L\) of the B exciton-polariton. The different modes are analyzed in detail by simulating the spectra with a novel optical model, including not only the propagation of electromagnetic waves in uniaxial anisotropic media, but also their spatial dispersion and the existence of an exciton free surface layer (“dead layer”). Based on earlier works of Thomas, Hopfield and Pekar, the parameters of the modeling deliver the values of the transverse-longitudinal splitting which are compared to those found in our photoluminescence data. We also identify the higher excitations of \(n=2,3\) apart from the ground \(s\)-state. The scattering with the longitudinal optical phonon near \(k=0\) shows up in a replication of the main excitonic structure every 0.07eV.

In ZnO, the low lying \(d\)-levels of the Zn-cation are in near resonance with the O \(2p\) part of the \(sp^3\)-hybridized valence-band and therefore participate the chemical bonding, too. This feature is believed to have an extreme influence on symmetries and binding energies of the split states at the valence band maximum due to the strong \(p-d\) repulsion. A possible reversal in the two upper valence bands \(\Gamma_7\) and \(\Gamma_9\) due to a negative spin-orbit-splitting is considered as a result. Calculations reveal that the magnitude of the \(p-d\) coupling increases when the crystal is compressed, because the chemical bond length is reduced. Cross-section Raman scattering and XRD measurements showed even in homoepitaxial grown samples the existence of strain, which can vary with the depth.

In order to estimate the position of the \(d\)-bands relative to the conduction band critical points (e.g. at the \(\Gamma\) and the \(A\) point in the Brillouin Zone) the energy range is extended to 32eV. Interband transitions from the O \(2p\) dominated \(sp^3\)-valence band and from the Zn \(3d\) semicore level are detected for energies 4-10eV and 10-18eV. The found energy gaps are applied to the bandstructure diagram. A strong anisotropy is observed mainly for energies above 10eV, in contrast to all other wurtzite compounds, like the nitrides. Here, anisotropy seems to be induced by different properties and cannot be described clearly by symmetry considerations based on the quasi-cubic approximation in hexagonal crystals. This is seen as a result of the large deviation from the internal parameter \(u=0.382\) from the ideal value for the wurtzite structure (\(u=0.375\)). This anisotropic behavior could also be verified by ab-initio calculations. At higher energies above the plasmon frequency (\(\hbar\omega_p = 18.12\) for \(E_{llc}\) and 18.95 eV for \(E_{lc}\)) the transitions of the O \(2s\)-core-level occur.
Since the prediction of room temperature ferromagnetism in ZnO doped with Mn a lot of effort was directed towards investigation of this material[1]. The scope of potential applications of systems based on ZnMnO is widened by the fact that apart from the magnetic phenomena introduced by the Mn ions, the ZnMnO has larger fundamental energy gap than ZnO. Although high quality ZnMnO/ZnO heterstructures have been already reported in the literature [2] the variation of the fundamental energy gap with the Mn concentration is not yet clarified. Similarly the precise structure of the ZnO valence band is still under debate. One obvious obstacle on the route towards room temperature ferromagnetism in ZnMnO comes from the fact that doping with Mn$^{2+}$ ions does not generate valence holes so other techniques such as co-doping must be applied in order to obtain a p-type material. On the other hand it has been proposed that the built-in and external electric field in ZnO quantum wells with ZnMnO barriers may be used to control the coupling of photo-generated valence holes with manganese ions in the barriers and thereby changing the Curie temperature [3]. The detailed knowledge of the absorption spectra in the vicinity of the fundamental gap is therefore of fundamental importance in studying such systems, especially in the presence of the magnetic field. Already for the case of ZnO films it has been demonstrated that any approach to this question ignoring the excitonic nature of optical transitions leads to mis-interpretation of the valence band structure [4]. We therefore present a multiband magnetoexciton absorption model in ZnO/ZnMnO quantum wells which takes into account the details of the valence band structure. In our model we incorporate the k.p coupling between valence subbands as well as the Coulomb coupling including the exchange interaction between the electron and hole [5]. The s,p-d interaction between the carriers and the magnetic ions in the barrier is taken into account within the mean field approximation. The effect of the electric field is accounted for using proper potential profile of the quantum well. As a result we obtain electric and magnetic field dependent excitonic absorption spectra from which the exciton binding energies and life-times as well as the overlap with the magnetic barrier material may be deduced. The calculations are performed for the circular polarization of light (Faraday configuration). Our model is valid both in the regime of low and high magnetic fields and therefore may be useful in interpretation of experiments investigating the electronic structure near the fundamental gap of both ZnO and ZnMnO.

Optical properties of MgO, ZnO, and CdO in a wide spectral range from first principles

A. Schleife, C. Rödl, F. Fuchs, and F. Bechstedt

Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena and European Theoretical Spectroscopy Facility, Max-Wien-Platz 1, 07743 Jena, Germany

Rapid progress in semiconductor technology of novel electronic and optoelectronic devices drives the extension of the variety of relevant materials. Following the nitrides, also the group-II oxides gain importance for devices operating with deep blue or even ultraviolet light. Due to their large band gaps and large exciton binding energies, especially MgO and ZnO are of interest. As a candidate for heterostructures and for alloys operating in the wave-length region reaching even into the visible spectral range, also CdO plays a role because of its smaller band gap. The group-II monoxides, especially ZnO and CdO, are also important for transparent and conducting layers in photovoltaic devices.

Modern materials science allows precise tailoring of specific properties for specific tasks if those of the basic materials are known. It therefore can essentially benefit from the fundamental understanding provided by parameter-free calculations. Though the optical properties of the bulk materials are of significant interest, their parameter-free description is still a challenge and, hence, contains several open problems. Strong excitonic and local-field effects dominate, e.g., the absorption and the electron-loss properties. The description of the direct or indirect band edge, the strength of the excitonic effects, the energy variation of the interband transitions, and the influence of crystal structure, e.g., wurtzite or rocksalt, are also of great interest.

In order to clarify these questions by a parameter-free approach, we apply modern ab-initio methods together with many-body perturbation theory to calculate optical properties up to photon energies that correspond to high-energy valence-conduction band transitions. We combine the computation of electronic structures including quasiparticle effects with the treatment of the screened attractive electron-hole Coulomb interaction as well as local-field effects in the form of the unscreened electron-hole exchange in the kernel of a Bethe-Salpeter equation. Due to the extreme computational demand for converged computations of the frequency-dependent dielectric function, energy eigenvalues and wave functions in the starting electronic structure are obtained using a GGA+U scheme. Together with hybrid k-point meshes, the electron-hole pair states in the excitonic Hamiltonian lead to converged results for the dielectric function in a wide spectral range up to 32.5 eV. The importance of excitonic effects is demonstrated even far away from the absorption edge.

The computed dielectric functions allow us to derive reflectivity curves and electron-energy loss functions that compare excellent to experimental results. Furthermore, we are able to clarify in detail the origin of peaks in the reflectivity and energy-loss functions in terms of optical interband transitions and plasmon effects. The impact of many-body effects is pointed out in detail and chemical trends for the three oxides are discussed.
Transition metal (TM) doped zinc oxide (ZnO) is attracting considerable interest because of its potential application in spintronic devices. Due to their relative chemical similarity the TM ions of the iron group are isovalent with zinc in the ZnO host matrix. Thus, they are expected to easily substitute for the zinc ions with little lattice distortion and without severely changing the valence or conduction bands. However, due to the incomplete occupation of the 3d shell TM ions develop localized states around the Fermi level that can act as deep hole or electron traps. Hence, TM dopands exhibit a number of stable charge states according to the energetic position of the Fermi level. Since the experimental realization of dilute ferromagnetic ZnO is still challenging a detailed knowledge of the charge states and their respective transition levels is essential.

Density functional theory (DFT) is a feasible tool for the prediction of both, the local structure and the energetics of single TM ions in a ZnO host matrix. In this study we calculate the charge transition levels of common TM ions (Mn, Fe, Co) by employing the DFT in the framework of the local spin density approximation with additional on-site coulomb interaction (LSDA+U). However, DFT shows significant deficiencies in describing excited states. Therefore, electronic properties especially the dopand levels in wide gap materials like zinc oxide (ZnO) have to be carefully interpreted. Hence, we follow two different approaches to carefully correct the calculated charge transition levels for the band-gap error in ZnO. On the one hand we apply an \textit{a posteriori} correction of the gap states that is based on a formalism proposed by Janotti and Van de Walle\cite{Phys. Rev. B 76, 165202 (2007)}. It refers to relative changes of transition levels while introducing the on-site coulomb interaction. This approach will be compared to an \textit{a priori} calculation based on a method by Paudel and Lambrecht\cite{Phys. Rev. B 77, 205202 (2008)} which includes an additional correction for the Zn 4s states and thus does not require further band-gap scaling.

\textsuperscript*) formerly Hahn-Meitner-Institut Berlin
Two-dimensional polaron mass in ZnO quantum Hall systems

Yasutaka Imanaka¹, Tadashi Takamasu¹, Hitoshi Tampo², Hajime Shibata² and Shigeru Niki²

¹National Institute for Materials Science, 3-13 Sakura, Tsukuba, Ibaraki 305-0003, Japan
²National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

ZnO is a transparent semiconductor because of its large band gap energy, and it is absolutely one of attractive materials from the viewpoint of new applications like UV light emitting diodes, transparent conductive electrodes and power devices. The optical properties of ZnO have been studied for long time since late 60’s. On the other hand, the transport properties, however, have not been investigated well because of the mobility of specimens. Cyclotron resonance in ZnO, which is most direct method to study effective mass of carriers in semiconductors, was also difficult to be performed and very few for low mobility samples at lower magnetic fields [1]. The detailed study of the polaron mass in a ZnO bulk sample was performed below a LO phonon energy at higher magnetic fields above 10T [2]. The larger electron-phonon coupling and the bare effective mass of ZnO were also obtained from the magnetic field dependence of the cyclotron resonance beyond the LO phonon energy recently [3].

Recent progresses of the epitaxial growth technique enable us to study quantum Hall effect in ZnO/ZnMgO heterostructures [4]. The mobility of the ZnO 2 dimensional electron gases (2DEGs) reaches more than 10,000cm²/Vs at low temperatures. This means that the cyclotron resonant condition (ωcτ>1) can be satisfied even at low magnetic fields. Moreover, the carrier density can be controlled beyond n=10¹²cm⁻² by changing Mg concentration of a ZnMgO layer without doping and gate techniques. In weak polar semiconductor heterostructures with dense 2DEGs above n=10¹²cm⁻², the resonant polaron effect around a LO phonon energy was found to be anomalous because of the higher plasma frequency than other excitation energies. A strong polar material, that is, ZnO is definitely good candidate for studying the 2D resonant polaron problems.

In this study, we have performed the cyclotron resonance experiments for high quality ZnMgO/ZnO heterostructures, in which the integer quantum Hall effect is observed clearly at steady high magnetic fields up to 25T. The mobility of a sample reaches 10,000cm²/Vs at most. The carrier concentration of the samples is obtained between 10¹²cm⁻² and 10¹³cm⁻² from shubnikov-de Haas oscillation measurements. The oscillation can be observed until higher Landau index up to 100.

In cyclotron resonance measurements, a millimeter vector network analyzer and a Fourier transform infrared spectrometer were used with a superconducting magnet up to 15T. The effective polaron mass of 2DEGs in ZnO has been obtained as m*=0.32±0.01m₀ and the enhanced mass in 2D systems is found out in comparison with the bare electron mass of ZnO bulk samples (m*=0.25m₀) [2]. We will discuss the magnetic field and the carrier density dependence of cyclotron resonance with the 2D polaron theory in the magnetic field.


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Solar-blind 4.55 eV band gap Mg_{0.55}Zn_{0.45}O components fabricated using quasi-homo buffers

Z. L. Liu, Z. X. Mei, T. C. Zhang, Y. P. Liu, Y. Guo, X. L. Du*  
Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

A. Hallen  
Ion Technology Center, Uppsala University, Sweden

J. J. Zhu, A. Kuznetsov*  
Department of Physics, University of Oslo, P.O.Box 1048 Blindern, NO-0316 Oslo, Norway

*E-mail: xldu@iphy.aphy.ac.cn (X. L. Du), andrej.kuznetsov@fys.uio.no (A. Yu. Kuznetsov)

The synthesis of wurtzite MgZnO alloy, an indispensable issue in band gap engineering of ZnO-based semiconductors, is attracting great interests for its practical applications in optoelectronic devices. Specifically, solar-blind UV detectors, i.e. those dedicated detecting only photons having energies > 4.4 eV, can be used for example for a flame detection, biological/chemical analysis, optical communications within ozone layer, etc. Recently, many efforts have been dedicated in the fabrication of wider band gap MgZnO alloys; however, phase separation and lacking of reproducibility greatly hamper the progress in this field [1] due to the structural discrepancy between wurtzite ZnO and rock-salt MgO. Moreover, theoretical studies have shown that wurtzite MgO has an unusual 5-fold coordinated structure induced by strong ionicity of Mg-O bonds [2], which is quite different from that 4-fold W-ZnO explaining that the phase separation is an issue even if considering that both components having a wurtzite structure. The influence of the strong ionicity of Mg-O bond on the structural distortion induced into the wurtzite ZnO matrix during synthesis of MgZnO alloys was practically ignored in most of the previous experimental studies. In this study, quasi-homo buffer, Mg_{0.17}Zn_{0.83}O, is employed in the realization of Mg_{0.55}Zn_{0.45}O with a band gap in solar-blind region addressing the issues mentioned above.

Firstly, an Mg_{0.17}Zn_{0.83}O film was grown on sapphire substrate by MBE as a template. Then, Mg flux was raised to increase the Mg fraction. In-situ reflection high-energy electron diffraction (RHEED) was used as structural monitor during the whole growth procedure; and no phase separation was observed, as was confirmed by ex-situ x-ray diffraction (XRD) ZnO (002) θ-2θ scan and ZnO (102) Φ-scan. The Mg fraction in the single-phase wurtzite epilayer, Mg_{0.55}Zn_{0.45}O, was confirmed by Rutherford backscattering spectrometry (RBS). The band gap of Mg_{0.55}Zn_{0.45}O film was characterized by a combination of transmittance spectrometry (TS) and reflectance spectrometry (RS) at room temperature to be 4.55 eV. In TS, two absorption edges are revealed, corresponding to Mg_{0.17}Zn_{0.83}O (340 nm) and Mg_{0.55}Zn_{0.45}O (270 nm) layers, respectively. Our results suggest that the above-mentioned process is promising for synthesis of wide band gap MgZnO.


The Effect of MgO Layer on Suppression of Visible Light

Photoresponse in n-ZnO/MgO/p-Si UV Detector


Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

Recently, UV photodetectors based on a wide band-gap semiconductor material, such as ZnO (E_g = 3.37 eV), have attracted more attentions because of their extensive applications in civil and military areas. Both Schottky contact and p-n junction type of ZnO-based UV photodetectors have been realized and reported.\(^1\) Because of the lack of stable and controllable p-type ZnO films, in most cases, heterojunctions were used to fabricate ZnO-based UV photodetectors with a different p-type semiconductor, such as Si\(^2-4\). However, reported n-ZnO/p-Si photodetectors remain an obvious photoresponse to visible light, although the UV photoresponse is increased due to ZnO, which would limit its direct application in UV detection under a visible light background.

In this work, we report a new design and realization of n-ZnO/insulator-MgO/p-Si visible-blind UV photodetector and demonstrate the key role of MgO on the suppression of visible light photoresponse in our device. The double heterojunction is grown by molecular beam epitaxy. The photoresponse spectrum of our device indicates a visible-blind UV detectivity of our devices with a sharp cut off of responsivity at the wavelength of 378 nm. To further indicate the effect of the middle i-MgO layer in our device, an n-ZnO/MgO(~6 nm)/p-Si double heterojunction is prepared and its photoresponse characteristic is compared with that of the n-ZnO/insulator-MgO(~50 nm)/p-Si heterojunction. Both dark current and photocurrent increase a lot as the thickness of the i-MgO layer decreases in the p-insulator-n heterojunction, which results in a lower UV/Visible rejection ratio. Therefore, it is necessary to form a MgO layer with a good insulation, which can effectively prevent the electron injection from p-Si side to n-ZnO side at a reverse bias in both cases of dark and visible light illumination due to the high potential barrier of MgO layer for electrons.

Reference


E-mail: yangguo@iphy.aphy.ac.cn (Y. Guo) & E-mail: xldu@iphy.aphy.ac.cn (X. L. Du)
Impact of acceptor states in Mg$_x$Zn$_{1-x}$O Schottky photodiodes

A. Hierro, G. Tabares, J.M. Ulloa, E. Muñoz

ISOM and Departamento de Ingeniería Electrónica, Universidad Politécnica de Madrid, Ciudad Universitaria s/n, 28040 Madrid, Spain

A. Nakamura, T. Hayashi, J. Temmyo

Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Hamamatsu, Shizuoka 432-8011, Japan

The incorporation of Mg to ZnO can provide great potential for tunability of the bandgap, thus allowing to spectrally cover part of the UV region. Provided that the Mg content remains below 35-40%, a wurtzite structure can be maintained and grown on sapphire. Particularly, by using an r-plane sapphire substrate, a-plane ZnO with the added functionality of being non-polar can be obtained. The addition of Mg to ZnO has also been used by several groups to enhance the incorporation of p-type dopants, which has resulted in the demonstration of p-n junctions. However, the origin for this enhancement in p-type doping efficiency still remains unknown.

In this work we have used remote plasma enhanced MOCVD to deposit a-plane Mg$_x$Zn$_{1-x}$O films on r-plane sapphire. The films have varying Mg concentrations ranging from 5.6 to 18 %, and absorptions edges covering the 3.38 to 3.58 eV spectral region. Semitransparent 10nm-thick Au-Schottky photodiodes have been formed on the films with excellent rectification characteristics.

At -1.5V the MgZnO Schottky photodiodes show responsivities of 240 A/W for 5.6 % Mg, decreasing down to 33 A/W for 18 % Mg, and rejection ratios as high as 5 orders of magnitude. The response time of the photodiodes under a reverse bias is also highly dependent on the Mg content, increasing quite noticeably from 13s to 35s as the Mg content is increased. As expected, under photovoltaic conditions the responsivities decrease by several orders of magnitude whereas the response time improves dramatically.

In parallel to the degradation of the responsivity with the Mg content, the net electron concentration determined by C-V profiling decreases from $8.5 \times 10^{16}$ to $1.6 \times 10^{16}$ cm$^{-3}$ from the 5.6 to the 18 % Mg photodiodes, respectively. To search for the origin of the decrease in carrier concentration, deep level optical spectroscopy (DLOS) and C-V-light measurements have been then used to probe the deep level spectrum of all the photodiodes. Regardless of the Mg content or the bandgap energy, two deep levels are observed at 280 and 580 meV above the valence band edge. The trap concentration of these levels is highly dependent on the Mg content, ranging from $1.1 \times 10^{17}$ cm$^{-3}$ at 5.6% Mg, to $1.0 \times 10^{18}$ cm$^{-3}$ at 18 % Mg. These deep levels are thus acting as a carrier compensating centers, and can explain the decrease in net electron concentration, the decreased responsivity, and the longer response time of the photodiodes with higher Mg content. This result also provides a reasonable mechanism to explain why p-type doping is more efficient in MgZnO than in ZnO alloys.
Characteristics of ZnO thin film transistor prepared by two different methods

K. Haga, M. Sakuma, Y. Takizawa, S. Seki
Sendai National College of Technology, Ayashi-Chuoh, Aoba-ku, Sendai, 989-3124, Japan

We succeeded the fabrication of bottom gate ZnO-TFT on thermal oxidized p-type Si substrate with the high-resistivity ZnO active layer which was prepared by two different methods. The first preparation methods was MO-CVD using the fibrous bis(acetylacetonato)-zinc(II) (Zn(C₅H₇O₂)₂) and ozone(O₃). Commercially produced Zn(C₅H₇O₂)₂ powders was vaporized in a vacuum vessel and then re-crystallized at the cooled part as fibrous Zn(C₅H₇O₂)₂. Zn(C₅H₇O₂)₂ gas carried with N₂ flows in the reaction chamber. The temperature of the substrate was maintained at 500 °C. O₃ was generated in the range of 0.60 - 2.04 g/h by adjusting both the flow rate of O₂ and the discharge voltage in the ozonizer. The second one was rf (13.56MHz) sputtering using a ceramic oxide target ZnO with a purity of 99.99% and 2 in. diameter. Sputtering was carried out oxygen mixtures at pressure of 1.33 Pa with an rf power of 50-200W. The temperature of the substrate was at RT-250°C.

The thickness of the ZnO active layer was measured with an electromechanical stylus instrument, and was a range of 20-186 nm. The crystallinity and surface composition of the ZnO films using as active layers of the ZnO-TFT were analyzed by X-ray diffractometry, atomic force microscopy and X-ray photoelectron spectroscopy. For all the ZnO films prepared by different methods, the ZnO (0001) peak at 2θ = 34.4° was mainly observed. The films are polycrystalline with a hexagonal structure and a preferred orientation with the c-axis perpendicular to the substrate.

The electrical characteristics of ZnO-TFT were measured using a semiconductor parameter analyzer. All of the ZnO active layers are n-type through the I-V measurement. The ZnO-TFT prepared by rf sputtering show drain current at off state for the gate voltage of V_G=0 and operate in enhancement mode. The ZnO-TFT prepared by MO-CVD has significant drain current at V_G=0 and that the drain current do not turn off without the application of negative gate bias indicating in depletion mode. Photoresponse was measured by continuously monitoring the rise and decay of the conductivity between source and drain electrode upon illumination and extinction of the UV light. For all of sample, the rise and decay photoresponse were very slow. The ZnO-TFT prepared by two different methods shows good electrical properties with a field effect mobility of above 0.2 cm²/V s, an on to off ratio greater than 10⁶, the off current of less than 10⁻¹⁰ A.
Humidity Detection Measurement ZnO nanodots using Quartz Crystal Microbalance (QCM) Method

A. Erol¹, B. Comba¹, S. Okur², N. Üzar¹, N. Tekgüzel²

1. Istanbul University, Science Faculty, Physics Department Vezneciler, 34134 Istanbul, Turkey
2. Izmir Institute of Technology, Faculty of Science, Department of Physics Gülbahce Koyu Kampüsü, Urla, İzmir, 35430, Turkey

In this work, we present the use of ZnO nanodots with diameters about 10nm, synthesized by sol-gel method, as a potential humidity sensor. The morphology and crystal structure of ZnO nanodots were characterized with Scanning Electron Microscopy (SEM), and X-Ray Diffraction, respectively. The optical band gap energy of the ZnO nanodots was determined by using Photoluminescence (PL). The humidity sensing properties of ZnO nanodots were investigated by QCM technique based on resonance frequency shift of quartz crystal coated with ZnO nanodots. Our results show that the ZnO nanodots can be used as a very sensitive relative humidity sensor.
SHG enhancement from one-dimensional polarity inverted structures in ZnO films

T. Minegishi¹,², S. Park², J. Park², T. Yao³ and K. Domen¹

¹ Department of Chemical System Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
² Center for Interdisciplinary Research, Tohoku University, Aramaki-Aoba, Aoba-Ku Sendai 980-8578, Japan

ZnO is a very promising material for photonic devices in the wavelength range from the THz region to the ultra violet owing to its wide transparent range. ZnO possesses relatively large nonlinear optical coefficients. Spontaneous polarization field exists in ZnO crystal and piezo polarization field is induced if the crystal is strained. In addition, the binding energy of exciton is as large as 60 meV. All of those properties are favorable in terms of nonlinear optical device applications.

In order to achieve efficient wavelength conversion, the phase-matching condition should be satisfied, which can be achieved for bulk ZnO crystals, but is not easy for films. In the case of films, however, nonlinear effects can be enhanced if the quasi-phase matching conditions are satisfied by fabricating periodically polarity inverted (PPI) structures. In this paper we will demonstrate the successful fabrication of PPI structures of ZnO films and will show an enhancement in the generation of second-harmonic generation of light from the PPI ZnO films.

The details of the fabrication procedure are described in ref.1. In brief, the selective growth of PPI ZnO layers is performed on MgO templates with line-and-space pattern with a periodicity of 580 nm. The formation of the PPI structure is unambiguously confirmed by the piezo-response microscopy.

SHG experiments are performed under a transmission geometry, in which the incident light with peak wavelength of 780 nm and pulse width less than 10 fs from a Ti-sapphire laser is focused onto the PPI specimen. We have clearly observed SHG at around 390 nm. When the light configuration satisfies the quasi-phase matching condition, resonant-like enhancement as shown in Figure is observed, where the enhancement in SHG intensity is plotted against effective period of the PPI structure. The quasi-phase matching condition is satisfied at the PPI periodicity of 1.49 μm.

Electroluminescence from a n-ZnO/p-GaN Hybrid LED

A. Behrends, A. Bakin, and A. Waag
Institute of Semiconductor Technology, Hans-Sommer Str. 66, 38106 Braunschweig, Germany
Ho-Sang Kwack, Le Si Dang
Institut Néel, CNRS-UJF, 25, rue des Martyrs, 38042 Grenoble, France

ZnO and GaN are both wide-band-gap materials with wurzite structure and a direct band-gap of 3.37 eV and 3.4 eV, respectively. Although the exciton binding energy of ZnO makes the material interesting for optoelectronic devices based on excitonic recombination even at room temperature, GaN is the material of choice for commercial applications. This is due to the lack of a controllable, reproducible and long-term stability p-type doping in ZnO. To combine the excellent optical properties of ZnO with the well established p-type doping capabilities of GaN, the interest in n-ZnO/p-GaN-hybrid structures increased in the last few years. Furthermore, GaN and ZnO have a similar lattice structures with a lattice mismatch of only 1.9 %. These hybrid structures show electroluminescence (EL), even though the interface is type II with a valence band offset of 0.8 eV – 1 eV.

We present a detailed description of the fabrication of p-GaN/n-ZnO hybrid structures using metallorganic chemical vapor deposition (MOCVD) and vapor phase transport (VPT). The diodes were contacted on the GaN and ZnO layer by evaporating Pd/Au and Ti/Au, respectively, showing ohmic behavior. These structures show a broad EL emission around 2.3 eV which can be clearly seen by the naked eye. Cathodoluminescence (CL) gives evidence that the luminescence has its origin in the ZnO. Possible recombination mechanisms will be discussed taking the type II band offset into consideration.
Sodium doped room temperature ZnO ultraviolet-blue light-emitting diodes employing ZnO/ZnMgO multi-quantum wells on silicon substrate

Z. Z. Ye, S. S. Lin, , H. P. He, X. Q. Gu, L. P. Zhu

State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, People’s Republic of China

Ultraviolet-blue light-emitting diodes (LEDs) employing an 8-periods ZnO/Zn$_{0.9}$Mg$_{0.1}$O quantum wells (QWs) are reported. $p$-type ZnO and Zn$_{0.85}$Mg$_{0.15}$O films are fabricated using sodium as acceptor dopant. The room temperature electroluminescence from ZnO-based LEDs is dominated by a band with peak wavelength around ~382nm and the green emission is negligible. The mechanism of the electroluminescence is discussed based on the photoluminescence spectra from QWs structure and $p$-type area of the LEDs.
Nitrogen Doping of ZnO

M. R. Wagner, C. Nenstiel, M. Alic, G. Callsen, A. Hoffmann
Institute of Solid State Physics, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

M. Hoffmann, M. Pinnisch, A. Laufer, S. Zöller, S. Eisermann, S. Lautenschläger, B. K. Meyer
Justus Liebig Universität Giessen, I. Physics Institute, Heinrich-Buff-Ring 16, 35592 Giessen, Germany

Nitrogen as group V dopant on the O-lattice site in ZnO is a promising candidate for shallow acceptor states in order to achieve p-conductive material. However, the controlled incorporation of acceptors into the ZnO matrix is still a not well understood obstacle for the fabrication of bipolar ZnO devices. We investigated the incorporation of nitrogen during homoepitaxial growth at low temperatures with different nitrogen precursors. The influence of polar and non polar ZnO substrate surfaces is studied.

The nitrogen thin films grown by chemical vapour deposition are characterized by micro-Raman spectroscopy, temperature dependent photoluminescence, photoluminescence excitation spectroscopy (PLE) and secondary ion mass spectrometry (SIMS). We report on specific conditions, especially substrate polarity and growth temperature, which favour the nitrogen incorporation. Low temperature PL measurements show the presence of donor acceptor pair (DAP) transitions at different energies between 3.19eV and 3.24eV. In addition, additional luminescence peaks in this energetic range can be observed in some of the samples. Based on the PLE data, we are able to identify all transitions in the DAP regime. The 3.24eV DAP luminescence shown an efficient excitation channel at 3.383eV which coincides with the energy of the free B exciton. However, we contribute this exciton not a B exciton but rather an E_g-D_0 process with a typical donor binding energy of 54meV. A second luminescence at 3.224eV can be clearly attributed by PLE to a D_0X-2LO process. Both transitions also exhibit very narrow excitation channels in the range of the dominant bound exciton line. These excitation channels are identified as 1_6 and 1_6 excited states.

In addition, some of the nitrogen doped samples show a second DAP transition at 3.19eV which possibly involves a deeper acceptor with the same shallow donor of 54meV. Temperature dependent measurements further allow an unambiguous differentiation between DAP and free to bound transitions, which are both observed in selected samples. The results of the optical characterization are correlated with SIMS and Raman in order to determine optimal growth conditions for efficient incorporation of shallow nitrogen acceptors in ZnO.
Effect of annealing on nitrogen-doped ZnO grown by MOVPE with a high-speed rotating disk reactor

N. Nishimoto1,2, Y. Matsuo2, Y. Fujita2

1 Innovation Plaza Hiroshima, Japan Science and Technology Agency, 3-10-23 Kagamiyama, Higashihiroshima 739-0046, Japan
2 Interdisciplinary Faculty of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue 690-8504, Japan

ZnO is an attractive material for the high performance light emitting devices because that has some superior intrinsic properties. Recently, the growth of p-type ZnO films was achieved by MBE, PLD, and MOVPE [1, 2, 3]. MOVPE has an advantage in the ability of mass-production compared with the other growth methods. ZnO films have been studied in our laboratory by MOVPE using diisopropylzinc and tertialy-butanol as a zinc source and an oxygen source, respectively [4, 5]. Previously, we tried the growth of nitrogen-doped ZnO films by using conventional horizontal-type reactor [6]. The post-annealing was carried out to remove the hydrogen bonded with nitrogen. The results showed the significant decrease of the electron concentration, however, p-type films were not obtained due to the high residual electron concentration in the as-grown samples. Recently, we developed the MOVPE system with the vertical-type reactor having a high-speed rotating disk [7]. This system has some advantages for the growth of high quality ZnO films. Growth of the undoped ZnO films with low residual electron concentration was achieved by using this system as compared with that by horizontal-type MOVPE system.

In this work, we tried to grow the nitrogen-doped ZnO epitaxial films with good property for fabricating the p-type films by using the MOVPE system with the vertical-type reactor. Thin films were grown at 350 °C, and the growth pressure was 76 Torr. The ratio of oxygen and zinc sources, $\frac{O}{Zn}$ was 2. Those films were annealed for removing the hydrogen bonded with nitrogen. The annealing at various conditions were investigated, such as annealing time, gas atmosphere, and the time at which rising and falling temperature. The characterization of the crystalline qualities were evaluated by Hall effect measurement, and Raman scattering spectroscopy.

Thin films in the above growth condition showed the good crystallinity compared with the samples grown by conventional horizontal-type reactor. The residual electron concentration and the mobility were $1.12 \times 10^{18}$ cm$^{-3}$ and 60.8 cm$^2$/Vs, respectively (our previous work [6] : $3.37 \times 10^{18}$ cm$^{-3}$ and 12.6 cm$^2$/Vs). The nitrogen concentration was $2.0 \times 10^{19}$ cm$^{-3}$. As a result of post-annealing, the residual electron concentration was decreased with maintaining the high mobility. It is expected that the p-type films will be achieved by optimizing the annealing conditions.

Effectiveness of using a ZnO substrate with an off-axis angle for growth of nitrogen-doped ZnO films

A. Nakagawa¹, T. Abe¹, M. Nakagawa¹, S. Chiba¹, H. Endo², K. Meguro², T. Abe², Y. Kashiwaba¹, T. Ojima¹, K. Aota¹, I. Niikura¹, Y. Kashiwaba¹, and T. Fujiwara¹
¹Iwate University, 4-3-5 Ueda, Morioka 020-8551, Japan
²Iwate Industrial Research Institute, Japan
³Sendai National College of Technology, Japan

High-quality ZnO:N films were successfully grown on single-crystal ZnO substrates with various off-axis angles by the plasma-assisted reactive evaporation (PARE) method. It was found that crystallinity and surface morphology of the ZnO:N films depend on the value of the off-axis angle.

We have reported the growth of ZnO:N films on single-crystal ZnO substrates by the PARE method and have also reported ultraviolet radiation emissions of wavelength of 375-380 nm from diodes formed from a ZnO:N film/ZnO substrate homojunction [1]. It is necessary to grow high-quality ZnO:N films in order to prepare UV light diodes. Effectiveness of using a ZnO substrate with an off-axis angle for ZnO high-quality film growth has not been reported. In this study, we investigated characteristics of ZnO:N films grown on single-crystal ZnO substrates with various off-axis angles.

ZnO (0001) substrates with several off-axis angles from the c-axis to m-axis, about 0º, 0.5º, 1º, 2º, 3º, 5º and 10º, were cut from the +C sector of a ZnO single crystal grown by the hydro-thermal growth method. The surfaces of ZnO substrates were polished by the chemical mechanical polish method and the substrates were annealed at 1,150 for 3.5 hrs. ZnO:N films were grown on these substrates at 650-750 by the PARE method. The surface morphology of ZnO substrates and ZnO:N films was observed using an atomic force microscope. Crystallinity of ZnO:N films was evaluated by X-ray diffraction. Photoluminescence (PL) was excited by a He-Cd laser (325 nm).

Values of root mean square roughness of the surfaces of as-polished ZnO substrates were very small (0.10-0.17 nm), but a step-and-terrace structure was not observed on the surface. A step-and-terrace pattern appeared clearly on the annealed ZnO substrates. Terraces with widths over 500 nm were observed on the surface of the ZnO substrate with an off-axis angle of about 0º, but the width of the terrace was not uniform. The shape of the step-and-terrace pattern changed uniformly and the terrace width became narrow with increase in the value of the off-axis angle. On the surface of the ZnO substrate with an off-axis angle over 3º, step bunching was observed.

Characteristics of ZnO:N films strongly depend on the surface condition of ZnO substrates. ZnO:N films on substrates with wide terraces often showed three-dimensional growth. The diffusion length of atoms on the terrace may be shorter than the width of the terrace. Films on substrates with narrow terraces had large RMS values because of step bunching. Under our film deposition conditions, an off-axis angle of about 0.5º was best for homoepital growth. In this case, two-dimensional growth was observed and the RMS roughness value was about 0.20 nm. The FWHM value of the X-ray rocking curve for the (0002) plane was about 23 arcsec., and acceptor-related peaks in PL spectra were observed in the ZnO:N film.

Using a ZnO substrate with an off-axis angle is advantageous for growth of high-quality ZnO:N films, and selection of an appropriate off-axis angle is important for obtaining for excellent device characteristics.

Depth-resolved Photoluminescence Studies of Na+H co-doped ZnO grown by MBE

A. Galeckas¹, L. Vines¹, A. Yu. Kuznetsov¹, Y. P. Liu², X. L. Du², T. C. Zhang², Z. X. Mei², Z. L. Liu², Y. Guo²

¹Department of Physics, Centre of Material Science and Nanotechnology, University of Oslo, P.O. Box 1048 Blindern, N-0316 Oslo, Norway
²State Key Laboratory for Surface Physics, Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100080, China

Substitutional group-I elements are expected to behave as shallow acceptors in ZnO, however in practice such dopants also occupy interstitial sites, acting as donors and thus leading to self-compensation. A possible way to resolve this problem is co-doping with hydrogen (H) which is known to suppress formation of compensating interstitials and to considerably increase solubility limits of dopants. In this work, we report on studies of p-type [Na+H] co-doping of ZnO and subsequent activation of Na by thermal annealing. The investigated samples were ZnO:[Na+H]/ZnO/MgO structures grown by RF-MBE on sapphire. The nominally 300nm-thick layers were doped in the concentration range [Na] ~ 2.6×10¹⁸ - 2×10¹⁹cm⁻³. The post-growth annealing was performed at 600-800°C in air to break Na-H complexes apart and remove hydrogen.

Secondary ion mass spectrometry (SIMS) measurements confirmed successful incorporation of [Na+H] co-dopants and also exposed relevant changes in the depth distribution of the concentration at different stages of post-growth annealing, suggesting that more than 90% of the incorporated H can be removed in the course of thermal treatment.

Hall-effect measurements have indicated n-type conductivity for all as-grown samples and semi-insulating (compensated) behavior as well as p-type conductivity for some of the annealed samples.

Differential spectroscopy approach was implemented in the conducted low-temperature photoluminescence (PL) measurements to enhance susceptibility to Na-related emission. More specifically, first the in-depth luminescence properties of ZnO:[Na+H]/ZnO/MgO structures were investigated by spatially-resolved PL probing of a series of SIMS craters of variable depth, and then spectra from undoped (buried) ZnO layers were used as references in analysis of the corresponding differential spectra. Several indications of NaZn-acceptor related optical activity were observed in the near-band-edge (A''X ~ 3.353 eV and (eA'') ~ 3.277 eV) and deep-level related emission regions (broad band around 2.17eV). We correlate depth-resolved PL results with SIMS data and discuss possible sources of [Na+H] co-doping induced spectral changes.
High quality p-type ZnO film grown on ZnO substrate by nitrogen and tellurium codoping

S. H. Park\textsuperscript{1}, T. Minegishi\textsuperscript{1}, J. S. Park\textsuperscript{1}, H. J. Lee\textsuperscript{1}, D. C. Oh\textsuperscript{2}, J. H. Chang\textsuperscript{3}, S. K. Hong\textsuperscript{4}, and T. Yao\textsuperscript{1}.

\textsuperscript{1}Center for Interdisciplinary Research, Tohoku University, Sendai, 980-8577, Japan
\textsuperscript{2}Department of Defense Science and Technology, Hoseo University, 336-795, Korea
\textsuperscript{3}Major of Semiconductor Physics, Korea Maritime University, Pusan 606-791, Korea
\textsuperscript{4}Nano Information Systems Engineering, Chungnam National Univ., Daejeon, 305-764, Korea

ZnO has attracted a substantial attention as a replaceable material for GaN in the optoelectronic applications. However, low solubility of acceptor and self-compensation hampered its p-type conductivity.

For the successful p-type conductivity control, high-quality ZnO film with high acceptor concentration is inevitably required. To achieve the mission, new growth technique for high-quality p-ZnO layers with high acceptor concentration is necessary. Tellurium atoms act as pseudo-donor, which can reduce the Madelung energy by codoping with nitrogen atom. Therefore, it is expected to grow high-quality ZnO doped with high N concentration beyond the solubility limit. In this presentation, nitrogen and tellurium codoping is proposed as a new solution to achieve p-type ZnO films.

Nitrogen doped ZnO film (ZnO:N) and nitrogen+tellurium codoped ZnO film (ZnO:[N+Te]) were prepared on (0001) ZnO substrate by plasma-assisted molecular beam epitaxy. Growth temperature was as low as 500 °C and growth parameters such as polarity, V/I ratio, Te-flux, and N-flux have been optimized carefully.

Under the optimum growth conditions, acceptor concentration of $\sim 10^{21}$ cm\textsuperscript{-3} (hole concentration $\sim 10^{16}$ cm\textsuperscript{-3} and hole mobility $\sim 18$ cm\textsuperscript{2}/Vs) was obtained from codoped ZnO film (ZnO:[Te+N]), while only n-type conduction was obtained from ZnO:N sample. Furthermore, in compare to ZnO:N, ZnO:[Te+N] revealed superior properties such as narrow x-ray rocking curve line width (30 arcsec), smooth surface morphology (RMS=1.0 nm) and strong excitonic emissions. Especially, narrow acceptor bound exciton (A\textsuperscript{o}X $\sim 3$ meV) and weak deep level emission prove the considerable improvement of optical properties, in comparison with those of previously reported ZnO:N. Such behaviors are tentatively attributed to the decrease of Madelung energy of ZnO by incorporation of Te, which increases the solubility and decreases the compensation ratio of acceptors.

In summary, high acceptor concentration p-type ZnO film has been achieved by codoping of nitrogen and tellurium into homoepitaxial ZnO.
Nitrogen doping in ZnO is prevented by spontaneous formation of compensating defects. A perfect control of the nitrogen doping concentration is required since high concentration of nitrogen could induce the formation of donor defects involving nitrogen. In this work, we investigate the effect of post-growth annealing in oxygen ambient on ZnO thin films grown by metalorganic chemical vapor deposition with NO as both oxidant and nitrogen dopant. After annealing at 600 °C, low-temperature photoluminescence shows the appearance of a transition at ~ 3.23 eV which is interpreted as DAP transition involving nitrogen acceptor. A second transition at ~ 3.15 eV is also discussed. This work suggests annealing as a potential means for nitrogen p-type doping.
The role of hydrogen in p-type conductivity conversion of in-situ Na-H codoped ZnO films by MBE

Y. P. Liu¹, L. Vines², X. L. Du¹,²*, A. Galeckas², T. C. Zhang¹, Z. X. Mei¹, Z. L. Liu¹, Y. Guo¹, J. J. Zhu², A. Yu. Kuznetsov²

¹Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
²Department of Physics, University of Oslo, P.O.Box 1048 Blindern, NO-0316 Oslo, Norway

*E-mail: xldu@aphy.iphy.ac.cn (X.L.Du), andrej.kuznetsov@fys.uio.no (A.Yu.Kuznetsov)

It’s well known that hydrogen, as an impurity, strongly affects the electronic properties of many semiconductors[1]. For example, formation of Mg-H complex in Mg doped GaN films result in a significant compensation, so a post-annealing technique has been developed to move out the hydrogen for activating the acceptors and hence achieving p-type GaN[2]. Bonding with oxygen, H was found to be a shallow donor in ZnO, making contribution to n-type conductivity in undoped ZnO[3]. In our attempts of p-type doping of ZnO film, hydrogen has been used to intentionally codope ZnO film with Na for purpose of forming NaZn-H complex[4]. We found that H can be removed from the Na-H codoped film, leaving Na on substitutional sites, resulting in a p-type ZnO film.

The samples were synthesized at 450 °C on undoped ZnO/sapphire templates by in-situ Na-H codoping using different doping levels by MBE. In comparison, Na solo-doped ZnO films were also prepared which are all insulative. Although the substitutional Na is promising shallow acceptors [5], however, stable p-type conductivity in Na solo doped ZnO is difficult to achieve due to formation of interstitial Na, resulting in a significant self-compensation. But the Na-H codoped as grown film, which demonstrates n-type conductivity with an electron concentration of ~2x10¹⁷ cm⁻³, converts to p-type one with a hole concentration of ~2x10¹⁶ cm⁻³ and a mobility of ~2 cm²/Vs after annealing at 950°C. SIMS measurement shows examples of Na and H concentration/SIMS intensities versus depth profiles in an as-grown sample and the 950°C annealed sample. A sharp interface between the doped and undoped layers is observed at a depth of ~0.2µm, indicating simultaneous incorporation of Na and H. After annealing, more than 90% H was removed from the doped layer. Moreover, a peak assigned to the substitutional Na was detected at 3.355 eV in PL spectrum at low temperature, and the peak at 3.355eV was enhanced in the annealed samples, indicating that NaZn-H complex is formed during codoping and the complex breaks by subsequent annealing, so that H is removed leaving Na on substitutional sites, achieving a p-type ZnO film.

To further increase the population of substitutional Na due to formation of NaZn-H complex, extra H was introduced during material synthesis so that to increase the Femi level and hence reduce the formation energy of NaZn [4]. The results are discussed in detail in this report.

On the electrical characteristics of Pd Schottky contacts deposited on the O-polar and Zn-polar faces of Bulk ZnO crystals

W. Mtangi, J. M. Nel, F. D. Auret, A. Chawanda, C. Nyamhere, and P. J. Janse van Rensburg

Department of Physics, University of Pretoria, Pretoria 0002, South Africa.

Abstract

After Mead reported the first Schottky contacts to ZnO in 1965, an increasing amount of research based on the quality of the contacts has been carried out. Of these reports, several researchers have reported the dependence of contact quality on the metals used and the type of methods used in sample cleaning prior to contact fabrication. Very little work has been reported on the effect of polarity of the bulk ZnO samples. In this regard, we report on the electrical behavior of palladium Schottky contacts deposited on the Zn and O-polar faces of melt-grown, bulk ZnO crystals. Room temperature current-voltage (I-V) measurements have been performed on the hydrogen peroxide treated samples. Results obtained on the Schottky contacts with a diameter of 0.6 mm on the O-polar face have revealed the presence of generation/recombination while contacts with the same diameter on the Zn-polar face have indicated pure thermionic emission. The best contact to the O-polar face has yielded an ideality factor of 1.65, a reverse leakage current of $1.42 \times 10^{-10}$ A at bias voltage, $V = -1$ V and a barrier height of 0.87 eV while the best contact to the Zn-polar face produced an ideality factor of 1.15, a reverse leakage current of $4.74 \times 10^{-11}$ A at bias voltage, $V = -1$ V and a barrier height of 0.90 eV. Generation/recombination on the O-polar face has been attributed to oxygen adsorption on the surface of the sample. Based on the current transport processes, ideality factors and reverse leakage currents at room temperature, we conclude that the Zn-polar face produces contacts of the best quality.
Effects of a high humidity environment and air anneal treatments on the electrical resistivity of transparent conducting ZnO-based thin films

A. Abduev, A. Akhmedov, A. Asvarov, A. Abdullaev, and A. Murtazaliev
Institute of Physics, Dagestan Scientific Center of RAS, Yaragskogo str. 94, Makhachkala 367003, Russia

Transparent conducting oxide (TCO) thin films are in practical use as transparent electrode in liquid crystal display, light-emitting diodes, and solar cells applications. Most TCO electrodes are based on indium-tin-oxide (ITO) thin films. However, because of the high cost and scarcity of indium, ZnO-based TCO thin films have attracted much attention as promising alternative material. ZnO-based films also have advantages in terms of their chemical stability in the reductive ambient containing H⁺ which is used for hydrogenated a-Si depositions. Thus ZnO-based TCO thin films have been extensively studied in the fields of their preparing methods and their physical properties. The electrical resistivity of ZnO has been reported to decrease by doping both trivalent atoms (B, Al, Ga, In) and four-valent atoms (Si, Ge, Ti). Among these dopants, Al and Ga have been widely used for the decreasing of resistivity of ZnO thin films. However, the resistivity of ZnO thin films has been found to increase when used in high temperature oxidizing environments and in a high humidity environment.

In this work the stability of transparent conducting Al-doped and Ga-doped ZnO thin films in a high humidity environment (air at 85% relative humidity and 85 °C) and in a high temperature oxidizing environment (air, 360 °C) will investigated for purpose of finding substitutes for ITO used in TCO applications.

The AZO and GZO films deposited by dc-magnetron sputtering of ceramic targets and used in the stability tests are prepared with thickness in the range from 200 to 1000 nm at a substrate temperature in the range from 50 to 280 °C. The effect of the stability tests on the electrical properties have been studied by X-ray diffraction measurements, scanning electron microscopy, Hall measurements and UV/visible spectrophotometry.

In the first part of this work, we will report the results of our investigations of the physical properties and the humidity and thermal stabilities of ZnO-based TCO thin films. Then we will discuss how a stability of ZnO-based thin films could be improved to realize a substitution for ITO electrodes in hi-tech applications.
Mechanism of Resistive Memory Effect in Ga Doped ZnO Thin Films

K. Kinoshita¹, T. Hinoki¹,², K. Yazawa², K. Ohmi¹,³, and S. Kishida¹,³
¹Department of Information and Electronics, Graduate School of Engineering, Tottori University, 4-101 Koyama-Minami, Tottori 680-8552, Japan
²Oike & Co., Ltd., 63 Daimotsu-cho, Kamitoba, Minami-Ku, Kyoto 601-8121, Japan
³Tottori University Electronic Display Research Center

Resistive random access memory (ReRAM), utilizing an electric field-induced resistive memory effect, has attracted enormous attention as a next-generation substitute for flash memory. This phenomenon has been observed in various metal oxides. Among them, ZnO is one of the most attractive materials because of its simple constituents and compatibility with complementary metal oxide semiconductor (CMOS) process. In this paper, a resistive memory effect has been first found out in Ga doped ZnO (GZO) thin films. The electrical polarity dependences of resistive memory effect have been investigated compared with NiO.

GZO and Ga-undoped-ZnO thin films were deposited on Al-bottom-electrode coated glass substrates by dc magnetron sputtering with rf plasma assist [1]. The thicknesses of GZO and ZnO films were 200nm and 160 nm, respectively. The Ga concentration was 5.7 wt.% for all GZO films. Resistive characteristics were analyzed by Conducting Atomic Force Microscopy (C-AFM). For the C-AFM measurement, the Rh-coated Si tip (Rh-Tip), which acts as mobile top electrode, was grounded, and a bias voltage was applied to the Al bottom electrode.

No change in resistance was observed for the ZnO film irrespective of the polarity and the amplitude of the applied bias voltage, even when the maximum voltage (±10 V) was applied. On the other hand, for the GZO films, the resistance changed from a low resistance state (LRS) to a high resistance state (HRS) by applying a bias voltage of +4 V, whereas a change from HRS to LRS was observed by applying a bias voltage of -4 V. This suggests that not only strong electric field but also high current density originated from Ga-doping was necessary to cause the resistance change, since the GZO film was thicker than the ZnO film. It has been also confirmed that resistance change in the GZO films was stably rewritable at room temperature.

In addition, a remarkable difference in polarity-dependence of resistance change effect was found between GZO and NiO [2], i.e., the opposite bias polarity was required to make the same resistance state. NiO is known as a metal-deficient p-type semiconductor, and ZnO is an oxygen-deficient n-type one. If some of the O²⁻ ions were removed from Zn-O [Ni-O] bonds in ZnO [NiO] film by the synergy effect of a strong electric field and Joule heating, it leads to the increase [decrease] in carrier concentration. Therefore, our result is consistent with crystallographic nature of these materials and supports the theoretical model of resistive memory effect based on locally induced redox reaction [3]. GZO is a candidate for n-type resistive memory material, which enables us to achieve transparent ReRAM devices.

[1] T. Hinoki et al., Proceedings of the 14th International Conference of II-VI compounds 2009 to be published
Schottky barrier contacts formed on polar-, nonpolar-Mg$_x$Zn$_{1-x}$O film grown by remote-plasma-enhanced MOCVD

A. Nakamura, T. Hayashi, and J. Temmyo
Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Hamamatsu, 432-8011 Japan

A. Hierro, G. Tabares, J.M. Ulloa, E. Muñoz
ISOM and Departamento de Ingeniería Electrónica, Universidad Politécnica de Madrid, Ciudad Universitaria s/n, 28040 Madrid, Spain

A selective growth of polar- and nonpolar orientation in film is an important technique, which for opto-electric devices such as light-emitting diodes, data storage devices, sensing applications and polarization-sensitive photodetectors. Recently, there has been considerable interest in the growth of nonpolar ZnO based epitaxial films for p-type doping\(^1\), heterostructures and quantum wells\(^2\). ZnO and its related ZnO-based Mg$_x$Zn$_{1-x}$O present advantage of having a large exciton binding energy, which is beneficial for opt-electronic devices at a high temperature. However, Mg$_x$Zn$_{1-x}$O has a tendency to have high resistance with an increase of Mg content, and a surface condition on film is an obstacle to form Ohmic contacts or Schottky contacts.

In this report, we characterized Schottky contact on both of polar face of c-plane (0001) Mg$_x$Zn$_{1-x}$O and nonpolar face of a-plane (11-20) Mg$_x$Zn$_{1-x}$O grown by remote-plasma-enhance MOCVD. Forming of Schottky contacts and the carrier concentration of MgZnO Schottky diodes with varying Mg content have been discussed. Polar Mg$_x$Zn$_{1-x}$O had been grown on a-plane (11-20) sapphire substrate on the other hand nonpolar Mg$_x$Zn$_{1-x}$O had been grown on r-plane (10-12) sapphire substrate at the same time. The typical substrate temperature was 600°C. The Mg content with 0 to 18% in the film was controlled by a flow ratio of DEZn and EtCp$_2$Mg. The optical bandgap of Mg$_x$Zn$_{1-x}$O has changed from 3.3 eV at x=0 to 3.6 eV at x=0.18. Prior to the metal deposition, the samples were cleaned in organic solvents (acetone and methanol), rinsed in de-ionized water, and dried by a nitrogen stream. The extended back ohmic contacts were defined with a Ti/Al/Ti/Au layer thermally annealed. Schottky contacts have been treated through a surface passivation with H$_2$O$_2$ at 100°C for 1 min. The morphology of the films was analyzed by a field emission scanning electron microscopy (FESEM). Current-voltage (I-V) and capacitance-voltage (C-V) measurements were performed on these Schottky diodes at room temperature.

The polar face of as-grown film had a vertically aligned columnar growth with respect to the sapphire (11-20) substrate. These columns had an average diameter of about 40 nm. In contrast, the nonpolar face of as-grown film had a sword-shape lying with an average width of 250 nm on the sapphire (10-12) substrate. The H$_2$O$_2$ treatment led to a smooth surface morphology for the films and resulted in Schottky contact of Au formed on the treated films with barrier heights of 0.8-1.0 eV. A rectifying behavior had been achieved with 6 to 8 order of magnitude between forward and reverse biasing. A series resistance was increased with Mg contents in both polar- and nonpolar diodes. A residual electron concentration were decreased with the Mg content performed by C-V measurement, typically from $3 \times 10^{17}$ cm$^{-3}$ at x=0 to $4 \times 10^{15}$ cm$^{-3}$ at x=0.18, it suggest that Mg atoms play a role of compensation.


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RPE-MOCVD grown ZnCuO films for green light emitting structures

B. Hu, K. Yamamoto, A. Nakamura and J. Temmyo

Research Institute of Electronics, Shizuoka University 3-5-1 Johoku, Naka-ku, Hamamatsu, Shizuoka, 432-8511 Japan
e-mail: hubo1219@gmail.com

ZnO has some typical features such as a wide band-gap energy (Eg) of 3.28 eV, which suggests potential applications for novel optical devices. We have already demonstrated ZnO-based alloy film systems exhibiting a band-gap energy lineup from 1.9 eV to 3.7 eV with cadmium and magnesium1). Here, undoped ZnO-based films show n-type conductive nature. A variety of group-V doping at the oxygen site for achieving p-type ZnO has been examined and possible stable reproducibility should be addressed yet. An introduction of Ib element such as Cu doped ZnO has been proposed to achieve p-type conduction2) and has been recently reported on RS-MBE grown Cu-doped ZnO-based pn junction was demonstrated3). On the contrary, we have already grown Zn1-xCuxO alloy films by remote-plasma-enhanced MOCVD with Cu2+ substituting at the Zn site with nitrogen carrier gas, and succeeded to control the Cu composition up to 3 % with the optical band gap energy up to 3.30 eV4). In this paper, we discuss the control of Cu valence in a ZnCuO system and a green emitting heterostructure with green Zn0.8Cd0.2O/p-ZnCuO films.

ZnCuO films were grown on a-plane sapphire substrates by RPE-MOCVD, using Diethyl zinc, Copper bis(diisobutryl methane) (Cu(dibm)2) with a carrier gas of hydrogen. Growth temperature was changed with 300 ~ 400 °C. The crystallinity was characterized using x-ray diffraction (XRD). The electrical specification of the films was done by Van der Pauw method. The diode performance was characterized by I-V and electroluminescence measurements.

The typical growth rate of ZnCuO was 2 nm/min at 300 °C, which is confirmed that the growth rate has decreased down from 14 nm/min of ZnO film at a dash by about 80 %. By evaluating the relation between c axis length calculated from XRD and conductivity of ZnCuO films, we can find that the c axis length became to smaller, having a tendency of n-type conduction nature at 400 °C. It can be seen that Zn2+ was substituted with Cu2+, because Cu2+(0.057 nm) ion is smaller than Zn2+(0.060 nm). In contrast, with ZnCuO films grown at 300 °C, we can see the tendency of c axis length became to large, and shown the possibility of p-type conductive nature. Thus, it is considered that there is a possibility of Cu2+ mixing with Cu+ in p-ZnCuO films. The DAP photoluminescence of 3.27 eV available from a low-temperature PL spectrum also suggests the result. We have successfully demonstrated a green heterostructure with Zn0.8Cd0.2O/p-ZnCuO on 4H-SiC. The I-V rectification characteristics were observed and a green EL emission fairly corresponding to the PL peak of Zn0.8Cd0.2O was confirmed.

A Novel Chrysanthemum-like ZnO Nanostructure synthesized by the Ultrasonic Spray Pyrolysis Method

Yun Guo*, Xiaoyin Wei, Bin Wang, Yue Zhao, Jiahua Min, Wenbin Sang
School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China

Abstract: Due to the outstanding performance in electronics, optics and photonics, nanostructured ZnO materials have received broad attention. Different growth techniques have been developed to fabricate various morphological ZnO nanostructures, which may exert a great influence on their properties for potential applications. Structurally, ZnO has much more variable shapes probably than any of the other known nanomaterials. In this work, a novel chrysanthemum-like ZnO nanostructure was synthesized by the ultrasonic spray pyrolysis method, and characterized using X-ray Diffraction (XRD), Raman Spectroscopy, Scanning Electron Microscopy (SEM) and Energy-Dispersive Spectroscopy (EDS) for the structural, surface morphological and chemical analyses respectively.

The XRD pattern confirmed the hexagonal polycrystalline structure of wurtzite. All diffraction peaks can be indexed according to the standard card (JCPDS 36-1451), with lattice constants: \(a=3.2448\text{Å}, \ c=5.1909\text{Å}\), while ZnO grew more preferentially along \((101)\) plane than \((002)\) plane and \((100)\) plane. Raman Spectrum was normalized by the main peak at 437 cm\(^{-1}\), which was assigned to the strongest \(E_{2H}\) vibration of Zn-O bond, diagnostic of wurtzite crystal structure. The peaks at 330 and 384 cm\(^{-1}\) were assigned to the \(2E_2\) and \(A_{1T}\) modes, respectively. The mode with \(E_{1L}\) symmetry at 584 cm\(^{-1}\) was ascribable to the defects such as \(V_0\), \(Zn_i\) and the free carriers. The morphological features were examined using SEM. Under the lower magnification of 1500 times, ZnO nanostructure exhibited a novel chrysanthemum-like configuration. The petals of chrysanthemum were fantastic to be built up from numerous particles linked together under higher magnifications. These particles showed relatively uniform dimensions with the grain diameters of 100-200 nm. The strong peaks for Zn and O in the EDS spectrum clearly indicated the main chemical composition. The growth process and mechanism of the as-obtained ZnO nanostructure were further discussed. This unique nanostructure was assumed to follow the dendrite growth mode, whose evolutive process was proposed in a granule-petal-flower way.

Key words: ZnO nanostructure; the Ultrasonic Spray Pyrolysis Method; X-ray Diffraction; Raman Spectroscopy; Scanning Electron Microscopy

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Corresponding author: guoyun@shu.edu.cn Tel: +86 021 5633 5357
Multiple diffraction effects occur when a single crystal is so oriented in x-ray beam that two or more sets of planes in the crystal simultaneously satisfy Bragg law. In reciprocal space two, or more, lattice points lie on the Ewald sphere at the same moment. Multiple diffraction is measured when a crystal is set in a diffractometer for a primary reflection and then rotated around the diffraction vector (ϕ-scan). If the primary reflection is forbidden or very weak, multiple diffraction events appear as peaks of “umweganregung” on the diffraction pattern (Renninger scan). Recently the multiple diffraction was at first used for study of wurtzite type epitaxial films [1-2].

In this paper, the multiple diffraction was applied for detailed study of ZnO and GaN epitaxial layers. An aim of the study is to reveal a connection between a defect structure of the layers and features of the multiple diffraction patterns. Several samples of ZnO and GaN epitaxial films grown by different methods on c-sapphire were under study. A thickness of the layers was in range 0.5 – 30 μm. Renninger scans were measured with using the primary forbidden reflection 0001. In most of them 7 triple diffraction peaks in each angular range of ϕ=30° are observed. Intensity and FWHM of the peaks measured in ϕ- and ω-scanning modes were analyzed. It is shown that FWHM of the ω-scan peaks is very sensitive to a type and density of dislocation ensembles. In particular the most intense triple diffraction peak (10̅10)/(1̅0̅1) is mostly broadened due to contribution of threading edge and screw dislocations. From a dependence of the multiple peak intensity on the layer thickness, a penetration depth in each triple wave combination was estimated.


r.kyutt@mail.ioffe.ru
ZnO epitaxial layers are promising materials for the fabrication of high-temperature devices operating in the ultraviolet spectral range. Large misfits of the lattice parameter and thermoelastic coefficient between ZnO and sapphire lead to a high stress and high defect density in the epitaxial structures. The special growth conditions (temperature, buffer and Zn / O flux ratio) are necessary to minimize such unfavourable influence. The purpose of this communication is a detailed study of X-ray diffraction in epitaxial ZnO layers with a different thickness and growth parameters.

The three epitaxial ZnO layers were grown on the (0001) sapphire with a complex buffer layer by radical-source molecular beam epitaxy (RS-MBE) technique [1]. A thickness of layers was 0.4 – 4 mkm.

X-ray diffraction was used for structural characterization of the films. Measurements were performed at triple crystal diffractometer using symmetrical and asymmetrical Bragg and symmetrical Laue diffraction geometry. Diffraction peaks were measured in two direction of scanning: $\hat{H}$–20-mode along the diffraction vector $\hat{H}$ and $\hat{0}$–mode normal to $\hat{H}$. Intensity distribution around the reciprocal lattice point (mapping) for the asymmetrical Bragg reflection 11-22 was obtained also. On basis of the analysis of the peak broadening in different geometry the parameters of microstructure (components of the microdistortion tensor and the size of coherent regions in directions parallel and normal to the surface) were obtained and densities of different dislocation ensembles were calculated [2].

It is shown that for RS-MBE (Zn / O >1) the layers are under a biaxial tensile stress while for Zn / O <1 the layer is undeformed. On the other hand the RS-MBE layers grown in the Zn rich regime were more perfect than the sample with Zn / O <1. Narrow diffraction peaks in symmetrical Bragg geometry indicate that there are no (or very few) threading dislocations with screw components. But density of the threading edge dislocations is high that is evident from the comparison of FWHM of 0-20-peaks measured in symmetrical Bragg and symmetrical Laue cases. The MBE Zn-rich grown layers contain dominating ensemble of the pure edge threading dislocations perpendicular to the surface ($\rho$ (vert. screw) = $10^5$ – $10^6$ cm$^{-2}$, $\rho$ (vert. edge) = $10^9$ – $10^{10}$ cm$^{-2}$). For the O-rich grown MBE layer the densities of the all dislocation types are approximately identical ($10^{10}$ cm$^{-2}$) and the layer is characterized by the quite small lateral dimension $\tau_x$ of the coherent regions.


1 r.kyutt@mail.ioffe.ru
Spin Selector by Ferroelectric Triple Barrier Resonant Tunnel Diode

M. K. Li\textsuperscript{1}, N. M. Kim\textsuperscript{2}, S. J. Lee\textsuperscript{1} and T. W. Kang\textsuperscript{1}

1. Quantum-Functional Semiconductor Research Center, Dongguk University, 3-26 Pildong, Joong-gu, Seoul 100-715, Korea
2. Department of physics, Soongsil University, 511 Sangdo-dong, Dongjak-gu, Seoul 156-743, Korea

People tried to develop the electron spin alinement in circuit in recent years.\cite{1,2} Conventional method of manipulating spin usually involved an external magnetic field.\cite{3} Many efforts are focused on aligning spin without magnetic field.\cite{4,5}

In this paper we propose a spin selector of ferroelectric triple barrier resonant tunnel diode with diluted magnetic quantum wells of ZnMnO theoretically. The spin transport properties are investigated by non-equilibrium Green's function method. It shows that the potential of barrier slopes due to the spontaneous polarization in the barriers. The positive and negative charges accumulate on the both surfaces of barriers, which leads the potential bending up or down. The transmission peaks are splitting to two sub peaks for each spin direction respectively due to three barriers. And the transmission peaks for spin-up and spin-down are separated due to the spin splitting in the quantum wells.

Our results show that the spin polarizations oscillation at low bias voltage due to the resonant peak splitting into sub peaks. And by reversing the ferroelectric dipole moment, the spin polarization can be changed from one direction to the other direction not only spin polarized status and spin mixed status. It is possible to apply as a spin selector. Furthermore, at different bias voltage the spin polarization is changed on opposite path by reversing the dipole from the left to the right. It can be used as a multi status spin selector device.

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New tendencies of deposition high quality ZnO films for designing of UV photodetectors on their basis

A. Ievtushenko1, G. Lashkarev1, V. Lazorenko1, V. Khranovskyy1, V. Karpyna1, O. Kutsay2, V. Batyrin3, A. Karpenko3, M. Lunika3, L. Kosyachenko4, V. Sklyarchuk4, O. Sklyarchuk4

1Institute for Problems of Material Science, Krzyzhansovskyy 3, Kiev 03142, Ukraine
2V.Bakul Institute for Superhard Materials, Avtozavodskaya 2, Kiev 04074, Ukraine
3Institute of Applied Physics, Petropavlovskaya 58, Sumy 40030, Ukraine
4Chernivtsi National University, Kotsyubinsky 2, Chernivtisi 58012, Ukraine

Zinc oxide (ZnO), a direct band gap II-VI semiconductor has been intensively studied as a promising material for ultraviolet detectors and light emitting devices because of its wide band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature. Recently, a great attention has been devoted to the growth of ZnO films and to produce different devices on their basis. However the properties of ZnO films strongly depend on following conditions such as deposition technology, choosing of substrate material, treatment procedure and further processes which take place in as-grown ZnO films. These troubles lead to the problems of deposition high quality ZnO films, including stability of PL, p-type doping and reproducibility of photoconductivity properties.

For improvement of quality ZnO films we developed the new approach in magnetron sputtering of ZnO films - layer by layer growth. This process was carried out by several stages of deposition on different substrates: Si, Si3N4/Si, Al2O3, ITO/Glass and Glass. Crystal quality of ZnO films was estimated by film stress magnitude and was examined by XRD analysis. The results of investigation structural, morphological and optical properties of ZnO films are discussed. This multistage magnetron sputtering method allows us to grow ZnO films of required thickness with higher crystal quality than ones deposited by single-stage rf magnetron sputtering (for similar thicknesses). Also it allows depositing the qualitative thick ZnO films (more than 1 mkm).

For stabilization of photoelectrical properties UV detectors based on ZnO we introduce N in films by dc magnetron sputtering in nitrogen plasma. Investigations of structure, morphology and optical properties of ZnO:N thin films were carried out. Ni/ZnO:N/Al metal-semiconductor-metal structures were prepared. For investigation nitrogen impurity effect, we deposited non-doped ZnO thin films on p-Si (100) substrate and fabricated the same contact structures to them. All photodiodes based on ZnO:N films demonstrated the maximal responsivity about 0.1 A/W (at 365 nm) and the time constant 100 ns as well as high stability in time. Opposite to ZnO:N case the photodiodes based on non-doped ZnO films displayed poor stability in time and scant persistence of photoconductivity (about several minutes).

Taking into account mentioned above approaches we deposited non-doped and nitrogen-doped ZnO films by rf magnetron sputtering on n"-Si (100) substrates using layer by layer growth method. We studied the properties of as-grown ZnO films by XRD, SEM and PL methods. The influence of processing technology of ZnO films on the photoelectrical characteristics of Ni/ZnO:N/n"-Si photodiodes on theirs basis are discussed.
Properties of Ga-doped ZnO thin films prepared by dc magnetron sputtering: Effect of O₂ deficiency in ceramic targets.

A. Abduev, A. Akhmedov, A. Asvarov, A. Abdullaev, and A. Murtazaliev
Institute of Physics, Dagestan Scientific Center of RAS, Yaragskogo str. 94, Makhachkala 367003, Russia

Transparent conducting Ga-doped ZnO thin films are used as transparent electrode in the various optoelectronic devices. However, the experimental facts that impurity doped ZnO thin films are poor in the heat resistance in an oxidizing atmosphere and that oxygen vacancy doping and extrinsic doping (by Al or Ga atoms) lead to the same mobilities and the data of theoretical scattering models could be an indication that the oxygen vacancies play more important role in the electrical transport in ZnO-based transparent electrodes [1]. Moreover, the electrical parameters of ZnO thin films often do not show a pronounced dependency on the deposition parameters (like temperature, pressure, sputtering power) for magnetron-sputtered films, which is argued to be due to differences in the sputtering arrangements, also including the residual oxygen in sputtering chamber. Hence, the search of ZnO-based materials, providing the insensitivity of the electrical properties of ZnO thin films to small values of the partial pressure of oxygen during the film growth, is relevant.

In this work we report the results of investigations of Ga-doped ZnO thin films, deposited by dc magnetron sputtering using high density ceramic sintered Ga-doped ZnO targets with various Ga content (3-6 at.%) and some oxygen deficiency. Depositions were carried out under various substrate temperatures (50 – 300 °C) and O₂ addition ratios (0 – 10 %) in working gas. The structural, morphological, electrical, and optical properties, as well as the humidity and thermal stabilities of the deposited films was estimated by using X-ray diffraction measurements, scanning electron microscopy, Hall measurements and UV/visible spectrophotometry.

The investigations have shown that increasing the Ga doping level in sputtering targets with O₂ deficiency leads to lower resistance at the substrate temperatures below 200 °C and to an increase of resistivity - at temperatures of more than 200 °C compared with the resistance, obtained when the targets without O₂ deficiency were used. Thus, it seems appropriate to optimize the level of doping of the ceramic targets, taking into account the requirements for permissible temperature of synthesis of ZnO-based transparent electrodes. Studies have also shown that the ceramic target, having some oxygen deficiency, provide the insensitivity of resistivity of as-deposited Ga-doped ZnO thin films to the presence of oxygen in the working gas up to 3%.

Growth conditions and structural properties as limiting factors of electrical parameters of zinc oxide thin films grown in Atomic Layer Deposition process with diethylzinc and water precursors


aInstitute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland
bDepartment of Mathematics and Natural Sciences, College of Science, Cardinal Stefan Wyszyński University, ul. Dewajtis 5, 01-815 Warsaw, Poland

Zinc oxide is nowadays a very extensively studied II-VI semiconducting compound with regards to its numerous potential applications in electronics and optoelectronics. Most of these applications (including e.g. memory cells built in cross-bar architecture, gas sensors, piezoelectric transducers and light emitting diodes) require stable in time and controllable electrical properties (both \( n \)- and \( p \)-type) of ZnO.

In this work we present our latest results for zinc oxide thin films obtained in the low temperature Atomic Layer Deposition (ALD) growth from diethylzinc (DEZn) and deionized water precursors. ZnO layers were polycrystalline when deposited on a glass substrate (used for electrical measurements). Films were grown at the temperature range between 60°C and 250°C with different relations between precursors’ doses.

The electrical investigations (based on classical Hall effect) made at room temperature on as-grown ZnO films revealed that by adjusting ALD process conditions (growth temperature, precursors’ pulsing times and purging times) we are able to control electrical parameters of films, such as free electron concentration, Hall mobility and resistivity. In particular, low \( n \)-type doping was achieved without any post-growing treatment, such as annealing at a high temperature, which is important for some of the predicted ZnO applications.

The so-obtained as-grown ZnO films have free electron concentration between \( 10^{16} \) cm\(^{-3} \) and \( 10^{21} \) cm\(^{-3} \) (depending on growth conditions) with Hall mobility at the level of 50 cm\(^2\)/Vs. As we have already shown (e.g. in [1, 2]) the level of \( n \) concentration scales perfectly with the growth temperature. In the present investigations we focused on examining correlations between structural, optical (obtained respectively from Atomic Force Microscopy, X-ray diffraction patterns and room temperature photoluminescence spectra) and electrical parameters of our ZnO layers. We will present how such factors as layer thickness, surface roughness, ZnO grains’ size and their crystallographic orientations affect the electrical characteristics of ZnO films.

Homo-epitaxy is a promising approach to prepare ZnO thin films of high quality. It avoids the problems arising from the lattice mismatch and the difference in thermal expansion which are inherent to the hetero-epitaxy. However, the quality of the epitaxial films is widely dependent on the quality of the underlying substrate crystals. In order to determine the impurity and defect content of the ZnO substrates we comprehensively investigated samples of various suppliers by photoluminescence (PL), electron paramagnetic resonance (EPR) and secondary ion mass spectroscopy (SIMS). The residual shallow donors are identified to be Al, Ga, In and H and Zn-interstitials in typical concentrations of about $10^{17}$ cm$^{-3}$. In most substrates transition metal impurities such as Mn, Co, Ni and Cu are found in a similar concentration range. Naturally, high concentration of Li, and Na are present in the hydro-thermally grown crystals, and N is unintentionally present in samples of one supplier. To change the Fermi level position in the samples which allows recharging defects and impurities into a paramagnetic state high energy electron irradiation was performed. In these materials new triplet centers are observed by photo-EPR which are likely to be caused by impurities interacting with intrinsic defects.
Correlation of Structural and Electrical Characteristics of Pulsed Laser Deposited ZnO Thin Films on Annealing

Raja Ramanna Centre for Advanced Technology, Indore -452 013 INDIA
*Corresponding Author Email: pmisra@rrcat.gov.in

Current surge for the development of ZnO based electronic and optoelectronic devices demands growth of its thin films and nanostructures with superior properties. ZnO when grown on commonly used Sapphire substrate, exhibits mosaic structure consisting of columnar grains separated by the boundaries, due to large in-plane lattice mismatch between the two. These grain boundaries and other structural defects are primarily responsible for the low electrons mobility in ZnO films. We have carried out systematic studies on the relationship of grain size and other structural parameters with electrical characteristics of ZnO films grown by pulsed laser deposition and annealed at different temperatures. The results of these studies will be presented in this paper.

About 400 nm thick ZnO films were grown on (0001) sapphire by using 3rd harmonic of a Q-switched Nd:YAG laser (355 nm, 6 ns and 10 Hz) as an ablation source at a fluence of ~ 0.6 J/cm². The films were grown in oxygen ambient at 1x10⁻⁴ Torr and at substrate temperature of 500°C, which were subsequently annealed at different temperatures in the range of 600-1000°C in air for 4 hours. The structural parameters such as crystallographic tilt, lateral and vertical coherence length, micro-strain and twist in as grown and annealed ZnO films were studied from the detailed analysis of the line width of symmetric (000 l) and skew symmetric (10-11) ZnO peaks of high resolution x-ray diffraction (HRXRD) using Williamson–Hall analysis. These were further substantiated by SEM and AFM measurements. The electron density and their mobility at room temperature were investigated using Hall measurements.

All the ZnO films were found to be highly c-axis oriented with their in-plane lattice 30º rotated with respect to that of Sapphire. The crystallographic tilt and twist of the grains in the ZnO layer and micro-strain was found to decrease significantly on annealing up to 800°C and then increase marginally on further increase in the annealing temperature up to 1000°C. The lateral coherence length i.e. the grain size which was ~ 50 nm for as grown films increased up to ~ 700 nm on annealing at 800°C and remained nearly constant with further annealing up to 1000°C. The lateral grain size measured using SEM and AFM was found in close agreement with that extracted from HRXRD. The as grown ZnO films were degenerate with high carrier concentration (~ 8x10¹⁸ cm⁻³) and low electron mobility (~ 22 cm²/V-s) primarily due to presence of point defects such as oxygen vacancies and Zinc interstitial, dislocations and grain boundaries. The carrier concentration was found to reduce up to ~ 7x10¹⁶ cm⁻³ and their mobility increased up to ~ 81 cm²/V-s on annealing at 800°C, beyond which marginal deterioration in electrical characteristics was observed. This was attributed to the replenishment of oxygen vacancies which is one of the potential donor defects in ZnO, increase in grain size and reduction of structural defects respectively. Although the grain size in ZnO film saturated on annealing beyond 800°C, the electrical characteristics deteriorated marginally perhaps due to slight but monotonic increase in the dislocations and point defect density as reflected through the micro-strain and deterioration in the chemical quality of the films due to the diffusion of Al into ZnO at the interface. From these observations a correlation between the annealing temperatures and structural and electrical characteristics of ZnO thin films was established. These studies resulted in elucidation of the optimal annealing conditions of the ZnO films grown on sapphire.
Switching Characteristics of ZnO based Transparent Resistive Random Access Memory Devices grown by Pulsed Laser Deposition

P. Misra*, A. K. Das and L. M. Kukreja
Raja Ramanna Centre for Advanced Technology, Indore -452 013 INDIA
* Corresponding Author Email: pmisra@rrcat.gov.in

Resistance switching characteristics, observed in metal oxide thin films, has recently attracted a great deal of attention to develop next generation low power, low cost, high speed, rugged and nonvolatile resistive random access memory (RRAM) devices. The memory effect in these materials is realized through the switching of the resistance of their thin films between two states of high and low resistances. Amongst the known metal oxides currently being explored for the development of RRAM, ZnO has been demonstrated to be a potential candidate. ZnO is an n-type wide bandgap semiconductor and is highly transparent in the visible spectral region. Moreover its conductivity can be tailored in a broad range from metal like to insulator like by suitable impurity doping. Therefore it is possible to develop a fully transparent RRAM entirely based on ZnO. In this paper we report growth of a novel transparent RRAM devices based on ZnO and its variants. We studied the resistive switching characteristics of these devices and associated conduction mechanisms responsible for the switching. The details of this study will be presented in the paper.

About 250 nm thick film of Zn_{1-x}Ga_xO (x=0.0075) with resistivity ~ 1×10^{-4} ohm-cm, grown by pulsed laser deposition (PLD) on Sapphire substrates at 500°C and in 1x10^{-4} Torr of Oxygen ambient using 3rd harmonic of a Q-switched Nd:YAG laser (355 nm, 6 ns and 10 Hz) at a fluence of ~ 0.6 J/cm², was used as transparent bottom electrode. A high resistive ZnO film of typical thickness ~ 90 nm was grown over it at room temperature using a novel in-house developed DC discharge assisted PLD. As a top electrode of the device, about 150 nm thick Zn_{1-x}Ga_xO (x=0.0075) film with a typical diameter of ~ 300 µm was grown in the same conditions as that of the top electrode. The current-voltage (I-V) characteristics of the device were investigated using Kiethley 206 source measurement unit in the top-bottom configuration.

The as grown RRAM device appeared highly transparent and shiny to naked eyes with measured average transmission of ~ 80% in visible spectral region. The device was found to be initially in high resistance state (HRS) ~ 1.3 kΩ (measured at ~0.16 V) and did not show any resistance switching behavior until the applied bias voltage was increased to ~ 3.5 V (initial forming voltage) with a current compliance of 10 mA at which the resistance of device dropped suddenly to a low value of ~ 120Ω (measured at ~ 0.16 V). The low resistance state (LRS) of device persisted even when the applied voltage was reduced to zero. After this initial forming process, which rendered the devise in LRS, as the voltage was swept again form 0 to 2 V switching of the device from LRS to HRS (ON state) was observed at a voltage of ~ 1.6 V. The RRAM device again switched to LRS (OFF state) at ~ 2.2 V as the voltage was swept from 0 to 2.5 volt. The repeatable nonvolatile switching of the resistance of RRAM device was obtained between LRS and HRS at small and well defined switching voltages with a narrow dispersion. The current conduction mechanism of the device in low and high resistance states was found to be dominated by the Ohmic behavior and Poole-Frenkel emission respectively. Resistance ratios of the high resistance state to low resistance state were found to be nearly constant up to 10 test cycles. Further optimizations and studies of the device structure are underway to achieve better endurance and switching characteristics and understand the associated mechanisms.
Seeded growth of bulk ZnO by Chemical Vapor Transport

P. Skupiński\(^1\), K. Grasza\(^{1,2}\), A. Mycielski\(^3\), W. Paszkowicz\(^1\), E. Lusakowska\(^1\), E. Tymicki\(^2\), R. Jakiela\(^1\)

\(^1\) Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland
\(^2\) Institute of Electronic Materials Technology, Wólczyńska 133, 01-991 Warsaw, Poland

To obtain large single crystals suitable for applications in electronics it is necessary to develop seeded growth from the vapor, instead of using spontaneous nucleation. Silicon carbide growth method is an example of the successful application of the seeded growth initialization for production of four inch diameter single crystals from the vapor. In the case of zinc oxide, the largest progress in the development of the growth technique was observed for the hydrothermal method (Tokyo DENPA reported 3” diameter wafers). The growth of ZnO from the vapor was limited by problems with selection of an effective transport agent, because of the slow sublimation rate of ZnO at a reasonably high temperature (which would allow using of quartz tubes). The other important challenge in ZnO growth is the complicated morphology of the crystallization front, which depends on crystal orientation/polarization and hydrogen/zinc pressure. [K. Grasza et al., J. Crystal Growth 310 (2008) 1823].

Grains growing in parallel, with different orientations, exhibit extremely different structural quality. Therefore, a combination of two factors: the seed crystallographic orientation and specific growth conditions is of primary importance for successful growth of large single crystals.

In this work, ZnO crystals with a diameter up to one inch were grown using as seeds oriented platelets. Hydrogen and optionally carbon were used as transport agents. The most visible difference in the implementation of those two transport agents is the difference between ZnO growth rates, proving an advantage of the hydrogen atmosphere. Complementary experiments of spontaneous nucleation were also seeds. The surface orientation dependence of the crystallization front morphology, specific for optimal growth conditions of differently oriented grains, was investigated. The seed-crystal interface was studied in details (Fig. 1). The mechanism of the first stage of nucleation on the seed in various growth conditions was investigated. The method of the seed front surface preparation was optimized for a given crystallographic orientation and applied growth conditions. The structural and electrical properties of the crystals were found to be dependent on the imposed growth conditions.
Properties of hydrogen doped ZnO films prepared by RF magnetron sputtering


I. Physics Institute, Justus-Liebig-University, Heinrich-Buff-Ring 16, 35392 Giessen, Germany

N-type conducting ZnO films are of special interest for applications like transparent conducting oxides (TCO) used in flat panel displays or solar cells. It is well known that hydrogen incorporated into ZnO induces shallow donor levels while in most other semiconductors hydrogen counteracts the prevailing conductivity by being incorporated as H⁺ (a donor) in p-type and as H⁻ (an acceptor) in n-type material. Therefore, besides the Group III elements Al, Ga and In, hydrogen is suitable to control n-type conductivity in ZnO.

In our work hydrogen doped ZnO thin films were prepared by reactive radio frequency magnetron sputtering using a ceramic ZnO target. In the deposition process argon was used as sputtering gas and hydrogen and oxygen as reactive gases. Highly conductive transparent layers were prepared by double-doping the films deposited from an aluminum (2 wt% Al₂O₃) or a gallium (1 wt% Ga₂O₃) doped target with additional use of hydrogen.

The structural film properties were analyzed by x-ray diffraction (XRD). Hall-effect measurements were performed to determine film-resistivity, free carrier-concentration and mobility. The influences of the carrier concentration on the position of the optical band gap and on the transmittance in the near infrared were investigated. Secondary ion mass spectrometry (SIMS) was used to quantify the hydrogen incorporation and electron spin resonance (ESR) measurements were used to detect the shallow donor concentration.

The thermal stability of hydrogen in the ZnO layers was examined by annealing experiments in vacuum and in nitrogen atmosphere. Also the dependence of the hydrogen incorporation on the substrate temperature during the deposition process was investigated.

By varying the deposition parameters we were able to adjust the electric properties of the films in a wide range from semiconductor like to degenerated-metallic behavior with carrier concentrations from $10^{13}$ cm⁻³ up to the $10^{20}$ cm⁻³ leading to film resistivities of $10^3$ Ωcm down to $10^{-4}$ Ωcm, respectively.
Ga doped ZnO thin films prepared by RF-Plasma assisted DC magnetron sputtering without heating substrates

T. Hinoki1,3, K. Yazawa3, K. Kinoshita1, K. Ohmi1,2 and S. Kishida1,2

1Department of Information and Electronics, Graduate School of Engineering, Tottori University, 4-101 Koyama-Minami, Tottori 680-8552, Japan
2Tottori University Electronic Display Research Center, 522-2, Koyama-Kita, Tottori 680-0941, Japan
3Oike & Co., Ltd., 65 Daimotsu-cho, Kamitoba, Minami-Ku, Kyoto 601-8121, Japan

ZnO based transparent conductive film is a candidate of transparent conductive oxide (TCO) replacing to ITO film. Al doped ZnO film deposited at elevated temperature beyond 200°C on glass substrate has been used as transparent conductive electrodes of thin film photovoltaic cells[1]. ZnO film prepared by sputtering at low temperature on plastic film substrate has not been yet applied as TCO film application due to its weak stability in resistance under high temperature and high humidity environmental conditions. ZnO film by DC magnetron sputtering has another problem of anomalous distribution of resistance. The resistance tends to be higher value at the corresponding positions facing the erosion area of target. This phenomenon has been explained as ZnO film deposited at facing erosion area is bombarded by energetic oxygen atoms or oxygen ions in several previous works[2].

This paper investigates effects of RF plasma assist for DC magnetron sputtering, which has not been practically applied to Ga doped ZnO (GZO) TCO films, improving spatial distribution of resistance. GZO films were deposited at ambient temperature on glass substrates (100 mm x 100 mm) by DC magnetron sputtering. Substrate was set at distance of 120mm from ZnO target (5.7wt.%Ga2O3-ZnO) for space of coil arrangement. The 2.5 turns coil for RF plasma generation was located between the target and substrate. Ar gas was introduced for sputtering over the surface of target, whereas Ar-H2 mixture gas was flowed beneath substrate holder. The electrical properties of deposited films were measured by Van der Pauw method. The environmental reliability was evaluated by resistance changing ratio R/R0 (R: sheet resistance after 250hr under storage condition of 60°C-95%RH, R0: sheet resistance as deposited).

The spatial distribution of sheet resistance was changed to be flattened with increasing RF power, and resistivity decreased with increasing RF power up to 300W. Beyond 300W in RF power, the distribution of sheet resistance showed convex shape and resistivity was increased again. Environmental reliability was also improved with increasing RF power. R/R0 of deposited film with RF plasma at 200W showed 1.12, while R/R0 of films without RF assist was ranging from 10 to 100. The RF plasma assisted DC magnetron sputtering is markedly effective to improve environmental reliability.

This work indicates that the RF plasma assisted DC magnetron sputtering affects sheet resistance, resistivity and environmental reliability. Spatial distribution of sheet resistance is improved by applying suitable RF power. Resistivity also shows the lowest value at RF power 300W. It is thought that the great resistance change under environmental storage condition of high temperature and high humidity of GZO film deposited at low temperature would also be improved by the RF plasma assisted DC magnetron sputtering technique.

The role of excitons in the excitation of deep-level emission in ZnO single crystals

I.V. Markevich, V.I. Kushnirenko, L.V. Borkovska, and B.M. Bulakh
V. Lashkarev Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 45 Prospect Nauky, Kyiv, 03028, Ukraine

Zinc oxide is a promising material for UV light emitters, so investigation of different factors that can influence ZnO UV emission is important.

In undoped ZnO single crystals, photoluminescence (PL), PL excitation (PLE) and photocurrent (PC) spectra were measured in 350-800nm range at 77K. In PL spectra, UV exciton emission and deep-level visible PL were present, the latter consisting of two overlapping green (500nm) and orange (620nm) bands. In PLE spectra of both visible bands as well as in PC spectra, some peaks whose energy positions coincided with that of free exciton and its excited states were observed. The intensities of PL and PC excited in these peaks were found to be essentially higher than under excitation by zone-to-zone light. At the same time, a sharp minimum was found in PLE and PC spectra at the position of donor-bound exciton. Obtained results indicate that a strong interaction of excitons with centers responsible for visible PL takes place in ZnO, which leads to nonradiative exciton annihilation [1] and, thus, to the decrease of UV emission intensity.

A number of longer wavelength PLE and PC peaks whose energy positions coincided in fact with that of the first, second and third phonon replicas of free exciton were also observed. The origin of these peaks was discussed.

MOVPE Growth of ZnO using Zn(C₉H₁₅O₃)₂ as a Zn source

Y. Nabetani, I. Hatanaka, T. Kobayashi, T. Muranaka, T. Kato and T. Matsumoto
Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, Takeda 4-3-11, Kofu 400-8511, Japan

ZnO is known as a multi-functional material that can be applied to optoelectronic devices in short wave length region, transparent conductive films, phosphors, gas sensors, and so on. The current research stage of ZnO is the improvement of crystalline quality to realize active electronic devices such as LED, LD, and FET. Similar to III-V and nitride compound semiconductors, MBE and MOVPE are the key growth techniques. Especially, productivity of MOVPE is high. Two Zn sources have been used to grow ZnO; DEZn(diethyl zinc) and Zn(acac)₂. However, DEZn is highly active, and Zn(acac)₂ cannot be supplied by bubbling. These may not be the best source for ZnO growth. On the other hand, Zn-MOPD(Zn(C₉H₁₅O₃)₂) has advantages; low activity in air and water, and it can be supplied by bubbler. Therefore, Zn-MOPD is one of the candidates for MO sources. In this work, we have grown ZnO using Zn-MOPD and investigated the properties of obtained films.

Samples were grown by MOVPE. Zn-MOPD was used as Zn source and O₂ gas was for O source. N₂ was used as carrier gas of Zn-MOPD. The growth pressure was 18 Torr. The growth temperature was 500°C. We used glass and sapphire (c and a planes) substrates.

The main peak of XRD θ/2θ spectra was (0002) and other diffractions were very weak, regardless of the substrates. The grown ZnO films were c-axis oriented. The FWHM of (0002) rocking curve spectra were the smallest for ZnO grown on a-sapphire. In order to investigate the in-plane orientation, XRD θ scans were measured. The in-plane orientation was ZnO[1010] // Al₂O₃[1120] on c-sapphire and ZnO[1120] // Al₂O₃[0001] on a-sapphire.

The PL spectra measured at 14 K were dominated by D₀X at 3.359 eV. Free exciton, A, was observed in all samples. We have observed only A exciton at room temperature. At low temperature, free excitons, B and C were observed in some samples. It is usual that luminescence of C exciton is hardly measured from film samples, because C exciton cannot be observed from c-direction. Considering the wide FWHM of XRD rocking curve, the observation of the C exciton can be explained by the fact that the c-axis orientation of grown ZnO was not so high especially on the glass substrate.

The resistivities of ZnO were 10⁻² – 10⁰ Ωcm, greatly depend on the conditions at after growth. When sample was cooled down from the growth temperature in vacuum, the resistivity was low while that of sample cooled in O₂ gas flow was high. From the AES spectra, it was found that surface region of sample cooled in vacuum contained considerable amount of C. This surface C may be deposited during sample cooling down.

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**XRD characterization of ZnO layers grown on GaAs(111), sapphire c-plane and a-plane substrates by Plasma-Assisted MBE**

T. Muranaka¹, T. Sakano¹, K. Mizuguchi¹, Y. Nabetani¹, T. Akitsu¹, T. Matsumoto¹, S. Hagihara², O. Abe³, S. Hiraki³ and Y. Fujikawa³

¹ Department of Electronic Engineering, University of Yamanashi, Takeda 4-3-11, Kofu, Japan
² Yamanashi Industrial Technology Center, Otsu 2094, Kofu, Japan
³ Nakaya Corporation, Tsukijiirai 1641-8, Showa-cho, Nakakoma, Yamanashi, Japan

Zinc Oxide (ZnO) is a wide band gap semiconductor with a room temperature band gap of 3.4 eV and an exciton binding energy as large as 60 meV, and is an expected material for blue-to-ultraviolet optical devices, transparent electronic devices. We have reported for high quality ZnO epitaxial layers were grown on GaAs(111)B substrate by plasma-assisted molecular beam epitaxy (PAMBE) [1, 2]. In this paper, we describe the comparison of the structural properties of the ZnO epitaxial layers grown on GaAs (111)B, and sapphire c-plane and a-plane substrates by PAMBE.

ZnO epitaxial layers were grown on GaAs(111)B, α-Al₂O₃(0001) and α-Al₂O₃(11-20) substrates by using plasma-assisted molecular beam epitaxy (PAMBE). The ZnO layers were grown at 330°C on GaAs(111)B substrates, and grown at 500°C on α-Al₂O₃(0001) and α-Al₂O₃(11-20) substrates, respectively. Zinc (Zn) vapor was supplied by heating of metallic Zn at 350°C, and oxygen was supplied via a plasma cell excited by capacitive coupled RF power of 200 W. Oxygen flow rate was from 0.7 sccm to 1.0 sccm. The atomic oxygen radical is produced in a plasma cell and only neutral atomic radical is effused toward the substrate surface.

Structural evaluation of the ZnO layers was carried out by using high-resolution X-ray diffractometer (HR-XRD) with Cu Kα₁ radiation. Φ scans of asymmetric reflections were performed to confirm the orientation relationship, and reciprocal lattice mappings (RLMs) were also performed to determine the lattice parameters of the ZnO layers.

From Φ scans of asymmetric reflections, the in-plane orientation relationships between the ZnO layer and the substrates were confirmed to be ZnO(0001)<11-20>||GaAs(111)<1-10>, ZnO(0001)<11-20>||α-Al₂O₃(0001)<1-100> and ZnO(0001)<11-20>||α-Al₂O₃(11-20)<0001>. The RLMs around the (10-15) reflections for the ZnO layers on GaAs(111)B and α-Al₂O₃(0001) substrates, and the (11-24) reflections for the ZnO layers on α-Al₂O₃(11-20) substrates were carried out. The ZnO layers on both α-Al₂O₃(0001) and α-Al₂O₃(11-20) substrates showed smaller mosaicity values in comparison with those of the ZnO layers on GaAs(111)B substrates. The lattice deformations of the ZnO layers along the c-axis and a-axis, described as (c_{layer} - c_{bulk})/c_{bulk} and (a_{layer} - a_{bulk})/a_{bulk}, were evaluated. The in-plane compressive strain in the ZnO films on both α-Al₂O₃(0001) and α-Al₂O₃(11-20) substrates, and the in-plane tensile strain in the ZnO films on GaAs(111)B substrates were observed.


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We succeeded the preparation of the bis(acetylacetonato)zinc(II) anhydrate (Zn(acac)$_2$) fiber by the original process as the raw material, and the preparation of high-flatness zinc oxide (ZnO) thin film by MO-CVD method using this raw material. MO-CVD method which is superior of industrial production is suggested as one of the preparation techniques of ZnO film. It was reported that dimethyl zinc (Zn(CH$_3$)$_2$), zinc chloride (ZnCl$_2$) and powdery Zn(acac)$_2$ hydrate (Zn(acac)$_2$·H$_2$O) were suitable raw materials as Zn source for the MO-CVD method. From the standpoint in consideration for the global environment, we pushed forward the study of the ZnO films by using the Zn(acac)$_2$·H$_2$O powder which had less toxicity and high stability in the ambient atmosphere. High purity and sublimation characteristics with less aging deterioration are necessary in the condition of powdery raw materials for MO-CVD method. However, the most of commercial Zn(acac)$_2$ is the monohydrate, the steam from this commercial one delays the sublimation of Zn(acac)$_2$ in the process of deposition of the ZnO film. Furthermore, it is estimated that this steam also deteriorates the cleanliness surface of substrate and obstruct crystal growth. We obtained the Zn(acac)$_2$ anhydrate fiber by the original process as the raw material for solving these problems. This fiber which was obtained from the commercial powder by sublimation-recrystallization process can be expected improvement of the purity. Furthermore, we can expect stable supply of the vapor phase Zn(acac)$_2$ by the fiber shape that are hard to cohere. We report the new MO-CVD raw materials on the structure, composition, and sublimation characteristics. In addition, we also report the structure of the ZnO film and those properties.

Zn(acac)$_2$·H$_2$O powder (Nihon Kagaku Sangyo) was introduced in our hand-made apparatus for sublimation-recrystallization process, and then heated at 155°C with 5 °C/min for 30 min in N$_2$ atmosphere before taking out the Zn(acac)$_2$ fiber from the apparatus cool off to room temperature. An r-plane sapphire substrate was annealed at 1000°C for 30 min in O$_2$ atmosphere. The Zn(acac)$_2$ fiber and the sapphire substrate were introduced in a MO-CVD apparatus. Inner pressure of the apparatus was lowered in 1×10$^{-4}$ Pa before introducing N$_2$ carrier gas (98 sccm). The substrate was heated at 520°C, and then 500 sccm of O$_2$ gas was introduced. The Zn(acac)$_2$ fiber was heated at 115°C in 1×10$^{-4}$ Pa. ZnO film was deposited on the substrate for 240 min before annealed at 520°C for 10 min in 1×10$^{-5}$ Pa. The ZnO film and the Zn(acac)$_2$ fiber were removed at room temperature. The Zn(acac)$_2$ fiber was analyzed by TG-DTA and XRD. The ZnO film was evaluated by RHEED, AFM and Hall Effect.
Characterization of ZnO thin films grown on glass at different O$_2$/Ar ratios

Kyu Hwang Lee, Nam-Ihn Cho, and Hyoun Gin Nam
Sun Moon University, Asan, Chungnam 336-708, South Korea
Eui-Jung Yun
Hoseo University, Asan, Chungnam 336-795, South Korea
Se Jong Lee
Kyungsung University, Busan 608-736, South Korea

We investigated ZnO thin films deposited on glass substrates at various O$_2$/Ar ratios. Rf magnetron sputtering was carried out at the substrate temperature of 250°C using a ZnO target. The rf power was maintained at 240W and the working pressure at 20 mTorr. The Ar and O$_2$ flow rates were independently adjusted from 16 to 64 sccm. Typical film thicknesses were in the range of 100-120 nm. ZnO films were subsequently immersed in 30% H$_2$O$_2$ for 1 min. at 30°C and finally annealed at 520°C in constant O$_2$ flow at 7.5 L/min for 60 min.

Hall measurements revealed that the film prepared at O$_2$/Ar ratio of 0.25 (O$_2$-deficient condition) is p-type whereas the film deposited at O$_2$/Ar ratio of 4 (O$_2$-rich condition) is n-type. Inconsistent results were obtained from ZnO prepared at intermediate O$_2$/Ar ratios, namely 1.5 and 2.0. These findings are contradictory to some of the previous reports by others who investigated conductivity of ZnO deposited on various substrates other than glass. The most outstanding difference observed in photoluminescence analyses depending on O$_2$/Ar ratio was the strength of orange luminescence related to single ionized oxygen interstitial (O$_{i-}$) as well as yellow luminescence attributed to oxygen interstitial (O$_i$) indicating that the dominant acceptor-like defect is oxygen interstitial. XPS analyses showed that the binding energies (BE) of Zn$_{2p3/2}$ and O$_{1s}$ shift toward lower energies as a consequence of annealing. BE shift was claimed to indicate O$_i$ formation and V$_{Zn}$ formation due to O$_2$ diffusion and decomposition of ZnO followed by subsequent out-diffusion of Zn, respectively.

The observed property variations were accounted for in terms of O$_2$ as well as Zn diffusion. It was claimed that formation of p-type ZnO film when prepared at O$_2$/Ar ratio less than unity is brought about owing to O$_2$ diffusion from the substrate into ZnO film resulting in O$_i$ and O$_{i-}$ formation. Instead, the measured n-type conductivity was suggested to be a consequence of V$_{o}$ creation due to out-diffusion of O$_2$ from ZnO.
Intrinsic defect evolution resulted from II/VI ratio variation in MOVPE ZnO


Department of Physics, University of Oslo, PO Box 1048, NO-0316, Oslo, Norway
Royal Institute of Technology, SE-16440, Kista-Stockholm, Sweden

ZnO is a II-VI compound semiconductor with a direct wide band gap (3.37 eV) and high exciton binding energy (60 meV) at room temperature. To proceed with device applications, an imperative issue is to master both p-type and n-type ZnO films. Several fundamental intrinsic defects, e.g. zinc interstitials and oxygen vacancies, are associated in literature with shallow donors determining n-type conductivity in “intrinsic” material and/or acting as compensating traps when making p-type doping [1]. Thus, it is essential to control the fractions of different intrinsic defects in ZnO and one route for doing that is by varying II/VI precursor ratios during synthesis. For example, an interesting evolution from n- to p-type conductivity in ZnO changing II/VI ratios in the range of 0.05 - 0.75 was investigated by Hall measurements and the observation was attributed to a change in the zinc/oxygen vacancy balance [2]. However the characteristics of the defects, e.g. corresponding PL signatures, have not been determined calling for more studies of II/VI ratio effect on the intrinsic defect concentration in ZnO films.

In the present study ZnO films were synthesized by MOVPE using different II/VI precursor ratios keeping all other parameters (growth rate/pressure/temperature, film thickness, etc) constant which somewhat narrows the ratio range (0.1 – 1.0) but allows attributing all trends conclusively to the changes in II/VI ratios. Results of XRD, SIMS, PL, Hall and other electrical characterization measurements are reported. For example, in PL spectra measured at 10K, there are three prominent peaks observed at 2.8 eV, 2.53 eV and 1.98eV which intensities follow unique trends when changing the II/VI precursor ratios – thus providing reasonable arguments for the identification (in progress). Importantly, all as-grown samples demonstrate similarly high crystalline quality – a rocking curve FWHM is at ~0.45° based on XRD measurements – making the rest of comparisons feasible.

References:
Optical and Structural Properties of ZnO Substrates for Homoepitaxial Growth

Institute of Solid State Physics, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

J. S. Reparaz, A. R. Goni
Institut de Ciència de Materials de Barcelona (ICMAB), CSIC, Esfera UAB, 08193 Bellaterra, Spain

Homoepitaxial growth of ZnO films requires high quality ZnO substrates with minimal strain and a low impurity concentration. Justified by these requirements we evaluate ZnO substrates of several main suppliers. In this contribution, we present a comprehensive study of ZnO substrates for high quality homoepitaxial growth. It is shown that the variations of defects in the substrates of different suppliers lead to different values of the lattice parameters and strain distribution which also influences the optical properties. XRD measurements clearly show that the c/a ratio is not a constant throughout the selection of our samples. This is mainly due to a varying compressive strain and defects in the samples as revealed by micro-Raman spectroscopy.

In addition, uniaxial pressure dependent luminescence measurements were performed. The pressure dependent shift and splitting of free and bound excitons are studied. High resolution luminescence spectra show large variations in the positions and energetic spacing of the A, B and C exciton-polaritons. Uniaxial and hydrostatic pressure dependent Raman measurements provide phonon pressure coefficients and deformation potentials for the intrinsic Raman modes. The pressure coefficients of the Raman modes are compared for samples with different lattice constants. The controlled change of the piezo-electric field of the ZnO crystal under external applied pressure also provides information concerning the strain induced shift of the bound excitons with their different localization energies. The results are discussed regarding substrate requirements and possible improvements for high quality homoepitaxial grown ZnO epilayers.
Transport properties of microstructured MF-sputtered Al$_x$Zn$_{1-x}$O

M. Piechotka*, M. T. Elm*, T. Henning*, M. B. Szyszka+ and P. J. Klar*

* I. Physikalisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 16, 35392 Giessen, Germany
+ Fraunhofer-Institut für Schicht- und Oberflächentechnik IST, Bienroder Weg 54 E, 38108 Braunschweig, Germany

The Al$_x$Zn$_{1-x}$O layers (AZO) were grown on a glass substrate by medium-frequency (MF) magnetron-sputtering with an Al concentration of $x \approx 2.2\%$. The film is about 700 nm thick and consists of grains with a lateral dimension of about 50 nm. We investigated the optical, vibrational and electrical properties of the AZO-films using PL, Raman spectroscopy and magnetotransport, respectively. The PL-measurements were performed at room temperature using a 325 nm He-Cd-laser and reveal a shift of the band gap to higher energies due to the Burstein-Moss-effect. The analysis of vibrational modes using resonant Raman spectroscopy with the same laser confirms this result. The magnetotransport measurements show that, on the one hand, the mobility at low temperatures down to 2 K is dominated by ionized impurity scattering. On the other hand, the phonon scattering is the dominating effect at high temperatures close to room temperature. Between these limits, grain boundary scattering plays a significant role for the transport mechanism. The temperature dependence of the charge carrier density is described using a merged-band model based on the DOS-calculations of Serre and Ghazali for highly doped semiconductors.

In the second part of this paper we discuss the effect of miniaturization on the transport behavior of the AZO samples. For this purpose, we prepared a series of wire arrays by photolithography followed by wet-chemical etching of the AZO-films. The nominal wire width was varied between 8 and 32 µm. The correlation of results obtained by scanning electron microscopy, atomic force microscopy and temperature-dependent resistivity measurements allows one to assess the extension of the surface layer affected by the microfabrication process and its effect on the electronic transport through the wire. We show that the extension of this surface layer is determined by the grain structure of the sputtered layer and is independent of wire thickness and degree of under-etching. This results in a minimal threshold of reliable structures due to the structural limit of the surface layer extension.

E-mail: markus.piechotka@exp1.physik.uni-giessen.de

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Sign reversal of the Seebeck coefficient of metallic Zn_{0.98}Al_{0.02}O

G. Homm, J. Teubert, T. Henning, P. J. Klar and B. Szyska

Institute of Experimental Physics I, Justus Liebig University Giessen, Germany and Fraunhofer Institute for Surface Engineering and Thin Films, Braunschweig, Germany.

We studied the Seebeck coefficient $S$ of sputtered Zn$_{0.98}$Al$_{0.02}$O samples with free carrier concentrations varying from $10^{18}$ to $10^{21}$ cm$^{-3}$. It is widely believed and often stated that n-type semiconductor materials must exhibit a negative Seebeck coefficient whereas the coefficient must be positive in the case of p-type material. We will show and explain that this is a misconception. The typical temperature dependence of the Seebeck coefficient of a sample with the low carrier concentration of $1.5 \times 10^{18}$ cm$^{-3}$ is the following. The Seebeck coefficient $S$ is negative and its absolute value decreases slightly in the range from 300 K down to about 80 K, on decreasing the temperature further the absolute value increases again due to the phonon drag effect. Samples with higher carrier concentrations show a decrease in the absolute value of $S$ and, as expected for non-degenerate semiconductors, the phonon drag effect becomes weaker. In contrast, metallic as grown Zn$_{0.98}$Al$_{0.02}$O shows a sign reversal of the Seebeck coefficient with decreasing temperature. The sign reversal is related to the non-parabolic density of states of the degenerately doped metallic Zn$_{0.98}$Al$_{0.02}$O. Here the sign of the Seebeck coefficient does not reflect the majority carrier type, thus, the assumption of parabolic bands which is the foundation of a strict correlation between sign of the Seebeck coefficient and sign of the charge of the majority carriers is no longer given.

Furthermore we studied the effect of microstructuring on the Seebeck coefficient $S$ of above mentioned Zn$_{0.98}$Al$_{0.02}$O films with a thickness of about 700 nm grown by RF sputtering on a glass substrate and free carrier concentration of $8.0 \times 10^{20}$ cm$^{-3}$ at room temperature. Specimens were microstructured by photolithography and wet-chemical etching with a pattern based on a square grid (pitch $a$ varied between 32 and 4 µm) with a unit cell consisting of a centered square-hole (pitch $a/2$). Dividing $a$ by halves corresponds to a doubling of the additional surface due to the hole sidewalls created in the etching process, whilst keeping the sample volume constant. Throughout the series the additional surface due to the sidewalls of the etched holes increases by a factor of 8 from $a = 32$ µm to $a = 4$ µm. The Seebeck coefficient changed systematically throughout the series, e.g. at 150 K from -1.0 µV/K for the reference sample to -1.7 µV/K for those with $a = 4$ µm specimen, which is in contrast to the predictions of the effective medium theory. As the artificial structuring was performed on the micrometer scale, changes of the densities of states of phonons as well as of electrons can be ruled out. Thus, the observed changes of the Seebeck coefficient are not due to electronic or phononic confinement. In addition to the micrometer scale of the artificial structuring, there are other structural length scales of importance which are the grain size of the crystallites as well as the distance between the Al impurities which act as scattering centers for the electrons. Both are much smaller than the characteristic length $a$. We believe that the etching of micrometer holes causes additional surface traps which lower the Fermi-energy leading to significant alterations of the Seebeck-coefficient.
Giant ultrasonic attenuation in ZnSe:Cr$^{2+}$ and its possible application in crystal characterization

V.V. Gudkov$^1$, A.T. Lonchakov$^2$, I.V. Zhevstovskikh$^1$, V.I. Sokolov$^1$, Yu.V. Korostelin$^1$, A.I. Landman$^2$, and V.T. Surikov$^3$

$^1$Institute of Metal Physics, Ural Department of the Russian Academy of Sciences, 18, S. Kovalevskaya st., Yekaterinburg 620041, Russia

$^2$P.N. Lebedev Physical Institute of the Russian Academy of Sciences, 53, Leninskiy prospect, Moscow, 119991, Russia

$^3$Institute of Solid State Chemistry, Ural Department of the Russian Academy of Sciences, 91, Pervomaiskaya st., Yekaterinburg 620041, Russia

Ultrasonic investigation of a number of II-VI crystals doped with 3d elements have revealed peak of attenuation $\alpha(T)$ at low temperatures (see [1] and references therein). These anomaly proved to be due to relaxation in the Jahn-Teller system discussed in [2]. In this case attenuation can be described with the following expression:

$$\alpha' = \frac{k_0}{2C_0} \frac{\omega \tau}{1 + \omega^2 \tau^2} = \frac{k_0}{2C_0} \frac{\omega n b^2}{k T} \frac{\omega \tau}{1 + \omega^2 \tau^2},$$

where $\omega$ is cyclic frequency of ultrasond, $\tau$ is relaxation time, $C$ is the elastic modulus, $C'$ is contribution of the relaxation to $C$, $k$ is the wave number, $C_0$ and $k_0$ are the values measured at a reference temperature, $w$ is the factor accounting the direction of the propagation and the polarization of the wave, $n$ is the dopand concentration, $b$ is the deformation potential, $\kappa$ is the Boltzmann constant. One may see that $\alpha(T)$ has a peak at $T = T_0$ which corresponds to $\omega \tau = 1$. The values of $\alpha' = \left[ (\alpha')_{\text{max}} / n \right]$ i.e., peak attenuation per the impurity ion, were determined as $1.9 \times 10^{-18}$ dB·cm$^{-2}$ (ZnSe:V$^{2+}$), $1.6 \times 10^{-18}$ dB·cm$^{-2}$ (ZnTe:Ni$^{2+}$), $0.06 \times 10^{-18}$ dB·cm$^{-2}$ (ZnSe:Ni$^{2+}$), and $0.008 \times 10^{-18}$ dB·cm$^{-2}$ (ZnSe:Fe$^{2+}$). These data were obtained at $\approx 54$ MHz with the use of shear waves propagated along the <110> crystallographic axis. Anomalously large magnitude of $\alpha' = 23 \times 10^{-18}$ dB·cm$^{-2}$ was found in ZnSe:Cr$^{2+}$ that corresponds to the peak attenuation of 90 dB/cm at $n_{C_r} = 3.8 \times 10^{18}$ cm$^{-3}$. Our high-frequency bridge technique makes it possible to measure $\alpha'(T)$ with the accuracy of 0.02 dB. So, the peak attenuation of 0.2 dB/cm can be perfectly well measured on the specimen of 1 cm long. It means that ultrasonic technique can be used for non-destructive measuring of the concentration of the Cr$^{2+}$ ions in ZnSe crystal as low as $10^{16}$ cm$^{-3}$. The measured dependence $\alpha'(T)$ was used for reconstruction of $\tau(T)$ with the help of the method described in [1]. Below 3 K relaxation time was about $10^3$ s decreasing till rapidly with heating and approaching to $10^2$ s at 10 K. Simulation of $\tau(T)$ made it possible to determine a number of the parameters of the Jahn-Teller cluster and to discuss the mechanisms of relaxation. This work was done within Russian Academy of Sciences Program (project No. 01.2.006 13395), with partial support of Russian Foundation for Basic Research (grant No. 04-02-96094-r2004 ural_a).

STM probe as a tool for low-energy-electron pumping of ZnSe/CdSe/ZnSe heterostructure

S.A. Masalov, M.G. Rastegaeva, S.V. Sorokin, and V.P. Evtikhiev
Ioffe Physical Technical Institute of RAS, St.-Petersburg 194021, Russia
sergeym@mail.com

The main advantage of electron beam pumped (EBP) lasers is employing of undoped laser heterostructures without p-n junction, i.e. without requirements of p-type doping of the materials. This is especially critical for wide gap compounds, like II-VI or III-N. The electron beams energy commonly used for laser pumping is relatively high and varied within the 5-100 keV range. One of the problems on this way is the high energy losses accompanying high energy electrons pumping.

Here we propose to utilize the effect of electronic field emission for the electron beam pumping. In this case, the metal W-probe in ultrahigh vacuum (UHV) scanning tunneling microscopy (STM) is used as the source of electrons. The investigated structure has been grown by molecular beam epitaxy on GaAs (100) substrate and consists of single CdSe quantum dot (QD) sheet with the nominal CdSe thickness of ~2 monolayers, embedded in the ZnSe matrix at a distance of 5nm from the surface. The STM measurements using the UHV microscope LS SPM produced by OMICRON were performed at a maximum value of a bias voltage (potential difference between the metal W-probe and GaAs substrate) ~10V. The electrons are injected under the electric field from W-probe to the ZnSe conduction band. The distance of 11 nm between the W-probe and the heterostructure surface (inter-electrode distance) has been estimated experimentally. The dependencies of emission current on bias voltage have been measured and studied in detail. These dependencies are described well by the Fowler-Nordheim theory and enable one to estimate both the effective area of field emission ($S \sim 8 \times 10^{-15} \text{ cm}^2$) and emission current density ($j \sim 5 \times 10^4 \text{ A/cm}^2$), as in Ref. [1]. When the electron energy approaches to $E \sim 3E_g (~ 8 \text{ eV in ZnSe})$ the processes of impact ionization are initiated. The injection of electrons to conduction band of ZnSe as well as the impact ionization processes result in formation of a local excited area ($S$) with the concentration of non-equilibrium carriers as high as $n \sim 10^{21} \text{ cm}^{-3}$. This value is governed by experimental conditions and may be increased by 3 orders of magnitude by changing the distance between the W-probe and the structure surface.

In conclusion, STM in the electronic field emission regime may be employed as an efficient tool in investigations of low-energy-electron pumping. Moreover, we believe that our results show a principle ability of using the electronic field emission from an extended area electrode for pumping of laser heterostructures with low energy electrons.

Synthesis and Characterization of Cu$_2$ZnSnS$_4$

Christine Chory, Florian Witt, Holger Borchert, and Jürgen Parisi

*Carl von Ossietzky University Oldenburg, Department of Physics, Energy- and Semiconductor Research, D-26129 Oldenburg, Germany*

We report on a facile wet-chemical synthesis of Cu$_2$ZnSnS$_4$ (CZTS) nanoparticles in gram quantities. CZTS can be used as absorber material for thin film photovoltaics, having a band gap of approximately 1.5 eV and an absorption coefficient $> 10^4$ cm$^{-1}$.

The particles were characterized by simultaneous thermogravimetry and differential scanning calorimetry (TG-DSC) to show the temperature range for decomposition of the organic shell and to depict temperature-induced reactions, especially the growth of the nanocrystals.

X-ray diffraction was used to verify the proper crystal structure, namely kesterite, and hence to confirm the corresponding chemical composition.

With light induced electron spin resonance (l-ESR) the dynamic excitation processes as they appear in solar cells were investigated. While the amplitude of the sample's spin resonance is monitored, an external laser source excites the investigated material. The laser induced changes of paramagnetic moments are good indications for several effects like modification in the material's electronic shell structure or for charge generation processes like exciton separation.
Influence of low-temperature buffer layer on properties of ZnTe grown on GaAs substrates

Q.X. Guo\textsuperscript{1,2,3}, K. Saito\textsuperscript{3}, Y. Sueyasu\textsuperscript{2}, Y. Ding\textsuperscript{3}, T. Tanaka\textsuperscript{2}, and M. Nishio\textsuperscript{2,3}

\textsuperscript{1} Synchrotron Light Application Center, Saga University, Saga 840-8502, Japan
\textsuperscript{2} Department of Electrical and Electronic Engineering, Saga University, Saga 840-8502, Japan
\textsuperscript{3} Venture Business Laboratory, Saga University, Saga 840-8502, Japan

ZnTe has potential applications for a variety of optoelectronic devices such as pure green light emitting diodes, solar cells, terahertz detectors, wave-guides and modulators. GaAs is a desirable substrate due to its large role in the electro-optic industry. If ZnTe could be grown epitaxially on GaAs, device integration would be possible. We have shown that high-quality ZnTe epilayers can be grown on (100) on GaAs substrates by metalorganic vapor phase epitaxy (MOVPE) [1,2]. In this work, efforts are devoted to the revealing of the influence of low-temperature buffer layer on the crystal quality and surface morphology of ZnTe epilayers grown on GaAs substrates.

ZnTe layers were grown on (100) GaAs substrates using a home-built MOVPE system at atmospheric pressure. Dimethylzinc (DMZn) and diethyltelluride (DETe) were used as source materials and H\textsubscript{2} was used as a carrier gas. Polished (100)GaAs substrates were chemically cleaned, degreased in organic solvents, and then etched in a solution composed of H\textsubscript{2}SO\textsubscript{4}+ H\textsubscript{2}O\textsubscript{2}+ H\textsubscript{2}O (5:1:1) for about 20s at 60\degree C followed by deionized water rinse. First, the substrate was heated at 580\degree C for 30 min in a stream of H\textsubscript{2} in order to remove the native oxide on the surface of the substrate. Next, the substrate temperature was decreased to 320\degree C for growing low-temperature ZnTe buffer layer. Then, the substrate temperature was increased to 430\degree C for growing the ZnTe epilayer. During the growth, the transport rates of DMZn and DETe were kept at 15\,\mu mol/min. The crystalline quality of the ZnTe layers was evaluated using an X-ray rocking curve of a high-resolution double-crystal method. The surface morphology of the ZnTe layers was characterized by an atomic force microscope. It was found that both the crystal quality and surface morphology of the ZnTe layer can be improved by introducing the low-temperature buffer layer with a suitable thickness between the ZnTe epilayer and the GaAs substrate. The growth mechanism will also be discussed.

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Temperature dependence of photoluminescence from P-doped ZnMgTe bulk crystals of high quality grown by Bridgman method

K. Saito¹, S. Shimao², T. Tanaka², Q.X. Guo¹, and M. Nishio²
¹Synchrotron Light Application Center, Saga Univ., 1 Honjo, Saga 840-8502, Japan
²Department of Electrical and Electronic Engineering, Faculty of Science and Engineering, Saga Univ., 1 Honjo, Saga 840-8502, Japan

Zn¹₋ₓMgₓTe ternary alloy is expected as a cladding layer and a transparent substrate for improving a performance of ZnTe based pure green LED, because it has wider band gap than ZnTe. There are only a few works on P-doped Zn¹₋ₓMgₓTe bulk crystals that are very important for fabricating ZnTe based LED. So far, we have prepared P-doped Zn¹₋ₓMgₓTe crystals by means of Bridgman method and also clarified the fundamental properties such as Mg composition (x), optical and electrical properties, lattice constant, and so on [1,2]. Very recently, we have successfully prepared the high crystalline quality of P-doped Zn¹₋ₓMgₓTe crystal for ZnTe based LED [3]. In this study, we report for the first time on the measurement temperature dependence of photoluminescence (PL) up to room temperature (RT) attained by using P-doped Zn¹₋ₓMgₓTe of high crystalline quality crystals. The measurement results will give useful information about the x dependent energies of band gap, P acceptor levels and so on.

P-doped Zn¹₋ₓMgₓTe crystals were grown by vertical Bridgman method in almost the same manner as was employed in the previous studies [1-3]. Zn, Mg, Te and Zn³P₂ were used as source materials. A pyrolytic boron nitride crucible containing the source materials was sealed in a quartz ampoule. The synthesis of Zn¹₋ₓMgₓTe was carried out using single zone electric furnace with abrupt temperature gradient to prevent explosion of the quartz ampoule. Then, the ampoule inserted into a four-zone growth furnace with a maximum temperature of about 1,150 °C. The growth was started with a downward rate of 25 mm/day. The grown ingots were sliced into (100) wafers, and then lapped. The crystallinity and x of the wafers were evaluated by X-ray rocking curve (XRC) measurement and energy dispersive X-ray analysis, respectively. Temperature dependent PL measurement (4.2 ~ 300 K) was performed using 405 nm blue-violet laser diode as an excitation light source.

P-doped Zn¹₋ₓMgₓTe crystals with x between 0.09 and 0.3 were successfully prepared. The typical value of the full width at half maximum of (400) XRC was 65.7 arcsec, which is relatively smaller than previous ones [3]. This result indicates that the P-doped Zn¹₋ₓMgₓTe crystals of high crystalline quality were obtained. All the crystals show not only low temperature PL spectra consisted of a bound excitonic emission due to neutral P acceptor and a P acceptor related free-to-bound (FB) transition emission as reported previously but also RT PL band originated from interband transition with no significant deep emissions in the wavelength range longer than 580 nm. The relationship between x and the peak energy of RT PL band is consistent with x dependent band gap obtained using RT cathodoluminescence measurement [2]. From the temperature dependent PL intensity of FB emission, the relationship between x and the energy of P acceptor level (𝐸ₓ) was estimated by the use of one-step model of thermal quenching mechanism. The result showed that 𝐸ₓ monotonically increases with increasing x. This relationship seems to be reasonable by comparing with the energy difference between FB emission and estimated band gap.

Growth of low-resistivity p-type ZnMgTe layers by MOVPE

K. Saito 1, N. Nonaka 2, Y. Inoue 2, T. Tanaka 2, Q.X. Guo 1, and M. Nishio 2
1Synchrotron Light Application Center, Saga Univ., 1 Honjo, Saga 840-8502, Japan
2Department of Electrical and Electronic Engineering, Faculty of Science and Engineering, Saga Univ., 1 Honjo, Saga 840-8502, Japan

Zn1-xMgxTe epitaxial layer is expected to be a promising for a variety of optoelectronic applications, such as a cladding layer of ZnTe based pure green light-emitting devices. In the previous study, we have investigated the growth characteristics of undoped Zn1-xMgxTe layer on ZnTe to control Mg composition [1] and to improve optical property [2] by metalorganic vapour phase epitaxy (MOVPE). For device applications, electrical property is also fundamental factor. With respect to MOVPE growth of Zn1-xMgxTe, to our knowledge, doping studies are not existed at all. In this study, we focused mainly on the realization of low-resistive p-type Zn1-xMgxTe layers grown by MOVPE.

P-doped Zn1-xMgxTe layers were grown on semi-insulating Ga-doped (100) ZnTe substrates by atmospheric pressure MOVPE system with vertical reactor employing hydrogen as a carrier gas. Dimethylzinc (DMZn), diethyltelluride (DETe) and bis-methylcyclopentadienyl-magnesium (MeCp)2Mg were used as the source materials. As a p-type dopant source, tris-dimethylamino-phosphine (TDMAP) was selected. The substrate temperature, transport rates of DMZn, DETe and TDMAP, and total flow rate of carrier gas were fixed at 395 °C, 20, 19 and 0.2 µmol/min and 800sccm, respectively, which correspond to the growth conditions for the transition between the mass transport and surface kinetic limited regions for ZnTe. The transport rate of (MeCp)2Mg was varied from 0 to 8 µmol/min. The thicknesses of the layers were fixed at around 4 µm.

High-resolution X-ray diffraction analysis was performed to determine the Mg composition (x). The electrical properties of the layers were determined by van der Pauw’s method using electroless Pd electrode as ohmic contact. Photoluminescence (PL) measurement at 4.2 K was performed using 405 nm blue-violet laser diode as an excitation light source. The laser power was attenuated by neutral density filters only when the excitation intensity dependence of PL was investigated. The effect of post annealing treatment in nitrogen at 420 ºC for 2 hours was also investigated for P-doped Zn1-xMgxTe layers, which is very effective in improving electrical and optical properties for P-doped ZnTe layers [3].

P-doped Zn1-xMgxTe layers with x between 0 and 0.1 were grown by varying (MeCp)2Mg transport rate. PL spectra at 4.2 K of as-grown layers were dominated by strong donor-acceptor pair (DAP) emission and relatively weak P acceptor-related excitonic (Ia) emission. The values of resistivity and hole concentration were, respectively, 3-5 Ωcm and (2-3)×1016 cm-3 for the layers with x less than 0.03, while those were 26Ωcm and 6×1015 cm-3 for the layer with x = 0.1. By the post-annealing treatment, PL property at 4.2 K of layers was significantly improved, i.e. DAP emission vanished and instead free-to-bound transition emission and enhancement of Ia emission were observed. The value of resistivity reduced to the order of 102 Ωcm and that of carrier concentration increased to (1-2)×1018 cm-3, independent of x. Then we have succeeded the preparation of low-resistive p-type Zn1-xMgxTe layers by MOVPE.

The electronic energy band spectra of ZnS, ZnSe, and ZnTe crystals evaluated with the new GGGA approximation of the exchange potential

S.V. Syrotyuk

Lviv Polytechnic National University, 12, S Bandery Street, 79000 Lviv, Ukraine

The electronic energy bands of ZnS, ZnSe, and ZnTe crystals have been calculated within the mixed basis approach grounded on the core Bloch states and plane waves [1–3]. The aims of this paper are as follows: (1) in the employing more accurate generalized gradient approximation (GGA) for solids, suggested in [4], within the mixed basis approach; (2) in using the simplest generalization of GGA (denoted GGGA in [5]); (3) in applying for crystal the new exchange-energy functional, derived in [5] and successfully employed to atoms; (4) in verifying of the parameter $\beta$ found to be good for atoms in application in crystals; (5) in searching for the parameter $\beta$ reliable for crystals.

The electronic energy band spectrum is searched from Kohn-Sham equation. The unknown wave function is represented in the mixed basis as a linear combination of core Bloch states and plane waves.

The unknown electronic band energies are evaluated as solutions from the system of linear equations in the block form [1–3].

Here the new exchange-energy functional suggested in paper [5] is employed. The exchange enhancement factor defined by Perdew, Burke and Ernzerhof (PBE) is used.

The exchange potential is derived from the exchange-energy functional, suggested in paper [5].

The semicore states energies obtained within the mixed basis approach by means of the new exchange-energy functional, suggested in [5], are in better agreement to experiment than ones calculated with pseudopotentials in LDA approach.

PbTe-CdTe monocrystals: growth by physical vapor transport method and theoretical analysis of structural stability

M. Bukala, M. Galicka, A. Szczerek, O. Domukhovskii, T. Story, R. Buczko, and P. Kacman

Institute of Physics PAS, Al. Lotników 32/46, 02-668 Warsaw, Poland

PbTe and CdTe semiconductors form an intriguing material system with excellently matching lattice parameters but different crystal and electronic structure. Recent technological and theoretical activity on PbTe-CdTe system is related to the discovery of high crystal quality PbTe-CdTe epitaxial multilayers and PbTe nano-dots in CdTe matrix, important for mid-infrared optoelectronic applications. Under thermodynamic equilibrium conditions the mutual solubility of PbTe and CdTe is extremely limited and in the bulk form only quenched PbCdTe polycrystals were so far available with multiphase material obtained by standard Bridgman technique.

We report the successful growth of Pb$_{1-x}$Cd$_x$Te monocrystals with Cd content up to 11 at.% by the application of the physical vapor transport method. X-ray diffraction analysis of the structural properties revealed high quality monocrystals of 1 ccm volume with (100) crystal facets and the X-ray rocking curve width parameter of about 100 arcsec.

Using ab initio methods, we study the stability of such crystals. We calculate the total energies of unit cells with 64 atoms in zinc-blende (ZB) CdTe and rock-salt (RS) PbTe, in which we exchange successively the cations by Pb and Cd ions, respectively. Thus, for any value of x we can compare the energy of the Pb$_{1-x}$Cd$_x$Te compound in both ZB and RS structures. As expected, close to CdTe the energy is lower for ZB, whereas close to PbTe the RS structure has lower energy. Our study shows, however, that the difference between ZB and RS for PbTe is much bigger than for CdTe and the hypothetical Pb$_{1-x}$Cd$_x$Te crystal would have RS structure for Cd concentrations x up to ca 0.75. Moreover, the total energy of the mixed crystal is higher than the appropriate energy of separated phases for any x value. This energy difference calculated per atomic pair is lower, however, than kT in growth conditions for x up to 0.2, what may suggest that the Cd content in our samples is close to the solubility limit. On the other hand, adding Pb to CdTe leads to much faster phase separation. These results are in agreement with the well known fact that it is much easier to obtain good quality RS PbTe crystals doped with Cd than vice versa.

The calculated lattice parameters, although smaller than the observed by ca 1%, as typically obtained in the ab initio calculations, diminish with x like $da_0/dx = -0.0034$ (for x≤0.2), in full agreement with our experimental data on monocrystals $da_0/dx = -0.0033$. 
Influence of P, As, Sb on CdTe properties

P. Fochuk, Yu. Obedzyns’ka, and O. Panchuk
Chernivtsi National University, 2, vul. Kotziubinskoho, 58012 Chernivtsi, Ukraine

R. Grill
Charles University, Faculty of Mathematics and Physics, Institute of Physics,
Ke Karlovu 5, Prague 2, CZ-121 16, Czech Republic

Ye. Nykonyuk
National University of Water Management and Nature Resources Use,
11, vul. Soborna, Rivne, 33028, Ukraine

J. Krustok
Department of Materials Sciences, Tallinn University of Technology,
Ehitajate tee 5, Tallinn, 19086, Estonia

N. Armani
CNR-IMEM Institute, Parco Area delle Scienze, 37/A Parma, 43010, Italy

CdTe, doped by elements of the VA group of the Periodic table (P, As, Sb), possesses interesting properties: a wide range of p-type conductivity ($10^1 - 10^7$ Ohm$\cdot$cm) and a reduced quantity or absence of inclusions in the crystals. Therefore it can be used in photovoltaics and substrate production. There are quite few publications which study such material. The goal of this work was the investigation of electrical, optical and structural properties of CdTe:P(As, Sb) single crystals in order to define the influence of these dopants on the point defect nature and the structural quality of the material.

The high-temperature Hall effect measurements of the electrical properties were performed under well-defined Cd (P$_{Cd}$) and Te (P$_{Te}$) vapor pressure at 600-1100 K, the photoluminescence and cathodoluminescence – at 10 and 77 K correspondingly, whereas the inclusions were studied using IR microscopy. For point defect structure modeling the Kröger’s quasichemical formalism was used.

All investigated samples revealed p-type conductivity up to 800-900 K. Above this temperatures the presence of large quantity of acceptors still has been felt even at 1200 K, although electron density was observed. The Cd vapor pressure and temperature dependences of the free electron density differed sufficiently comparing to undoped CdTe. In a majority the samples didn’t contain any inclusions. A large density of small inclusions was present only in the end of ingot at high dopant content. Low temperature PL measurements showed that in doped CdTe samples usually potential fluctuations due to charged defects can be observed and sometimes this leads to a shifting of PL bands to lower energy.

The modeling of the point defect structure in the investigated crystals was successful only with the assumption that several dopant centers were considered. Besides the main acceptors, when the dopant atoms (P, As, Sb) occupy the Te sites, the localization of the dopant atoms in interstitial and Cd positions was also taken into account. The experimental results showed a satisfactory agreement with the calculations in component vapor pressure and temperature dependences.
Stoichiometry and electron spectrum of non-doped CdTe and ZnTe compounds under rapid crystallization from vapor phase

V. Krivobok, V. Bagaev, S. Chernook, Yu. Klevkov, S. Kolosov, V. Martovitskii, A. Shepel’
P.N. Lebedev Physical Institute, Leninskii pr. 53, Moscow 119991, Russia

The effect of a rapid low temperature crystallization from vapor phase of non-doped CdTe and ZnTe compounds upon their electron spectrum and crystal structure was studied by REM, X-ray diffractometry and low temperature photoluminescence. It was shown that the change of rapid crystallization conditions (temperature, vapor oversaturation, reagent concentration, relation of stream intensity of reagents) allows us to realize a normal (atomic roughness) growth along the three crystallographic directions [111], [110], [100]. Both the growth direction and crystallization rate therewith determine the sizes, shape and mechanisms of defect formation.

The twins turn out to be the dominating kind of defects under conditions of rapid growth along [111]. The twins affect significantly optical and thermal properties of a material for crystals under studies (with the dislocation density < 10^5 cm⁻² and absence of a second phase inclusions) [1,2]. In addition, in the case of CdTe non-coherent twin boundaries can result in the formation of electrically active acceptor centers with the activation energy of 0.16 - 0.25 eV, and, in the case of ZnTe, these boundaries can change significantly a composition of the point defects nearby. The use of modulation spectroscopy with infrared illumination allowed us to draw preliminary conclusions on the nature of some kinds of point defects forming nearby the twin boundaries.

It was found that under conditions of ZnTe and CdTe free growth from vapor phase the crystallite structure is improved noticeably while turning to the growth by non-polar planes {110} or {100}. As a result, the twin density decrease by 1.5 – 2 order of magnitude and more. The rapid crystallization allowed us to overcome the problems of complex formation and low solubility of some impurities.

An opportunity to obtain conductivity of both p- and n-type was realized for as-grown crystals by using the different growth regimes. The large-grained n-type CdTe polycrystals with mobility of ~10⁵ cm²/V*s for electrons and resistivity of ~10⁹ Om/cm at the room temperature were produced. The samples grown had a high luminescence yield in the near bandgap region that is determined by the recombination of free and bound excitons. An emission of donor-acceptor pairs and bands close to A-centres emission occurred in the more long-wavelength region. An analysis of low temperature photoluminescence spectra recorded at a resonant excitation showed that all transition observed are not related to the intrinsic defects of crystal lattice but are determined by residual impurities - acceptors (Ag, Li) and hydrogen-like donors.

New features in the spectra of intrinsic emission in the vicinity of the exciton band bottom was found out. The features observed are caused both by the inelastic exciton scattering at different defects and scattering processes with participation of free carriers [3].

The influence of metallic layers on the diffusion of highly mobile dopants in CdTe

J. Kronenberg¹, F. Wagner¹, H. Wolf¹, Th. Wichert¹, and The ISOLDE collaboration²

¹Technische Physik, Universität des Saarlandes, D-66123 Saarbrücken, Germany
²CERN, CH-1211 Geneva 23, Switzerland

The presence of an external Cd pressure leads to unusual concentration profiles in CdTe, if the diffusion is performed at temperatures around 800 K, as was shown by previous studies, e.g. in the case of Ag [1]. In this contribution it will be shown that metallic layers evaporated onto CdTe crystals affect the diffusion of highly mobile dopants, like Ag, in a significant way and lead to unusual concentration profiles, as well, but at much lower temperatures.

The diffusion of Ag in CdTe crystals after annealing at 828 K under Cd pressure frequently leads to symmetrically and peak-shaped depth profiles with respect to the center of the 800 µm thick crystals. These profiles are called unusual because the Ag atoms must have diffused from regions of low concentration to regions of higher concentration contrary to what is usually expected in diffusion experiments. Simulations of the diffusion profiles taking into account the charge state and drift of the different defects and, thereby, reproducing the profiles observed in a quantitative way yield the following information: The dopant atoms are dominantly present as positively charged interstitials. The penetration of interstitial Cd atoms from both sides of the crystal, originating from the external Cd pressure, changes the initially Cd-vacancy rich, p-type material, into n-type. As a consequence, the dopant profile maps the position of the Fermi level across the depth of the crystal, reflecting at the same time the profile of the intrinsic defects, and the steep gradients of the dopant profile indicate the positions of pn junctions [2,3].

If a Cu layer of 20 nm is evaporated onto the implanted surface before the diffusion step, at a diffusion temperature of 550 K (30 min) the implanted Ag atoms are moved nearly completely to the backside of a 450 µm thick crystal; without this metal film, at the same temperature a Ag profile monotonously decreasing from the implanted surface is observed, as is expected on the basis of Fick’s laws. A similar effect, but less pronounced, is observed if the metals Au, Ni or Al instead of Cu are evaporated onto the crystal.

As mentioned above, the formation of the unusual concentration profiles requires that an initial deviation from stoichiometry is substantially changed by an external source of Cd atoms at diffusion temperature. These latter experiments indicate that the interstitial Cd atoms required can either be generated by the external Cd vapor pressure or by a Cd layer formed at the interface between the evaporated metallic layer extracting Te atoms and the CdTe crystal. The quantitative differences observed for the different metallic layers of Cu, Au, Ni, and Al might be connected to the different efficiencies to extract Te atoms at the interface to the CdTe crystal.

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Investigation of Influence of Accelerated Rotating Wave on Solid-liquid Interface in CdZnTe ACRT Crystal Growth

Chenying Zhou*, Jiahua Min, Changjun Wang, Xiaoyan Liang, Wenbin Sang, Linjun Wang
School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China

Compound semiconductor CdZnTe (CZT) has become a novel material for its high atomic number, large enough bandgap and high intrinsic $\mu\tau$ product. It could be used as X-ray and $\gamma$-ray detecting material, and has great potential applications for medical imaging, industrial process monitoring, national security and treaty verification, environmental safety and remediation, and basic science. So far most commercial CZT crystals were grown by high pressure Bridgman method (HPB), but their extensive applications were limited due to their high cost of production. Meanwhile, vertical and low pressure Bridgman method (VLPB) has been paid extensive attention because of its advantages such as equipment requirement achieved easily and process controlled easily. In the process of VLPB, the use of accelerated crucible rotation technique (ACRT) could produce stable and effective Ekman flow, so that the material crystallizability, crystal growth rate and quality could also be improved.

In this paper, the VLPB crystal growth process of Cd0.9Zn0.1Te with ACRT has been numerically analyzed by the finite element method. The two-dimensional system model with the characteristic of transient axial symmetry has been established, and ACRT was achieved by coupling the centrifugal force which caused by rotation into the volume force of fluid momentum equation (Navier-Stokes equation). In the process of crystal growth, the shape of solid-liquid interface is changing continuously. The crystal growth rate, crucible dropping rate and curvature for solid-liquid interface were all studied in this research, and the definition of relative crystal growth rate and standard deviation of curvature for solid-liquid interface were given on these bases so as to track changes of solid-liquid interface. There are four accelerated rotating waves in ACRT, which are trapezoidal wave, sine wave, square wave and triangle wave, and their simulations were achieved by the application of Heaviside function and the expansion of Fourier Series. In simulation, the maximum angular velocity was 60rpm, the simulation cycle was 32s, the temperature gradient was 10K/cm, and the crucible dropping rate was 1mm/h. Results showed that, after 280 hours’ growth, the solid-liquid interface was appreciably convex in trapezoidal wave, compared with that in sine wave, square wave or triangle wave, and the crystal growth rate was also a little greater than crucible dropping rate (1mm/h) in trapezoidal wave, which made the solid-liquid interface smooth and kept the crystal grow up spontaneously.

Keywords: ACRT; Crystal growth; Numerical simulation; Solid-liquid interface

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*Biography: Chenying Zhou (1984–), female, Shanghai, China. She received the B.S. degree and now is studying for M.S. degree in the School of Materials Science and Engineering, Shanghai University. Her technical research is mainly about the process of CdZnTe crystal growth.

Corresponding author: zhouchenying1984@yahoo.com.cn. Tel.: +86 139 1794 6156.
ZnSe based films characterization by local cathodoluminescence

A.A. Shakhmin1, I.V. Sedova1, S.V. Sorokin1, H.-J. Fitting2, M.V. Zamoryanskaya1
1Ioffe Physical Technical Institute, Polytekhnicheskaya 26, St. Petersburg 194021, Russia
2Institute of Physics, University of Rostock, Universitätsplatz 3, Rostock 18051, Germany

Investigation of the heterostructures based on wide band gap AII VI semiconductors attracts considerable attention as a result of wide applications in compact blue-green semiconductor lasers production. These lasers become essential in projection laser television systems, laser navigation and location, high quality color printing devices and other. From this point of view a solid solutions ZnCdSe, ZnSSe, ZnMgSSe are of particular interest since they are presently used in active, waveguide and emitter blue-green laser regions.

The aim of the study was the research of the electron structure (the depth of trap levels and defects levels in band gap) of ZnSe, ZnSSe and ZnMgSSe films. These films with a different composition were grown by molecular beam epitaxy on GaAs substrate. The thickness of the films was about 1 µm.

The local cathodoluminescence is used as primary analyzing technique. The experimental results were obtained on X-ray microanalyzer Camebax Microbeam with the original cathodoluminescence system. The film composition was measured by electron probe microanalysis. The cathodoluminescence spectra of binary ZnSe, ternary ZnSSe and quaternary alloy ZnMgSSe were obtained. For these materials the cathodoluminescence intensity time variation were measured in dependence on the electron beam current density and sample temperature for interband electron transitions under electron beam irradiation. The intensity rise and then decay was observed and these processes are from 50 ms for rise to minutes for decay. The investigation was performed at different temperatures in the range from liquid nitrogen to room temperature and various electron beam current density.

The rise of emission intensity relates with the presence of electron traps in the films. If the depth of trap energy level is comparable with kT the trap deactivation process has high probability and radiative recombination occurs. The catch of electron by the trap and an electron transition from trap energy level to upper level leads to radiative recombination. The cathodoluminescence intensity rise time increases with lowering temperature and raising the electron beam current density. The intensity decay is caused by electron transition from conducting band to the defect energy level. This defect energy level considered to be the reason of nonradiative carrier recombination. The cathodoluminescence intensity decay time remains constant with the electron beam current increase so we assume that the intensity does not concerned with temperature decay due to electron beam irradiation.

The depth of the electron trap and defect energy levels in band gap was calculated. For different samples it varies from 0.02 to 0.06 eV below conducting band depending on its structural perfection. We attribute it to impurity or intrinsic defect levels.

The cathodoluminescence can be used in analysis of barrier layers inside the complex heterostructure with quantum wells. It allows studying the internal layers as well as the surface layers.
Enrichment Mechanism of the Surface of CdTe Single Crystals with Excess Te in the Br₂-HBr-H₂O Polishing Bromine Etchant

S.V. Belyaev¹, V.A. Gnatyuk¹,², A.V. Stronski¹, T. Aoki²
¹V.E. Lashkaryov Institute of Semiconductor Physics of National Academy of Sciences of Ukraine, Kyiv 03028, Prospekt Nauky 41, Ukraine
²Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Hamamatsu 432-8011, Japan

Surface resistivity of CdTe single crystals can be sufficiently lowered because of enrichment of the surface with excess electronegative tellurium and formation of surface chemical compounds. This effect is typical for a high-ohmic state of CdTe due to a high Debye screening depth. In the paper, the enrichment mechanism of the surface of CdTe single crystals with excess overstoichiometric Te in the Br₂-HBr-H₂O polishing bromine solution is analyzed on the base of general regularities of the acid-alkaline interaction theory.

At the interaction of bromine with CdTe chemical compound the displacement of the relatively weaker acid (chemical element Te) by the stronger acid (bromine) should be observed. The displacement reaction should proceed:

CdTe + Br₂ = CdBr₂ + Te (free).    (1)

Having acidic properties chemical element Te should react with the oxidizer (bromine), but the intensity of this interaction should be relatively low as compared with the interaction of the oxidizer and CdTe compound:

Te (free) + Br₂ = Te Br₄.      (2)

At the condition that the rate of the direct reaction (1) is sufficiently higher than that of (2), segregation of the free tellurium on the surface is a natural process and does not require attraction of additional mechanisms.

Full interaction of CdTe with the oxidizer in accordance with reaction equations (1) and (2) has a two-stage character and is described by equation (3):

2CdTe + 4Br₂ = 4CdBr₂ + TeBr₄ + Te (free).  (3)

The third stage is the interaction of the reaction products with the selected solvent. Besides the interaction with the oxidizer, CdTe can interact with the solvent (HBr acid):

CdTe + 2HBr = CdBr₂ + H₂Te.    (4)

Gassing H₂Te is easily oxidized by Br₂ according to the reaction:

H₂Te + Br₂ = 2HBr + Te (free).    (5)

Interaction intensity of CdTe with HBr is low and the effect of the segregation of the elementary tellurium according to reactions (4) and (5) is insignificant. The effect of enrichment of the surface with excess tellurium is caused by a relative decrease of its solubility in acid solution. Note that in the polishing solution near the CdTe surface there simultaneously are three reaction products but not two: CdBr₂, TeBr₄ and elementary Te.

The proposed use of a mixed solvent with defined components allows us to shift the chemical equilibrium in the system and solubility of the reaction products to obtain the surface with desired chemical and physical properties.
Adsorption Shift of the Surface Potential in CdTe and Cd$_{1-x}$Zn$_x$Te Crystals

S.V. Belyaev$^1$, V.A. Gnatyuk$^{1,2}$, T. Aoki$^2$

$^1$V.E. Lashkaryov Institute of Semiconductor Physics of National Academy of Sciences of Ukraine, Kyiv 03028, Prospekt Nauky 41, Ukraine
$^2$Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Hamamatsu 432-8011, Japan

CdTe and Cd$_{1-x}$Zn$_x$Te single crystals are attractive for applications as a substrate and detector material due to their high resistivity. However, a decrease in the surface resistivity, due to the adsorption of atmospheric oxygen, is typical for high resistivity crystals. This is due to a large Debye screening depth.

The influence of adsorption of atmosphere oxygen on the physical properties of the surface of (110) orientated Cd$_{1-x}$Zn$_x$Te single crystals with $p$-type conductivity ($\rho = 6 \times 10^5$ Ohm-cm) is investigated. In order to prevent the formation of a natural oxide film and enrichment with free tellurium during etching process and to obtain a clean surface the non-water organic solvent was matched as the etching solution. The following repeated rinsing of the surface was carried out in several stages with the use of high purity non-water organic solvents. The electrical contacts were deposited on the freshly etched surface and the photoconductivity spectra and resistivity were investigated. Then the Cd$_{1-x}$Zn$_x$Te surface was stabilized in the air atmosphere starting from several minutes up to 140 hours and mentioned above measurements were carried out again.

As a result of the series of the consequent measurements, which were carried out after certain time intervals, the following features were experimentally established: an increase in the intrinsic photoconductivity spectra maximum, decrease in the slope of the short wavelength wing and monotonic increase in the surface conductivity. A decrease in the slope and increase in the surface conductivity reflect the reconstruction of the surface structure and increase in the concentration of the surface states during chemical adsorption.

A decrease in the dissociation energy of O$_2$ molecules in the adsorbed state leads to the appearance of an atomic oxygen migrating along the surface.

The change of the surface charge state to the side of negative values of the electrostatic potential, which is caused by adsorption of atmosphere oxygen, is accompanied by the corresponding shift of the electron-hole equilibrium in the subsurface layer of the Debye screening depth. The effect of a decrease in the surface resistivity due to adsorption of atmospheric oxygen or presence of surface contaminations is accompanied by the occurrence of the surface leakage currents, which hinder recognition of a useful signal and result in deterioration in the functional parameters of devices based on high resistivity CdTe and Cd$_{1-x}$Zn$_x$Te.
Isothermal close space sublimation of II-VI semiconductors using alternated exposure to the elemental sources in different environments

O. de Melo, M. Sánchez, B. J. García¹, M. Hernández Vélez¹²

Physics Faculty, University of Havana, Cuba

¹Applied Physics Department, Faculty of Sciences, Autonomous University of Madrid, Spain

²Instituto de Ciencia de Materiales de Madrid, ICMM-CSIC, Cantoblanco 28049, Madrid, Spain

In the last years, our group has developed the isothermal close space sublimation of II-VI semiconductors using alternated exposure to the elemental sources. With this technique, epitaxial ZnTe, CdTe and CdSe compounds and also alloys have been obtained. By controlling the exposure and purge time it has been possible to attain different growth regimes. For example, for large purge times and short exposure times, atomic layer epitaxy regime has been obtained. However for short purge times, multilayer adsorption of the elements has led to not self-regulated growth and consequently, thicker films were obtained. The growth process was performed in a graphite boat with a movable upper part containing the substrate and a bottom fixed part where the sources were located. The substrate was cyclically exposed to the elemental Zn, Cd, Te and/or Se sources in the growth experiments.

In the first part of this presentation we present results on ZnTe, CdZnTe, CdTe and CdSe systems, showing the structural and optical properties of the films obtained with this simple technique. The influence of the used ambient (Argon, Hydrogen, vacuum) is explained. It is shown that hydrogen is able to transport Se by forming H₂Se compound while growth processes performed in vacuum present a large growth rate as a consequence of an improved precursor transport toward the growth surface. We have studied the dissociative adsorption of the group VI molecules (Se and Te) which is favored by using hydrogen since H₂Se seems to be more easily decomposed than Se₂ ones. This imposes a low temperature limit for efficient growth that is near 380 °C for Te compounds and 350 °C for Se compounds. High resolution transmission electron micrographs are presented as well as transmission diffraction patterns showing the epitaxial character of these films.

In the second part, we present recent results showing that using vacuum environment promotes the transport of vapors towards the surface and allows decreasing the low temperature limit for efficient growth. Film thickness ranged between 200 and 600 nm for 50 cycles samples. ZnTe and CdTe films were obtained even at temperatures as low as 310 °C. This is important because low temperatures worsen the inter-diffusion processes allowing the growth of relatively abrupt interfaces. Such structures have been grown in the ZnTe/CdTe system. Its compositional, structural and optical properties are presented. These results offer new possibilities of this low cost technique for growing heterostructures.
The local electron interaction with crystal lattice defects in ZnHgSe and ZnHgTe solid solutions

O. Malyk
Semiconductor Electronics Department, Lviv Polytechnic National University, Bandera Street 12, Lviv 79013, Ukraine

Usually the electron scattering models in ZnHgSe and ZnHgTe are considered in relaxation time approximation. However, these models have essential shortcoming – they are long-range which contradict special relativity. From the other side in [1,2] the short-range models of electron scattering were proposed for Cd$_x$Hg$_{1-x}$Te and Cd$_x$Hg$_{1-x}$Se in which the above mentioned shortcomings were absent. The purpose of the present work is to use this approach for description of the electron scattering in ZnHgSe and ZnHgTe solid solutions.

For the charge carrier scattering on the nonpolar optical and acoustic phonons, neutral defects, disorder and static strain potential the interaction radius of the short-range potential is limited by one unit cell. For the charge carrier scattering on the ionized impurity, polar optical and piezoelectric (piezoacoustic and piezooptic) phonons the interaction radius of the short-range potential is founded in a form $R = \gamma a$ ($a$ - lattice constant, $\gamma$ – the respective adjusting parameters).

To calculate the conductivity tensor components the method of a precise solution of the stationary Boltzmann equation was used [3]. The temperature dependences of the charge carrier mobility in the range 4.2 – 370 K in Zn$_x$Hg$_{1-x}$Se (0.02 ≤ x ≤ 1) and Zn$_x$Hg$_{1-x}$Te (x=0.15) crystals are calculated. The influence of the different scattering mechanisms on the charge carrier mobility is considered. A good agreement between theory and experiment in all investigated temperature range is established. The scattering parameters $\gamma$ for different scattering modes are determined.

A new type of surface electronic states in $p$-type $\mathrm{Hg}_{1-x}\mathrm{Cd}_x\mathrm{Te}$ were observed and studied. These states are characterized by rather high surface concentration $N = (5-7) \times 10^{11}$ cm$^{-2}$.

At relatively high temperatures ($T > 15-20$ K) these surface states does not effect essentially on the crystal photoelectrical properties. However, at low temperatures ($T < 10$ K) these states can recharge due to trapping of non-equilibrium carriers, generated by a radiation with photons energy $\hbar \omega > E_g$.

It was shown, that the observed surface states are acceptors, and have an energy level near the valence band top. It was also demonstrated that these states are located not in the oxide layer, which is always present on $\mathrm{Hg}_{1-x}\mathrm{Cd}_x\mathrm{Te}$ surface, but on crystal surface directly.

After the recharging of these states a space charge near the crystal surface occurs. This space charge can effect essentially the photoelectrical phenomena at low temperatures, especially the photo-gradient effects. We have observed the double change of sign of photoelectromagnetic effect (PME) current with magnetic field $H$ (PME is normal at small $H$, then it becomes anomalous with the increase of magnetic field, and at large $H$ it becomes normal again).

The study of low-temperature anomalies of the PME had enabled us to detect the presence of the unusual surface states. We have proposed the model of anomalous PME with an account of the surface states recharging by light.
Arsenic incorporation in MBE-grown HgCdTe studied with the use of ion milling


1R&D Institute for Materials SRC "Carat", Stryjska 202, Lviv 79031, Ukraine
2Institute of Semiconductor Physics, SB RAS, ac. Lavrentieva 13, Novosibirsk 630090, Russia
3Institute of Physics PAS, Lotnikow 32/46, Warsaw 02-668, Poland
4Institute of Physics, Rzeszow University, Rejtana 16A, Rzeszow 35-310, Poland
5Ioffe Physical Technical Institute, Polytekhnicheskaya 26, St. Petersburg 194021, Russia
6Pidstrygach Institute for Applied Problems of Mechanics and Mathematics NASU, Naukova 3b, Lviv 79060, Ukraine

Arsenic is the acceptor dopant of choice in HgCdTe, the basic material for photodetectors operating in the infrared part of the spectrum. Its advantages include easy incorporation during growth, low diffusivity and the fact that it is a shallow acceptor. A problem related to arsenic doping of HgCdTe is caused by its amphoteric nature: it occupies cation sites as a donor AsHg and Te sites as an acceptor As Te. Currently, HgCdTe is grown mostly by molecular beam epitaxy (MBE), and this growth occurs under Te-rich conditions; this means that in the as-grown films arsenic is generally incorporated on cation sites as a donor, and a transfer of the As to Te sites is necessary. Such a transfer (activation), which is achieved by a post-growth anneal, is becoming one of the critical issues in HgCdTe technology.

Both arsenic incorporation during the growth and its activation are believed to be accompanied by the formation of a number of by-side defects, which affect the electrical and optical properties of the material. This makes a study of arsenic incorporation and its effect on the defect structure of HgCdTe a very topical task. For the first time we performed such a study with the use of ion milling, a unique means to reveal point defects and defect complexes in HgCdTe. Strongly non-equilibrium processes, which take place in HgCdTe under ion milling, when a crystal is oversaturated with interstitial mercury atoms HgI, produce specific donor defects and complexes that may not form under other conditions. The complexes may comprise intrinsic point and extended defects that normally do not show their presence due to their electrical neutrality or compensation. By studying electrical properties of HgCdTe before ion milling, straight after it, and during so-called ‘relaxation’, when the induced defects gradually disintegrate, one can obtain information on the defect structure of the specimen.

We have studied MBE-grown Hg0.8Cd0.2Te films, doped with arsenic during the growth using an effusion cell and a cracker cell, with both activated and inactivated arsenic. Our results show that the most efficient incorporation of electrically active arsenic occurs under doping from the cracker cell, at the arsenic cracking zone temperature $T_{cr}$~600–700°C. By varying the arsenic flow, the concentration of electrically active arsenic can be easily adjusted within the range $10^{15}$–$10^{17}$ cm$^{-3}$. In the films grown at the lower $T_{cr}$ arsenic tended to incorporate in MCT in electrically inactive form, yielding low carrier concentration ($<10^{15}$ cm$^{-3}$). Doping from the effusion cell, while giving high concentration of electrically active arsenic, leads to the high concentration ($>10^{17}$ cm$^{-3}$) of Te-related initially neutral defects, which ion milling activates electrically.

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HgCdTe, while continuing to be one of the most important semiconducting materials for infrared (IR) detectors, also possesses attractive properties for emitting IR light between 3 and 5 µm. This is due to its interband recombination, which can be easily adjusted by controlling the CdTe mole fraction $x$ in the alloy. It was shown theoretically back in 1991, that the Auger recombination rate in a HgCdTe potential well with size quantization is significantly smaller that that in bulk material [1], but problems with HgCdTe growth led to a serious lag of HgCdTe heterostructure technology in respect to the III- VI materials. It was only recently, that a step has been made from HgCdTe light-emitting structures with homogenous ‘active’ layer with constant $x$ towards structures with potential wells, resonant cavities and separate confinement [2-4]. Such structures are typically grown by molecular beam epitaxy (MBE), which allows for the growth of structures having different thicknesses and compositions.

We report on the study of optical properties of MBE-grown HgCdTe structures with potential wells and separate confinement, suited for light emission in the mid-IR range. The structures were grown at A V Rzhanov Institute of Semiconductor Physics, Novosibirsk, on (013) GaAs substrates with ZnTe/CdTe buffer layers. The $x$ value in the ‘active’ layer (potential well) in the structures varied from 0.33 up to 0.42, and the width of the wells varied from 50 up to 200 nm. The composition of the ‘barrier’ layers was $x \sim 0.72$, and in some of the structures these layers were doped with In with concentrations of $\sim 3 \times 10^{15}$ cm$^{-3}$. Part of the structures was subjected to the post-growth annealing in mercury vapors at 250 °C for 3 hours.

The structures were subjected to the studies of optical transmission and photoconductivity at 300 K and 77 K, and extensive photoluminescence (PL) investigations. The PL was studied in the temperature range 4.2–300 K and in magnetic fields of up to 6 T (at 4.2 K) under pulse excitation with InGaAs/GaAs and AlGaAs/GaAsP semiconductor lasers emitting at 0.98 and 0.84 µm, respectively. The PL spectra were recorded with a cooled InSb photodiode.

We discuss the optical properties of the structures, including those related to the presence of multiple layers, as well as statistical (microscopic) and technological alloy composition fluctuations in the ‘active’ layers (potential wells). We shall also consider the advantageous effect of barrier layer doping and post-growth annealing on the PL intensity in the structures and discuss the prospects of various types of HgCdTe-based structures for light emitters in the mid-IR range.

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Multicarrier Analysis of Free Carrier Absorption in Mercury Cadmium Telluride

O.V.S.N. Murthy¹, V. Venkataraman¹, and R.K. Sharma²
¹Department of Physics, Indian Institute of Science, Bangalore 560012, India
²Solid State Physics Laboratory, Lucknow Rd, Timarpur, Delhi 110054, India

Mercury Cadmium Telluride (HgCdTe) is a widely used material for infrared absorption especially in the important atmospheric window of 8-14 µm for its high efficiency. Even though free carrier absorption at lower energies may not be an impediment to devices operating at the absorption edge, it nevertheless gives important information regarding the carriers present in the material and their dynamics.

We compare free carrier absorption (FCA) inferred from infrared transmission measurements in bulk and epilayer Hg₁₋ₓCdₓTe (x~0.2) with calculated curves.

Various carrier species present in the system are taken into account by a nonlinear fitting procedure using a multicarrier expression for the free carrier absorption on experimental data. Associated magnetotransport measurements are also used to correlate the carrier information. The FCA expressions utilize known relevant scattering mechanisms, e.g. polar optical phonon and ionized impurity at high temperatures.
Raman scattering in CdHgTe epitaxial layers grown on CdZnTe substrates

A. Belogorokhov, L. Belogorokhova, I. Denisov, N. Smirnova
Institute of Rare Metals, B.Tolmachevsky per., 5, Moscow 119017, Russia

Cd$_{x}$Hg$_{1-x}$Te (MCT) is well recognized for its importance in the infrared detector industry. The performance of an infrared system is based on a high spatial resolution and on a high thermal resolution. An increase in spatial resolution means an increase in number of pixels [1]. So it essential to know the crystal perfection and composition homogeneity over the whole MCT volume. To gain insight into the problem of crystal perfection over the whole volume in Cd$_{x}$Hg$_{1-x}$Te/Cd$_{1-y}$Zn$_{y}$Te epitaxial structures we performed micro-Raman scattering experiments.

The Cd$_{x}$Hg$_{1-x}$Te (0.20 <x <0.3) epitaxial layers with a diameter of 30–50 mm were grown from Te base melts in a soldered quartz ampoule at T$_{g}$ = 495-515°C on the single crystal Cd$_{0.96}$Zn$_{0.04}$Te (111) substrates.

After saturated Hg vapor annealing the layers reveal n- and p- type conductivity with different carrier concentration.

To study the spatial distribution of structural defects, all over the layer volume, the samples were cleaved perpendicularly to the epilayer/substrate interface just before the Raman measurements and the cleaved surfaces were investigated. The temperature of the samples was estimated to be 90K. The Raman microprobe was found to be useful in identifying vibrational modes induced by crystal defects. Thus, we have obtained $A_1$ and two $E$- modes of tellurium located at 123, 90 and 142 cm$^{-1}$, correspondingly; mode, activated by Hg vacancy (107 cm$^{-1}$); optical phonon modes at 116.5, 139.5, 157.8 cm$^{-1}$. In all spectra we have not seen any additional features at 132-136 cm$^{-1}$ that were tentatively assigned to a clustering mode [2].

Correlation between carrier concentration in epitaxial layers and presence of tellurium precipitates in hetero-structures is established.

The work was supported by the Russian Foundation for Basic Research (No. 09-02-01215).

Mercury cadmium telluride (MCT) is extensively used for infrared detector applications. Indium (In) can be incorporated as a donor and arsenic (As) as an acceptor. The incorporation of dopants as well as the different annealing procedures used for the activation of the dopants lead to significant changes of the luminescence properties. Thus the different levels due to As or In doping can be studied by PL. Modulated photoluminescence (PL) measurements using a continuous-scan Fourier transform infrared spectrometer (FTIR) have been performed on a large variety of MCT samples: Excitation-power dependent and temperature dependent comparative studies were done using undoped, As doped and In doped samples with a Cd composition between 22% and 70%. The samples were grown by molecular beam epitaxy (MBE) or liquid phase epitaxy (LPE).

The activation of the dopants by specific annealing procedures corresponds to the appearance of new emission peaks in the PL spectra. The energy levels are investigated. The emission energy temperature dependence and excitation power dependence of the different peaks allow to investigate the origin of the peaks.

For instance, in the case of an As-doped sample, the PL results tend to show that the annealing procedure can transfer the As atoms from a donor site (As_{Hg}) to an acceptor site (As_{Te}).

The temperature dependences of the PL lines are compared to the band gap temperature dependence. Localization level can be evidenced in this way, possibly due to dopant incorporation or alloy disorder.
HgCdTe quantum wells (QW) are attractive objects for generation of new knowledge about physical process in quantum narrow gap semiconductors and for future practical application in IR and THz emitters and detectors. HgCdTe zone diagram allows to fabricate direct gap and inverse gap QW’s. The possibility to grow symmetric and asymmetric QW expands the science field of investigations. Really the small effective electron mass and high mobility leads to wider Landau levels splitting, weaker electron localizations and increasing Rashba effect. It is very important for construction and developing spintronic devices.

We developed the method of zone engineering of HgCdTe/HgTe/HgCdTe QW at growing by MBE method with in situ ellipsometric control of composition and thickness. The growth of QW with step-like composition variations is accompanied by sectionally spiral curve trajectory of ellipsometric parameters in $\psi$-$\Delta$ plane. The sharp turns in the curve occur when the composition changes abruptly. The form of the spiral fragments and their extension from fracture to fracture allow determination of growing layer composition and its thickness. The precision in thickness determination is not worse than 1 ML. The precision of QW composition determination depends both on its thickness and difference in composition between spacer and QW. In case of 0.03 molar fractions difference and 16 nm thickness the precision amounts $\delta x=0.002$ and will be improved when difference increases.

In case of QWs with gradient interfaces the ellipsometric trajectory in $\psi$-$\Delta$ plane is smooth and without character breaks. We deduced that breaks becomes visible clearly in coordinates $d\Delta/d\psi$-$\Delta$ or $d\Delta/d\psi$. The numerical calculations show the possibility to control the composition gradients from 0.06 to 0.6 of molar fraction/nm.

The Cd$_{\varphi}$Hg$_{1-\varphi}$Te/HgTe/Cd$_{\varphi}$Hg$_{1-\varphi}$Te QWs with abrupt changes of composition were grown reproducible with in situ ellipsometric control. The HgTe thickness was in range of 5 – 22 nm. The central part of Cd$_{\varphi}$Hg$_{1-\varphi}$Te spacers were doped by In with concentration of $10^{14}$-$10^{17}$ cm$^{-3}$. The composition distribution in QW was checked by ex situ measuring of reflection spectra with precise step etching. It was found good coincidence between ellipsometric and reflection spectra data. We observed 2D electron in QW with mobility $5\times10^{5}$ cm$^2$/V×s at concentration $3\times10^{11}$ cm$^{-2}$. QW are sensitive in IR and THz ranges.

The asymmetric QW’s were grown with composition gradient 0.04 mol.fr./nm. The measurement of its parameters now is in process.
Determination of Shockley-Read recombination center parameters in MBE p-Hg_{0.78}Cd_{0.22}Te/GaAs via photoconductivity in magnetic field

D.Yu. Protasov\textsuperscript{1}, V.Ya. Kostuchenko\textsuperscript{2}, V.S. Varavin\textsuperscript{1}, S.A. Dvoretsky\textsuperscript{1}, N.N. Mikhailov\textsuperscript{1}

\textsuperscript{1}Institute of Semiconductors Physics SB RAS, Lavrentiev Prospect, 13, Novosibirsk, 630090, Russia
\textsuperscript{2}Siberian State Geodetic Academy, Plakhotnov street, 8, Novosibirsk, 630108, Russia

The lifetime of minority charge carriers is a critical parameter for infrared photodetectors on base p-Hg_{1-x}Cd_{x}Te (MCT). In this material the lifetime is limited by Shockley-Read recombination at low temperatures. It is rather difficult to study this mechanism in p-Hg_{1-x}Cd_{x}Te and compare theory with experiment because it’s strong dependence from such recombination parameters of center as ionization energy $E_i$, density $N_t$, capture rates for electrons $\mathcal{L}_n$ and holes $\mathcal{L}_p$.

In this work a values of $E_i$, $N_t$, $C_n$ and $C_p$ in vacancy-doped MBE MCT films with various density of major holes were determined at 77 K. The parameters of recombination centers were founded via measurements of steady-state photoconductivity in magnetic filed for Faraday’s geometry \cite{1}. This method allows to divide the contribution of excess electrons and holes in photoconductivity, as well as to obtain the mobility of minor electrons $\mu_n$ and the ratio between electrons and holes lifetimes $\tau_p/\tau_n$ \cite{1}.

We compare our experimental values $\tau_p/\tau_n$ with lifetime ratios calculated on theoretical expressions \cite{2}, take into account a radiative, Auger-7 and Shockley-Read recombination mechanisms. The parameters $E_i$, $C_n$ and $C_p$ were used as fitting parameters and density $N_t$ was computed by obtained expression

$$N_t = \frac{P_0 \cdot \left(\frac{C_n}{C_p}\right) N_1}{\left(\frac{\tau_p}{\tau_n} + 1\right)}$$

where $N_1$ – density of state in conduction band reduced to energy of recombination center. Results are shown in the table:

<table>
<thead>
<tr>
<th>$P_0$, m$^{-3}$</th>
<th>$\mu_n$, m$^2$/V\cdot$s</th>
<th>$\mu_p$, m$^2$/V\cdot$s</th>
<th>$\left(\frac{\tau_p}{\tau_n}\right)_\text{exp}$</th>
<th>$\left(\frac{\tau_p}{\tau_n}\right)_\text{theor}$</th>
<th>$\tau_n$, ns</th>
<th>$\tau_p$, ns</th>
<th>$N_t$, m$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.7$\times$10$^{21}$</td>
<td>0.036</td>
<td>7.5</td>
<td>15.3</td>
<td>14.0</td>
<td>12</td>
<td>166</td>
<td>4.0$\times$10$^{19}$</td>
</tr>
<tr>
<td>8.3$\times$10$^{21}$</td>
<td>0.045</td>
<td>6.4</td>
<td>6.1</td>
<td>6.1</td>
<td>17</td>
<td>105</td>
<td>2.5$\times$10$^{19}$</td>
</tr>
<tr>
<td>2.5$\times$10$^{22}$</td>
<td>0.026</td>
<td>5.6</td>
<td>43.3</td>
<td>40</td>
<td>0.8</td>
<td>32</td>
<td>5.3$\times$10$^{20}$</td>
</tr>
</tbody>
</table>

The capture rates and ionization energy did not depend from density of major holes and their values are equal to $\mathcal{L}_n=2.3\times10^{-12}$ m$^3$/s, $\mathcal{L}_p=8.2\times10^{-16}$ m$^3$/s, $E_i=53$ meV, but the centers density in samples is various. Correspondence of received values with published data and a nature of recombination centers are discussed.

CdHgTe is today one of the main materials for manufacture of IR photodetector arrays. Deposition of the CdTe layer on the CdHgTe surface is one of the most promising passivation methods for such devices.

In this paper the electric properties are investigated of a CdTe-CdHgTe structure grown in single MBE process on a GaAs substrate. The structure includes an operating layer CdxHg1-xTe with d=7.5 µm width and composition value x=0.343, a graded gap layer with d=0.2 µm x=0.343–0.4 and CdTe layer with d=0.2 µm. The Hall measurements gave the electron concentration and mobility values of n=1.10^{14} \text{cm}^{-3} and 1.1.10^4 \text{cm}^2/\text{V.sec} correspondingly. The volt-farad characteristics corresponded to n-type CdHgTe, but in inversion region an indicative hump was observed, the hump amplitude dramatically increased at illumination. The wafer was illuminated from the frontal side, the gate electrodes being opaque. The measurements using narrow light probe have shown that the photoelectric sensitivity did not change when the probe was moved off to 0.3 mm distance from the gate electrode (the electrode dimensions and the distance to the closest one were 0.5x0.5 and 0.5 mm correspondingly).

The total experimental data and analysis of band diagram structure lead to the consequent conclusions: 1) on the entire wafer area in the CdHgTe near the CdHgTe/CdTe boundary exists an inversion layer, that is, a layer of mobile holes; 2) the hump, that is, the structure capacity increase in comparison to usual high-frequency inversion capacity, occurs due to the spreading effect – the test current lines cross the structure not only in the gate electrode area, but disperse on the inversion layer to excess area; 3) the high photoelectric sensitivity can be attributed by photo holes captured in inversion layer and leaking to the MIS structure and, besides, from greater area; 4) the calculations give the value of donors effective concentration in CdHgTe as N_d=3.10^{14} \text{cm}^{-3}; CdTe has a p-type conductance with acceptor concentration value N_a=1.10^{16} \text{cm}^{-3}.

The structure volt-ampere characteristics demonstrate that dramatic current increase occurs at such negative voltages where the hump begins to decrease, that is when the holes begin to drift out from the inversion layer through the CdTe to the gate electrode, and their concentration in the inversion layer decreases.

The experimental data analysis allows to estimate the valence band offset value for holes on the CdTe/CdHgTe interface as 0.1 eV or even less.
An investigation of gold and nickel contacts to MBE grown p-type MCT

A.V. Predein, V.V. Vasiliev
Institute of Semiconductor Physics, Lavrentyeva av. 13, Novosibirsk 630090, Russia

Investigations of metal contact to p-type Cd$_x$Hg$_{1-x}$Te (MCT) are stimulated by difficulty in producing low-resistance contacts especially for infrared detectors, where it is impossible to manufacture large area contact. The theoretical studies predict that contact of most metals to clean p-type MCT surface give Schottky barrier higher than the band gap, but nevertheless it is possible to try achieve low contact resistance by introducing some interface layers between the metal and semiconductor or by special surface processing.

An opportunity was investigated of ohmic contacts manufacture by thermal evaporation of Au and Ni to p-type heteroepitaxial Cd$_x$Hg$_{1-x}$Te structures grown by molecular beam epitaxy (MBE) method. The contacts parameters were investigated by measuring the volt-ampere characteristics at 78 K. The operating layer composition of MCT wafers varied from x=0.2÷0.3, some wafers had graded layer of 0.4 µm width and composition x=0.45 on the surface, and the vacancy hole concentration value was $p=5\times10^{15} \div 5\times10^{16}$ cm$^{-3}$. After metal deposition the wafers were annealed at 120º C in air.

For nickel contact to p-type MCT a volt-ampere curve was obtained closely to linear one and the resistivity value was 0.003 Ohm.cm$^2$. The gold contact gave a rectifying volt-ampere curve of Schottky diode and the resistance value of ~1 Ohm.cm$^2$. The effect of geometric factors (electrodes geometry and contact area) on the contact resistance was investigated and amount and kind of previous processing operations as well.
Hydrogenation of \( \text{Cd}_{x}\text{Hg}_{1-x}\text{Te} \) films at chemical treatments

G.Yu. Sidorov, Yu.G. Sidorov, V.S. Varavin

Institute of Semiconductor Physics of the Siberian Branch of the RAS, Russia,
630090, Novosibirsk, Lavrentiev avenue 13

The effect of hydrogenation of mercury cadmium telluride (\( \text{Cd}_{x}\text{Hg}_{1-x}\text{Te} \) or MCT) epilayers with \( x=0.22 \), grown by molecular beam epitaxy (MBE) on GaAs substrates, has been investigated. The layers used were n-type with an electron concentration \((2-5)\times10^{14} \text{ cm}^{-3}\) and vacancy-doped p-type with a hole concentration about \(10^{16} \text{ cm}^{-3}\). The hydrogenation of films was carried out by boiling samples in DI water and by means of electrochemical treatment.

It is found that after boiling p-type layers for 30 minutes in DI water no significant changes of concentration and carrier mobility occur, but the minority carrier lifetimes increase. Incrementing boiling time up to 90 minutes causes an increase in the hole concentration up to \((2-5)\times10^{17} \text{ cm}^{-3}\), which agrees with the data of other researches.

After boiling n-type layers for 30 minutes in DI water a decrease in conductance and effective carrier mobility has been obtained, which can be explained by the introduction of acceptors. Incrementing boiling time up to 90 minutes causes conductivity type conversion from n to p, with increase of hole concentration up to \((2-5)\times10^{17} \text{ cm}^{-3}\). The minority carrier lifetimes in such samples are sufficiently higher than in vacancy-doped samples with comparable hole concentrations.

Analogous effects have also been observed after electrochemical treatment of samples in electrolytic solution with negative potential applied to the sample.

Treated samples with the highest hole concentrations obtained (up to \(10^{18} \text{ cm}^{-3}\)) have been analyzed by SIMS. There were no impurities found in concentrations capable to provide such hole concentrations.

The observed phenomena can be explained by the effect of hydrogenation of MCT layers when atomic hydrogen diffuses into the film volume. In case of a p-type material hydrogen forms acceptor complexes with mercury vacancies that changes the recombination levels which cause the magnification of a minority carrier lifetimes observed. In the n-type material diffusing atomic hydrogen displaces mercury atoms from sites of a metal sublattice and forms complexes with induced vacancies. The same process occurs at high concentrations of hydrogen in a p-type material. The interstitial mercury having high diffusivity comes out of the volume of sample.

The technology of IR photodetectors on the basis of \( \text{Cd}_{x}\text{Hg}_{1-x}\text{Te} \) involves procedures in which the MCT interacts with chemical mediums, resulting in hydrogenation of material. This can further be the cause of changes of photodetectors parameters.
Defects of crystal structure in Cd$_x$Hg$_{1-x}$Te layers grown on Si(310) substrates

M. Yakushev, A. Gutakovsky, I. Sabinina, and Yu. Sidorov
Institute of Semiconductors Physics, Lavrentiev av. 13, Novosibirsk 630090, Russia

CdHgTe/CdTe/ZnTe/Si heteroepitaxial structure is the most perspective material for the development of photodetector arrays for near- and mid-infrared. In comparison with CdHgTe (MCT), grown on the matched CdZnTe substrates, devices on the basis of MCT, grown on Si, are distinguished by high stability at a thermal cycling, cheapness of production and a major size of substrates.

There is a number of problems in the process of growth of MCT heteroepitaxial structure on Si substrate. These problems associate with a major mismatch of lattices constants, non-isovalentness and monatomic of silicon. As a result, considerable quantities of defects are formed. The high density of defects leads to the degradation of electrophysical properties of heterostructures, as well as parameters of the devices which are made of grown films.

The mechanisms of formation of antiphase domains and stacking faults in CdHgTe/CdTe/ZnTe/Si (310) heterostructures have been investigated by the methods of selective etching and transmission electron microscopy. It is demonstrated that the ensemble of structural defects is determined by the conditions of ZnTe/Si (310) interface formation.

It is established that the density of antiphase boundaries depends on relation of Zn and Te$_2$ vapor pressures and substrate temperature at the initial moment of ZnTe growth. High pressure of Zn vapor results in the formation of monodomain layers. The increasing of growth temperature and Te$_2$ vapors pressure results in the precipitation of antiphase boundaries and magnification of their density up to polycrystalline growth.

Stacking faults can be situated in four equivalent planes \{111\} in a crystal with a sphalerite type lattice. It is revealed that stacking faults of one type dominates in MCT/Si (310) heterostructure. Stacking faults are situated in the (111)-plane which is traversing the (310)-plane under the angle of 68 degrees. The precipitation of stacking faults has heterogeneous character and occurs on ZnTe/Si (310) interface. The annealing of heterostructures at 350°C in tellurium atmosphere leads to the annihilation of stacking faults. The reason of the dominating of particular type stacking fault consists in the following: the formation of Zn-Zn bonds in a stacking fault plane under high Zn vapor pressures and the gain of the internal energy of heterostructure at the expense of the decreasing of the square of stacking fault which is situated under a major angle to the interface.
Kinetics of CdTe and CdHgTe layer growth on a (310) surface

M. Yakushev, D. Brunev, and Yu. Sidorov

Institute of Semiconductors Physics, Lavrentiev av. 13, Novosibirsk 630090, Russia

The growth of CdHgTe layers by a molecular beam epitaxy (MBE) method takes place at a low temperature. The low temperature of a substrate results in the growth of CdHgTe which is carried out in conditions when two crystalline phases - (HgTe)$_2$ and Te$_2$ - can appear. The probability of formation of this or that phase is determined by the kinetics of matching phases formation. As a result, CdHgTe films grown by MBE contain specific defects with the density up to $10^4$ cm$^{-2}$. It is known that the origin of intergrowing defects occurs on the relief perturbations. In this connection, the morphology of CdHgTe surface layers and CdTe buffer layers extensively determines the density of intergrowing defects.

The surface morphology of CdTe buffer layers and the growth kinetics of CdHgTe films grown by MBE on GaAs (310) substrates are investigated by the methods of RHEED and ellipsometry.

It is established that Cd-stabilized CdTe(310) surface is atomic-smooth. Its reconstruction is featured by the lattice cell which coincides with the lattice cell of the unreconstructed (310) surface. It is determined that the adsorption of Te$_2$ in the quantity of less than 0.2 monolayers results in the reconstruction of a surface with the formation of (100) terraces divided by two-atomic steps. The system of (100) – (210) facets forms on CdTe (310) surface if the thickness of Te$_2$ adsorbed layer more than 0.3 monolayers.

It is established that the minimum Hg vapor pressure necessary for the growth of HgTe on (310) surface is 4 times smaller than on (100) surface. It is found that there is no formation of Te$_2$ adsorbed layer during the growth of HgTe on (310) surface whereas the Te$_2$ adsorbed layer with the equivalent thickness of 1 angstrom is formed on (100) surface.

Low values of permissible pressures of mercury vapor and the lack of tellurium adsorbed layer indicate that there is no difficulties in the CdHgTe films crystallization processes on a (310) surface. As a result, more favorable conditions for the molecular beam epitaxy of CdHgTe layers are created on the surface with (310)-orientation in comparison with the surfaces oriented on other planes.
The current baseline for infrared focal plane arrays (IRFPAs) is a hybrid technology wherein the HgCdTe (MCT) detector array and the Si readout integrated circuit (ROIC) chips are fabricated separately and connected element by element with indium. The number of pixels, as well as mechanical and thermal capability, is limited. A technology for which HgCdTe detector arrays are monolithically integrated with Si ROICs would obviate these deficiencies.

We have investigated issues concerning the development of the monolithic technology based on HgCdTe photosensitive elements grown on Si multiplexer.

We have analyzed processes of growth of CdTe and HgCdTe on Si(310) with SiO₂ layer in which growth windows were opened. The windows represent squares with the side from 30 µm to 100 µm. The influence of preepitaxial annealing on the parameters of CMOS transistors of 128×128 MX-4 multiplexer have been investigated. It was demonstrated that p- and n-channel transistors save their characteristics during annealing till 580°C and 520°C respectively. The decreasing of preepitaxial annealing temperature from 600°C to 450°C – 500°C have no influence on the structural quality of MCT layers.

“MCT-32” crystal has been developed. It consists of 32×32 photosensitive cells. Each cell includes MCT photodiode and n-MOS transistor. The size of the single cell is 150×150 µm². Multiplexer contains test electronic components for the process checking being able. The size of the crystal is 7.1×7.8 mm². The crystal is assembled by the n-MOS technology with polysilicon gates and Al interconnections on Si(310) substrate. The developed multiplexers provide free access to the elements of photodetector array, high uniformity of photodiode bias and opportunity to operate with the dark and background high-degree currents. The selected photodiode connects to readout common bus. Photodiode bias is specified by external precision low-noise read-out circuit which averages and transforms photocurrent into output voltage. Multiplexer provides a read-out in the range of frequencies from 4 to 40 frames per second.

“MCT-32” multiplexer has been fabricated, and its characteristics have been measured. The technology of preepitaxial preparation which does not destroy multiplexer elements has been developed. MCT layers have been grown on a substrate with the multiplexer. The operations for the development of the monolithic infrared photodetector based on “MCT-32” multiplexer have been performed. These operations are listed further: 1) Annealing in inert atmosphere for obtaining the p-type conductivity; 2) Obtaining n-p junctions in the process of ion implantation of boron; 3) Selective etching of polycrystal; 4) Deposition of protective dielectric; 5) Formation interconnections between MCT photodiodes and multiplexer elements.

Measuring results of electrooptical parameters of monolithic photodetector are presented.
Effect of post-implantation anneal on the current-voltage characteristics of IR photodiodes based on p- Cd$_x$Hg$_{1-x}$Te

A.V. Vishnyakov, V.S. Varavin, M.O. Garifullin, A.V. Pridein, V.G. Remesnik, I.V. Sabinina, G.J. Sidorov

Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, pr. Ak. Lavrent’eva 13

Dark currents of IR photodiodes and doping profiles of n$^+$-n-p structures based on p-type Hg-vacancy-doped Cd$_{0.22}$Hg$_{0.78}$Te films grown by molecular-beam epitaxy on GaAs substrates were examined. The films contained variable-band-gap layers on their surface used to reduce surface recombination. The IR diodes were prepared by implantation of B$^+$ ions into the Cd$_{0.22}$Hg$_{0.78}$Te films. A differential Hall analysis showed that, following the ion implantation, there formed an n$^+$-n-p structure with n-layer whose thickness, 1 to 2 $\mu$m at ion doses (1-9)$\cdot10^{13}$ cm$^{-2}$, increased with increasing the ion dose. A post-implantation anneal at 120°C for 4 hours resulted in the formation of an extended n-layer with an electron concentration, uniform across the layer, matched to the level of background donors. Measurements of current-voltage characteristics of the diodes showed that the post-implantation anneal slightly increased the diffusion current component and reduced the tunnel current component, which lead to increased values of the differential resistance at reverse bias voltages. Numerical modeling of 3D distributions of charge-carrier concentration in annealed photodiodes was performed. Simulations were made using Sentaurus Synopsys TCAD. The formation of n$^+$-n-p junctions during anneals due to mercury outdiffusion from the implanted region was taken into account. The resulting doping profiles were used to calculate the dark current in the photodiodes. The tunnel currents were modeled taking into account a nonzero thickness $\Delta x$ of the layer near the n-p junction in which the Hg-vacancy concentration increased from zero to a peak value. The thickness $\Delta x$ was found to amount to 0.4-0.5 $\mu$m, showing no changes during the anneal. The thickness $\Delta x$ of 0.4-0.5 $\mu$m results in a tunnel current component being substantially smaller than that in abrupt p-n junctions. It follows from the simulated data that the high tunnel current experimentally observed in implanted diodes could result from an increased (in excess of $10^{15}$ cm$^{-3}$) donor concentration in the n$^-$-layer, which enhanced tunneling due to decreased thickness of the space charge region in the p-n junction, and also from a small (less than 3 $\mu$m) thickness of the n-layer. Since, according to differential Hall measurements, the charge-carrier concentration in the n$^-$-layer after implantation reached values of $3\cdot10^{15}$ cm$^{-3}$ and decreased to the background level in annealed samples, this could be a primary reason for the large value of the tunnel current in implanted samples and the lower value of this current in annealed diodes.

The simulation showed that, following the post-implantation anneal, the diffusion current in the samples could be increased up to 2 times as a result of increased volume of the n-layer. According to simulated data, an additional reason for the increased tunnel currents could be a built-in positive charge in the dielectric (~$10^{11}$ cm$^{-2}$), acting to increase the strength of the electric field near the surface.
INFLUENCE OF GERMANIUM ON HIGH TEMPERATURE ELECTRICAL CHARACTERISTICS OF CdTe

U.M. Pysklynets, I.V. Gorichok¹
Ivano-Frankivsk National Medical University, Halytska St. 2, Ivano-Frankivsk, 76000, Ukraine
pysklynets@pu.if.ua
¹Precarpathian National University, Shevchenko St. 57, Ivano-Frankivsk, 76025, Ukraine

The aim of this article was to conduct computer modeling of defected subsystem of CdTe:Ge crystals under high temperature annealing in cadmium vapor on basis of quasi-chemical approach with possibility of dopant Ge behavior in CdTe lattice analysis and agreement of experimental data with theoretical calculation. Three models were examined: isolated point defects GeCd, GeTe, associative centers (GeCdVcd) and model of point defects with restricted solubility of the dopant Ge [1]. It is achieved, that the model of point defects with restricted solubility of the dopant Ge gives satisfactory agreement with experiment in examined annealing temperature range $T = 800-1250$ K and cadmium vapor partial pressure $P_{Cd} = 10^2-10^4$ Pa, whereas calculation made only on basis of isolated point defects or associative centers does not give the same result.

When developing the model of point defects with restricted solubility of the dopant Ge it was taking into account that not all dopant atoms, contained into CdTe, are in solid solution, portion of them may be in the form of precipitates. An increase in temperature or a decrease in partial pressure of cadmium vapor results in dissolution of precipitates with subsequent transition of the dopant into solid solution.

Dependences of free carrier charge concentration, intrinsic and extrinsic point defects in CdTe:Ge crystals upon pressure and temperature have been calculated on basis of quasi-chemical equation of their formation. Partial coefficient of compensation have been calculated for identification of dominant defects under their broad spectrum realization. It has been established that within annealing temperature range $T = 800-1250$ K, and partial pressure of cadmium vapor $P_{Cd} = 10^2-10^3$ Pa, germanium is located mainly in cadmium sublattice, therefore free carrier charge concentration in crystal is controlled by extrinsic centers GeCd and native point defects. At increasing of $P_{Cd}$ content of germanium centers in tellurium sublattice increases.

Dependences of germanium solubility at different partial pressure of cadmium vapor upon temperature have been calculated. Germanium solubility in CdTe increases with the increase in annealing temperature. Within a certain annealing temperature interval, which width is a function of cadmium vapor partial pressure, the calculated values for germanium solubility are lower than experimental values of electron concentration that is caused by predominance of intrinsic point defects over extrinsic ones under above-mentioned conditions. At increasing $P_{Cd}$ this annealing temperature interval increases and germanium solubility decreases.

Equilibrium constant and enthalpy of quasi-chemical reaction that describes germanium transition from one to other sublattice of the main matrix have been determined.

The electron transport properties of thin films of sol–gel processed undoped and Al-doped zinc oxide nanoparticles with variable doping level were investigated. We provide estimates of the conductivity and the resulting charge carrier densities with respect to the doping level. The increase of electron density due to extrinsic doping was compared to the accumulation of charge carriers in field effect transistor structures. This allowed us to assess the scattering effects due to extrinsic doping on the electron mobility. The latter decreases with increasing doping density. In contrast, the accumulation leads to an increasing mobility. We conclude that the conductivity of sol–gel processed nanocrystalline ZnO:Al is governed by an interplay of the enhanced charge carrier density and the doping-induced charge carrier scattering effects./1/

To enable an ambipolar charge carrier transport, organic/inorganic bulk heterojunction systems can be useful. We studied nanocrystalline ZnO:Al, as an n-type semiconductor, and an organic semiconductor, the so called rr-poly(3-hexylthiophene), as a p-type counterpart. The p-type conjugated polymer was infiltrated in the inorganic porous structure. We show that by doping the zinc oxide nanoparticles as well as by tuning the morphology of the blend it is possible to adjust a balanced electron and hole mobility in the hybrid material, which is indispensable for the performance of an ambipolar transistor.

Our data will be discussed in terms of the charge transport in field effect transistors as well as the morphology of the thin films which was monitored via X-ray reflectance measurements.

/1/ M. Hammer et al., Nanotechnology 19, 485701 (2008)
Effects of thermal annealing on the structural, the optical, and the electronic properties of ZnO nanoparticles formed on Si substrates by using spin coating

Young Soo No¹, Dong Yeol Yun¹, Su Youn Kim¹, Dong Ick Son², and Tae Whan Kim¹,2,a)

¹Department of Electronics and Communications Engineering, Hanyang University, Seoul, 133-791, Korea
²Department of Information Display Engineering, Hanyang University, Seoul, 133-791, Korea

ZnO/Si heterostructures, which are fabricated by utilizing the combined advantages of the large excitonic binding energy of the ZnO thin film and the cheap Si substrates, have been particularly interesting due to their promising applications for optoelectronic devices operating in the blue region of the spectrum. Because the structural, the optical, and the electronic properties of the ZnO/Si heterostructures are very important for fabricating electronic and optoelectronic devices, systematic studies of the physical properties of ZnO nanoparticles and ZnO/Si heterostructures are necessary for achieving high-performance devices. Even though some studies on the formation and the physical properties of ZnO nanoparticles via a simple method have been performed [1], systematic studies concerning the effects of thermal annealing on the structural and the optical properties of ZnO nanoparticles formed on the Si (100) substrates are very important for enhancing the efficiency of optoelectronic devices based on ZnO nanoparticles.

This paper presents data for the effects of thermal annealing on the structural, the optical, and the electronic properties of ZnO nanoparticles formed on p-Si (100) substrates by using a spin-coating and thermal-treatment method. Atomic force microscopy images showed that the size of ZnO nanoparticles formed on Si substrates by using spin coating and thermal annealing increased with increasing annealing temperature. X-ray diffraction patterns showed that the ZnO nanoparticles formed on Si (100) substrates had a c-axis preferential orientation in the [0001] crystal direction and that the (0002) peak intensity corresponding to the ZnO nanoparticles increased with an increase in annealing temperature up to 700°C, indicative of the improvement of the crystallinity of the ZnO nanoparticles. The photoluminescence spectra at 13 K for ZnO nanoparticles formed on the Si substrates showed that the strong exciton peak related to the near-band-edge emission was shifted to lower energy with increasing annealing temperature resulting from the increase in the size of the ZnO nanoparticles. The X-ray photoelectron spectroscopy spectra showed that the peak positions corresponding to the O 1s and the Zn 2p slightly shifted after thermal treatment. These results can help improve understanding of the effects of thermal annealing on the structural, the optical, and the electronic properties of ZnO thin films grown on p-Si (100) substrates.

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Reference

a)Corresponding author E-mail: twk@hanyang.ac.kr
Ab initio calculation and Curie temperature of acceptor and donor defects in (Ga,Fe)N and (Zn,Mn)O


1 Laboratoire de Magnétisme et de Physique des Hautes Energies Département de physique, B.P. 1014, Faculté des sciences, Rabat, Morocco.
2 Laboratoire de Physique des Hautes Energies Département de physique, B.P. 1014, Faculté des sciences, Rabat, Morocco.
3 The Institute for Nanomaterials and Nanotechnology, INANOTECH, Rabat, Morocco.
4 Hassan II Academy of Sciences and Technology, Rabat, Morocco.
5 Institut Néel, CNRS-UJF, B.P. 166, 38042 Grenoble Cedex, France.

In order to understand and to explain the half-metallicity and ferromagnetism stability, observed in Mn-doped ZnO and Fe-doped GaN with acceptor defects like Zn vacancies in ZnO [1,2] and Ga vacancies in GaN [3], the energy stability is studied using the Korringa-Kohn-Rostoker (KKR) method combined with the coherent potential approximation (CPA) [4]. We calculated the electronic structure and magnetic properties of Mn-doped ZnO and Fe-doped GaN in the presence of acceptor and donor vacancy defects sites. The mechanism of exchange interaction between magnetic ions with acceptors and donors defects is also investigated. Furthermore, comparison between the electronic structure of the substitutional and interstitial defect is given for co-doping method. The Curie temperature, $T_c$, is evaluated by using effective field approximation [5]. Computed by ab-initio calculations, we calculated magnetisation versus external magnetic field $M-H$ curve and saturation moment of p-type Ga$_{0.95}$Fe$_{0.05}$N and p-type Zn$_{0.9}$Mn$_{0.1}$O. Hydrogenation effect on magnetization and stability is also investigated with and without defects. The contribution of the hyperfine interaction for the disordered alloy systems is calculated. Finally, we propose a model which describes the origin of strong ferromagnetism stability observed in p-type Ga$_{0.95}$Fe$_{0.05}$N and p-type Zn$_{0.9}$Mn$_{0.1}$O by vacancy defects sites.

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