12\textsuperscript{TH} INTERNATIONAL CONFERENCE
ON II-VI COMPOUNDS
Warsaw, Poland
September 12 – 16, 2005

PROGRAM
&
ABSTRACTS

FACULTY OF PHYSICS
Warsaw University

INSTITUTE OF PHYSICS
Polish Academy of Sciences
CONFERENCE ORGANIZED UNDER AUSPICES AND SPONSORED BY:

COMEF

APARATURA NAUKOWO-BADAJCZA

European Office of Aerospace Research and Development

UPAP

International Union of Pure and Applied Physics

Office of Naval Research Global

PAN

Polish Academy of Sciences

PROM

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RIBER

Products and Services for the Compound Semiconductor Industry

Warsaw University

The President of the City of Warsaw

Conference co-organized by the Committee on Physics of the Polish Academy of Sciences
The 12th International Conference on II-VI Compounds will be jointly organized by the Faculty of Physics of the Warsaw University and the Institute of Physics of the Polish Academy of Sciences and will be held at Warsaw University on September 12-16, 2005. The Conference will be a continuation of a successful series of topical, truly international conferences which started in Durham (UK) in 1983 and through two decades of serving the semiconductor physics community were organized in various European countries as well as in U.S. and Japan. The main goals of this series of conferences are to provide a well organized international forum to review and stimulate the progress in basic and applied research on II-VI compounds, to facilitate the exchange of new ideas and to establish new scientific contacts and international consortia aimed at solving outstanding basic and applied problems. These conferences have also served educational purposes by attracting PhD students from various countries.

II-VI semiconductors provide a variety of unique optical, electrical, and magnetic properties. The conference will cover all aspects of basic and applied research on wide- and narrow-gap II-VI compounds and their alloys, including diluted magnetic semiconductors. Special emphasis will be given to various low dimensional quantum structures and new technological and application concepts (e.g., spintronics, ultrafast magneto-optical phenomena, quantum dots, infrared and visible range detectors, light emitting structures, and new materials for radiation detection).

The Conference will be conducted in accordance with IUPAP principles as stated in the ICSU-Document "Universality of Science" (sixth edition, 1989) regarding the free circulation of scientists for international purposes. In particular, no bona fide scientist will be excluded from participation on the grounds of national origin, nationality, or political considerations unrelated to science.

TOPICS

- Growth and characterization
- Doping and defects
- Theory and band structure
- Optical and electrical properties
- Magnetism and spintronics
- Wide bandgap materials
- Infrared, visible and radiation detectors
- ZnO-based materials and structures
- Quantum dots and nanocrystals
- II-VI organic biomaterials
- Hybrid structures
- New devices
SCIENTIFIC PROGRAM

Monday, September 12th, 2005

8:50– 09:00 Opening
Chair: C. Klingshirn

09:00 – 09:45 R. R. Gał ˛azka — II-VI compounds — Polish perspective
(Mon-I-1)

09:45 – 10:30 F. Henneberger — Optical quantum control using II-VI quantum dots
(Mon-I-2)

10:30 – 11:00 COFFEE BREAK
Chair: J. K. Furdyna

11:00 – 11:45 K. Ando, H. Saito — Ferromagnetism in (Zn,Cr)Te
(Mon-I-3)

11:45 – 12:30 L. Besombes, Y. Leger, L. Maingault, D. Ferrand, J. Cibert, H. Mariette —
Magnetic properties of a single magnetic atom embedded in a quantum dot
(Mon-I-4)

12:30 – 14:00 LUNCH BREAK
Chair: T. W. Kang

14:00 – 14:15 F. Perez, B. Jusserand, G. Karczewski — Spin density wave and single
quasiparticle excitations of the spin polarized two-dimensional electron gas
(Mon-O-1)

14:15 – 14:30 E. A. Zhukov, D. R. Yakovlev, M. Bayer, G. Karczewski, T. Wojtowicz, J. Kossut —
Spin coherence of two-dimensional electron gas induced via trion
formation in CdTe//CdMgTe quantum wells
(Mon-O-2)

14:30 – 14:45 M. Goryca, D. Ferrand, P. Kossacki, M. Nawrocki, W. Pacuski, W. Maślana,
S. Tatarenko, J. Cibert — Dynamics of magnetization relaxation in (Cd,Mn)Te
quantum wells
(Mon-O-3)

14:45 – 15:00 R. Andre, I. C. Robin, A. Balocchi, S. Carayon, S. Moehl, J. M. Gerard —
Purcell effect on CdSe//ZnSe quantum dots in pillar microcavities
(Mon-O-4)

15:00 – 15:15 BREAK
Chair: D. Hommel

Becker, H. Buhmann, L. W. Molenkamp — Direct observation of geometric
phases in HgTe ring structures
(Mon-O-5)

Determination of the number of Mn ions inside CdMnTe self assembled
quantum dots
(Mon-O-6)

15:45 – 16:00 L. Chen, P. J. Klar, W. Heimbrodt, T. Kurz, H.-A. Krug von Nidda, A. Loidl,
Kouzema, M. Froba — (II,Mn)VI nanostructures in mesoporous silica - from
powder samples to thin films
(Mon-O-7)

16:00 – 16:15 J. Liu, H. Buhmann, E. G. Novik, Y. S. Gui, V. Hock, C. R. Becker, L. W.
Molenkamp — Enhanced exchange interaction in magnetic
HgMnTe-quantum well structures
(Mon-O-8)

16:15 – 17:00 COFFEE BREAK

17:00 – 19:00 POSTER SESSION 1
<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Speaker(s)</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>09:00 – 09:45</td>
<td>(Tue-I-1)</td>
<td>J. Kasprzak, M. Richard, R. Andre, R. Romestain, Le Si Dang, G. Malpuech, A. Kavokin</td>
<td>Evidence for Bose condensation of microcavity polaritons</td>
</tr>
<tr>
<td>09:45 – 10:30</td>
<td>(Tue-I-2)</td>
<td>Gyu-Chul Yi</td>
<td>ZnO nanorod heterostructures and nanodevices</td>
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<tr>
<td>10:30 – 11:00</td>
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<td>COFFEE BREAK</td>
</tr>
<tr>
<td>11:00 – 11:45</td>
<td>(Tue-I-3)</td>
<td>R.J. Warburton</td>
<td>Excitons in CdSe/ZnSe quantum dots and exciton-photon coupling in ZnCdSe/ZnSe quantum wells</td>
</tr>
<tr>
<td>11:45 – 12:30</td>
<td>(Tue-I-4)</td>
<td>G. Karczewski</td>
<td>CdTe-CdMnTe quantum dots</td>
</tr>
<tr>
<td>12:30 – 14:00</td>
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<td></td>
<td>LUNCH BREAK</td>
</tr>
<tr>
<td>14:00 – 14:15</td>
<td>(Tue-O-1)</td>
<td>N. Le Thomas, O. Schops, M.V. Artemyev, U. Woggon</td>
<td>Optical Spectroscopy of Single CdSe Nanorods</td>
</tr>
<tr>
<td>14:15 – 14:30</td>
<td>(Tue-O-2)</td>
<td>A. El Shaer, A. Bakin, A. Che Mofor, A. Waag, M. Heuken, J. Blasing, A. Krost, J. Stoimenos</td>
<td>CBE growth of high-quality ZnO epitaxial layers and heterostructures</td>
</tr>
<tr>
<td>14:30 – 14:45</td>
<td>(Tue-O-3)</td>
<td>T. Moriyama, S. Fujita</td>
<td>Epitaxial growth of non-polar ZnO by MOVPE</td>
</tr>
<tr>
<td>14:45 – 15:00</td>
<td>(Tue-O-4)</td>
<td>C. Morhain, X. Tang, B. Lo, M. Laugt, P. Vennegues, B. Vinter, J-M. Chauveau, M. Teisseire-Doninelli, C. Deparis, G. Neu</td>
<td>Large built-in electric fields in c-oriented wurtzite ZnO/ZnMgO quantum well heterostructures</td>
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<tr>
<td>15:00 – 15:15</td>
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<td>BREAK</td>
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<tr>
<td>15:30 – 15:45</td>
<td>(Tue-O-6)</td>
<td>H. Z. Xu, K. Ohtani, M.Yamao, H. Ohno</td>
<td>Control of ZnO/Al₂O₃ (11-20) surface morphologies using plasma assisted molecular beam epitaxy</td>
</tr>
<tr>
<td>15:45 – 16:00</td>
<td>(Tue-O-7)</td>
<td>F. Tuomisto, K. Saarinen, D. C. Look, A. Mycielski, K. Grasza, G. Cantwell, G. M. Renlund, R. H. Burgener II</td>
<td>Observation of Zn vacancies in ZnO</td>
</tr>
<tr>
<td>16:00 – 16:15</td>
<td>(Tue-O-8)</td>
<td>F. Bertram, S. Giemsch, J. Christen, A. Dadgar, A. Krost, M. Wagner, A. Hoffmann</td>
<td>Direct Observation of As-related (e,A⁺)-emission in ZnO</td>
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<tr>
<td>16:15 – 17:00</td>
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<td>COFFEE BREAK</td>
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<tr>
<td>17:00 – 19:00</td>
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<td>POSTER SESSION 2</td>
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</tbody>
</table>
Wednesday, September 14th, 2005

Chair: U. Woggon

09:00 – 09:45
(Sec-I-1)


09:45 – 10:30
(Sec-I-2)

J. Gaj — Optical probing of interactions in II-VI semiconductor structures

10:30 – 11:00
COFFEE BREAK

Chair: J.J. Davies

11:00 – 11:45
(Sec-I-3)

S-J. Park — Phosphorous-doped p-type ZnO and ZnO LED

11:45 – 12:30
(Sec-I-4)


Thursday, September 15th, 2005

Chair: D. Wolverson

09:00 – 09:45
(Thu-I-1)

S.H. Lee, M. Dobrowolska, J.K. Furdyna — Inter-dot spin exchange interaction in coupled II-VI semiconductor quantum dots

09:45 – 10:30
(Thu-I-2)

A. Efros — Semiconductor nanorod optical properties

10:30 – 11:00
COFFEE BREAK

Chair: Le Si Dang

11:00 – 11:45
(Thu-I-3)

R. Akimoto, B.S. Li, K. Akita, T. Hasama — Ultrafast intersubband optical switching in II-VI-based quantum well for optical fiber communications

11:45 – 12:30
(Thu-I-4)

T. Voss, H.G. Breunig, I. Kudyk, L. Wischmeier, I. Ruckmann, J. Gutowski — Coherent control of excitonic transitions in II-VI quantum wells

12:30 – 14:00
LUNCH BREAK

Chair: S.V. Ivanov

14:00 – 14:15
(Thu-O-1)


14:15 – 14:30
(Thu-O-2)


14:30 – 14:45
(Thu-O-3)


14:45 – 15:00
(Thu-O-4)


15:00 – 15:15
BREAK
15:15 – 15:30 
(Thu-O-5) 
K. Miki, T. Abe, J. Naruse, K. Ikumi, T. Yamaguchi, H. Kasada, K. Ando — **High sensitive ultraviolet pin photodiodes of ZnSSe n^+-i-p structure // p^+-GaAs substrate grown by MBE**

15:30 – 15:45 
(Thu-O-6) 

15:45 – 16:00 
(Thu-O-7) 
I. Nomura, A. Manoshiro, A. Kikuchi, K. Kishino — **Yellow-green lasing operations of ZnCdTe/MgZnSeTe laser diodes on ZnTe substrates**

16:00 – 16:15 
(Thu-O-8) 

16:15 – 17:00 
__________________________ COFFEE BREAK __________________________

17:00 – 19:00 
__________________________ POSTER SESSION 3 __________________________

**Friday, September 16th, 2005**

09:00 – 09:45 
(Fri-I-1) 
M. Kawasaki — **Converting ZnO into p-type**

09:45 – 10:30 
(Fri-I-2) 

10:30 – 11:00 
__________________________ COFFEE BREAK __________________________

11:00 – 11:45 
(Fri-I-3) 
A.A. Toropov — **III-V//II-VI heterovalent double quantum wells**

11:45 – 12:30 
(Fri-I-4) 
P. Kossacki — **Spectroscopic studies of ferromagnetic (Cd,Mn)Te quantum wells**

12:30 
Closing
### CONFERENCE SCHEDULE

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<thead>
<tr>
<th>Time</th>
<th>Sunday September 11</th>
<th>Monday September 12</th>
<th>Tuesday September 13</th>
<th>Wednesday September 14</th>
<th>Thursday September 15</th>
<th>Friday September 16</th>
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<tbody>
<tr>
<td>08:00 – 09:00</td>
<td>Registration</td>
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<tr>
<td>08:50 – 09:00</td>
<td>Opening</td>
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<tr>
<td>09:00 – 09:45</td>
<td>R.R. Gałązka</td>
<td>J. Kasprzak</td>
<td>S.C. Enwin</td>
<td>S. Lee</td>
<td>M. Kawasaki</td>
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<tr>
<td>09:45 – 10:30</td>
<td>F. Henneberger</td>
<td>G.-C. Yi</td>
<td>J.A. Gaj</td>
<td>A. Efros</td>
<td>R. Grill</td>
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<td>10:30 – 11:00</td>
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<tr>
<td>11:00 – 11:45</td>
<td>K. Ando</td>
<td>R.J. Warburton</td>
<td>S.-J. Park</td>
<td>R. Akimoto</td>
<td>A.A. Toropov</td>
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<tr>
<td>11:45 – 12:30</td>
<td>L. Besombes</td>
<td>G. Karczewski</td>
<td>M. Adachi</td>
<td>T. Voss</td>
<td>P. Kossacki</td>
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<tr>
<td>12:30 – 14:00</td>
<td>Lunch</td>
<td>Lunch</td>
<td>Lunch</td>
<td>Lunch</td>
<td>Closing</td>
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<tr>
<td>14:00 – 14:15</td>
<td>F. Perez</td>
<td>N. Le Thomas</td>
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<td>J.-H. Lim</td>
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<td>14:15 – 14:30</td>
<td>E.A. Zhukov</td>
<td>A. El Shaer</td>
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<td>S. Moel</td>
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<tr>
<td>14:30 – 14:45</td>
<td>M. Goryca</td>
<td>T. Moriyama</td>
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<td>R. Hauschild</td>
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<tr>
<td>14:45 – 15:00</td>
<td>R. André</td>
<td>C. Morhain</td>
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<td>Y. Imanaka</td>
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<td>15:00 – 15:15</td>
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<td>15:15 – 15:30</td>
<td>M. König</td>
<td>E. Kamińska</td>
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<td>15:30 – 15:45</td>
<td>P. Wojnar</td>
<td>H. Z. Xu</td>
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<td>15:45 – 16:00</td>
<td>L. Chen</td>
<td>F. Tuomisto</td>
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<td>16:00 – 16:15</td>
<td>Liu</td>
<td>F. Bertram</td>
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<tr>
<td>16:15 – 17:00</td>
<td>Coffee</td>
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<tr>
<td>17:00 – 19:00</td>
<td>Poster session 1</td>
<td>Poster session 2</td>
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<tr>
<td>18:00 – 21:00</td>
<td>Welcome party</td>
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<td>Conference banquet</td>
<td>20:00</td>
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<tr>
<td>Reception</td>
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</table>

Registration open: on Sunday, September 11th, 2005 from 14:00 till 21:00 and through all the conference days from 8:00 till 19:00.

Exhibition: Monday/Tuesday 9:00 – 18:00. The sessions as well as the exhibition will be held in the conference center at Warsaw University, Krakowskie Przedmieście 26/28, Warsaw. Conference banquet: restaurant "Biblioteka", Dobra 56/66, Warsaw.
TRAVEL/LOCAL INFORMATION
From Warsaw F. Chopin International Airport (www.polish-airports.com) the conference site as well as Sofitel Victoria, Harenda, and Ibis Stare Miasto hotels can be conveniently reached by public transportation system using bus line No. 175. The bus No. 175 departs from the stop right in front of the arrival hall of the airport (direction "Dw. Gdański"). The airport is located about 10 km south from the center of the city. Bus trip takes about 25 min. to the city center and about 30 – 35 min. to the conference site located at Warsaw University, 26/28 Krakowskie Przedmieście Street (bus stop "Uniwersytet", also for Harenda and Victoria hotels). For Ibis hotel – bus stop "Muranowska" (about 35-40 min. from the airport).

The conference registration will be open since Sunday, September 11th, from 14:00 till 21:00 and through all the conference days from 8:00 till 19:00.

The bus No. 175 also stops in front of the Warsaw Central Railway Station (www.pkp.pl) where all the international trains arrive (south exit, bus stop across Jerozolimskie Street in front of the Marriott Hotel/LOT Airline Office).

The single fare ticket valid for all bus, tram, and subway day lines is 2.40 PLN and can be purchased in all newspaper kiosks. The ticket can also be obtained from bus driver (cash only, additional administrative charge of 0.60 PLN). Variety of other special tickets (e.g., 24 hours, 3-day, one-week) is also available. For details on public transportation system, tariffs, and regulations see Warsaw Transportation Authority (ZTM) web page www.ztm.waw.pl.

Further information concerning the City of Warsaw, in particular the map of Warsaw, you can find at the web-pages: www.e-warsaw.pl or www.warsawtour.pl.

The TAXI service is available at the airport (follow the TAXI sign outside the airport building) and the Central Railway Station. To avoid overcharging, we advice you to use one of the following Taxi companies operating in Warsaw: MPT Taxi (phone number 9191), Super Taxi (9622), Sawa Taxi (644 4444) or Taxi Merc (677 7777). For the cost estimate 2 PLN/1 kilometer fare can be used. For ordering taxi by mobile phone dial 48-22 before the number given above.

The time zone of Poland is Central European Time (one hour ahead of GMT).

The Polish currency is zloty (PLN): 1 PLN=100 gr (grosz). The current exchange rate to Euro is: 1 EUR ≃ 4 PLN. One can easily change major foreign currencies to zloty in banks and many exchange offices (Kantor). All major credit cards can be used in cash machines of various banks as well as in hotels and many restaurants and shops.

The electricity supply in Poland is 230 V (50 Hz).

The weather in Warsaw in September is usually pleasant with the daytime temperature in the range 15 – 20 degrees Centigrade. For detailed weather forecast you can check, e.g. the web site: http://weather.icm.edu.pl/index2eng.php.

LUNCHES
Lunches are not included in the conference fee and are available at University campus, typically for the prize below 20 złoty (i.e. 5 EUR). Variety of restaurants serving lunches can be found at nearby Krakowskie Przedmieście and Nowy Świat Streets (see attached maps).
SOCIAL EVENTS

Welcome party on Sunday, September 11th, 2005 from 18:00 till 21:00 in the Conference Center (first floor) — free of charge to all registered participants and accompanying persons.

President of the City of Warsaw reception on Monday, September 12th, 2005, City Hall, Bankowy Square 3/5, from 19:45 — free of charge (busses depart from the Conference Center at 19:15)

Conference excursion on Wednesday, September 14th, 2005 — free of charge. Busses depart from the parking lot nearby Conference Center at 14:00. Excursion program includes, in particular, a visit to Łazienki Palace and park with piano and violin concert.

Conference dinner in restaurant "Biblioteka" in the new University Library at 56/66 Dobra Street (see attached map) — banquet ticket: 50 EUR.

CONFERENCE EXHIBITION

A vendors exhibition will be held on Monday and Tuesday, September 12–13th, 2005 as an integral part of the conference. The exhibition room is located on the first floor of the Conference Center nearby poster session and coffee breaks area (see the plan of the floor). For the complete list of vendors see the attached leaflet.

FEE

<table>
<thead>
<tr>
<th>Conference fee:</th>
<th>before July 31, 2005</th>
<th>after July 31, 2005</th>
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</thead>
<tbody>
<tr>
<td>Regular participants:</td>
<td>395 EUR</td>
<td>410 EUR</td>
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<tr>
<td>Students:</td>
<td>265 EUR</td>
<td>280 EUR</td>
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<tr>
<td>Accompanying person:</td>
<td>30 EUR</td>
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<tr>
<td>One-day participation fee:</td>
<td>50 EUR</td>
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<tr>
<td>Conference dinner:</td>
<td>50 EUR</td>
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</tbody>
</table>

Regular participants and students are entitled to admission to all conference sessions, coffee breaks, welcome party, conference excursion and (excluding students) the volume of conference proceedings published as a special issue of *physica status solidi* c.

For accompanying persons the conference fee covers: welcome party, conference excursion and coffee breaks.

One-day participation fee covers: admission to all conference sessions on a given day and coffee breaks. It, however, does not entitle to the submission of manuscript to the conference proceedings.

Refunds: No refunds of conference fee are possible after August 15th 2005.

ACCOMODATION Blocks of rooms have been reserved for conference participants at special discount rates (from about 30 to 122 EUR) at Sofitel Victoria, Harenda, Ibis Stare Miasto, Atos and MDM hotels. For details see conference web page.

PRESENTATIONS

Poster presentation: Board dimensions: height 155cm x width 115cm.

Oral Presentations: Time allotted for oral presentations is:

- for invited talks: 45 min. (including 5-10 min. for discussion)
- for contributed talks: 15 min. (including 3 min. for discussion).
For ORAL presentations overhead and PC video projector will be available. Please, prepare your computer presentation in format PowerPoint or PDF (CD-ROM or USB (pen drive)).

We strongly suggest that (with the help of our staff responsible for organization of oral sessions) you check your computer presentation a day before your scheduled talk and transfer the presentation to our host computer.

CONTACT
Prof. Tomasz Story
Institute of Physics, Polish Academy of Sciences
Al. Lotników 32/46, PL 02-668 Warsaw, POLAND
phone: (48-22) 843 66 01 x. 3325, fax: (48-22) 843 09 26
e-mail: II-VI-2005@ifpan.edu.pl

PROCEEDINGS
The proceedings of the conference will be published as a special issue of physica status solidi (c).

Manuscript submission, formats, and length restrictions
For general guidelines please see: http://www3.interscience.wiley.com/cgi-bin/jabout/102519628/instruct-c.html

Manuscripts should be delivered on the first day of the Conference in three copies and accompanied by a disk (DOS format floppy or CD-ROM) containing text and figures. Please make sure that disk files and hardcopies are identical. Do not send your manuscript to the Editorial Office of physica status solidi.

The length of the paper must not exceed 4 printed journal pages for contributed oral or poster presentations and 6 printed journal pages for invited papers.

Prepare your manuscript using Microsoft Word (preferred) or LaTeX. It is essential that you use the provided template and style files, respectively, to enable an easy length estimate of your article. All textual material (incl. tables, captions, etc.) should be in a single file.

Microsoft Word: Please use the document template package http://www.ifpan.edu.pl/II-VI-2005/pssc_word.zip an example is the file instruct.doc which contains extended author instructions in the style of a manuscript.

LaTeX 2e: The style file package http://www.ifpan.edu.pl/II-VI-2005/pssc_latex.zip is available (with instruct.tex as sample file).

In addition to the Word or LaTeX + dvi file (and separate figures, if any), please accompany your submission by one printable file (PDF or Postscript), using only standard fonts Times New Roman and Symbol; some fonts such as Asian or Russian character fonts may cause problems) of your entire manuscript including the text as well as all tables and figures.

Review of the papers will be performed during the Conference.
For publication in physica status solidi (c), production will be done using your publication-ready manuscript file. You will not receive page proofs for correction.
1. Main Gate
2. Conference Center (arrow points the main entrance) – Old Library
3. Kazimierzowski Palace (availability of lunches)
4. Audytorium Maximum (optional eatery)
5. New Library (restaurant "Biblioteka")
6. "Hareda" hotel
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II-VI Compounds – Polish Perspective

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The purpose of the lecture is to review the main achievements of the investigations of II-VI compounds and point out Polish contribution to this part of solid state physics. Because the Polish physicists were particularly active in the area of narrow gap semiconductors as well as in the area of semimagnetic semiconductors producing several pioneering papers in this field, special attention will be paid to narrow gap, mercury based semiconductor alloys, and to the II-VI semimagnetic semiconductors, both narrow and wide gap. Some problems connected with material processing, the most sparking experimental results as well as theoretical ideas will be presented. Because the history of II-VI compounds lasts for many decades (also in Poland) only selected achievements will be reviewed. The lecture will concentrate mostly on the properties of bulk crystals, low dimensional structures and other current and hot problems of II-VI compounds will be only mentioned.
Optical Quantum Control Using II-VI Quantum Dots

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The control of quantum states is a key prerequisite in quantum information processing. Owing to the large Coulomb energies, the exciton-biexciton system in II-VI quantum dots is well suited to study and to implement optical concepts for this control.

The exciton, split by anisotropic electron-hole exchange in a fine structure doublet, enables to prepare a quantum bit by proper photon polarization. Distinct quantum beats in the exciton emission confirm indeed the formation a coherent superposition. The quantum coherence times are longer than the radiative life-time of the exciton.

Entangled states that have no classical counterpart are of particular importance in quantum information. The biexciton is an entangled state of two excitons and exhibits a binding energy as large as 20 meV in II-VI quantum dots. Direct coherent control of the biexciton is achieved by using resonant two-photon excitation with a pair of phase-correlated ultra-short pulses. On the other hand, by stimulating the biexciton-exciton transition with a subsequent pulse, the biexciton can be disentangled in a controlled way. Applications in quantum logics as well as how this allows to trigger single-photon as well as photon-pair emission are discussed.

Charged quantum dots enable the control of the carrier spin. The potential of the trion state, representing the fundamental optical excitation in these dots, is investigated. Novel optical and magnetic anisotropies are observed that are crucial for the spin manipulation. The low-temperature spin relaxation times are on the 10 ns-time scale.
Ferromagnetism in (Zn,Cr)Te

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After discoveries of ferromagnetism in (In,Mn)As and (Ga,Mn)As [1], ferromagnetic diluted magnetic semiconductors (DMSs) have been attracting much attention. A theoretical prediction [2] of high Curie temperature (Tc) in DMSs based on wide-gap semiconductors have triggered enthusiastic quests for high-Tc DMSs. A variety of "high-Tc DMSs" have been reported up to now, but the origin of the observed ferromagnetism is still controversial both theoretically [3] and experimentally [4]. In most of the reports, the ferromagnetic DMSs have been claimed based on SQUID and XRD data. However, we have shown that SQUID is too sensitive and XRD is too insensitive for that purpose [4]. For the essential confirmation of the syntheses of DMSs, we must prove the spin-dependent splittings of the band structures of the host semiconductors. Indeed, the detection of these band splittings by means of the magneto-optical spectroscopy has been the main topic in the field of traditional II-VI DMSs. We will show how the ferromagnetism observed in Zn$_{1-x}$Cr$_x$Te can be considered to be intrinsic [5].

Magnetic circular dichroism (MCD) spectra of ZnTe films implanted with various transition metal ions showed a peculiar character of ZnTe:Cr. The intensity of its MCD structure at the band gap energy $E_0$ of ZnTe, which reflects the spin-dependent splitting of the conduction and valence bands, is about one order larger than those observed for ZnTe:Mn, ZnTe:Fe, and ZnTe:Co.

SQUID data of Zn$_{1-x}$Cr$_x$Te films grown by MBE showed ferromagnetism. Tc was determined to be 300 K for a x=0.2 sample by the Arrot-plot analyses of the magnetic data. In order to know if the observed ferromagnetism really originates from ZnTe based DMS, we did detailed MCD spectral analyses. The MCD intensity of Zn$_{1-x}$Cr$_x$Te around $E_0$ was much enhanced as compared with that of ZnTe. However, it was not easy to make clear correspondences of the observed MCD structures around $E_0$ to the ZnTe band structure since its spectral shape was anomalously broadened. Such anomalously broadened MCD structure around $E_0$ was not observed in ordinary DMSs such as (Zn,Mn)Te. But it should be noted that a prototype ferromagnetic DMS (Ga,Mn)As shows the same anomaly. In contrast to the MCD anomaly around $E_0$, the MCD structures of Zn$_{1-x}$Cr$_x$Te at the L critical points clearly showed the existence of the spin-dependent band splittings. This is an unambiguous verification of a fact that Zn$_{1-x}$Cr$_x$Te is a DMS with the s,p-d exchange interactions. Furthermore, we found that the temperature and magnetic field dependences of the intensity of the MCD structures at L, which reflect the DMS nature of Zn$_{1-x}$Cr$_x$Te, showed clear ferromagnetic behaviors. Tc estimated from the Arrot-plot analyses of the MCD intensity of Zn$_{1-x}$Cr$_x$Te coincided with Tc determined from the magnetic measurements. Thus the intrinsic nature of the ferromagnetism of Zn$_{1-x}$Cr$_x$Te DMS was experimentally proved unambiguously.

High Tc of Zn$_{1-x}$Cr$_x$Te is explained theoretically [6], but its interesting transport properties such as high resistivity have not been well understood yet [7].

Magnetic Properties of a Single Magnetic Atom Embedded in a Quantum Dot

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Several proposals for quantum information storage and processing using electron spins in quantum dots (QDs) have been put forward recently. Spin qubits are an attractive choice for the development of solid-state quantum information processing devices due to their long coherence time [1]. Developing such devices requires, however, the ability to detect and manipulate individual spins. Magnetic ion-doped QDs seem promising for the detection and manipulation of spins in the nanometer scale [2]. They have been proposed as single-spin filters or single-spin aligners in spintronics devices [3]. QDs based on II-VI semiconductor compounds offer the unique possibility of incorporating magnetic ions (Mn$^{2+}$) isoelectronically into the crystal matrix. This provides a way to study the interaction between a controlled number of injected carriers and the localized magnetic ions.

In this work we show how we can optically probe the magnetic state of a single Mn atom embedded in an individual QD. We use magneto-optic micro-spectroscopy to study the optical properties of individual Mn doped self-assembled CdTe/ZnTe QDs [4]. The fine structure of a confined exciton in the exchange field of a single Mn atom (S=5/2) is analyzed in detail. The exciton-Mn exchange interaction shifts the energy of the exciton depending on the Mn spin component and six emission lines are observed at zero magnetic field. It is then possible to probe the statistic spin state of the Mn atom through the emission intensities of the different discrete exciton levels. The Mn spin temperature depends on the lattice temperature but is also found to strongly depend on the density of photo-generated carriers.

Investigating both the biexciton and exciton transitions in the same Mn-doped QD we analyze the influence of the number of confined carriers on the spin splitting of the Mn atom. The injection of a second electron-hole pair cancels the exchange interaction with the magnetic atom and the Mn spin splitting is significantly reduced [5]. The biexciton level remains split by the perturbation of the carriers wave function induced by the interaction with the Mn atom. Magneto-optics measurements permit the determination of all the parameters controlling the interaction between the confined carriers and the magnetic atom. The effect of the position of the magnetic atom and the effect of the anisotropic shape of the QD have been analyzed. More generally, it follows from this study that the spin state of a single magnetic atom can be controlled by the injection of a discrete number of carriers in a single QD.

Spin Density Wave and Single Quasiparticle Excitations of the Spin Polarized Two-dimensional Electron Gas

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We present a new understanding of previous observations we did on two-dimensional electron gas confined in a CdMnTe/CdMgTe semimagnetic quantum well. Semimagnetic II-VI systems exhibit a giant Zeeman effect which provides the unique feature to significantly spin-polarize the high density (few $10^{11}$ cm$^{-2}$) electron gas with low magnetic field below orbital quantization and quantum Hall regime. This experimental system is a model object to study electronic properties of a two spin-subband electron gas. We did angle resolved Raman spectroscopy and measured magnetic and wavevector dispersions of the low energy excitations. Apart from the well-understood collective spin-flip mode [1], Raman crossed polarized spectra (see Fig. 1 and 2) exhibit a new excitation characterized by a broad line at higher energy than the spin flip mode, with positive magnetic and wavevector dispersion. This line is attributed to single quasiparticle flipping their spin. Its energy is well above the energy of the collective spin flip mode which at vanishing wavevector coincides with the Baro Zeeman energy (Larmor’s theorem). The origin of this mode wasn’t understood [2] as a comparison with fermi-liquid theory gave no line attributed to single quasiparticle excitation. We show indeed that its observation is realized under specific resonance conditions.


Decoupled from spin-flip excitations (transverse excitations) a longitudinal spin density wave propagates through the intra-spin-subband single quasiparticle excitations continuum. This point prevents the wave to be a well defined collective mode. No line attributed to this excitation is found in the parallel Raman spectra, but its existence strongly modifies the shape of the broad line attributed to both minority and majority spin conserving single quasiparticle excitations. Excitations of the majority spin subband are suppressed.
Spin Coherence of Two-Dimensional Electron Gas Induced via Trion Formation in CdTe/CdMgTe Quantum Wells

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Coherent spin beats of electrons have been studied by a picosecond pump&probe Kerr rotation in CdTe/(Cd,Mg)Te quantum wells with a diluted two-dimensional electron gas (2DEG). We suggest that formation of trion states, either by direct photoexcitation in the trion resonance or by binding photogenerated excitons, is the leading mechanism that provides spin coherence of a 2DEG. A long spin lifetime for resident electrons (up to 3 ns) has been measured.

CdTe/(Cd,Mg)Te heterostructures consists of 5 periods of a 12 nm or 8 nm quantum wells separated by 20 nm barriers. Concentration of 2DEG provided by the modulation doping of barriers was varied from $5 \times 10^9$ to $10^{11}$ cm$^{-2}$. Experiments have been performed in magnetic field (0 \textendash 7 T) applied perpendicular to the structure growth axis, i.e. in the Voigt geometry, for a temperature range 2 \textendash 150 K. Polarization induced in the electronic system by circular polarized pump pulses (duration 1 ps, repetition at 76 MHz) has been detected by means of the Kerr rotation of linearly polarized probe pulses. The decay of the beats shows two characteristic times. The fast component is about 20\textendash30 ps and the long component of 2\textendash3 ns. Their relative intensities depend on excitation energy, which was either resonant with trion or exciton ground state or detuned from these resonances, and on excitation density. Comparison with characteristic times of exciton radiative decay measured by means of a streak-camera allows us to assign the short decay component to spin beats of excitons. The beat component with decay of 2\textendash3 ns is due to the coherent precession of resident electrons from the 2DEG. The detected frequency of the spin beats corresponds to the Zeeman splitting of conducting electrons with g-factor of 1.626.

Only long-lived beats were observed under resonant excitation of trion state. Due to the singlet spin structure of the trion ground state the trion itself can not contribute to the spin beats. In this case the spin coherence is induced and held by the 2DEG, when part of its electrons with certain spin orientation is taken out for the trion formation.
Dynamics of Magnetization Relaxation in (Cd,Mn)Te Quantum Wells

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Most of previous studies of the dynamics of magnetization relaxation in semimagnetic materials were done in an experimental set-up in which the sample was placed in a constant magnetic field and the evolution after a short heating pulse was analyzed. Such an approach is limited to quite large values of the magnetic field. Here we present a study of the magnetization relaxation after a short pulse of magnetic field. This experimental approach allows us to go down to very small magnetic field.

The quantum wells of (Cd,Mn)Te with (Cd,Mg,Zn)Te barriers were placed in an optical cryostat. Short pulses of magnetic field were produced with magnetic coil mounted at the surface of the sample and applied in the Faraday configuration. The small size of the coil (about 0.5 mm in diameter) assured short pulses of the magnetic field with rise and fall times of about 10 ns. The 2 A current produced a magnetic field of about 400 Oe. We analyzed the evolution in time of the giant Zeeman shift of the photoluminescence line during and after the pulse with resolution down to 10 ns. This shift reproduces the dynamics of the magnetization of the system of Mn ions in the (Cd,Mn)Te quantum well. Quantum wells with a Mn content from 0.2 % to 1.5 % were analyzed. The magnetization relaxation after the pulse was found to be faster than 40 ns and to depend on the Mn content, from 40 ns for 1.5 % Mn down to below 20 ns for 0.2 % Mn. Such a time scale is characteristic for the spin decoherence time $T_2$ in bulk (Cd,Mn)Te [1].

Applying an additional, constant magnetic field resulted in a dramatic increase of the magnetization relaxation time, up to 2 $\mu$s at 0.5 T. We attribute this to the contribution of the Zeeman interaction to the internal energy of the system.

\textsuperscript{1} D. Scalbert et.all, Sol. State Comm. 66 (1988) 571
Purcell Effect on CdSe/ZnSe Quantum Dots in Pillar Microcavities

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Single CdSe/ZnSe QDs are very interesting candidates as single photon emitters [1]. They provide blue-green photoluminescence (PL) and exhibit well separated multi-exciton lines. To develop single photon sources that can be used for quantum optics, one possibility is to have a single QD in resonance with a pillar microcavity mode [2]. First, the optical cavity can filter spectrally the emission from the fundamental exciton state after an excitation pulse and reject emission from multi-excitons to ensure single photon emission. Second, the Purcell effect enhances drastically the spontaneous emission into a given mode of the pillar microcavity and yields optimized single photon collection. Moreover the shortening of radiative lifetime preserves from dephasing or non-radiative decay of the PL. We report here the first observation of Purcell effect on II-VI QD with Purcell factors as high as 4.

The active layer was grown by molecular beam epitaxy on a GaAs substrate. It consists of a single layer of QDs sandwiched between two $\lambda/4$-ZnSe layers. To enclose the CdSe QDs into a hybrid microcavity we have developed TiO₂/SiO₂ Bragg reflectors. A mirror with 8.5 periods of $\lambda/4$ layers was deposited on top of the epitaxial layer. Then the substrate was selectively etched before deposition of a 4.5 periods second mirror. Micropillars were then etched by reactive ion etching and chemical etching to provide the lateral optical confinement. Optical characterizations demonstrating the Purcell effect were performed at 4K: variations of decay times from 317 ps to 77 ps have been measured (fig. 1). The maximum shortening, with respect to non-processed samples, is of a factor of 4. Moreover PL spectra at 100K, under high excitation density, allow us to identify the different optical modes thanks to the filtering effect on the broadband emission, typical under such conditions. The quality factor of the cavity is measured to be $Q = 270$. The PL decay time changes are explained by the calculated Purcell factors of the different pillar modes involved in the emission process.

Direct Observation of Geometric Phases in HgTe Ring Structures

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Since its prediction in the 1980s the concept of geometric phases has aroused much interest. Only a few years after the seminal paper by Berry \cite{berry1984} describing the geometric phase of a quantum system for an adiabatic parameter change, it was shown by Aharonov and Anandan \cite{aharonov1987}, that such a phase exists for the non-adiabatic case as well. Experimentally, direct evidence for the existence of a geometric phase has been given only for polarized neutrons \cite{bitter1987}.

In solid state physics the existence of a geometric phase was predicted for systems with strong spin-orbit coupling. The Aharonov-Bohm (AB) effect in such systems has been investigated intensively in order to reveal signatures of an additional geometric phase. So far only additional structures in the Fourier transform of the AB oscillations were found, which were taken as indirect evidence \cite{morpurgo2004}.

In this contribution we show by numerical calculations for a multichannel ring that a change in the spin-orbit coupling leads to significant phase shifts in the AB oscillations (top figure). Experimentally, we investigated the conductance of HgTe quantum well based ring structures, where the Rashba splitting can be tuned by a Schottky gate. The experimental observation (bottom figure) is in good qualitative agreement with theoretical predictions and therefore provides direct evidence of a geometric phase in a solid state system.

Determination of the Number of Mn ions Inside CdMnTe Self Assembled Quantum Dots

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We have grown CdMnTe diluted magnetic quantum dots (QDs) in ZnCdTe matrix, using the self assembly method. The composition of the ternary Zn0.8Cd0.2Te barrier was chosen in order to shift the energy of the excitonic emission from the QDs well below the strong luminescence due to intra-Mn emission. The quantum dots layer was formed from 6 monolayers of a CdTe that has larger lattice constant than ZnCdTe matrix. Mn ions were added only into two middle CdTe monolayers. Using such a growth procedure we achieved a large dilution of Mn ions in our CdMnTe quantum dots. Formation of the QDs was induced using the procedure applied by Tinjod et al [1] for pure CdTe QDs.

Photoluminescence (PL) and microphotoluminescence (µ-PL) measurements in a magnetic field in the Faraday geometry were performed. For excitation we used either UV lines or 514nm line of the Ar:ion laser (non-resonant, above the barrier excitation). Diameter of the excitation spot was about 0.1mm or 1µm in the case of PL or µ-PL experiments, respectively. The temperature was maintained at 1.6K or 8K.

Typically PL spectrum of our QDs layer shows very broad band from 1.72 eV to 1.95 eV. Its width is determined by inhomogeneity of the sizes and chemical compositions of the quantum dots. The band was nearly fully polarized already at 2 T, indicative of the exchange interaction of the excitons confined in the QDs with the Mn-ions.

µ-PL spectrum splits into a large number of lines with the spectral widths not exceeding 3 meV. These lines, attributed to individual diluted magnetic quantum dots, are relatively broad, what is caused by magnetic moment fluctuation inside the dot. We observed giant Zeeman splitting of the excitonic emission from individual diluted magnetic QDs. We found that there are only several nearly discrete values of the Zeeman splitting in our QDs-ensemble. We attribute this effect to a discrete, small number of Mn⁺⁺ ions incorporated in each dot. Depending on the energy (and, thus, on the size of a dot), it may contain from 7s (in larger dots) to 3 (in smaller ones) Mn ions.

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Recently, we demonstrated the possibility of synthesizing ordered arrays dilute magnetic (II,Mn)VI semiconductor nanostructures inside the channels of mesoporous silica host structures [1,2]. Here, we expand this procedure from mesoporous powders to thin mesoporous films. The diluted magnetic semiconductor Cd$_{1-x}$Mn$_x$S with $x$ up to 0.3 was synthesised within the pores of mesoporous thin film silica host structures by a wet impregnation technique from an aqueous solution of the respective metal acetates, followed by drying steps and a conversion to sulphides by thermal H$_2$S treatment. The presence of Cd$_{1-x}$Mn$_x$S nanoparticles inside the pores was proved by powder X-ray diffraction, infrared and Raman spectroscopy, and transmission electron microscopy. Photoluminescence excitation measurements clearly demonstrate the quantum size effect of the incorporated nanostructured guest species. Due to the quantum confinement of the excitons in the nanostructures an increase of the direct band gap with decreasing particle size as well as a stronger band gap bowing is observed. Electron-paramagnetic resonance (EPR) measurements on low $x$ samples are used to prove that Mn is incorporated on cation site of the II-VI host. The corresponding EPR spectra are typical for exchange-coupled Mn$^{2+}$ ions in (Cd,Mn) and (Zn,Mn) chalcogenide mixed crystals. The features consist of a sextet of sharp lines with a splitting of about 7 mT between neighboring lines, each line with a pair of satellites at lower magnetic field on a broad background. The whole spectrum is centered around a $g$-factor of $g = 2$. The sharp lines and their satellites correspond to the allowed and forbidden hyperfine transitions of the six Zeeman-split $m_S = -5/2, ..., +5/2$ levels of the $^4S_{3/2}$ (or $^6A_1$) ground state of the Mn$^{2+}$ 3d-electrons. Our measurements show that the quality of the nanoparticles incorporated into the mesoporous films is comparable to those inside the mesoporous powders. This presents an important step towards the technological use of these nanostructures.

Enhanced Exchange Interaction in Magnetic HgMnTe-Quantum Well Structures

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Magnetic two-dimensional electron gas (M2DEG) systems have become a very interesting material class for potential applications in spintronics. Important are parameters which characterize the d-d and the sp-d exchange interactions and hence lead to a strongly enhanced temperature and magnetic field dependent effective g-factor. In thin magnetic narrow gap materials such as HgMnTe quantum well (QW) structures, standard optical and magnetometer measurements fail to produce parameters such as the antiferromagnetic temperature $T_0$ and the effective spin $S_0$. An alternative method to determine these parameters is the analysis of the anomalous Shubnikov-de Haas (SdH) behavior [1]. The effective g-factor causes an oscillatory SdH amplitude with distinct nodes. The position of these nodes is a function of the total subband spin splitting $\delta$ and are influenced by temperature and the spin orbit coupling induced Rashba effect, which is strong in these narrow gap materials.

Here, we present an analysis of the temperature dependent SdH amplitudes of Hg$_{1-x}$Mn$_x$Te QW structures with $x = 1.5$ and 6.5% Mn. We used an 8x8 $k\cdot p$ band structure calculations [2] in order to obtain the modified Landau level fan chart. From a comparison of the density of states oscillations with the experimental SdH-oscillation, we were able to deduce the corresponding antiferromagnetic temperature $T_0$ and the effective spin $S_0$. We found that the exchange interactions are enhanced in these confined structures compared with equivalent bulk samples [1]. Moreover, for low Mn concentrations the effective spin is comparable with that of isolated Mn atoms, $S_0 = 5/2$, and remains constant for temperatures up to 10 K. However, the antiferromagnetic d-d exchange reduces the effective spin for samples with higher Mn content, but this value is not constant. It increases with increasing temperature. This observation indicates a weakening of the antiferromagnetic coupling of the localized moments which leads to an enhancement of the sp-d exchange interaction in the temperature range up to 10 K.

Defect-related Emission in CdS Films Grown Directly on Hydrogen-terminated Si(111) Substrates

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The defect-related emission due to lattice-mismatch, which is called Y-band in photoluminescence spectra, has frequently been observed in heteroepitaxial films of II-VI compounds with a zincblende structure such as CdTe/GaAs [1] and ZnTe/GaAs [2]. Up to now a similar emission band has not been reported in wurtzite-type II-VI compounds. Recently, we have reported the successful growth of wurtzite CdS films directly on hydrogen-terminated off-orientated Si(111) substrates without preheat treatment.[3] In these CdS film on off-orientated Si(111) substrate, a newly broad emission band at 2.45 eV, which is denoted “Y” in Fig. 1, can be observed in 100 meV below the band edge. The intensity of the new band disappears in a relatively low temperature (70 K) similar to that of the bound exciton, as can be seen in Fig. 1. In addition, the peak energy is unchanged even though the excitation intensity increases by two orders of magnitude, and the integrated intensity of Y emission increases super-linearly with the excitation power intensity as shown in Fig. 2. These behaviors on the newly emission band in the CdS films are evidently different from the donor acceptor pair emissions. However, it should be noted that the behaviors on the Y emission observed in the grown wurtzite CdS film are similar to those of the Y-band observed in II-VI semiconductors with a zincblende structure. To our knowledge, these are the first experimental evidences of the so-called Y-band in wurtzite II-VI compounds.

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Thermoelectric Properties of ZnTe, ZnSe and ZnS Single Crystals at Ultrahigh Pressure up to 20 GPa

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In the present work the thermoelectric power (Seebeck coefficient) $S$ and electrical resistance $R$ were investigated in ZnTe single crystals in pressure $P$ range of 0-20 GPa using the automated setup (Fig. 1). By the $R(P)$ dependencies the phase transitions in ZnTe $[1]$ (zinc blende $\rightarrow$ cinnabar $\rightarrow$ Cmcm) were observed. At the $S(P)$ dependencies of ZnTe the anomaly drops were observed both at increasing and at decreasing pressure circles. So, thermopower’s sign even changed during the return circle (Fig. 2). The observing anomalies are related by authors to a transition in an intermediate phase, probable with a NaCl lattice. A comparison with investigated earlier high-pressure thermopowers of other zinc chalcogenides (ZnSe, ZnS) $[2]$ was performed.

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Photoelectricals and Noises Processes in CdTe Crystals

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Cadmium telluride and its ternary alloy mercury cadmium telluride are mainly employed in the field of radiation detection, ranging from middle infrared to X-ray and further, up to γ-ray energies. Structural defects and residual impurities create deep levels in the band gap, which degrade the performance of the devices fabricated on the basis of these materials. Photoluminescence (PL), thermally stimulated current (TSC), deep level transient spectroscopy (DLTS), photoinduced current transient spectroscopy (PICTS) are widely used to study these defects, especially in the case of CdTe and CdZnTe. Noise measurements also enable to investigate deep recombination traps and determined their type (n or p). It is possible to obtain more realistic model of the defect levels when comparing the results from different experimental techniques.

Low frequency noise spectroscopy method presented in this work is based on the Fourier transform application, considering the discrete time series of $n$ equal ranges. A digital converter connected with PC convert this series into the frequency domains by means of appropriate mathematical programs. Noise spectra in the range from 0.1 Hz up to 100 kHz were measured using digital oscillograph. Using of ultra low noise amplifier allow to extend the sensitivity of the measurements up to several nV. Transformation was carried out according to the expression: $U(t) \exp[i(2\pi f)t]dt$. Values of discrete voltage of rapid Fourier transform treatment were averaged in order to obtain the resulting noise spectra.

Spectra of noise density were represented in the coordinates $S_u(f) \cdot f^{-\gamma}$ to determine the energy position of the defect, which lorencian lie in the low frequency region. Free carrier lifetimes $\tau_i$ for $i$-th recombination trap were estimated from the slope of the falling part of the frequency dependence $f_{0i}$ for the $A_i$ amplitude. Defect activation energies $E_a$ were obtained from the temperature dependences of the parameter $\tau_i T^2$.

Structural imperfections considerably affect the noise processes in CdTe and HgCdTe. Dislocations and twins are easy created as a result of mechanical stresses or different types of ionization due to the low stacking fault energy and critical resolved shear stress. Therefore it is very important to distinguish the nature of noise at low and ultra low frequencies ($f < 1$ Hz) where noises concerning with these type of defects are often observed. It has been also taken into consideration when interpreting the results of experiments that the spectra of generation-recombination noise are imposed on the spectrum of the $f^{-\gamma}$-noise at low frequencies.
Hydrostatic Pressure Dependence of the Direct Gap, Transverse Effective Charge and Refractive Index of ZnTe System

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Especially for ZnTe in the II-VI family, the work of K. Sato et al \cite{1,2} demonstrates the fabrication of intrinsic pn-junctions and the realization of pure green ZnTe light-emitting diodes LEDs. Strained layer superlattices and heterostructures consisting of this compound have received a lot of interest, because they are considered to be promising materials for optoelectronic devices operating in the visible light range \cite{3,4}.

In particular the Cd\textsubscript{1-x}Zn\textsubscript{x}Te/ZnTe multiple quantum-well heterostructures were studied under high hydrostatic pressure \cite{5}. These II-VI compounds have a significant lattice mismatch of about 4-6 \%, which leads to heavy stress within the layers and thus strain effects upon the band offset must be considered. It is clear then that under the stress, the device’s optical properties are modified. Therefore, it would be interesting to study and understand the behavior of electronic and optical properties when the stress is applied. It is clear then that under stress, the device’s optical properties are modified. Therefore, it would be interesting to study and understand the behaviour of electronic and optical properties when stress is applied.

In this paper, we have determined the pressure dependence of the direct band gap, transverse effective charge and refractive index for ZnTe system. Using the sp\textsuperscript{3}s\textsuperscript{*} semi-empirical tight-binding method (TB) with the scaling law and the Murnaghan’s equation of state, we have shown that all these properties were found to have a sublinearity behavior with the pressure. The results are compared with other works.

\begin{thebibliography}{9}
\end{thebibliography}
Photoluminescence Characteristics of MBE-grown, Sn-doped ZnSe Crystal Layers

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Characteristic bright, blue photoluminescent emission has been observed in Sn-doped, MBE-grown crystal layers under 325nm light excitation at low temperatures. The emission shows distinct nonlinear dependence (n>1) on the excitation intensity. The nature of the blue emission seems analogous to the green emission in Pb-doped ZnSe crystal layers [1].

Crystal layers of Sn-doped ZnSe layers were grown using Eiko EW-2, water-cooled MBE growth machine, having liquid N₂ shrouds, using solid source materials. Homoepitaxial growth on ZnSe substrate crystals, obtained from RMT Ltd., Russia, has been performed as well as growth on SI-GaAs crystals. Photoluminescence characteristics have proved quite sensitive to the crystallographic properties of the layers. The blue emission has been observed in the crystal layers with higher perfection. Typical emission spectrum is shown in the figure along with the excitation intensity dependence. The emission shows nonlinear dependence on excitation intensity as shown in the figure with n value ranging from 1.2 to 1.5. The emission is susceptible to temperature quenching and almost disappears above temperature of 100 K.

The emission is accompanied with green emission peaking at 560 nm in less perfect crystal layers as well as with near band edge emissions.

These characteristics of the blue emission observed in ZnSe:Sn are in many respects analogous to those of the green emission previously reported on Pb-doped ZnSe crystal layers. An analysis based on phonon emission model has yielded a result S=4 for the blue emission in ZnSe:Sn, while S=13 is obtained for the green emission in ZnSe:Pb.

Dislocation of High Quality ZnO Single Crystal Examined by Transmission X-ray Topography

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Wide bandgap oxide-semiconductors have attracted much attention for applications such as optical devices, liquid crystal displays and solar cells. Due to its direct optical bandgap of 3.4 eV at room temperature, ZnO is a promising material for many different applications including: solar cells, optical devices, liquid crystal displays, gas sensors, heat mirrors, ultrasonic oscillators and acoustic wave transducers. Recently ZnO light emitting devices were demonstrated by Tsukazaki and Kawasaki et al [1]. Therefore the ZnO substrate, which has lower dislocation density, is very important for fabricating light emitting devices. X-ray topography is a useful technique to obtain dislocation information. However, there are few reports on the x-ray topography of ZnO single crystal.

In our previous paper [2], a transmission x-ray topograph using the Lang method was successfully obtained from a ZnTe (100) single crystal. In this work, the transmission x-ray topography was carried out to obtain dislocation densities of ZnO single crystal grown which was by the hydrothermal method. The x-ray topograph was successfully observed on the ZnO (0001) single crystal. The dislocation density was estimated to be approximately 200 cm\textsuperscript{−2}. This is the lowest dislocation density recorded for a ZnO single crystal. Furthermore, photoluminescence (PL) measurements were carried out at liquid helium temperature, to study dislocation. No deep emission was observed in the low dislocation density area, but a deep emission was observed in the high dislocation density area. The intensity of the deep emission increased proportionally with increasing dislocation density. Furthermore, the ZnO single crystal was annealed at 800 °C under oxygen atmosphere. The PL intensity was larger than that of the as-grown sample. The dislocation density of the annealed sample decreased in comparison with the as-grown sample.


Optical Characterization of High Quality Conductive ZnSe Single Crystal

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White light emitting diode (LED) has been fabricated from GaN-based semiconductors. The LED was produced by combining a blue InGaN chip with phosphor, and it emits an intense bluish white light. Recently \([1]\), a ZnSe-based white LED has been demonstrated, which utilizes a phenomenon unique to ZnSe homoepitaxial structures grown on conductive ZnSe substrates. N-type doping followed by heat treatments performed under certain conditions in ZnSe result in a broad deep luminescence band. However, the detailed deep luminescence properties of Al-doped conductive ZnSe are almost unknown.

In this work, undoped and Al-doped conductive ZnSe substrates were grown by the physical vapor transport method developed by Sumitomo Electric Industries, Ltd. \([2]\). Photoluminescence (PL), absorption and PL excitation (PLE) measurements were carried out at room temperature for undoped and Al-doped samples, to investigate the luminescence mechanisms of deep emissions. The substrates were annealed at temperature range from 500 to 1000 °C under Zn atmosphere. The carrier concentrations of the samples can be changed from \(10^{15}\) to \(10^{18}\) cm\(^{-3}\). The broad deep PL emissions are observed at 647, 615 nm for undoped and Al-doped ZnSe. The PLE emission is observed at 467 nm for undoped ZnSe, and at 470 nm for Al-ZnSe (Fig. 1). This indicates that the luminescence mechanism is different in the undoped and Al-doped ZnSe.


Luminescent Properties of ZnS:Ce,Y Phosphor

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Zinc sulfide (ZnS) is a well-known host material for phosphors. When a ZnS host is activated by rare earth ions, the phosphors exhibit various luminescence colors in the visible region. In the rare earth ions, Ce\(^{3+}\) center shows green luminescence with the peak wavelength of 510 nm, as shown in Fig. 1. Using Li\(^{+}\)-charge compensator and thermal quenching technique, the phosphor showed blue-green luminescence with the peak wavelength of 480 nm. In this paper, we report that Y ion is greatly effective on blue shift of the luminescence. The ZnS powder mixed with appropriated amounts of CeF₃ and Y₂S₃ powders was fired at 1100 °C for 3 hours in a H₂S atmosphere. The prepared ZnS:Ce,Y phosphor showed photoluminescence (PL) with the peak wavelength of 450 nm which was greatly blue-shifted from ZnS:Ce, as shown in Fig. 1. The luminescence color was a saturated blue color whose color coordinates were x=0.15 and y=0.09. The PL spectrum and luminance were closed to those for the ZnS:Ag,Cl CRT phosphor.

The origin of the saturated blue luminescence was thought to be localized or unlocalized luminescence centers. For donor-acceptor pair luminescence, the emission peaks shift toward higher energies with increasing excitation intensity. However, the shift was not found for ZnS:Ce,Y through our experiment. This leads to the origin that the luminescence is due to the 5d-4f intra-transition of Ce\(^{3+}\) ion. For weaker crystal fields around Ce\(^{3+}\) 2D state of the 5d configuration is higher. This results in the blue shift of the luminescence. Since Y\(^{3+}\) is not the charge compensator of Ce\(^{3+}\), the blue shift due to Y\(^{3+}\) is a new phenomenon.

In conclusion, we have found that with the Y\(^{3+}\) co-activator the ZnS:Ce,Y phosphor emitted the bright saturated blue luminescence. The detail mechanism of the blue shift induced by Y\(^{3+}\) is under investigation. However, the mechanism will contribute to the development of new activation technique in phosphors.

Fig. 1 PL spectra of ZnS:Ce,Y, ZnS:Ce and ZnS:Ag,Cl phosphors

Optoelectronic Devices Based on Colloidal HgTe Nanocrystals Emitting at Wavelengths Between 1.5 and 3.5 $\mu$m

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While bulk HgTe is a zero-gap semiconductor, the band gap of chemically synthesized nanocrystals (NCs) from this material offers a huge infrared tuning range strongly depending on the particle size. Here, we demonstrate HgTe NCs prepared by an aqueous-based colloidal synthesis exhibiting strong photoluminescence at wavelengths between the near infrared and the mid-infrared. By the choice of the capping thiol-molecules, which can be changed by a ligand exchange procedure, different surface functionalities can be provided. This makes the NCs soluble in a variety of different liquids, resulting in a high flexibility for thin film preparation and incorporation of NCs in different optoelectronic devices. As examples, we demonstrate (a), light emitting microcavity devices operating close to a wavelength of 1.5 $\mu$m and (b), polymer/nanocrystal hybrid solar cells with an infrared extended photosensitive wavelength region.

(a) The microcavity devices consist of a TiO$_2$/SiO$_2$ Bragg interference bottom mirror on glass substrates, followed by the active NC layer, a SiO$_2$ spacer layer and a metallic top mirror. The NC layer is assembled by layer-by-layer deposition to obtain densely packed nanocrystal films with well controllable thicknesses. The thickness of the spacer layer is varied to tune the wavelength of the cavity resonance to the desired target wavelength of 1.5 $\mu$m. The emission spectra give clear evidence for a single cavity resonance with a linewidth smaller by a factor of 8 than that of a NC reference layer (see Fig. 1). The emission of the devices is observed up to temperatures above 75 $^\circ$C and it is strongly forward directed with a beam divergence smaller than 3$^\circ$.

(b) The hybrid solar cells make use of a nanoporous TiO$_2$ layer for electron transport which is deposited on indium tin oxide (ITO) covered glass substrates. HgTe NCs for spectral sensitization are deposited on the TiO$_2$ by adsorption from aqueous solutions. Poly-3-hexylthiophene (P3HT) is drop-cast on top of the structure for hole transport. The best photovoltaic response is obtained when HgTe NCs are blended into the P3HT layer, in addition to the HgTe at the TiO$_2$/P3HT interface. For this kind of cell we achieved an open circuit voltage ($V_{oc}$) of 400 mV, a short circuit current ($I_{sc}$) density of 1.96 mA/cm$^2$ and a fill factor of 0.5. Most importantly, however, the photoreponse of these solar cells is extended up to a wavelength of 1.4 $\mu$m (Fig. 2), so that an even larger portion of the solar spectrum is used for energy conversion than from a classical Si solar cell.

![Fig. 1: Emission spectra of HgTe NC based microcavity devices with various cavity lengths compared to the emission of a reference layer.](image1)

![Fig. 2: Photon to current efficiency (IPCE) spectrum of a hybrid solar cell showing a photoreponse up to 1.4 $\mu$m.](image2)
Effects of Sub-gap Irradiation on the Time-of-Flight Current Waveforms of High Resistivity CdTe and CdZnTe

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Time-of-flight (TOF) drift mobility measurement is one of the most powerful tools to elucidate the carrier transport properties of high resistivity CdTe and CdZnTe for nuclear detector materials. The energy location and the concentration of shallow defects, which control the carrier mobility, were successfully obtained by measuring the temperature dependence [1]. Usually, however, the time scale of the measurements are less than 100 ns for electron and some microseconds for hole drift, therefore the thermal emission of trapped carriers from deep defects that dominate carrier lifetime can not be expected in the time interval under practical experimental conditions. In the present work, we attempt to utilize sub-gap illumination to change the occupancy of the deep level defects during carrier drift and the effects of the irradiation on the TOF current waveforms are investigated. In addition to the basic experimental setup of TOF measurement as described in [1], infra-red DC light source were settled to illuminate the side face of the sample.

This illumination brings a variety of effects on TOF current waveforms those depend on the contact material, the dopant or the growth method. As an example, the current waveforms obtained from a Cl-doped CdTe crystal with electroless gold contact are shown in fig. 1. Both of the current waveforms with and without IR (\(\lambda = 0.95 \mu m\)) irradiation are measured at exactly the same negative bias voltage applied on the front electrode (electron drift). The initial rapid decay of the current for both waveforms indicates that the carriers are captured by some deep defects immediately after photo-excitation. Obviously the number of carriers arrived at the counter electrode is reduced by IR irradiation. Namely, the occupancy of the deep lying states is modified and hence the number of deep electron traps is increased by IR irradiation. In addition, a slight increase of the transit time is recognized. The possibility of a selective excitation of a deep defect by tuning IR wavelength is thus suggested. We will discuss the results of IR irradiation at several different wave lengths to obtain spectroscopic information of the defect structure of high resistivity CdTe and CdZnTe.

Electron Interaction with a Short-range Potential of a Crystal Lattice Defect in CdHgTe Solid Solution

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Usually the electron scattering models in the solid solution Cd$_x$Hg$_{1-x}$Te are considered in relaxation time approximation. However, these models have essential shortcoming – they are long-range which contradict special relativity. Besides the use of a macroscopic parameter in these models, the permittivity, is not reasonable in microscopic processes. From the other side in [1,2] the short-range model of electron – polar optical phonon scattering was proposed in which the above mentioned shortcomings were absent. The purpose of the present work is to use the approach advanced in these works for construction of the short-range scattering models on various types of crystal defects.

For the electron scattering on the neutral defect, nonpolar optical and acoustic phonons the interaction radius of the short-range potential is limited by one unit cell. For the electron scattering on the ionized impurity (II), polar optical (PO) and piezoelectrical (PZ) 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 [3,4]. The temperature dependences of electron mobility in the solid solution Cd$_x$Hg$_{1-x}$Te ($0 \leq x \leq 1$) in the range 4.2 – 300 K are calculated. The scattering parameters for different scattering modes are presented in a table:

<table>
<thead>
<tr>
<th>$x$</th>
<th>0</th>
<th>0.08</th>
<th>0.17</th>
<th>0.26</th>
<th>0.36</th>
<th>0.52</th>
<th>0.59</th>
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</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_{PO}$</td>
<td>0.55</td>
<td>0.55</td>
<td>0.62</td>
<td>0.7</td>
<td>0.63</td>
<td>0.72</td>
<td>0.74</td>
<td>0.67</td>
</tr>
<tr>
<td>$\gamma_{PZ}$</td>
<td>0.40</td>
<td>0.43</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.65</td>
<td>0.65</td>
<td>0.5</td>
</tr>
<tr>
<td>$\gamma_{II}$</td>
<td>4.0</td>
<td>4.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

The influence of the different scattering mechanisms on the electron mobility in the temperature range 4.2 – 300 K is considered. A good agreement between theory and experiment in the temperature range 40 – 300 K is established. The discrepancy between the theory and experiment at lower temperatures can be explained by an incorrectness of the impurity defect structure model.

Nonequilibrium Effects and Formation of an Order in High Density Exciton Systems in Quantum Wells

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In spite of many investigations devoted to exciton condensation the role of nonequilibrium effects is not studied. In the report a statistical theory of exciton condensed phase formation in two-dimensional system is presented taking into account the nonequilibrium effects caused by both the finite value of exciton lifetime and the presence of pumping. It is suggested that condensed phase arises as a result of an attractive interaction between excitons. Due to the finite value of exciton lifetime the sizes of exciton condensed phase regions are restricted and the condensed phase arises in a form of systems of islands amid exciton gas. The joint solution of kinetic equations for island size and exciton diffusion equation in the space between islands has been obtained [1,2]. The both the size distribution function and the concentration of the condensed phase islands are calculated as functions of the pumping, the exciton lifetime, temperature and other parameters of crystal. It is shown that the radius distribution function has sharp maximum, its width growths in vicinity of threshold of exciton condensed phase appearance. There is a specific interaction between condensed phase islands through exciton concentration fields. This interaction causes a correlation in position of islands. The possibility of periodical distribution of exciton condensed phase islands is studied. The theory is applied to explanation of experimental manifestation of condensed phase in quantum well [3] and also to explanation of the periodical fragmentation appearance observed in luminescence spectrum from the ring around the laser spot in crystal with double quantum wells [4].

Detection Possibilities of CdTe X- / γ-Ray Detectors Based on Schottky Diodes

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Over decades CdTe has been a superior material for semiconductor X- / γ-ray detectors widely used in science, technology, medicine, and other fields. However, the manufacturers of CdTe detectors have faced a variety of problems related to preparation of homogeneous single crystals with semi-intrinsic electric conductivity. As far back as 1966-1967, a bright outlook for using Schottky barriers in CdTe X- / γ-ray detectors was discovered [1,2]. Later on repeated attempts were made to build detectors with barrier structures [3,4]. However, these works ceased to be topical after the development of commercial detectors based on CdTe single crystals (and then on Cd1−xZnxTe) with characteristics acceptable for practical use. In the late 1990-s the results presented in a number of publications by T. Takahashi et al. [5,6] testified to a considerable improvement in the characteristics of CdTe detectors due to the use of In/p-CdTe Schottky diodes. Nevertheless, some important questions concerning the role of the Schottky barrier in these devices and its parameters remain unclarified. The present paper analyzes the key characteristics responsible for the detecting capability of such type detectors.

Solution of the Poisson equation for a Schottky diode based on a semiconductor with deep acceptor levels in the bandgap, and their compensation, indicates that the concentration of uncompensated impurity in a semi-insulating CdTe cannot be considerably less than the total concentration of all incorporated impurities. This, in turn, means that the width of the strong electric field region in the Schottky diode based on semi-insulating CdTe constitutes the minor portion of the substrate thickness. The very low capacitance value observed for a diode based on the high-resistivity material and its weak dependence on the bias voltage (if any) is attributable not to large thickness of the space-charge region, but to the effect of the substrate resistance. Analysis of the Hecht equation for the efficiency of charge collection shows that in the CdTe-based Schottky diode full collection of carriers generated by absorbed photons (including holes with their low mobility) is already achieved at the lifetime over \( \sim 10^{-8} \) s. The calculation results show that the sensitivity of a CdTe detector based on a Schottky diode can be determined not only by the generation of electron-hole pairs in the barrier region, but, largely, by the diffusion component. This is true in the case of long electron lifetime. With shortening of the electron lifetime, the total detection efficiency drops.

Vapor Phase Growth of Bulk (CdTe)$_{1-x}$Ga$_2$Te$_3$$_x$ Single Crystals

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Wide possibilities of CdTe crystals application in various fields (from IR-devices, γ-ray detectors up to solar cells etc) stimulate search of perfect crystals with predicted properties production technology. Fine doping of CdTe crystals by IIIA group elements allows obtaining both a n- and p-type material depend on thermodynamic conditions during the growth process. According to literature data, CdTe crystals doping by Ga from the melt results in poor structural perfection due to constitutional supercooling at the growing surface. Low-temperature (in comparison with the melt crystallization) vapor phase crystal formation is known as a method of native defects content decreasing but small crystal growing rates restricted such methods use usually.

According to the CdTe - Ga$_2$Te$_3$ system phase diagram a wide solid solution range is observed near CdTe, thus properties of such crystals are of a great interest. The aim of this work is to eliminate influence of Ga$_2$Te$_3$ content in the CdTe crystals grown from the vapor phase on their structural, electrical, optical characteristics. Bulk (CdTe)$_{1-x}$Ga$_2$Te$_3$$_x$ single crystals (Ø up to 50 mm) were grown by vapor transport in silica ampoules in a furnace with special shape using a polycrystalline ingots as initial source material. The last were synthesized previously from high pure (6N) elements Cd, Te, Ga in evacuated silica ampoules by compounding and homogenization in the melt during 24 h at 1370 – 1423 K followed by rapid cooling. Ga$_2$Te$_3$ content in the initial charge was regulated from 0,01 up to 1 mol %. Evacuated later in the growth ampoule the charge was held in the growth furnace at 1023 – 1123 K.

The natural faceting single crystals growth was initialized accidentally on a grain of certain orientation, predominantly (111), followed by overgrowth towards to a top of the container up to complete filling of the top according to Fig.1 and the initial charge recrystallization into the single crystal. The nucleation process was controlled by special optical adjustment.

It was shown that minimization of plastic deformation effect in preparation of the most structurally perfect crystals is possible if heat is removal from the crystallization front by radiation. The growth of high resistive material required careful preparation of the initial charge with near to stoichiometric composition. It was noted that the melt superheating value during the initial ingot compounding influence on the recrystallization rate velocity. The crystals microstructure was studied by optical and electron microscopy, X-ray diffraction. After optimization of cooling conditions the crystals with perfect crystal structure, Te-inclusion-free ones were obtained. The high resistive crystals were successfully tested as room temperature X-ray and gamma-ray detectors.
High p-type Doping of MgZnCdSe on InP Substrates by Inserting ZnTe Thin Layers

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Abstract

High p-type doping of ZnCdSe and MgSe/ZnCdSe superlattices (SLs) on InP substrates was successfully performed by periodically inserting N-doped ZnTe thin layers. ZnCdSe/ZnTe (4.0nm/0.73nm) samples yielded a high net acceptor concentration \( (N_A - N_D) \) of \( 8.0 \times 10^{17} \text{cm}^{-3} \) while the \( N_A - N_D \) of N-doped ZnCdSe samples was \( 3.6 \times 10^{16} \text{cm}^{-3} \) at most. \( N_A - N_D \) values more than \( 4 \times 10^{17} \text{cm}^{-3} \) were confirmed for MgSe/ZnCdSe/ZnTe samples with the MgSe layer thickness ratio less than 0.24. These results indicate that ZnTe-inserted MgZnCdSe materials are very promising for p-cladding layers of II-VI visible LEDs and LDs.

MgZnCdSe II-VI materials lattice-matched to InP substrates are very attractive for yellow-to-green LDs and LEDs. The bandgap energy of MgZnCdSe can be controlled from 2.1 to 3.8 eV, and high n-type doping was currently obtained. These suggest that MgZnCdSe can be applied for the active and the n-cladding layers. On the other hand, the p-type doping of ZnCdSe was \( 10^{16} \text{cm}^{-3} \) level at most, and a further doping level has never been reported for MgZnCdSe. In this paper, in order to obtain high p-type doping of MgZnCdSe, we propose novel doping method, i.e. periodically inserting heavily p-type doped ZnTe thin layers into MgZnCdSe layers. By inserting the ZnTe layers, p-carriers of the ZnTe layers diffuse into MgZnCdSe layers, which can bring high p-carrier concentration in the total layers.

In this study, we grew ZnCdSe and MgSe/ZnCdSe SLs on InP substrates by MBE with periodically inserting p-doped ZnTe thin layers. The samples consisted of ZnCdSe(4.0nm)/ZnTe (0-0.73nm) SLs or MgSe(0-1.4nm)/ZnCdSe(4.0nm)/ZnTe(0.73nm) SLs. P-type doping was performed for each layer of the SLs using an RF nitrogen source. \( N_A - N_D \) of the samples was evaluated by the double-Schottky C-V measurements at RT. Figure 1 shows the \( N_A - N_D \) values of the ZnCdSe samples as a function of ZnTe layer thickness. Figure 2 shows the \( N_A - N_D \) values of the MgSe/ZnCdSe SL samples as a function of MgSe layer thickness ratio in one period of the SLs.

Fig. 1 Net acceptor concentrations as a function of ZnTe layer thickness. Fig. 2 Net acceptor concentrations as a function of MgSe layer thickness ratio.
Luminescence Investigation of Ion Milled CdTe

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The ion milling (IM) is used to form relatively thick n-type layers on vacancy-doped p-Hg\textsubscript{1-x}Cd\textsubscript{x}Te substrates. This very simple technology ensures high-quality junction formation [1]. Since thin (\(\sim 1 \mu m\)) CdTe layers are the main passivation coating for HgCdTe photodiodes arrays so the possibility of conductivity type conversion in heterostructures CdTe/p-HgCdTe under IM is the very important question for such diodes technology. Some reports indicate about existence of p-to-n conversion at IM also in p-CdTe [2]. But according to [1] conversion depth in Hg\textsubscript{1-x}Cd\textsubscript{x}Te strong depended on composition x and at x > 0.5 after IM formed only thin (\(\leq 1 \mu m\)) damage layer. Conductivity type conversion in p-Hg\textsubscript{1-x}Cd\textsubscript{x}Te as well as in p-CdTe is caused by rebuilding of native defect system. So the main aim of this study was luminescence investigation of IM effect on defect structure of CdTe.

Single crystals wafers of undoped high resistivity bulk CdTe were used in these experiments. As grown wafers were annealed in Cd (group A) or Te (group B) vapour at 700 °C (see Fig.). The IB-3 (EIKO, Japan) etching system with Ar\textsuperscript{+} ions was used to perform IBM with ions energy E=500 V. Luminescence (CL) was excited at 77 K by shot electron pulses (3 \(\mu s\)) with repetition rate \(\sim 50 \text{ Hz}\) and energy 8.5 keV. Electrical measurements did not display the formation of any n-type layers in IM samples. It was revealed that in all samples (initial and milled) observed two emission bands related to exciton (at \(\sim 1.58 \text{ eV}\)) and donor-acceptor (at \(\sim 1.4 \text{ eV}\)) recombination. IM caused the increasing of exciton luminescence and some shift of its maximum to high-energy region with ion dose increasing for all samples. At the same time we observed the decrease of intensity and approximately constant intensity for acceptor-donor band in group A and group B samples respectively.

The comparison of CL spectra of initial and IM samples indicate that ion milling causes the rebuilding of native defects system - cadmium and tellurium vacancies. This effect is discussed in connection with possibilities of p- to n-type conversion of CdTe during ion milling.

Growth and Characterization of Cadmium Telluride Single Crystals with Access Tellurium

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In this report we present the results of the technology of CdTe crystals growing and such characteristics of the crystals as photoluminescence (PL) properties and sensibility to gamma-radiation.

Potential applications CdTe materials include digital radiography, transmission computed tomography, backprojection tomography and process control. These detectors may be used for creation of detecting blocs for X-ray and γ-ray medical and technical tomography due to the possibility to work at room temperature combined with small sizes.

We have been studying samples (p > 10⁸Ω·cm) with the impurity defect composition most frequently used in the technology for fabricating nuclear radiation spectrometric semiconductor detectors based on semi-insulating cadmium telluride [1].

CdTe single crystals were grown by the Bridgman method from a melt with access tellurium and by the methods from gas phase with nonstoichiometric source.

We investigated the initial unsaturated compound p-CdTe (p ~ 10¹⁴ cm⁻³, μ = 80–90 cm²/(Vs)) and the tellurium-saturated samples n-CdTe (n ~ 10¹⁴ cm⁻³, μ = 600–700 cm²/(Vs)), n-CdTe<In> (n ~ 10⁷ cm⁻³, μ = 400–800 cm²/(Vs)), and n-CdTe<Cl> (n ~ 10⁶ cm⁻³, μ = 300–500 cm²/(Vs)).

Analysis of the PL excited by Ar⁺-laser radiation at 4.5 K shows the following. It is seen PL intensity is very weak at 1.4 eV (A-centers), especially in the case of CdTe(Cl) single-crystals. The same refers to donor-acceptor for PL at 1.5 eV if doped concentration is more then 10¹⁷ cm⁻³. The exciton photoluminescence spectrum of the p-CdTe single crystals at 4.5 K contains the luminescence lines A (1.5900 eV), D (1.5935 eV), and C (1.5915 eV) due to the annihilation of exciton-impurity complexes and also the broadened lines Iβ (at 1.5860 eV) in the longer wavelength range and X (at 1.5965 eV) at the frequency of free excitons.

The saturation of cadmium telluride single crystals with tellurium (PTe₂ ~ 3.0 kPa) leads to an increase in the intensity and a narrowing of the lines Iβ (at 1.5860 eV) and X (at 1.5965 eV) and the appearance of the line Iα (at 1.5924 eV), the Iα line is attributed to the emission of ionized donor-impurity atoms (D⁺, X). Intensity of the Iβ line increases with rise of the tellurium partial pressure in the range 1.0–10.0 kPa. To explain the nature of the Iβ line a model is proposed for metastable DX centers formed through Jahn-Teller distortion of the crystal lattice of cadmium telluride, i.e., through the displacement of a DCd residual donor impurity atom (where D is a Group III element of the periodic table) to the region of a nearest neighbour interstice.

CdTe detectors have been produced in quasihemispherical configuration used when a medium energy resolution, stability and reliability of operation, small size and radiation hardness are needed. Detectors have been investigated by means of a measuring system consisting of a charge-sensitive amplifier, an amplifier and an AccuSpec A amplitude analyzer of Canberra firm. The noise of electronics ~10 keV had been the main limiting factor of reception < 8 % for energy resolution of photopeak at 122 keV (⁵⁷Co).

Monte Carlo Investigation of Dynamical Effects Under Intense Radiation Fields in Bulk II-VI Semiconductors

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Nonlinear processes involving high-order harmonic generation from a bulk semiconductor or semiconductor structure subject to intense radiation field have been widely investigated in recent years. This interest has been motivated by the possible applications to frequency converter in the sub- and near-THz region. For this sake, the nonlinearity of hot carrier velocity-field (v-E) relation in bulk semiconductors and the nonlinearity of the current-voltage (I-V) characteristic in n+n+ structures, are used. Harmonic generation in semiconductors is of interest in its own right, but it may prove useful also for the general understanding of the several features of this highly nonlinear process.

In the far-infrared region, linear as well nonlinear optical properties are mainly determined by the motion of the free carriers in the field of the incident wave. Numerous physical mechanisms may potentially act to produce harmonics generation, and the elucidation of their separate influence may well yield interesting informations for the general understanding of several features of the highly nonlinear process.

We have studied the efficiency of harmonic generation in bulk II-VII semiconductors using a Monte Carlo (MC) simulation for the motion of the free carriers in the external electromagnetic field combined with the nonlinear electrodynamic equations. From MC simulation we obtain the time dependent drift velocity; taking the Fourier coefficients of the drift velocity we calculate the dependence of the nonlinear dielectric susceptibility as function of the electric field amplitude; solving the nonlinear wave equation at the n-th harmonic frequency we get the amplitude and intensity of the n-th harmonics. The electron collision mechanism included are: collision with impurity, collisions with optical phonons polar and non polar, collisions with acoustic phonons.

We study and discuss the dependence of the high-order harmonic efficiency by some process parameters as: i) the frequency and the intensity of the alternating signal; ii) the value of the doping concentration; iii) the temperature. We compare the results obtained in II-VI compounds with our previous results obtained in GaAs, InP, and Silicon bulk.

More detailed analysis of the obtained results will be presented at the conference.
Long Range Lattice Distortions in Zn$_{1-x}$Cr$_x$Se and Zn$_{1-y}$Ni$_y$Se Solid Solutions

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Doping of II-VI wide bandgap semiconductors by 3d elements changes their optical and magnetic properties what is of considerable interest to creation of lasers (ZnSe:Cr [1]) and spintronic devices (ZnO:Co [2]). An influence of 3d elements on the lattice structure has been considered only as a local distortion around an impurity center due to change of electrostatic interaction with nearest ions. The low temperature structure phase transition in Zn$_{1-Y}$Ni$_Y$Se (Y=0.0025) induced by Ni ions has been recently observed [3]. Ultrasound measurements revealed that the shear elastic modulus C$_{44}$ exhibits a softening with lowering of the temperature [4]. So it seems to be very important to search the lattice distortion fine structure induced by 3d ions in ZnSe:3d at elevated temperatures.

The neutron diffuse measurements sensitive to fine structure of lattice changes were performed for Zn$_{1-X}$Cr$_X$Se and Zn$_{1-Y}$Ni$_Y$Se crystals at the temperatures 300K and 120K. The rocking curves near the (400), (220) and (022) Bragg reflexes have clear diffuse scattering profiles evidencing about lattice ions shear displacements. An average size of shear domains determined by the diffuse profile halfwidth depends on a shear displacement type and temperature. For the Zn$_{1-Y}$Ni$_Y$Se (Y=0.0025) crystal the average size of the $\langle 1-10 \rangle$ [110] shear distortions (in angle brackets the direction of scanning vector is shown, while in brackets is direction of ion distortion) is approximately equal 0.4 nm while for the $\langle 011 \rangle$ [100] displacements it is equal $\simeq$ 0.8 nm at the room temperature. The average size of the shear distortions $\langle 011 \rangle$ [100] at 120K is 2.5 times greater than this value at 300K. This result demonstrates a clear correlation with the softening of the shear elastic modulus C$_{44}$. For Zn$_{1-X}$Cr$_X$Se (X=0.045) an average size of shear distortions $\langle 1-10 \rangle$ [110] has larger size at the room temperature and increases with reducing of the temperature from 300K to 120K. The velocity of the $\langle 1-10 \rangle$ [110] shear ultrasound wave is decreased with lowering of the temperature what is the direct evidence of the (C$_{11}$ – C$_{12}$)/2 shear modules softening [5]. The obtained results reveal that Cr and Ni ions actually induce the long range shear displacements in Zn$_{1-X}$Cr$_X$Se and Zn$_{1-Y}$Ni$_Y$Se crystals. Thus a principally new problem may be formulated – nonlocal influence of many electron 3d impurities on the lattice structure in semiconductors with ion-covalent bonds.

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Characterization of the Vapor Grown CdTe Crystals for High Energy Radiation Detectors

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Growth steps and set-up for the pure and chlorine doped cadmium telluride and also cadmium zinc telluride single crystals preparation by sublimation traveling heater method (STHM) in vertical configuration without seeding is described. Rather large (18 mm in diameter and up to 50 mm length) crystals were obtained by using this technology.

The structural, electrical and transport properties of as-grown material were investigated by different techniques: infrared (IR) transmission spectroscopy, double-crystal X-ray diffractometry (DCD), Hall effect and conductivity measurements, photoelectrical measurements and chemical etching. It was concluded that most suitable material for preparing X-ray and γ-ray non-cooling detectors are single crystals with Cl concentration in the charge $N_{Cl} = 5 \times 10^{18} - 10^{19} \text{cm}^{-3}$. Their main parameters at room temperature are: resistivity $\rho > 10^9 \Omega \text{cm}$, major carrier (electrons) mobility $\mu = 400 - 500 \text{cm}^2 / \text{Vsec}$, carrier lifetime $\tau = 2 - 7 \mu \text{sec}$.

The transmission of the samples with Cl concentration $N_{Cl} \leq 10^{19} \text{cm}^{-3}$ is high (larger than 60% in the wavelength range of 2 – 25 µm), etch pit density (EPD) not exceed $10^5 \text{cm}^{-2}$, which confirmed their rather high crystalline quality. It was revealed, that such semiinsulating samples are highly compensated and their conductivity is controlled by mid-gap levels at room temperature.

Crystallinity of the material became poorer when doping level were increased up to $N_{Cl} = 5 \times 10^{19} \text{cm}^{-3}$. Such crystals contains second phase inclusions (with density $3 - 7 \text{cm}^{-2}$) and voids, which causes considerable reduction of IR transmittance and increasing of the etch pit density (EPD). Undoped and low-doped ($N_{Cl} < 10^{18} \text{cm}^{-3}$) samples exhibited rather high degree of structural perfection but their resistivities were not enough for application as non-cooling X- and γ-ray detectors.
The Binding Energy of an Exciton-Donor Complex in a Quantum Dot in a Magnetic Field

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The theoretical investigation of magnetic field influence on the binding energy of the quasiparticle complexes in a quantum dot (QD) of A²B⁶ semiconductor is very interesting for study of the magnetooptical properties of QDs and for practical applications in new optoelectronic devices. We have developed a variational approach to study the influence of magnetic field on the ground state energy of an exciton-donor complex (EDC), which consists of exciton bound to an ionized donor impurity in a QD with parabolic confining potential. The variation of the ground state total and hole wave functions [1]. We have chosen g in the form that takes into account Coulomb interaction between the particles and also the spherical confining boundary of the system. We use the units of the length \( \hbar^2/\kappa m_e \) and the energy \( \hbar^2/2\kappa a_0^2 \). The energy of the electronic system \( V(r) = -(g|H_e|g) \) becomes the potential energy for the motion of the hole [1]. We have chosen the hole trial wave function with the second variational parameter \( \lambda \), based on the results of [1] and on the solution of the system with Coulomb repulsive interaction in spherical QD with parabolic confining potential [2]. The variation of the ground state total and binding energies of EDC with respect \( \delta \) and \( \lambda \) were performed for different values of \( d, \sigma \) and \( B \). The behavior of the binding energy of EDC with the increasing of the magnetic field and the features of the magnetooptical absorption in a QD are discussed. Both cases of finite and infinite potential barrier on the QD surface are considered.

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Coherent Control of Polariton Modes in Pulse-transmission and Four-wave-mixing Experiments

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Optical properties of ZnSe/ZnSSe heterostructures with a ZnSe layer thickness corresponding to a few exciton Bohr radii are dominated by the presence of various polariton modes and their interactions. The quantization of the exciton’s center-of-mass motion in the active layer according to $k_n = n \pi / d$ (d layer thickness, n integer) results in heavy-hole polariton modes labelled as $hh_n$. By use of the coherent-control technique it is possible to manipulate the excitation of polariton modes on ultra-short time scales. We achieve the control by use of a pair of phase-locked pulses exciting a sample containing a 25 nm ZnSe well. The pulse pair is provided by an actively stabilized Michelson interferometer. The time delay between the two pulses is $t_{\text{int}} + \Delta t_{\text{int}}$, where $t_{\text{int}}$ denotes the basic temporal separation of the pulse pair in the fs range, and the fine tuning $\Delta t_{\text{int}}$ can be varied with an accuracy of 40 attoseconds. In the exciton spectral region of the sample four heavy-hole exciton-polariton modes $hh_1$ to $hh_4$ are observed. By changing the delay between the pulses the contributions of the different modes can be selectively enhanced or suppressed in the optical spectra.

First, we demonstrate the separate control of polariton modes in linear pulse-transmission experiments. The transients measured in real time show significant differences in dependence on the fine tuning $\Delta t_{\text{int}}$ due to the different radiative decay times of particular polariton modes. Second, we have investigated the coherent control of nonlinear polariton polarization obtained in four-wave-mixing (FWM) experiments. The pulse pair was incident on the sample from direction $k_1$, and an additional single pulse was applied from direction $k_2$. The $k_2$ pulse and the first pulse of the pair arrived at the sample simultaneously. In Figs. 1 and 2, contour plots of the FWM signals are depicted as emitted in directions $2k_1 - k_2$ and $2k_2 - k_1$, respectively. The signal intensity is encoded in a logarithmic grey scale. As a function of $\Delta t_{\text{int}}$ the spectrally resolved FWM signals show oscillations at the energy positions of the polariton modes due to constructive and destructive interferences of the respective polarizations. A clear phase shift is observed between the oscillations of the signals of various modes emitted in direction $2k_2 - k_1$ (Fig.1). This indicates that polariton modes can be separately manipulated in the coherent regime if the pulse pair contributes quadratically. Contrasting to that, in direction $2k_2 - k_1$ (Fig.2) all polariton modes are simultaneously enhanced or diminished showing that they are not separately controlled in this case. We will give a detailed analysis of the coherent control of the polariton modes in the nonlinear regime with respect to both directions of diffraction.

Fig. 1: Contour plot of coherent control of polaritonic FWM polarization measured in the direction $2k_1 - k_2$ ($t_{\text{int}} = 700$ fs).
Fig. 2: Contour plot of coherent control of polaritonic FWM polarization measured in the direction $2k_2 - k_1$ ($t_{\text{int}} = 450$ fs).
Far-infrared Spectroscopy of Hg$_{1-x}$Mn$_x$Te - MnSe Mixture
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The optical properties of an inhomogeneous material are described by the complex dielectric function that depends on 3D distribution of constituents. The investigated mixture consists of two dielectric components, of which one is treated as a host, and the other as the inclusion phase. The characterization of the inhomogeneous material by two dielectric functions is not very useful, since one need to know the exact geometrical arrangement of the constituents of the material. However, if the wavelength of the electromagnetic radiation is much larger than the particle size, classical theories of inhomogeneous materials presume that the material can be treated as a homogenous substance with an effective dielectric function. In the literature, many mixing models can be found for the effective dielectric permittivity of such mixture. Some are presented in [1]. Optical properties of such materials depend upon the properties of the constituents, as well as their volume fraction [2].

As the multicomponent alloy of A$_{1-x}$B$_x$C$_{1-y}$D$_y$ type grows, clusters of one or few constitutive elements can be formed in material. Some reasons for that is an insufficient knowledge of phase diagrams, impossibility of absolute control of components solubility etc. As a result, different complexes can be formed in material. For example, instead A$_{1-x}$B$_x$C$_{1-y}$D$_y$, the A$_{1-x}$B$_x$C alloy can grow with clusters of D elements or AD and BD compounds.

In this paper, we focused our interest on far-infrared spectroscopy of Hg$_{1-x}$Mn$_x$Te$_{1-y}$Se$_y$ (x ≤ 0.14, y ≤ 0.1) mixed crystals growth by Bridgman method. The phonon properties of constitutive elements, as HgTe, HgSe, MnTe, MnSe, Hg$_{1-x}$Mn$_x$Te and Hg$_{1-x}$Mn$_x$Se are well known [3, 4] and some of them are presented in this paper. The model for the phonon properties of multicomponent mixed crystal we made and applied for many systems (see for example [5]).

The analysis of the far-infrared spectra was made by a fitting procedure based on the model of coupled oscillators. Compared results obtained on that way with the theoretical prediction [5], we concluded that samples with x=0.14 and y=0.05 (composition from X-ray microprobe) consist of MnSe clusters randomly distributed in Hg$_{0.86}$Mn$_{0.14}$Te matrix. Because of that, for the analysis of FIR spectra of this specimen, we construct the new effective dielectric function, based on the Maxwell-Garnett model, which takes into account the above-mentioned reason. There is a good agreement between the experimental results and the applied model.

Cadmium Zinc Telluride (CZT) based semiconductor detectors have been under intensive research for quite a few years for its inherent advantages over traditional solid ones made of scintillant, high purity Germanium or Silicon, etc., like high atomic number (Z), large enough bandgap for low leakage current rendering its operating at room temperature, small enough bandgap for small the electron-hole ionization energy (<5eV), high product and so on thus better performances are foreseeable in the detection of high energy radiation such as X-rays, gamma-rays, and other uncharged or charged particles.

Further, unipolar CZT detectors with novel configurations, like coplanar grid and capacitive Frisch grid structures have drawn much attention recently for their successful solutions in handling the hole ‘tailing’ problem resulting from the great mismatch in mobilities between holes and electrons in the intrinsic matrix.

However, challenging can be the optimization in designing unipolar CZT detectors primarily due to two factors: the yield of material suitable is relatively low and this continues to limit to some extent the experiments due to the associated high material costs, and the effect of the non-uniformly distributed electrical field and potential formed by the grid shaped anode on the final collected signals and spectra, which is one of the keys to an optimized device, can not be easily explored by the classic theory, like Hecht relation.

Simulations on many occasions are adopted to predict detector performance, especially Monte Carlo method, which is mostly suitable to delineate the actual interactions happened in micro scale in the view of randomness and possibility. However, GP (general purposed) M.C. codes like Tigor, EGS4, MCNP series are hard to take anisotropic or non-uniform macro properties into account, like the non-uniform electric field or potential during the carrier tracking, which can be readily made up by finite element simulations.

Thus a new approach is present here to simulate the CZT detectors by a home-made M.C. code developed on Matlab to follow the history of a huge sum of incident γ photons and electrons within their respective lifetime, the latter of which are under the influence of the non-uniform electrical field and potential, calculated by commercial finite element software ANSYS with high accuracy. By adjusting the input parameters, such as various material parameters, device dimensions and anode shapes, the induced charge signals on the readout grids are evaluated using the Shockley–Ramo theorem to the charge carriers propagating inside the detector volume.

The approach can be fairly useful in the analysis of the weighted potential, charge transportation and final spectrum characteristics of unipolar CZT detectors with novel structures.

A simulated result of $10^{-6}$s $^{57}$Co radiation onto a $10 \times 10 \times 2$ mm CZT coplanar grid is compared with published experimental data to verify the accuracy of the simulation and discussed for future improvement.
Effects of Contact Interfacial Behavior on the Performance of CdZnTe Detectors

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Recently, Cadmium Zinc Telluride (CZT) has rapidly drawn a significant interest due to its high potential for many room temperature nuclear radiation detectors. The quality of CZT crystal plays a vital role in determining the performance of these detectors. Their failures are generally referred to as the degradation of bulk material properties. However, little work has been reported on the effect of the degradation of the interfacial layer between the contact and CZT surface on the performance of detectors. The effects of different metal contact treatments and aging tests on the performance of detectors have been investigated in this paper.

The CZT crystals with high resistivity of $10^9 \Omega \cdot \text{cm}$, grown in the same run, were cut into four wafers with dimensions of $5 \times 5 \times 2 \text{mm}^3$ as a sample set. They were mechanically grounded, then polished with alumina suspension and finally etched chemically with BMLB solution. The Au electrodes were made on both sides of the three CZT wafers by the electroless deposition, thermal vacuum evaporation and sputtering deposition process, respectively and a Au/Cr composite electrode on the fourth CZT wafer by thermal vacuum evaporation. All the four CZT wafers were passivated by a KOH-KCl solution followed by a NH$_4$F/H$_2$O$_2$ solution. The accelerated aging tests on the detector were performed by using the Thermal Cycle Testing System (ESPAC TSA-71H), in which the environment temperature of the detector was changed between $-65 \degree \text{C}$ and $150 \degree \text{C}$ within 240s.

The 3-D finite element simulation results indicate that the maximum thermal stress is concentrated on the midst of the electrode and rarely varies with the electrode thickness due to relatively thin metal layer for the contact electrode. The adhesion force between the electrodes and the CZT surface was measured by using a Dage PC2400 Micro tester with the shear-off-method, which indicates that the interfacial adhesion strength of the sputtered Au electrode is the greatest among the Au electrodes, and even greater than that of the Au/Cr composite electrode. The inhomogeneities and discontinuities of the contact layers were investigated by using a Sonoscan D9000 scanning acoustic microscopy (SAM) and the interfacial composition identified by using a Physical Electronics Phi 550 ESCA analyzer. The current-voltage characteristics were determined by using ZC36 micro-current testing instrument. In particular, the CZT detector response to gamma-rays for different metal contact treatments and aging effects are presented and discussed.

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Study on In-Diffused CdZnTe Under Controlled Partial Pressures

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There is a growing interest in the Cd$_{1-x}$Zn$_x$Te (CZT) crystals of high resistivity for fabricating X, $\gamma$-ray detectors, but high quality CZT crystals are hard to obtain by conventional low pressure Bridgman growth technique (LPB) directly. In recent years, In-doped CZT crystals with high resistivity have been obtained by LPB, and found to be sensitive to gamma radiation. Taking into account the relatively high $D_{In}$ values at 700-900°C, an uniform In distribution with sufficient time under defined thermodynamic conditions could be achieved by using In-diffusing into as grown intrinsic CZT, instead of In-doped melt growth. In this paper, we will present our recent attempts of realizing In-doped crystal by In-diffusing into as grown intrinsic CZT wafers from an external source (vapor or In deposited layer) under the controlled partial pressures using a Cd$_{1-y}$Zn$_y$ alloy reservoir. The as-grown intrinsic CZT crystals of $\rho \sim 10^8$ Ω·cm were grown by LPB method. The ingots were cut into wafers along (111) direction, which are about 2mm in thickness. After some mechanical polishing and chemical treatments on the surfaces, the wafer was put into the specially designed quartz ampoules, in which the CZT sample, the wafer, the high pure In and the Cd$_{1-y}$Zn$_y$ alloy reservoir were separated spatially from each other. The evacuated and sealed ampoule was inserted into a horizontal 3-zone resistance furnace.

The In-diffusion of the CZT wafers was carried out at temperature of 700-1000°C for 1 to 10 days under different partial pressures, and then the ampoule was cooled down to room temperature at a rate of 1-5°C per min or quenching to 0°C within a few seconds. The structural, constituent and electrical properties of the In-diffused CZT wafers were identified by using a JSM-6368 LA Scan Electronic Microscopy, a FTS-175 Fourier transform spectroscopy, Electronic probe microscopy, and a HL5500 Hall Effect System.

The results show that the resistivity can be raised by two or three orders up to $5.7 \times 10^{10}$ Ω·cm, IR transmissivity raised by 10%, up to 65% or even more, and EPD density are $7.5 \times 10^4$ cm$^{-2}$. In particular, the effects of the parameters, such as Cd/Zn partial pressures, diffusion duration and temperature, rate of cooling after diffusion, on the electrical properties are analysed. In addition, the In diffusion mechanism and its compensation effect in CZT are discussed, and based the experimental results and established theoretic model, the In effective diffusion coefficient $D_{In}$ in CZT is obtained in the temperature range of 873K to 1073K, at maximal Cd saturation. Here it is worth noticing that the In diffusion rate depends on the vacancy or interstitial concentration, determined by P$_{Cd}$ value in the ampoule.

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Positive Magnetoresistance Behaviour in the Variable Range Hopping Regime in CdSe

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Experimental results are reported on high field positive magnetoresistance in CdSe sample in which range hopping occurs at low temperatures. Positive magnetoresistance associated with variable range hopping conduction has been observed. Experimental data are tentatively compared with available models in the insulating regime. Doped semiconductors with an impurity concentration just nearly the critical density \( n_c \) for the metal-insulator transition (MIT) exhibit hopping conductivity with a variable jump length. This variable range hopping (VRH) transport is described by the following temperature dependence of the conductivity \( \sigma = \sigma_0 \exp \left[ -\left( T_0/T \right)^s \right] \). According to Mott [1], and assuming a constant density of states at the Fermi level, \( s=0.25 \). If long-range Coulomb interactions are considered, as proposed by Shklovskii and Efros (SE) [2], a parabolic Coulomb gap exists and the exponent is \( s=0.5 \). The experimental situation has been confusing for some time, with both values of \( s \) being observed. It is more difficult to choice between the Mott VRH regime with \( T^{-1/4} \) and the SE VRH regime with \( T^{-1/2} \). In previous work the value of the exponent \( s \) has been calculated in InP sample using regression methods [4, 5, 6]. In this work we have attempted to slice for one of the two VRH regimes by studying the behaviour of positive magnetoresistance in the insulating regime of the (MIT). The theory has been developed by Shklovskii and Efros [2] for low magnetic field and by Tokumoto et al. [3] for high magnetic field, and in both cases the VRH exponent \( s \) can be estimated. We have respectively fitted experimental data using the equations of positive magnetoresistance given by Shklovskii and Efros for low magnetic field, and Tokumoto et al. for high magnetic field, and we have determined the value of the VRH exponent \( s \).

\[ \ln(\sigma/\sigma_0) - \ln(T/(K)) \]

- Experimental results
- \( \alpha = 0.333 \) regime of Mott
- \( \alpha = 0.6 \) regime of Shklovskii

\[ B = 0.57T \]
\[ B = 0.95T \]
\[ B = 1.33T \]
\[ B = 1.91T \]
\[ B = 3.05T \]
Energy Spectrum, Charge State and Electron Configuration of Transition Metals in n-ZnSe Single Crystals

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Hall effect, electric conductivity and charge carriers mobility in n-ZnSe single crystals doped with different concentrations of Cu, Ag or Au impurities are studied in the temperature range from 55 to 500 K. The doping was made in the process of long-term (100 h) high-temperature (950°C) annealing in Zn+Cu, Zn+Ag or Zn+Au melts respectively.

It is found that low copper-doping of n-ZnSe samples (< 0.2 at% Cu in melt) leads to an inversion of both the Hall coefficient sign (Fig. 1a) and thermal emf sign, and to an anomalous temperature dependence of the electron mobility in the high-temperature region (T > 400 K). It is shown that these anomalies of kinetic coefficients are due to the mixed electron-hole impurity conductivity, which is caused by two charge states of copper ions: Cu\text{+}\text{Zn} with d\text{10} electron configuration and Cu\text{++}\text{Zn} with d\text{9} electron configuration. Cu\text{++}\text{Zn} ions form a shallower energy level near the valence-band edge in comparison with Cu\text{+}\text{Zn} ions.

A quite another character of kinetic coefficient dependences in the high-temperature region is observed for n-ZnSe crystals doped with Ag or Au. The $R_H = f(10^3/T)$ curves are typical for the crystals with two donor levels of different energies (Fig. 1b, c). Silver manifests itself as a usual compensating acceptor impurity (Fig. 1b), while gold atoms demonstrate the strongly marked amphoteric properties (Fig. 1c).

At low gold concentration, Au atoms form mainly the donor-type interstitial Au\text{i} defects. The increase of Au concentration in Zn+Au melt to (1 ÷ 2) at% leads to the formation of both simple Au\text{Zn} defects and associate acceptors (Au\text{Zn}-Au\text{Zn}), (Au\text{Zn}-D\text{Zn}) and (Au\text{Zn}-V\text{Se}). Thus, electrical measurements show that Ag and Au manifest itself as single-charged Ag\text{Zn}+ and Au\text{Zn}+ ions with d\text{10} electron configuration and form a single-energy levels near the valence-band edge of ZnSe crystals. A model explaining the existence of kinetic coefficient anomalies in n-ZnSe:Zn:Cu crystals and their lack in n-ZnSe:Zn:Ag and n-ZnSe:Zn:Au crystals is proposed.
Photoluminescence, Raman Scattering and Vertical Transport of CdSe/CdMgSe Superlattices

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It was shown recently that low-strained type-I CdSe/CdMgSe quantum wells could be grown on InAs substrates by molecular beam epitaxy [1]. We have studied for the first time photoluminescence (PL), photoluminescence excitation (PLE) and reflectance spectra as well as vertical transport (VT) of carriers and excitons in 40-periods superlattices (SL) CdSe/Cd_{0.8}Mg_{0.2}Se with periods of 3.7, 5.9 and 7.3 nm with equal width of wells and barriers. The VT was studied under various conditions by all-optical methods with the aid of an enlarged (10 nm) CdSe quantum well (EW) which was incorporated into the central part of the SL and served as a sink for the carriers that have performed a vertical transport across the SL. The VT efficiency is revealed in the relation of integral intensity of luminescence peaks from the EW and SL. The PL spectra from the SL and EW were measured at different temperatures in the range 2.2-100 K and under different excitation powers. The energy of excitation was above the gap energy of the SL. At He temperatures six peaks were observed in the photoluminescence spectra. They were identified as localized and free heavy-hole excitons from the EW and the SL and two donor-acceptor bands. The PLE spectra show that PL of the EW is mainly due to carriers excited in the SL and then trapped in the EW after tunneling through the SL. Distinct peaks of heavy-hole and light-hole excitons of the SL are observed in the spectra. This signifies that excitons play a significant and probably a dominating role in the VT. The temperature dependence of VT is very weak at low temperatures, but beginning from 17K it has an activation-like character with activation energy of 8.5 meV for the 3.7nm SL. This can be explained as excitons delocalization. The study of the VT dependence on the excitation power density W shows that at W>1W/cm² there exists only one main mechanism of the VT. This mechanism is probably diffusion of the heavy-hole excitons. The VT efficiency increases strongly with the SL period decreasing. VT was also studied in magnetic fields up to 12 Tesla in the Voigt configuration in the SL with 5.9 and 7.3 nm periods. However, we did not observe the threshold-like increase of the SL photoluminescence as a function of the magnetic field which according to the theory of Berezhkovskii and Suris [2] must signify the decrease of the vertical transport when the resonance between the heavy hole energy levels of the neighboring wells is destroyed by the magnetic field and the heavy-holes miniband gets narrower. Thus VT for these SLs is not of the Bloch type due probably to thickness fluctuations of the SL layers.

Calculations of the interband transition energies were performed and compared with those from the photoluminescence excitation spectra. An estimate of the excitons binding energies and valence band offsets for the CdSe/CdMgSe was obtained from this comparison. Study of Raman scattering by phonons was also performed and it indicates the two-mode behavior of the CdMgSe phonons.

We present results of photoluminescence study of CdMnSe/ZnSe disk-shaped quantum dots in a magnetic field up to 11 T in the Faraday and Voigt geometries at liquid He temperatures and various levels of laser excitation. We observed a strong increase (up to two orders of magnitude) of the quantum dot photoluminescence intensity in the Faraday geometry and a weak (less than two times) in the Voigt one within the range of B=0÷11 T. The magnetic field dependence of the photoluminescence intensity and its anisotropy is related with the dependence of non-radiative Auger recombination of excitons with excitation of Mn-ions on the spin of both exciton and Mn-ion. However, the existing theory is unable to explain the observed anisotropy [1]. In order to account it for the selection rules of the Auger process have been revised. The anisotropy is provided by a quick spin relaxation of photoexcited excitons into the ground state which spin structure depends on the direction and magnitude of the magnetic field. Our model of the Auger recombination fits well with the experimental data and allows to explain characteristic features in photoluminescence spectra of single CdMnSe/ZnSe QDs.

Magnetic, Electric, Optic Properties and Band Structure of Semimagnetic Solid Solutions Based on Mercury Chalcogenide

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From the investigation of temperature dependence of magnetic receptivity of the Hg$_{1-x}$MnSe, Hg$_{1-x}$Mn$_y$Te$_{1-x}$S$_x$, Hg$_{1-x}$Mn$_y$Se$_{1-x}$S$_x$, Hg$_{1-x}$Mn$_y$Se$_{1-x}$S$_x$, Hg$_{1-x}$Mn$_y$Fe$_{1-x}$S$_x$, Hg$_{1-x}$Mn$_y$Fe$_{1-x}$S$_x$, crystals, obtained by Bridgeman method, was determined that on the $\frac{1}{\chi_{\text{Mn,Fe}}} = f(T)$ dependence rectilinear segments with different slant, which can be described by Curie low or Curie – Wase low, with negative paramagnetic Curie temperature ($\theta$) can be distinguished. The rise of effective magnetic moment ($\mu_{\text{eff}}$) of Mn atoms with temperature increasing (which is determined on the basis of linear segments slant change on the $1/\chi_{\text{Mn}} = f(T)$ dependence) is caused by the transition to “paramagnetic” state of cluster groups with different size (Mn-Se-Mn-Se, Mn-Te-Mn-Te, Mn-S-Mn-S or mixed Mn-Te-Mn-Se, Mn-Se-Mn-S, Mn-Te-Mn-S), which are formed in a crystals. Indirect exchange interaction with antiferromagnetic character occurs between Mn atoms via chalcogen atoms in these crystals. The energy of indirect exchange interaction depends on chalkogen atom size. From the obtained results the basis of the method of appreciating the cluster sizes, their shapes and heterogeneities of semimagnetic solid solutions on the basis of $A^{I+}B^{V}$, the magnetic subsystem of which formed by the Mn atoms, were proposed. In the Hg$_{1-x}$Mn$_y$Fe$_{1-x}$S$_x$ crystals conductivity decreases with temperature rising (T), and Hall coefficient is independent of T, which indicates the degeneration of Hg$_1$ effective magnetic moment ($\chi$) increases with the temperature rise. The conductivity of Hg$_{1-x}$Mn$_y$Fe$_{1-x}$S$_x$ crystals has semiconductor character, and the temperature dependences of Hall coefficient indicate that both electrons and holes take part in the transfer process, $\alpha$ changes from $> 0$ (at low T) to $\alpha < 0$ (at high T) for the most of the samples, conditioned by the increasing of concentration with the temperature rise. The thermal treatment of Hg$_{1-x}$Mn$_y$Te$_{1-x}$S$_x$ in the vapour of S and increase of S content leads to thermal - electric quality factor increase. Optic investigations show that both direct and indirect interband optic transitions take place in the crystals. The difference between $E_{\text{g} \text{op}}$ for direct and indirect transitions is $\sim 0.05 – 0.07$ eV for Hg$_{1-x}$Mn$_y$Se (adjusted with Et:$0.07$ eV for HgSe), and is $\sim 0.02$ eV for Hg$_{1-x}$Mn$_y$Te$_{1-x}$S$_x$ (adjusted with Et:$0.02$ eV for HgTe) at the T $\sim 100 – 300$ K. The transmission coefficient is $\sim 60\%$ for $x > 0.1$. Direct and indirect interband optic transitions, most probably, occur between valence band of heavy holes and conduction band (indirect – begin from extreme point of heavy holes band, located in $k \neq 0$), that is the resemblance to Hg$_{1-x}$Cd$_x$Te band structure takes place at T $> 77$K. The replacement of the part of Mn atoms by Fe atoms in the Hg$_{1-x}$Mn$_y$Fe$_{1-x}$S$_x$ crystals ($x + y = 0.1; z = 0.01$) leads to increasing $E_{\text{g} \text{op}}$ in comparison with $E_{\text{g} \text{op}}$ for Hg$_{1-x}$Mn$_y$Se$_{1-x}$S$_x$ ($x = 0.1; z = 0.01$), $E_{\text{g} \text{op}}$ increases with the rising of Fe content in the Hg$_{1-x}$Mn$_y$Fe$_{1-x}$S$_x$. Band structure of Hg$_{1-x}$Mn$_y$Se and Hg$_{1-x}$Mn$_y$Te$_{1-x}$S$_x$ is unparabolic and is characterized by the availability of transition “gapless semiconductor – ordinary semiconductor” at the certain temperatures and compositions ($\Gamma_6$ and $\Gamma_8$ band inversion). It is determined, that change of unparabolicity of the band spectrum of Hg$_{1-x}$Mn$_y$Se with the composition and temperature change is responsible for $dE_{\text{g} \text{op}}/dT < dE_{\text{g} \text{op}}/dT$ (at $E_{\text{g}}>0$). This change also essentially influences on the temperature dependence of electron effective mass at the Fermi level and on the thermal coefficient of optic band gap value change. The higher the degree of filling the unparabolic conduction band by electrons and the nearer is “x” to compo-sition the inversion of $\Gamma_6$ and $\Gamma_8$ band takes place the stronger this influence shows itself.
Phonon Properties and Doping of Zn$_{1-x}$Mn$_x$Se Epilayers Grown by Molecular-Beam Epitaxy

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ZnSe-based materials are important II-VI semiconductors with a variety of potential applications in optoelectronics devices, e.g. blue-green laser diodes [1] and light-emitting diodes [2]. Recently, diluted magnetic semiconductors (DMS) like Zn$_{1-x}$Mn$_x$Se have been demonstrated as possible candidates for spin aligners in spin-based opto-electronic devices [3]. However, information regarding the influence of the Mn concentration on several fundamental material parameters is still poor.

In this contribution, polarized and non-polarized reflection measurements in the far-infrared to the mid-infrared spectral range are employed in combination with electrical Hall effect measurements in order to investigate the phonon and free-charge-carrier properties of Zn$_{1-x}$Mn$_x$Se as a function of composition and doping concentration. We observe an “intermediate-mode” behavior for the optical phonon modes in Zn$_{1-x}$Mn$_x$Se in the composition range $0 \leq x \leq 0.43$. In addition to the known ZnSe-like and MnSe-like phonon resonances a weak mode is found below the MnSe-like phonon band. We conclude from linear chain calculations that this mode is due to an impurity phonon resonance caused by Mn incorporation on the Se-sublattice sites. Furthermore, we report on the free-charge-carrier effective mass, mobility, and concentration in differently doped Zn$_{1-x}$Mn$_x$Se samples. A distinct reduction of the effective electron mass in ZnSe is observed upon Mn-incorporation [4,5]. Additionally, the dopability decreases drastically with increasing Mn concentration. The latter effect is likely due to the unintentional Mn co-doping caused by the Mn incorporation on the Se-sublattice sites as suggested by the phonon mode properties.

Concentration and Size Dependence of the Dynamics of the Mn 3d\(^5\) Luminescence in Zn\(_{1-x}\)Mn\(_x\)S Nanoparticles with x up to 0.3

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Bulk crystals of wide-gap (II,Mn)VI dilute magnetic semiconductors such as Zn\(_{1-x}\)Mn\(_x\)S show a strong concentration dependence of the characteristic decay times of the internal Mn 3d\(^5\) luminescence. It is found that the characteristic decay times decrease significantly from a few ms to \(\mu\)s with increasing Mn-content x [1]. This observation is explained by migration effects of the excitation within the Mn system allowing a more efficient transfer to non-radiative defects, i.e. so called killer centers. In corresponding nanostructures with low Mn-content x < 2%, a dramatic decrease of the decay times compared to bulk are commonly observed. The reasons for this decrease are still under discussion. They range from confinement effects [2] to surface effects [3].

We studied the concentration as well as the size dependence of the dynamics of the Mn-related luminescence in Zn\(_{1-x}\)Mn\(_x\)S nanostructures. The diameters of the spherical nanostructures studied were 3, 6, 7, and 9 nm, respectively. The Mn concentrations x exceeded those of all nanostructures studied previously and ranged up to x = 0.3. Clear trends with concentration as well as with diameter of the nanoparticles were observed. For the smallest diameter of 3 nm, it was found that, in contrast to bulk Zn\(_{1-x}\)Mn\(_x\)S, the decay times increase significantly with increasing Mn concentration. This unexpected behavior becomes less pronounced with increasing diameter of the nanostructures. A characteristic decay time almost independent of x was observed for the largest diameter of 9 nm. Furthermore, it was found that the characteristic decay times slightly increase with increasing diameter for x \(\approx\) 0.01 whereas for x \(\geq\) 0.1 this trend is reversed and the characteristic decay times decrease with increasing diameter. Possible explanations for this unusual behavior will be discussed.

Preparation Conditions in Molecular Beam Epitaxial Growth of High-Quality CdSe Quantum Dots for Green Laser Diodes

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Green laser diodes (LDs) are expected for light sources in plastic (PMMA)-fiber optical communications and in full-color displays together with red and blue LDs. Quantum dots (QDs) of CdSe is a candidate as an active layer material of the green LDs. Laser diodes with the QDs have advantages compared to those with the two-dimensional quantum well, that is, they have low threshold currents and the temperature dependence of the threshold current is small [1]. In this paper we describe preparation conditions in molecular beam epitaxial growth of high-quality CdSe QDs.

The sample structure is “ZnSe cap layer/ CdSe QDs/ ZnSe buffer layer/ GaAs (001) substrate”. Photoluminescence (PL) was measured at 14 K, and the high PL intensity and the narrow half width (FWHM) of the spectrum were used as measures of high quality.

The source material was CdSe compound and the substrate temperature was 330°C throughout the study. The amount of CdSe source supply was also fixed to 2.2 monolayers (MLs). The substrates of GaAs (001) without or with GaAs buffer layers grown in a separate MBE chamber were compared. As growth parameters, were changed the source supply rate and the growth interruption time between the growth of CdSe QDs and the ZnSe cap layer. The irradiation of the Se was also tried during the growth interruption.

As a result, the GaAs substrate with a GaAs buffer layer showing (2x4)β reconstruction is better than the substrate without buffer layer (only thermally deoxidized). The optimum source supply rate was between 0.02-0.003 ML/s. During the growth interruption, the ripening or coalescence of the QDs [2] almost finished in 30 seconds, which was revealed as a red-shift of the PL peak. The PL intensity decreased with coalescence, and it recovered with the interruption time to the almost same level as that without growth interruption, that is, the crystallinity of the QDs deteriorated once with coalescence and recovered during the long growth interruption (8 min.). The Se-irradiation during the growth interruption (1 min.) increased the PL intensity. In all cases the higher emission intensity accompanied the narrower FWHM. Thus, some of preparation conditions for high-quality CdSe QDs were established in this study. Also, the improvement of the qualities above accompanied the blue shift of the PL peak wavelength.

The wavelength value at room temperature is around 530 nm, which corresponds to the subminimum of the transmission loss of the PMMA optical fiber. The transmission loss at this wavelength is already smaller than that at 650 nm of the red LD used at present. The adjustment of the emission wavelength to 560 nm (minimum-loss wavelength) remains as a next problem [3].

The temperature dependences of the PL spectra are shown in the conference session.

Magnetization Dynamics of Diluted Magnetic Quantum Dots

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Diluted magnetic quantum dots (DMQDs) represent promising candidates for spintronic devices, as they allow for controlling single carrier spins confined on a nm length. Nowadays, their realization via self-organized growth of II-VI quantum dots under incorporation of magnetic Mn ions is well established and the static magneto-optical properties have been studied in detail [1..5]. Less attention has been paid so far to the dynamics of the Mn spin system. Besides the principle interest in knowing the time-scale on which the Mn magnetization can be switched incoherently in a device, the question arises wether the underlying spin-lattice relaxation (SLR) in diluted magnetic structures with sizes necessary for sufficient carrier confinement is already modified compared to the well studied bulk case. In this paper, the temperature and magnetic-field dependences of spin heating and cooling transients are studied systematically on (Cd,Mn)Se DMQDs with Stranski-Krastanov morphology using samples with an intermediate Mn content $x = 0.03..0.07$. The exponential dependences of the SLR rate $1/\tau$ both on the inverse temperature $T$ as well as on Mn content prove that the overall scenario of a SLR via the Orbach process on Mn clusters is qualitatively not altered at sizes down to the sub-10-nm range. Compared to several monolayer thick quantum wells, however, the SLR rate is reduced by nearly one order of magnitude. This points to the reduced formation of Mn clusters in the present structures. From the activation energy found in the $1/\tau = f(1/T)$ plot, it follows that Mn pairs play the major role here, in contrast to the bulk case.

Shorter Wavelength Intersubband Absorption Down to $\lambda = 1.55 \mu m$ in (CdS/ZnSe)/BeTe Type-II Super-lattices

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Intersubband transition (ISB-T) in semiconductor quantum wells (QWs) or super-lattices (SLs) has been paid considerable attention due to the potential application in infrared detector, quantum cascade laser, ultrafast all-optical modulators and switches. The recent attempt to extend the ISB-T to near infrared (NIR), in particular to the $1.55 \mu m$ (0.8 eV) fib-optic communication, has been developed exceedingly. So far, NIR wavelengths ($\lambda \leq 2 \mu m$), ISB-T, and ISB carrier relaxation times from sub-ps to ps have been reported in III-V material system such as GaN/AlGaN, InGaAs/AlAsSb, InGaAs/AlAs, and GaN/AlN. The recent development of ZnSe/BeTe and (CdS/ZnSe)/BeTe SLs, which has a huge band offset of 2.3-3.1 eV, has open up the application in the NIR spectral region for II-VI wide gap material [1-5]. In this contribution, we first present the dependence of ISB absorption on the electronic doping density in (CdS/ZnSe)/BeTe SLs grown on GaAs (001) substrates using molecular beam epitaxy. A streaky RHEED pattern as well as a clear Kikuchi band confirms two-dimensional mode in the whole growth. Superlattice satellites increase to 13 orders and peaks become narrow and intense in high-resolution XRD (HRXRD), revealing perfect structure. Clear interference fringes around zeroth-order peak in XRD spectra indicate a sharp interface in this heterostructure. An ISB-T energy as high as 0.79 eV is observed in this structure, covering $1.55 \mu m$ (0.8 eV) within its absorption bandwidth. The intensity of ISB absorption increases with increasing ZnCl$_2$ flux until reaches a maximum and then decreases with further more ZnCl$_2$ flux supplying. The ISB-T energy slightly red shifts from 0.79 to 0.775 eV with ZnCl$_2$ flux increasing and then blue shifts to 0.785 eV when the intensity of ISB decreases with more chlorine doping. To fully understand the ISB-T as well as further device application, we also study the effects of anneal on the ISB absorption and structural properties in (CdS/ZnSe)/BeTe SLs. For comparison, the anneal results on a reference structure, CdS/ZnSe multiple quantum wells, are also given. With annealed temperature increasing, the ISB-T shifts to longer wavelength in (CdS/ZnSe)/BeTe SLs, but to short wavelength in CdS/ZnSe structure, i.e., a red shift in (CdS/ZnSe)/BeTe and a blue shift in CdS/ZnSe heterostructure. The ISB absorption vanishes at the anneal temperature at 270$^\circ$C for CdS/ZnSe, while the ISB-T disappears until the temperature up to 440$^\circ$C for the (CdS/ZnSe)/BeTe SLs. HRXRD combined with dynamic simulation and photo-induced ISB-T are employed to investigate the anneal effects on both heterostructures. The explanations to result in the change in (CdS/ZnSe)/BeTe and CdS/ZnSe structures are given.

3d Transition Metal Impurities in Zn$_{1-x}$M$_x$Se and Zn$_{1-x}$M$_x$S Alloys

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Doping of wide-gap II-VI semimagnetic semiconductors (ZnS, ZnSe, CdTe, etc.) 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. Resonant photoemission spectroscopy is a powerful method to investigate the contribution of transition metal 3d states to the valence band electronic structure of doped semiconductors. Using Co L$_\alpha$ X-ray emission spectra and Co 2p X-ray photoelectron spectra, we have found that Co ions in ZnS:Co are in a Co$^{2+}$ configuration and that the Co 3d impurity states are localized above the top of the valence band by 1.0 ± 0.2 eV [1].

Here, we report metal-impurity 2p X-ray absorption and L X-ray resonant emission spectra of Zn$_{0.95}$Cr$_{0.05}$S, Zn$_{0.95}$Co$_{0.05}$Se, and Zn$_{0.95}$V$_{0.05}$Se. The results for Zn$_{0.95}$Cr$_{0.05}$S are shown in the figure. The X-ray results are compared with our optical and magnetic data.

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Polarization of Electron Spin in Two Barrier System Based on Semimagnetic Semiconductors

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A spin filter based on semimagnetic semiconductors was studied. A system of semimagnetic semiconductors with two barriers and well between them was investigated as the spin filter [1]. The spin polarization arises as a result of spin dependent electron tunneling through resonance quasilevels in the well, which are splitted due to an exchange interaction of electrons and magnetic ions. Moreover the tunneling processes the propagation of the polarized carriers injected into non-magnetic layer was studied. For that the kinetic transport equations for electrons and the Poisson equation were solved numerically. The investigation was made for (CdMn)Te/CdTe/(CdMn)Te and (CdMg)Te/(CdMn)Te/(CdMg)Te heterostructures. We have calculated 1) the current voltage characteristic for the electron with different spin projections in two barriers system, 2) the dependence of current voltage characteristic on magnetic field, temperature, concentration of magnetic ions, 3) the spin polarization in the sample as function of distance from barrier. The study has shown that the level of spin polarization of tunneled electrons strongly depends on magnetic field and such parameters of the spin filter as widths of barriers and well, the electron density in matrix and the concentration of magnetic ions in the barriers, time of electron spin relaxation.

Effects of Alloying, Ordering, and Strain on the Exchange Parameters of II-VI Dilute Magnetic Semiconductors

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The potential in spintronic applications has recent rekindled the interest in the study of dilute magnetic semiconductors (DMS), which exhibit an interesting combination of magnetism and semiconductivity, characterized by both impurity-like wavefunction localization and band-like behavior. One of the materials that have attracted much attention is Be\(_{1-x}\)Mn\(_x\)Te. BeTe can be doped with very high hole-carrier density (more than 10\(^{20}\) cm\(^{-3}\)). Unlike most other II-VI semiconductor hosts, it is possible to stabilize Mn-doped BeTe in the ferromagnetic phase, with potentially high Curie temperature. Furthermore, the alloying of BeTe with a few percent Mn can be lattice-matched to the two important optoelectronic materials ZnSe and GaAs, opening up promising applications for spintronics.

However, despite its promising potential in magnetoelectronics, many fundamental physical properties of BeMnTe are still unknown. For example, the exchange parameters \(N_{0a}\) and \(N_{0b}\) are the two most essential quantities related to the interaction between the magnetic ion \(d\) states and the host itinerant \(s\) and \(p\) electron states in dilute magnetic semiconductors. By symmetry, the coupling between the conduction band \(s\) state and the Mn \(d\) states is mainly through the direct (or potential) exchange, so \(N_{0a}\) is usually positive. On the other hand, the anion \(p\) and cation \(d\) states hybridize strongly in ZB semiconductors, so the coupling between the \(p\) states and Mn \(d\) states is dominated by the kinetic exchange caused by the hybridization and level repulsion between the magnetic ion \(d\) and the anion \(p\) states, and \(N_{0b}\) is usually negative. Recently, experimental measurement on a Be\(_{1-x}\)Mn\(_x\)Te/ZnSe found that \(N_{0b}\) of Be\(_{1-x}\)Mn\(_x\)Te is about -0.4 eV. This result is quite puzzling because the value is much smaller than the well-known value of -0.88 eV for Cd\(_{1-x}\)Mn\(_x\)Te, in contrast to the usual believe that the exchange parameters are not sensitive to alloy concentration; thus, \(N_{0a}\) and \(N_{0b}\) should be similar for Be\(_{1-x}\)Mn\(_x\)Te and Cd\(_{1-x}\)Mn\(_x\)Te as well as MnTe in the hypothetic ZB structure. To understand the general trend in the exchange parameters, we have studied the effects of alloying, ordering, and strain on \(N_{0a}\) and \(N_{0b}\) of Be\(_{1-x}\)Mn\(_x\)Te, Zn\(_{1-x}\)Mn\(_x\)Se, Zn\(_{1-x}\)Mn\(_x\)Te, Cd\(_{1-x}\)Mn\(_x\)Te and Be\(_{1-x}\)Mn\(_x\)Te/ZnSe superlattice, using the first-principles band-structure method [1]. We find that: (i) \(N_{0a}\) in the alloy is smaller than in the corresponding binary hypothetical ZB compounds MnTe and MnSe, due to wavefunction localization. In general, \(N_{0a}\) is not very sensitive to the Mn concentration. (ii) \(N_{0b}\) increases as the alloy volume decreases, due to increased p-d level repulsion. The change of \(N_{0b}\) on the Mn concentration depends on the system studied. For bulk Be\(_{0.75}\)Mn\(_{0.25}\)Te, \(N_{0b}\)=1.31 eV and increases as \(x\) decreases. (iii) Ordering of Mn atoms in the host can alter the wavefunction localization, and thus change the exchange parameters. (iv) \(N_{0b}\) is reduced from -1.31 eV in bulk Be\(_{1-x}\)Mn\(_x\)Te to a value as small as -0.3 eV in a Be\(_{1-x}\)Mn\(_x\)Te/ZnSe heterostructure. This can be explained by the strain-induced nonuniform distribution of the Mn atoms near the interface, and the reduced symmetry of the VBM wavefunction. Thus, our results explain why the measured \(N_{0b}\) of Be\(_{1-x}\)Mn\(_x\)Te/ZnSe is so small compared with what one would expect for bulk Be\(_{1-x}\)Mn\(_x\)Te.

Te-cluster doped ZnS\textsubscript{x}Se\textsubscript{1-x} (x=0.08) is a suitable system for high efficient blue-green light emitters because it reveals high quantum efficiency of photon-emission from Te-cluster bound excitons, and also has strong durability for device operation due to Te hardening effect. This paper presents a new green DH structure LEDs of ZnS\textsubscript{Se}:Te (active layer)-ZnMgS\textsubscript{Se} (cladding layer) on p-type GaAs substrates grown by MBE. Here we tried to improve the green LEDs from the viewpoints of (i) controlling Te-cluster doping and (ii) new device structure on p-type GaAs, which leads to efficient green LEDs with long device lifetime for its practical use.

(A) Te\textsubscript{n} -cluster (n\textgreater{}2) Modulation Doping
In order to improve green emission efficiency of Te\textsubscript{n}-clusters, we have examined three different doping profiles of Te\textsubscript{n}-clusters: (i) Te-cluster uniform doping (3%) in whole active ZnS\textsubscript{x}Se\textsubscript{1-x} layer, (ii) modulation doping (10 periods of 7% Te-doped layer (50 Å) and undoped layer (50Å)), and (iii) Te-bias modulation-doping (light uniform Te-doping of 2% + Te modulation doping of 5%). In comparison of these doping profiles, we have confirmed very efficient green emission (>0.2% in bare-LED chips) in the (iii) Te-bias modulation doping. This improvement in the green emission is due to a large thermal activation energy of Te\textsubscript{n}-cluster bound exciton (\textDelta{}H\textsubscript{T} > 250meV) in the Te bias-modulation doping system. Another big advantage of this doping method is to be able to maintain Te-hardening effect for the long device lifetime.

(B) New Green LEDs on p-type GaAs substrates
Present green LEDs (using Te-bias modulation doping) is grown on p-type GaAs for the first time. The p-type hetero-structure is achieved by a new technique of hetero-interface super-lattice (SL) buffer consists of ZnSe-ZnTe MQWs, inserted in GaAs(III-V)-ZnS\textsubscript{Se}(II-VI) hetero-interfaces, which can overcome a large energy barrier (>1eV) for hole ohmic conduction. This interface SL buffer enables us to design a simple LED structure of n\textsuperscript{+}-ZnMgS\textsubscript{Se} window-i(Te-doped ZnS\textsubscript{x}Se active layer)-p(ZnMgS\textsubscript{Se}) on p-GaAs without surface super-lattice structure required in conventional II-VI LED devices on n-GaAs. Because of a transparent surface n\textsuperscript{+}-window, an extraction efficiency of the green emission is found to be larger three times in magnitude than conventional LEDs.

We have carried out simple aging tests on the present green LEDs, coupled with DLTS/ICTS technique monitoring point defect diffusion and generation in devices. Typical device lifetime under 3A/cm\textsuperscript{2} at 300K is over 1300 hours, which undergoes through a so-called “slow-mode degradation process” due to point defect generation and diffusion in p-type ZnMgS\textsubscript{Se} cladding layer. The observed slow-mode degradation is quite similar to the case in ZnSe based white LEDs, and is found to be improved by utilizing double-cladding structure which prevent electron over-flow into p-type ZnMgS\textsubscript{Se} layer.
**Fig. 1** Schematic diagram of a ZnSSe:Te DH-LED on p-type GaAs.

**Fig. 2** Three different doping profiles of Te-clusters: (i) uniform, (ii) modulation, and (iii) Te-bias modulation in the active layer of the ZnSSe:Te DH-LEDs.

**Fig. 3 (a)** Comparison of the external quantum efficiencies between ZnSSe:Te LED on p-type GaAs and on n-type GaAs.

**Fig. 3 (b)** EL spectra of the ZnSSe:Te LED on p-type GaAs, and n-type GaAs under 3A/cm² at R.T.

**Fig. 4** Optical output power of the ZnSSe:Te LED on p-type GaAs and n-type GaAs versus aging time under 3A/cm² at room temperature.

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Electrophysical and Cathodoluminescent Properties of Low-dimensional CdSSe/CdS Structure

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Using hexagonal low-dimensional structures may solve a problem of reliable laser emitting in visible spectral range [1]. The first laser with such a structure was realized on CdSSe/CdS system by longitudinal pumping of a scanning electron beam at room temperature [2]. The CdSSe/CdS heterostructure is considered to have a type-II band alignment. However, up to date its zone diagram was not studied in detail. In this work we studied the band alignment of such a structure by the methods of cathodoluminescence (CL), CV characteristics and current deep level transient spectroscopy (CDLTS).

A diode-like sample was fabricated out of a low-dimensional CdSSe/CdS structure destined for an electron-beam pumped vertical-cavity surface-emitting laser (VCSEL). The structure was grown by metal-organic vapour phase epitaxy (MOVPE) on undoped CdS substrate. It contained a 0.35 µm thick CdS buffer layer and 40 pairs of a 3 nm thick CdS₀.₆₅Se₀.₃₅ layer and a 142 nm thick CdS layer. The CdSSe layers formed quantum wells (QWs) for holes and were semitransparent for tunneling electrons. The CdS substrate was partially eliminated by mechanical polishing and etching in the solution of CrO₃ in HCl. The residuary thickness of the CdS up to the first CdSSe layer was about 11 µm. The structure was bonded to a n+ GaAs substrate. An In contact to the back side of the GaAs substrate and a Ni contact to the CdS layer were made.

To determine peculiarities of the carrier distribution, first the CV characteristics were measured. Free carriers were found to be electrons. In the approach of depletion layer [3] average concentration of free electrons was found to be equal to 4·10¹³ cm⁻³. Two dips and one peak in the N(z) dependence are observed. We connected the peak with the first CdSSe layer. Based on this analysis we have determined conditions at that the edge of the space charge layer reaches the low-dimensional region of the structure. The CDLTS spectra consisted of peaks from deep electron traps with activation energies \( E_a = 0.331 \) and \( 1.145 \) eV in the CdS layers and the peak with \( E_a = 0.279 \) eV due to an emission of holes from the ground quantized level in the CdSSe layers. Using a calculation procedure described in [4] the valence band offset in the laser CdS₀.₆₅Se₀.₃₅/CdS structure was determined as 287±40 meV. The conduction band offset was estimated by the value of 83 meV. Finding band offsets allowed calculating the spontaneous emission line maximum. These calculations are in close fit with experimental data obtained by CL.

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Ultrasonic Investigations of ZnSe:Cr\(^{2+}\) Crystal

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Experiments in ZnSe:Ni\(^{2+}\) have resulted in discovery of anomalies in temperature dependences of ultrasonic absorption and phase velocity [1]. The anomalies were interpreted as due to the Jahn-Teller effect and had relaxation nature. The relaxation occurred in the system of the impurity electron levels, distorted by ultrasonic wave. We restored the temperature dependences of relaxation time \(\tau\), dynamic \(C_{44}^D\) (i.e., measured at a certain frequency \(\omega\)), unrelaxed \(C_{44}^{U}\) (adiabatic) and relaxed \(C_{44}^{R}\) (isothermal) elastic moduli. The moduli exhibited sufficient softening below 100 K, indicating lattice instability. The curve \(\tau(T)\) made it possible to estimate the energy of the 1st exited state \(\Delta E = 3.5\) meV.

Since the properties of II-VI:3d crystals are of great importance, we investigated ZnSe crystal with another type of dopand, namely, Cr. Its concentration was \(\approx 10^{20}\) cm\(^{-3}\). We found an absorption peak of longitudinal wave, similar to one in ZnSe:Ni\(^{2+}\), but of larger magnitude. However, there was not observed softening, except for \(C_{44}^{R}\). In Fig.1 symbols: • correspond to \(\Delta C_{eff}^D = C_{eff}^D(T) - C_{eff}^D(4.2)\), \(\triangle = \Delta C_{eff}^U = C_{eff}^U(T) - C_{eff}^U(4.2)\), and ◦ – \(\Delta C_{eff}^R = C_{eff}^R(T) - C_{eff}^R(4.2)\). It means that there is no such phase transition as in ZnSe:Ni\(^{2+}\). The relaxation time was calculated with the use of approach reported in [1] and the curve is shown in Fig.2. Symbols ■ relate to results obtained with the help of another method. It was based on the condition of relaxation maximum \(\omega \tau = 1\) and the measurements were done at 32.5, 75.4, 157 MHz. One may see that both the methods give similar results. Moreover, \(\tau\) proved to be of the same order as in ZnSe:Ni\(^{2+}\).

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Some New Aspects of the Low-Energy Excited States Problem in II-VI Selenides Doped with 3d Transition Metal Ions

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Wide bandgap semiconductors doped with 3d transition metal ions have attracted considerable attention for the last years due to their possible applications in laser technique [1] and spintronic devices. In the present paper heat capacity of the solid solutions Zn$_{1-x}$M$_x$Se (M = Ni, Cr, Fe; x = 2.7, 4.5 and 1.7 at.% respectively) have been measured in the temperature range (1.85-25)K. As a result, the additional contribution to the total heat capacity $C_{tot}$ due to the intra-configurational $d$-$d$ transitions from the ground state of 3d ion to the first excited one was separated (Schottky mechanism): $C_{Schott} = C_{tot} - C_{lat}$, where $C_{lat}$ is the heat capacity of the host material, i.e. ZnSe.

According to the theory, in the low temperature limit the amount $C_{Schott} T^2$ must be proportional to the exp($-\Delta/kT$) that make it possible to determine the activation energy $\Delta$. Applying this procedure for Zn$_{1-x}$Cr$_x$Se compound, we obtained $\Delta=7$cm$^{-1}$ in accordance with [2]. In contrast to ZnSe:Cr$^{2+}$, the energy of excited state for ZnSe:Fe$^{2+}$ and ZnSe:Ni$^{2+}$ proved to undergo noticeable jump from $\Delta_1$ to $\Delta_2$ at some temperature $T_c$ = 4 and 2.5K respectively, as one can see in Fig. 1. Using $C_{Schott}$ data after Ref.[3], we also found a similar $\Delta$-jump for Cd$_{1-x}$Fe$_x$Se (x = 0.034) and Hg$_{1-x}$Fe$_x$Se (x = 0.024) solid solutions at $T_c$ = 4.4 and 3.7K. The value of $\Delta_1 \simeq 14$cm$^{-1}$ for the Fe$^{2+}$ ion in ZnSe, CdSe and HgSe turned out to be close to the value of such energy gap in ZnS:Fe$^{2+}$ [4]. We also obtained $\Delta_1=24$cm$^{-1}$ for the Ni$^{2+}$ in ZnSe. This value is in a good agreement with activation energy estimation 28cm$^{-1}$ from our ultrasonic studies [5]. Note, the low-energy excited state for the Ni$^{2+}$ ion in II-VI compounds has been detected for the first time. As an important result, the $\Delta$-jump in Zn$_{1-x}$Ni$_x$Se probably indicates the low-temperature structural phase transition which has been found earlier in this compound by the neutron diffraction method [6]. Does the $\Delta$-jump in II-VI selenides doped with Fe$^{2+}$ ions have the same nature? This problem will also be discussed in the paper.

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Magneto-Optical Faraday Effect in II-VI Based Semimagnetic Semiconductor Nanocrystals

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The Faraday effect is a powerful tool for characterizing II-VI semiconductors especially in case of their semimagnetic counterparts type of II\textsubscript{1-x}Mn\textsubscript{x}VI. In fact, for these materials so-called giant Faraday rotation is one of the most interesting phenomena which are due to strong spin-spin exchange interaction between the localized magnetic moments of Mn\textsuperscript{2+} ions and band carriers. It is obvious that when one goes from bulk material to zero-dimensional structures the magneto-optical phenomena should be significantly modified by strong confinement in all three directions. There are several important aspects in the magneto-optical studies of semimagnetic semiconductor nanocrystals, but the key question is to elucidate how should change magneto-optical characteristics because of transition from 3D semiconductor crystal to 0D nanocrystal. Our previous findings \cite{1} suggest of large enhancement of the Faraday effect for Cd\textsubscript{1-x}Mn\textsubscript{x}Te nanocrystals when compared to the bulk Cd\textsubscript{1-x}Mn\textsubscript{x}Te crystal. However, this experimental result have to be still confirmed for other chalcogenide systems and for nanocrystals embedded in different matrices. In this work we present results of magneto-optical studies of II-VI based semimagnetic semiconductor nanocrystals prepared by different physical and chemical techniques.

The II\textsubscript{1-x}Mn\textsubscript{x}VI nanocrystals were prepared by growth of nanoparticles embedded in SiO\textsubscript{2} matrix with using pulsed laser deposition technique, embedding of semiconductor nanoparticles into polymer matrix and growth by melting of the semiconductor doped fine powder borosilicate glasses. In addition, new approach to synthesis of Cd\textsubscript{1-x}Mn\textsubscript{x}S semimagnetic semiconductor nanoparticles has been proposed. Four kinds of CdS nanoparticles doped with Mn\textsuperscript{2+} (with low, intermediate, high Mn\textsuperscript{2+} content and binary CdS, MnS sulfides) were synthesized by embedding in polymer matrix. A water-based synthesis was used to prepare the nanoparticles with mercaptoethanol as stabilizing ligand. MnS-Cd nanoparticles were synthesized to provide ion exchange type of Mn\textsuperscript{2+}-Cd\textsuperscript{2+}.

The observed changes in the Faraday effect for the studied nanocrystals are the following: i) increase of the Verdet constant near the fundamental absorption edge for nanocrystals as compared with that of bulk crystal; ii) almost linear dependence of the Faraday rotation as function of magnetic field strength for nanocrystals at liquid helium temperature in contrast to the dependence with saturation in bulk case; iii) changes in process of a transition of the semimagnetic nanoparticles from the paramagnetic state to a spin glass. It was considered opportunity to explain the observed features in framework of the interface paramagnetism enhancement effect on the Faraday rotation \cite{2} in the nanocrystals. Other possible mechanisms of the influence of the reduction of dimensionality on spin exchange parameters in semimagnetic zero-dimensional structures are discussed.

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Negatively Charged CdTe/ZnTe Single Quantum Dots: Valence Band Anisotropy and Optical Orientation

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Semiconductor quantum dots have been studied intensely in recent years as attractive candidates for quantum information processing. In this context, the spin of electronically charged QDs is especially exciting because of its long dephasing time. Knowledge of the discrete energy structure of doped QDs and the ability to control the individual charge state of the dots is essential for the development of these spin based devices.

In this work, using the negatively charged exciton as a probe, we investigate the valence band structure and hole spin relaxation in epitaxial CdTe/ZnTe QDs. Polarization sensitive magneto-pholuminescence and photoluminescence excitation spectroscopy are used to analyze the structure and polarization properties of the exciton, biexciton and negatively charged exciton in single QDs. Resonant excitation of the excited states of single charged QDs are observed and photo-depletion permits to efficiently control the presence of excess carriers in the dots.

FIG. 1 (a) Zero field PL spectra of a single n-doped QD. The insets show the zero field polarization anisotropy of the charged exciton and its characteristic splitting under a transverse magnetic field. (b) Polarization sensitive PLE spectra and circular polarization rate of the charged exciton. The inset shows the depolarization curves of the resonant PL in a transverse magnetic field.

In a transverse magnetic field the charged exciton splits into a quartet of linearly polarized lines (Fig1(a)). This spectral feature directly reveals an off-diagonal coupling of both electron and hole states. Large in plane hole g-factor are measured. At zero magnetic field, the heavy-light hole mixing and symmetry reduction of the quantum dot results in elliptical polarization of the optical transitions with a specific axis for each dot defined by strain and shape.

Despite this valence band mixing, we achieve an optical pumping of spin polarized charged exciton populations and demonstrate a control of the degree of polarization by applying an external magnetic field. We find that high efficient selective pumping of spin polarized $X^-$ can be achieved at all excitation energies below the onset of the wetting layer showing that spin-flip of the holes occurs on a time scale longer than the exciton life-time. Due to the hole in plane g-factor, a small transverse magnetic field erases the contribution of the oriented hole to the photoluminescence polarization (Hanle effect).
Complete Magneto-optical TE-TM Mode Conversion in Cd$_{1-x}$Mn$_x$Te Waveguide for Integrated Optical Isolator

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II-VI diluted magnetic semiconductor of Cd$_{1-x}$Mn$_x$Te is a very attractive magneto-optical material for integrated waveguide isolator in advanced fiber communication systems. Cd$_{1-x}$Mn$_x$Te has several merits for the integration. It can be grown epitaxially on GaAs substrate, it is transparent and it shows large Faraday effect near its absorption edge. To fabricate the waveguide isolator, high magneto-optical mode conversion efficiency between transverse electric (TE) and transverse magnetic (TM) waveguide modes with wider wavelength range is desired. For this purpose, we propose to use the graded-refractive-index clad layer of the Cd$_{1-x}$Mn$_x$Te waveguide and studied the effect of the thermal annealing. We designed and fabricated Cd$_{1-x}$Mn$_x$Te waveguide on GaAs(001) substrate at 300°C by the molecular beam epitaxy (MBE) method [1, 2] where 5000Å thick graded-refractive-index layer ($x = 0.225 - 0.26$) are inserted between the core layer (1µm) and air and between the core and clad layer (3µm). Cd$_{1-x}$Mn$_x$Te waveguide was grown with Te rich condition which we found very effective for the magneto-optical performance. After the growth, samples were annealed in the MBE chamber by increasing the substrate temperature between 400°C and 450°C with Cd flux for typically 5 min. Magneto-optical measurements were carried out at room temperature at several wavelength ($\lambda = 680 - 800$ nm) and magnetic fields up to 5.5 kG. Complete TE-TM mode conversion efficiency was obtained between 710 nm and 735 nm for the Cd$_{1-x}$Mn$_x$Te waveguide annealed at 425°C (solid circle) whereas the complete mode conversion efficiency was obtained only for 3 nm wavelength range (725 nm to 728 nm) for the waveguide without annealing (open circle) as shown in Fig. 1. The annealing expanded the operation wavelength range more than 8 times. Analyses showed that the absolute value of the phase mismatch between TE and TM modes, which reduces the mode conversion efficiency, was reduced by the annealing (less than 100 deg/cm). This result suggests that the annealing redistributed Mn atoms by diffusing along the waveguide thickness to result in the smoother refractive index distribution in the waveguide. The annealed Cd$_{1-x}$Mn$_x$Te waveguides also showed very low optical loss of 0.2 dB/cm, high magneto-optical figure-of-merit of more than 1000 deg/dB/kG, and isolation ratio more than 20 dB at $\lambda = 715 - 735$ nm. These results demonstrate the feasibility of monolithic integration of an optical isolator with semiconductor optoelectronic devices by using Cd$_{1-x}$Mn$_x$Te.

We study the transport properties of a II-VI semiconductor structure containing CdSe self-assembled quantum dots embedded within a ZnBeMnSe tunnel barrier. At zero magnetic field, the I-V characteristics of the structure are similar to that previously observed in non-magnetic III-V systems with many resonant peaks associated with tunneling through individual quantum dots.

Novel behavior however emerges under the application of an external magnetic field. Firstly, we observe peaks drifting apart following the Brillouin-like giant Zeeman splitting of the ZnBeMnSe barrier. Given that there is no Mn in the dots, and that the barrier height change due to the giant Zeeman splitting has a negligible effect on peak position, this is simply evidence that the individual electron levels in the quantum dots must couple to the Mn system in the barrier.

Far more intriguing however, is the fact that the splitting between pairs of states of opposite spin remains finite (and of the order of a few meV) even at zero magnetic field. This behavior stems from the electrons in the dots mediating a ferromagnetic interaction between Mn in the vicinity of the dots, which is strong enough to overcome the direct Mn-Mn antiferromagnetic coupling. This conclusion is supported both by our analytical modeling and by numerical simulation work done by others.
Colloidal Nanocrystals Integrated in Epitaxial Nanostructures: Structural and Optical Properties

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Semiconductor quantum wells, wires, and dots, grown epitaxially in molecular beam epitaxy, have emerged as the potential basis of active devices in modern telecommunication systems. In parallel, semiconductor nanocrystals, grown by colloid chemistry, are another important class of quantum nanostructures, particularly suitable for applications in wet-chemical environments such as biosensing and labelling. Here we present an epitaxial growth technique which allows to integrate colloidal II–VI nanocrystals into monolithic photonic devices. The obtained results demonstrate the compatibility of wet-chemical growth and molecular beam epitaxy (MBE) to create complex semiconductor nanostructures with nanocrystals as active optical material. As exemplary system we chose CdSe/ZnSe nanostructures and discuss the two limits of thin (d\textless;2R) and thick (d\textgreater;2R) ZnSe cap layers of thickness d for CdSe nanorods and nanodots of radii R between 2 nm and 4 nm \cite{1}. The hybrid growth samples were produced in three steps: Colloidal solutions of CdSe nanorods and CdSe(ZnS) core-shell nanodots have been synthesized by the standard high-temperature reaction of organometallic precursors in the strongly coordinating solvents. These nanocrystals were deposited ex-situ on a ZnSe buffer layer with a thickness of 45 nm which was grown on a (001)-GaAs substrate by MBE at 280 °C. In a third step, the sample was transferred back into the MBE chamber, heated to 240 °C and overgrown by migration-enhanced epitaxy (MEE), a special MBE technique which allows an enhanced movement of adsorbed atoms on the substrate surface. The growth was controlled by reflection high energy electron diffraction (RHEED), and the structural properties were examined ex-situ by high resolution X-ray diffraction (HRXRD) and reciprocal space maps (RSM), and high-resolution transmission electron microscopy (TEM). In contrast to the well known Stranski-Krastanow growth mode, the hybrid epitaxial growth of quantum dots is strain-free without forming a wetting layer. The ZnSe cap layer is of high crystalline quality and provides all parameters for a consecutive growth of Bragg-structures, waveguides or diode structures for electrical injection. As a possible mechanism for the epitaxial growth of the ZnSe on top of the nanocrystal we propose lateral epitaxial overgrowth from a neighboring epitaxial ZnSe region. The optical properties have been studied by temperature-dependent and time-resolved photoluminescence. The nanorod emission spectrum is maintained after ZnSe overgrowth, however efficiency, PL dynamics and photostability are modified. The PL decay of the hybrid structure is strongly non-exponential and characterized by a fast initial decay, which we assign to a capture in ZnSe-related traps, and a second component slightly longer than the decay time of the SK dots. The origin of PL decay modification of CdSe NRs in the hybrid structure can be attributed to various effects including changes in the optical transition dipole moment due to the extension of electron or hole wave functions into the surrounding barrier, reorganization of the nanorod surface, and changes in defect density during the thermal annealing, or a new, combined, decay time consisting of the radiative lifetime of the nanorod and a transfer time between the NR and the substrate.

\cite{1} U. Woggon et al., Nano Letters 5, 483 (2005).
Low-density electron systems in three-dimensional space (3D) may form Wigner phases: the electrons are localized around separate sites forming a lattice (Wigner crystal), or they may form a paired crystal in spin-singlet configuration [1].

In quantum dots (QDs) in high magnetic fields electron systems can form an island-like structure (Wigner molecule). In this paper we investigate the possibility of the spin-singlet paired phase in a QD in an external magnetic field.

We have developed a variational many-body description for few-electron systems in a two-dimensional (2D) parabolic QD in an external magnetic field. To fully account for the Coulomb interaction in a many-electron context we have used the Hamiltonian in standard second quantized form.

In the evaluation of the ground state energy and for the trial state of the Wigner molecule phase, each particle is associated with a definite value of spin.

In the paired electron phase, the two electrons participating in each pair no longer have definite spins, but are in a spin-singlet state. To construct the trial many-body wave function for the investigation of the paired electron phase we have used the two-electron variational wave function introduced in [2], which reduces to the exact eigenfunction for specific magnetic fields and QD potential [3].

We have obtained that there exist regimes where Wigner molecules and paired electronic configurations are the ground states of QDs. The calculations are performed for two and four electrons.

Excitons in ZnSe/CdSe Quantum Dot Heterostructures

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Coupling between quantum dots (QDs) is now a matter of great importance. In the "artificial molecules" formed by two or more coupled QDs interdot coupling can be tuned far out of the regimes accessible in natural molecules, and single-particle tunneling and Coulomb interactions can be varied in a controlled way.

In the present work electron-hole Coulomb interaction is calculated in the of ZnSe/CdSe QD molecules. 2D-like QDs formed by Cd fluctuation are considered. In quantum structures of this type lateral sizes few times exceeds the bulk exciton effective radius therefore only vertical confinement is considered. Lateral motion of carriers is described in the framework of two dimensional Coulomb problem.

For double stack of quantum dots realistic potential of Pöschl-Teller type was used as a single particle potential for describing space confinement in vertical direction. z-dependent Coulomb interaction between electron and hole is defined by direct diagonalization method. In this case exciton binding energy is very high. For 1 nm QD vertical size and 1.2 nm barrier thickness it is 0.078 eV, with increasing interdot distance it decreases to 0.065 eV for 4.2 nm barrier, then increases and gradually and approaches the binding energy of excitons in isolated QDs.

In order to describe the motion of carriers in heterostructures with arbitrary number of QD stacks the set of one dimensional rectangular potential wells with finite potential barrier is considered. We found recurrence relation between the wave functions describing electron (hole) motion in neighboring wells, which gives possibility to solve the problem for arbitrary number of wells. The electron-hole Coulomb interaction is considered the same way as for double stack of quantum dots.
Influence of Local Electric Field on Fine Structure of Excitonic Complexes in CdTe/ZnTe Self-Assembled Quantum Dots

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We study the fine structure of excitonic complexes in individual CdTe/ZnTe quantum dots under the influence of electric field caused by local charge fluctuations. The analysis is focused on the anisotropic exchange splitting (AES) of exciton (X) and biexciton (XX) lines.

The sample was grown by MBE on (001)-oriented GaAs substrate. It contains a single layer of CdTe self-assembled quantum dots (QDs). Individual dot lines are investigated using microphotoluminescence ($\mu$-PL) under non-resonant excitation. Our measurements are performed at 20K and under a magnetic field in Faraday configuration. Since the exchange splittings of X and XX are much larger than the linewidths, the two linearly-polarized components of each doublet are clearly resolved in the spectra. Contrarily to the usual observation in InAs quantum dots, the direction of optical anisotropy is not clamped to a simple crystallographic axis.

We analyse a set of well isolated lines appearing in the low energy tail of the dot distribution. Their relative energy positions [1] suggest that they originate from the exciton (X), the charged exciton (X*), and the biexciton (XX) from the same QD. The identification is confirmed by following observations: i) the intensity of XX is superlinear with excitation power; ii) AES has opposite sign and approximately the same magnitude for X and XX, while for X* the splitting is zero [2]. An additional confirmation of the common origin of the three lines is the observed equality of their effective Lande factors. Using short signal integration time, we observe synchronized spectral jumps of the lines [3] under the influence of local charge fluctuations. We insist that the jumps are perfectly synchronized for the three investigated transitions. These fluctuations can be reduced and even cancelled by reducing the excitation power. Information about the local field distribution is extracted from the Stark shift and the changes in AES. We observe that the influence of the electric field (measured by the Stark shift) is somewhat stronger for the X state than for the X* and XX states. The change in line intensity is correlated with the line position, as expected for a fluctuating Stark shift. More surprisingly, we also observe a strong correlation between the line positions and the value of AES for X and XX. Indeed, such correlation can exist only if the direction of the field is fixed with respect to the direction of native anisotropy [4]. We conclude that the direction of the fluctuating field is not random, and that the fluctuations are probably caused by charge-state variations of a localized center in the vicinity of the dot, such as a dislocation or another quantum dot.

Spin-polarised Carriers in CdS Quasi-spherical Quantum Dots

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Nowadays, the properties of spin-polarised carriers in semiconductors attract an increasing attention due to the envisioned applications of carrier spin for the processing, transport and storage of information. From the material point of view the spin dephasing time, that describes the loss of spin coherence, is one of the most important parameters as it directly determines the information survival. Recently, several groups reported a considerable enhancement of the spin dephasing time in semiconductor quantum dots (QD) \cite{1, 2} that make them very attractive for spintronics and quantum computation. Measurements of the spin dephasing time of charge carriers in semiconductors are usually performed using techniques of laser spectroscopy that enable the full control of the polarisation state of the light beams used. Both polarization of light and symmetry of semiconductor material/structure lead to the selection rules of the light-matter interaction, which make it possible to photogenerate and detect the spin-polarised carriers \cite{3}. The main point of this contribution is that the interpretation of optical measurements of the spin polarised carriers in QDs can differ substantially depending on QDs shape.

Semiconductor QDs are usually prepared with either pyramidal \cite{1} or spherical \cite{2} shape. We concentrate on photoluminescence and time-resolved absorption spectroscopy of CdS QDs of a quasi-spherical shape in glass matrix. We show that the information on the spin relaxation of electrons is encoded in the decay of the degree of circular polarization (DCP) while the decay of the degree of linear polarisation (DLP) is connected with the exciton relaxation between different sublevels of its lowest energy state. This finding is based on the experimental and theoretical analysis of the DLP spectral and temperature dependence and supported by the measurements of its dynamics. Further, we discuss the potential influence of a depolarisation field \cite{4} on DLP. The connection between the carrier spin orientation and the emitted/absorbed light polarization in our quasi-spherical QDs differs substantially from that found in pyramidal \cite{1} QDs due to the different symmetry of the energy states. We also compare results of time-resolved differential transmission and time-integrated photoluminescence measurements and we show that the use of time-resolved technique is strongly advantageous for the determination of the spin dephasing time.

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Magnetic Anisotropy of the Co$^{2+}$ Ion in ZnO

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AC magnetic susceptibility and magnetization have been investigated in cobalt based diluted magnetic semiconductor with the wurtzite lattice structure: Zn$_{1-x}$Co$_x$O. Single crystals of Zn$_{1-x}$Co$_x$O ($x \sim 0.01$) were grown by chemical vapour transport using chlorine as the transporting agent. The growth temperature was 900$^\circ$C. The Co concentration $x$ was determined using three methods: (i) from the Curie constant, obtained from a fit of the susceptibility to the Curie-Weiss law; (ii) from the saturation value $M_s$ of the magnetization; (iii) from the electron microprobe analysis. The measurements were performed in the temperature range 2-100 K. Magnetic susceptibility was investigated using a mutual inductance method. The measurements were carried out in ac magnetic field of frequency 625 Hz and amplitude not exceeding 10 Oe. Magnetization was investigated in the fields up to 9 T. At low temperatures the magnetic system is strongly anisotropic, that manifests itself in different dependences of magnetic susceptibility vs. temperature as well as of magnetization on the magnetic field, observed for two principal orientations of the magnetic field, i.e., $H \parallel c$ and $H \perp c$. The low temperature data were analysed within the framework of the crystal field model. The simple theoretical model has been used for the interpretation of the experimental data and for calculation of the zero-field splitting D of the orbital ground state of Co$^{2+}$ ion.
Synthesis and Characterization of Zn(Mn)O Nanoparticles

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In order to synthesize manganese-doped ZnO quantum dots with diameters in the range of few nanometers, wet-chemical synthesis methods have been developed. 2,2-Dimethylpropylenediamine and 1,2-diaminocyclohexane, respectively, were used as stabilizer molecules, and the base applied was tetramethylammoniumhydroxide. The particles obtained after precipitation from the ethanolic solution were redispersed and analyzed by UV/Vis absorption, photoluminescence and photoluminescence excitation spectroscopy.

The particles were characterized by X-ray powder diffraction. Particle sizes were determined from reflection line widths by means of the Scherrer equation. The diffraction pattern were also fitted directly by modelling the nanocrystals and using the Debye equation to calculate the powder pattern. Parameters refined include atom positions, crystal size and lattice constants. To study the local structure of the nanoparticles, the pair distribution function was calculated which is a diagram of the interatomic distances within the sample. The interpretation yields information on the local structure, i.e. the mutual arrangement of the atoms at short distances. The length of the longest significant inter atomic vector was comparable to the particle size from the Scherrer equation.

Raman spectroscopy from the lattice vibrations of the nanocrystals (e.g. the E\textsubscript{2} mode at 54 meV) was applied not only for an additional confirmation of the presence of ZnO and its crystallinity, but especially for the investigation of size effects, which manifest themselves in peak shifts and changes of the half width and line shape. Moreover, this spectroscopic method was employed in search of interfacial vibration modes, and for the verification of the Mn incorporation by atomic Mn spin flip transitions in an external B-field (transition energy \simeq 0.1 meV/T). Beside these signatures of the nanostructures, Raman spectroscopy also gives access to the ligand molecules by studying their internal vibration modes, originating essentially from the C-C and C-H bonds, in the energy range up to about 400 meV.

Figure 1: Photoluminescence and photoluminescence excitation spectra of Zn(Mn)O.
Fabrication of Low Dimensional Structures of ZnSe and ZnO
by Thermal and Mechanical Methods

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Fabrication of low dimensional structures of II-VI compounds as nanoparticles and elongated structures, such as nanowires or nanotubes, is a subject of increased interest due to their potential use in different technological applications. The aim of this work is the obtention of low dimensional structures of II-VI semiconductor compounds and to study their electronic and optical properties, which are often different from those of the corresponding bulk materials and may find applications in nanoscale electronics and optics. Two different preparation methods are followed in order to obtain either nanoparticles or elongated structures.

For the growth of elongated structures, the starting material is commercially available powder of the selected compound, this powder was compacted to form disk shaped samples which were placed on an alumina boat near the gas inlet in a furnace heated at temperatures ranging from 450°C for ZnSe to near 1300°C for ZnO. Micro and nanorods mainly of hexagonal shape have been observed to grow on the surface of the disc shaped ZnO samples under a high purity argon flow. The ZnO nanorods reach up to several hundreds microns in length and their diameter varies from 50 nm to several µm. In the case of ZnSe the most visible structures are nanorods which appear on the surface of the sample. Also the grain structure changes from the typical particulate morphology observed in powder materials to faceted grains with a lamellar or columnar structure which has been studied by Atomic Force Microscopy (AFM). Growth temperature and argon flow rate allow to control the process.

A comparison of the luminescence properties of the different kind of structures obtained in several II-VI [1] compounds is performed. In particular the differences between these structures and nanoparticles previously obtained by mechanical methods are analysed. As reported in previous works [2,3,4] the milling process was found to produce particles of wide range of sizes from several hundreds of nanometers down to several tens nanometers. These particles are composed of crystallites of a few nanometers in size as well as larger ones. The evolution of defect structure of the particles is highly dependent on the material.

It is well established that the group-I-elements Li and Na introduce deep acceptor states in ZnO. With 800 and 600 meV binding energies, respectively, they compensate the background shallow donors producing high resistive material rather contributing to a sizeable amount of free holes in the valence band. In photoluminescence the Li(Na) doped ZnO samples give rise to broad luminescence bands in the yellow spectral range (around 2.2 eV) explained by shallow donor to deep acceptor recombinations. It is also believed that selfcompensation of Li (Na) acceptors by interstitial Li(Na) donors is a limiting factor towards achieving p-type conductivity. Most of these experimental findings base on ZnO crystals diffused or grown at high temperatures (>1000 °C). In our report we compare results from low temperature diffusions of Li(Na) into bulk ZnO crystals with in-situ doping of epitaxial films grown by chemical vapour deposition at growth temperatures around 600 °C. Contrary to the earlier investigations we can demonstrate the Li(Na) give rise to a shallow acceptor level with a binding energy around 300 meV. It participates in a donor acceptor pair recombination band at 3.05 eV. In the diffusion experiments we can demonstrate that the acceptor level appears at diffusion temperatures between 350 and 400 °C and is no longer introduced for temperatures above 700 °C.
Self-assembling of two isoelectronic impurities was predicted for AlN- and GaAs-rich Al\(_{1-x}Ga_{1-x}N_{y}As_{1-y}\) alloys in the ultra dilute limit of the anion impurities [1]. The self-assembling appears as formation of the tetrahedral cells consisting only of the impurity atoms. The separated anion impurity atoms should be surrounded by the cation impurity in such cells. The main origin of this phenomenon is the thermodynamic preference of Al-N and Ga-As bonds over Al-As and Ga-N bonds due to the large cohesive energy of AlN. The cohesive energy of MgO is also very significant. Therefore, the preferential formation of Mg-O bonds in a number of the II-VI compounds co-doped with Mg and O can be expected. The conditions of the 1O4Mg tetrahedral cell self-assembling in ZnTe-rich Mg\(_{x}Zn_{1-x}O_{y}Te_{1-y}\) alloys are described. The free energy of the constituent compounds, strain energy and configurational entropy of the random and self-assembled alloys were taken into account. The free energy of the alloys decreases after assembling due also to the diminution of the strain energy. Thus, the decrease of the configurational entropy should be compensated by the diminution of the free energy of the constituent compounds and strain energy. The O concentrations in the ultra dilute limit from \(y = 1 \times 10^{-8}\) to \(y = 1 \times 10^{-3}\) was chosen. The Mg concentrations relevant for the self-assembling of Mg\(_{x}Zn_{1-x}O_{y}Te_{1-y}\) alloys were estimated for the growth and annealing temperatures of 300 and 500 °C, respectively. For the growth and annealing temperatures the Mg concentrations are also in the ultra dilute limit from \(x = 2.7 \times 10^{-4}\) and \(2.3 \times 10^{-3}\) to \(x = 0.004\) and 0.0046, respectively.

Majority-Carrier Mobilities in Undoped and n-type Doped ZnO Epitaxial Layers

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In recent years, the improvement in the growth technology of ZnO has been remarkable, and there have been several reports on the fabrication of high-quality thin films. This research compares the results of calculation with our experimental data to discuss how much the electron mobility of undoped and Ga-doped epilayers is approaching their physical limit. Our samples were deposited by a laser-molecular-beam epitaxy method. We performed theoretical calculation which took scatterings by ionized impurities, acoustic phonons, piezo-electric phonons, and polar optical phonons into consideration. Figure 1 shows theoretical and experimental results of room-temperature electron mobility as a function of carrier concentration. Since it is inappropriate to adopt the relaxation time approximation for polar optical phonons, the variational method was used for the calculation. The calculated mobility at nondegenerate concentration region is about 430 cm²/Vs [1]. As far as this case concerned, the theoretical value is in good agreement with the experimental value. We will also discuss the effect of electron-plasmon scattering on the electron mobility during the conference.

Sputter Deposition of ZnTe\(_{1-x}\)O\(_{x}\)

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Bandgap-bowing in II-VI-semiconductors is a topic of great interest with regards to the potential of bandgap-engineering. The variation of bandgap-energy is induced by anionic substitution with an isovalent element of distinctly different electronegativity. The alloy system Zn(Te,O) furthermore shows the formation of an intermediate band inside the forbidden bandgap [1]. This makes Zn(Te,O) a potential material for the realisation of an intermediate-band-solar cell.

We examine the possibility of substituting tellurium by oxygen in polycrystalline ZnTe\(_{1-x}\)O\(_{x}\) and Zn\(_{1-y}\)Mn\(_{y}\)Mg\(_{y}\)Te\(_{1-x}\)O\(_{x}\) thin-films and the effects on bandgap energy and crystal structure. Samples are synthesized in an rf (radio-frequency)-sputter process. ZnTe and ZnMnTe-ceramic targets of different composition are used as a source material. Argon serves as sputtering-gas with variable amounts of oxygen added as a reactive component.

X-ray diffraction (XRD) is used to analyse the crystal structure of the samples, the bandgap energy is determined by optical transmission measurement, and the amount of oxygen and manganese/magnesium in the films is examined by x-ray-photoelectron-spectroscopy (XPS) and energy-dispersive-x-ray-analysis (EDX).

Among II-VI semiconductors, ZnO is widely recognized from both points of view: as a diluted magnetic semiconductor (ZnO doped by 3d metals) and as promising optical material for various optoelectronic short wavelength devices such as detectors of UV radiation and light-emitting structures. On the way to obtaining high-temperature ferromagnetics many DMS materials have been investigated including zinc oxide. The advantages of ZnO include its high transparency and possibility of high doping by Al, Ga or In to achieve large carrier concentration. More recently, room-temperature ferromagnetism has been reported for ZnO doped by Co. However the origin of its ferromagnetism still remains a subject of debates.

The ZnO films of thickness about 0.2-0.6 mkm were deposited on sapphire substrates (0001) by rf magnetron sputtering and PEMOCVD. XRD analysis demonstrated hexagonal crystal lattice with a texture governed by technological conditions.

We suppose that valent state of Co ion play important role in the obtaining high temperature ferromagnetic ordering. Consequently, it is of interest to investigate valent state of Co ion in ZnO:Co films and get answer on question how Co incorporates into ZnO lattice. Is it a source of localized magnetic moment only (Co$^{2+}$) or it simultaneously supplies an electron to conduction band (Co$^{3+}$)? We performed investigations of Co states in ZnO:Co films by X-Ray absorption spectroscopy (XAS). They result in the intermediate value of Co ion charge between $+2$ and $+3$. Additionally we measured magnetic moment of films by SQUID magnetometer. Instead of ferromagnetic state we observed the strong paramagnetic behavior. Measured magnetic moment corresponds to $1\mu_B$ per Co ion being a consequence of $d^7$ states splitting in the crystal field. We believe that Co concentration (in our case 7 at%) and carrier concentration is not enough to obtain ferromagnetic ordering.

The second area of our interest is optical properties of undoped ZnO films. We performed investigations of PL spectra of ZnO films, deposited by magnetron sputtering and plasma-enhanced chemical vapor deposition. All deposited films were highly transparent and have carrier concentration less than $5\cdot10^{16}$ cm$^{-3}$. PL spectra were studied at 4.2 K, 77 K and room temperature. An excitation was carried out by nitrogen laser (high excitation) and He-Cd laser (low excitation). In PL spectra at low excitation we observed three peaks positioned at 3.36, 3.32, 3.24 eV. Taking into account exciton-phonon interaction (EPI) we have done fitting of theoretical curves to experimental ones by varying constant of EPI and considering exciton of small radius. Obtained results demonstrate good agreement between experimental and calculated curves. The energy of real LO phonon for ZnO was defined. At high excitation we observed only one peak positioned at 3.37 eV at 4.2K. The intensity of this peak increased with increasing excitation intensity. At higher excitation densities we observed new weak broad line at 3 eV connected as we suggest with formation of electron-hole plasma. Our results also demonstrate that ZnO films improve optical quality after thermal annealing in air. This leads to amplification of UV emission with lowering visible emission usually due to lattice defects.
The Structural and Photoluminescence Properties of Mn-doped ZnO Nanocolumns Grown by Cathodic Electrodeposition

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Application of semiconductor nanostructures in devices is one of the major focuses in recent nanoscience researches. Considerable efforts have been made to fabricate nanostructures of zinc oxide (ZnO), which was recognized as a promising photoelectronic material with significant potential in laser emission, field emission, and nanoscale heterojunction. By using carrier charge and spin degrees of freedom diluted magnetic semiconductor (DMS) is expected to exhibit novel physical character and apply in new devices [1]. By now, many works have showed Mn-doped ZnO nanostructures had ferromagnetism at $T_c=30\sim45\text{K}$ [2].

In this paper, Mn-doped ZnO nanocolumns were grown by cathodic electrodeposition on Si substrates. X-ray diffraction (XRD) and X-ray photospectroscopy (XPS) results suggested Mn ions doped into ZnO lattices successfully. Field-emission scanning electron microscopy (FE-SEM) images showed the sample was consisted of nanocolumns with diameters of 200 nm and lengths of 500 nm. A resonance-Raman shift was observed, which was induced by Mn ions doping. No magnetic signal was detected at room temperature. In photoluminescence (PL) spectrum, a strong ultra violet emission was obtained. The possible origination of this emission was discussed by analyzing low temperature PL spectra.

Photoluminescence Properties of Zn$_{0.93}$Cd$_{0.07}$O/Mg$_{0.03}$Zn$_{0.97}$O Heterostructures


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ZnO and its related alloys of Zn$_{1-x}$Cd$_x$O and Mg$_y$Zn$_{1-y}$O, continue to increase in importance for the UV-visible light emitting devices. Recently, p-type ZnO has been produced and the injected light emission have been demonstrated from the p-i-n ZnO structure\(^1\). In particular, a narrowing of the band gap is preferable to tune the emission wavelength of future optoelectronic devices into the visible. We have successfully achieved wurtzite Zn$_{1-x}$Cd$_x$O films with up to $x=0.697$ by remote plasma-enhanced metalorganic chemical vapor deposition (RPE-MOCVD)\(^2\). The band gap energy of wurtzite Zn$_{1-x}$Cd$_x$O was controlled from 3.3 eV ($x=0$) down to 1.9 eV ($x=0.697$). The blue-green emission was demonstrated from the heterostructures of Zn$_{0.92}$Cd$_{0.08}$O/ZnO system at room temperature\(^3\).

In this report, Zn$_{0.93}$Cd$_{0.07}$O/Mg$_{0.03}$Zn$_{0.97}$O heterostructures were successfully grown by RPE-MOCVD and were investigated by photoluminescence (PL) spectroscopy in order to examine the effects on the barrier and active bandgap energy. The details of the growth methods and characterization have been described in our previous paper\(^2,3\). Diethyl zinc (DEZn), dimethyl cadmium (DMCd) and bis-ethylcyclopentadienyl magnesium (EtCp$_2$Mg) were used as group-II sources. Plasma oxygen was a group-VI agent and used for the decomposition energy transfer of group-II sources. The substrate temperature was maintained between 350 and 450°C. A double-heterostructure typically consisting of 15nm-thick Mg$_{0.03}$Zn$_{0.97}$O / 30nm-thick Zn$_{0.93}$Cd$_{0.07}$O / 200nm-thick Mg$_{0.03}$Zn$_{0.97}$O was grown on a-plane sapphire substrate. PL measurements were carried out using a He-Cd laser (325nm) from 17K up to room temperature.

In the double heterostructure of Zn$_{0.93}$Cd$_{0.07}$O/Mg$_{0.03}$Zn$_{0.97}$O, temperature and excitation intensity dependencies of PL spectra were examined. Figure 1 shows the typical PL spectrum of the Zn$_{0.93}$Cd$_{0.07}$O/Mg$_{0.03}$Zn$_{0.97}$O double-heterostructure at low temperature. The PL emission is characterized as localized and free exciton emission. A dependence with a slope near unity is obtained from the excitation dependence of the PL intensity.

\[ \text{PL Intensity (arb. units)} \]

\[ \text{Photon energy (eV)} \]

\[ \text{MgZnO 15nm} \]

\[ \text{ZnCdO 30nm} \]

\[ \text{MgZnO 200nm} \]

\[ \text{Fig. 1. The PL spectrum of Zn$_{0.93}$Cd$_{0.07}$O/Mg$_{0.03}$Zn$_{0.97}$O double heterostructure at 17K.} \]


Growth Mode Control for ZnO Nanostructure

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We have studied the influence of the orientation (a, c, and R-plane sapphire substrate) and growth temperature on the surface morphology for well-assembled ZnO nanostructure. Remote plasma-enhanced metal-organic chemical vapor deposition (RPE-MOCVD) was employed with diethyl zinc (DEZn) and molecular oxygen introduced into hydrogen plasma atmosphere [1]. The film thickness is in the range of 200-500nm. The surface morphology of ZnO nanostructures are evaluated by field-emitting scanning electron microscopy (FE-SEM) and the corresponding results are shown in Fig. 1. It is found that the surface morphologies appear as island and needle-like crystals at low growth temperature (360°C). At an increased temperature (450°C), faceted terraces are observed on c and R-plane substrate and faceted needle-like crystals can be seen on a-plane substrate. When growth temperature is further increased (500-550°C), regular wavy surface is achieved on R-plane substrate, however, such an improvement is not observed on a, and c-plane substrates. We believe that the lattice mismatch plays a key role for the difference of surface morphology and the lattice mismatch with the R-plane substrate is relatively small compared with that with a, and c-plane substrates. Furthermore, with increasing temperature the surface morphology on R-plane substrate appears as island, faceted terrace, and wavy surface, which is attributed to an improved migration length of atoms and radicals absorbed on the substrate surface, but the trend is not observed on a, and c-plane substrates. The optical properties of the ZnO nanostructures grown on R-plane substrate at different temperatures was characterized by photoluminescence with an excitation laser source of 325 nm at low temperature and the result is shown in Fig.2. The PL spectrum is dominated by two main peaks; one is donor bound exciton and about the other peak located at around 3.2 eV we are not clear up to now.

Fig.1

![Scale bar: 100 nm](image)

Fig.2

![Intensity (a.u.)](image)

Photocorrosion Instability of Quantum-confined ZnO Nanocrystals

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Quantum confinement of charge carriers in semiconductor nanocrystals affects substantially their optical and photochemical properties. Principal factor, causing this effect, is a change in electronic properties of the nanocrystal in the size range, comparable with the Bohr diameter of exciton. In some cases the size-dependent increase in the energy of charge carriers, photo-generated in the quantum-confined nanoparticles, enables photochemical reactions, forbidden thermodynamically for the bulk crystals of given semiconductor. Cathodic photocorrosion of ZnO nanocrystals, stable towards reductive photodissolution in the form of microcrystals [1], can serve as the demonstrative example of this phenomenon.

Table.

<table>
<thead>
<tr>
<th>$E_g$ (eV)</th>
<th>$2R$ (nm)</th>
<th>$E_{CB}$, V (NHE)</th>
<th>$E^*$, V (NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.43</td>
<td>6.0</td>
<td>-0.58</td>
<td>-0.78</td>
</tr>
<tr>
<td>3.48</td>
<td>5.5</td>
<td>-0.61</td>
<td>-0.81</td>
</tr>
<tr>
<td>3.50</td>
<td>5.3</td>
<td>-0.63</td>
<td>-0.83</td>
</tr>
<tr>
<td>3.57</td>
<td>4.8</td>
<td>-0.68</td>
<td>-0.88</td>
</tr>
<tr>
<td>3.63</td>
<td>4.4</td>
<td>-0.72</td>
<td>-0.92</td>
</tr>
</tbody>
</table>

Colloidal ZnO nanocrystals of different size – 4.4-6.0 nm (with the band gaps $E_g = 3.63 - 3.43$ eV correspondingly, see Table) have been synthesized via the variation in the concentrations of precursors at basic hydrolysis of zinc acetate in ethanol. The irradiation of deaerated ZnO colloids results in the hypsochromic shift of the long-wave edge of the absorption band of the semiconductor ($\Delta E$), induced by the accumulation of excessive negative charge by ZnO nanoparticles (Burstein-Moss effect). At $\Delta E = 0.15 - 0.16$ eV, the changes in the absorption spectra of the solutions can be observed, indicating the formation of metallic zinc.

It has been found that the photoreaction rate neither depends on Zn(II) concentration, nor diminishes in the presence of alkalis, able to bound Zn(II). From these observations it has been concluded that the accumulation of metallic zinc is the result of reductive (cathodic) photocorrosion of ZnO nanocrystals. The photocorrosion rate decreases at the increase in the size of ZnO nanoparticles. Moreover, in the case of the largest of studied nanoparticles (6.0 nm), similarly to bulk ZnO crystals, we have not observed the photodissolution of the semiconductor at all. It has been assumed that the growth of the photocorrosion rate at the decrease in the size of ZnO nanoparticles results from a change in the energies of photogenerated charge carriers. Performed estimations (see Table) have shown that the conduction band potential of ZnO nanoparticles, influenced by Burstein-Moss effect, i.e. $E^* = E_{CB} + \Delta E$, can exceed the potential of cathodic corrosion of nanoparticulate zinc oxide (-0.8 V versus NHE [2]) only when the size of the nanocrystals is smaller than 6.0 nm. It has been concluded that the ability of ZnO nanoparticles to undergo cathodic photocorrosion is determined predominantly by simultaneous effects of quantum confinement of charge carriers and cathodic polarization of the nanocrystals induced by the accumulation of excessive negative charge.

Luminescence and Structural Properties of Defects in Ion Implanted ZnO

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Ion implantation is a well known technique to introduce defects in ZnO samples. After implantation the ZnO lattice damage recovery is nearly complete using air annealing conditions for temperatures above 1000°C. Intraionic emission is observed for samples implanted with rare earth (RE) or transition metal (TM) ions after air annealing at 800°C. However, with increasing annealing temperatures out diffusion occurs for some of RE ions. This is evidenced for both Tm and Er where the mobility of intrinsic and extrinsic defects assumes an important role on the ion lattice accommodation. The out diffusion processes is followed by significant changes on luminescence spectra.

In this work we report on the structural and optical properties of RE and TM ion implanted ZnO bulk crystals. High quality ZnO samples were implanted at room temperature with several fluences and subjected to different air annealing times. The crystalline quality and damage recovery were studied by Rutherford backscattering spectrometry and channeling (RBS/C). The ions optical activation was analyzed by photoluminescence.
Ultraviolet Electroluminescence of ZnO Based Heterojunction Light Emitting Diode


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Recently, ZnO had been paid more attention because of potential applications in ultraviolet light emitting diode and laser diode [1]. However, it is very difficult to fabricate p-type ZnO due to serious self-compensation effect [2], which results in no great progress in p-n homojunction diodes. ZnO heterojunction as another route has been paid attention except the effort on the fabrication of p-type ZnO. One attractive heterojunction is ZnO/GaN heterojunction because of similar crystal structure and small lattice mismatch of 1.8%. However, the emission of GaN plays a dominant role in the electroluminescence spectra of ZnO/GaN heterojunction light emitting diode [3].

In this paper, the main reason was analyzed and the new heterojunction was designed by introduced into different i-layer by plasma-enhanced molecular beam epitaxy (P-MBE). We make use of high resistivity of nitrogen doped ZnO [4] to fabricate n-ZnO/i-ZnO/p-GaN heterojunction light emitting diodes. The emission of i-ZnO was obtained in this heterojunction due to the limitation effect of i-ZnO on electrons and holes. Moreover, n-ZnO/i-MgO/p-GaN heterojunction light emitting diode was also fabricated. The limitation effect on electrons is increased in this heterojunction. The bright ultraviolet electroluminescence at 384 nm originated from the ZnO layer was observed in the room temperature electroluminescence spectra. It is very hopefully to realize the stimulated emission of ZnO using these heterojunctions by the improvement of crystal quality and the optimize of device structure.

Raman Spectra and Phonon Modes of Mg$_x$Zn$_{1-x}$O Alloy Films

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The MgZnO/ZnO heterostructure is potentially useful material for ultraviolet light emitting devices. The investigation of lattice vibration characteristics in Mg$_x$Zn$_{1-x}$O is very necessary to clearly understand the long-wavelength optical phonons, optical mode behavior. Raman scattering studies are important for examining the strain, composition, long-range order and local structure in alloy layers.

In this paper, Raman spectra and phonon modes of high quality wurtzite Mg$_x$Zn$_{1-x}$O alloy films with 0$<x<0.3$ prepared by plasma-assistance molecular beam epitaxy (P-MBE) on sapphire (0001) and Si (111) substrates were reported in detail for the first time. Four Raman modes ($E_{2}^{high}$, multiphonon processes, LO, TO) were observed in the Raman spectra of Mg$_x$Zn$_{1-x}$O alloys with different Mg content measured using 488nm line from Ar$^+$ laser by backscattering geometry. All samples were found to display one-mode behavior since no separate ZnO- and MgO-like modes were observed. The compositional dependence of long wavelength frequencies of optical phonons has been studied by the resonant Raman spectra measured using 325nm line from He-Cd laser and the results can be expressed as linear functions of the molar fraction x of the alloy. These behaviors can be explained within a modified random-element-isodisplacement (MREI) [1] model. The measured frequencies of the LO mode agree well with the calculated values.

Formation of p-type ZnO Films with Annealing in NH₃ Ambient

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ZnO is a II-VI compound semiconductor with a wide direct bandgap of 3.3 eV and a large exciton binding energy of 60 meV at room temperature. Because of these features, ZnO is considered as a promising material for various applications in light emitting devices (LDs and LEDs) which operate in the short wavelength range, from blue to ultraviolet. In general, for the development of optical devices based on ZnO, it is necessary to obtain n- and p-type ZnO films. Since undoped ZnO exhibits high n-type conductivity, however, ZnO has difficulty in obtaining good, reproducible p-type material. According to recent papers on the growth of p-type ZnO, p-type ZnO can be obtained by either the growth of N-doped ZnO films by chemical vapor deposition with NH₃ or molecular beam epitaxy using an atomic nitrogen source, which are understandable since nitrogen replaces oxygen to generate holes because of similar ionic radius. On the other hand, there have been recently another trials such as As and P doping. These approaches, however, leave room for further discussion since the ionic radii of P and As seem to be too large to occupy the oxygen site within the wurtzite host lattice and thus to serve as acceptors.

In this paper, we address the formation of p-ZnO films according to annealing in NH₃ ambient. First, we investigate the effects of thermal annealing with NH₃ on the structural, optical and electrical properties of ZnO films. Next, we examine and discuss the effects of N-doping on the pre-annealing of as-dep. ZnO and activation annealing in combination with post-annealing in NH₃.

For our experiment, ZnO films were deposited on SiO₂/Si(100) substrates and Si (111) substrate at room temperature by r.f. sputtering system. ZnO films were annealed in quartz tube with NH₃ ambient at 600 - 700 °C. The effects of thermal annealing in NH₃ on the structural properties of ZnO films were investigated by atomic force microscope (AFM), and X-ray diffraction (XRD). Hall effect measurements were carried out in the vander Pauw configuration using a commercial system. Photoluminescence (PL) spectra of ZnO thin films were obtained from 13 K to 300 K with a He-Cd laser.

Some results on the hall effect we obtained are shown in Table 1. Here the electron concentrations decrease from mid-10¹⁸ cm⁻³ to low-10¹⁶ cm⁻³ after thermal annealing with NH₃ at 600-700 °C. The p-type ZnO was obtained with electron concentration of low 10¹⁶/cm³ at 700 °C for 1 hr with post annealing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity [Ω·cm]</th>
<th>Mobility [cm²/V·s]</th>
<th>Carrier concentration [cm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂ annealing</td>
<td>0.24</td>
<td>6.27</td>
<td>−4.66 × 10¹⁸</td>
</tr>
<tr>
<td>NH₃ annealing</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600°C, 30 min</td>
<td>1.59</td>
<td>23.19</td>
<td>−2.12 × 10¹⁷</td>
</tr>
<tr>
<td>600°C, 1 hr</td>
<td>3.61</td>
<td>18.56</td>
<td>−2.66 × 10¹⁶</td>
</tr>
<tr>
<td>700°C, 1 hr</td>
<td>121.45</td>
<td>2.86</td>
<td>−1.10 × 10¹⁶</td>
</tr>
<tr>
<td>700°C, 1 hr (post-annealing)</td>
<td>40.18</td>
<td>15.80</td>
<td>+1.06 × 10¹⁶</td>
</tr>
</tbody>
</table>
Temperature Dependent Band Gap and Homogeneous Line Broadening of the Exciton Emission in ZnO


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Zinc oxide (ZnO) has a wide band gap of 3.44 eV, which makes it interesting for optoelectronic applications in the blue or near-UV spectral range. Since the excitonic binding energy of 60 meV is large, one may expect excitonic gain processes up to room temperature (RT). On the other hand the LO–phonon energy is with 72 meV even larger, allowing ionization of the exciton by absorption of a single LO–phonon. This fact together with a rather strong exciton–phonon coupling results in a very broad luminescence band ($h\omega_{\text{max}} \approx 3.31$ eV, FWHM $\approx 95$ meV) at RT.

By means of photoluminescence (PL) measurements we investigate the homogeneous line broadening of the exciton emission and the band gap narrowing with temperature which is an important input parameter for high temperature applications.

We excite high quality bulk ZnO samples with a cw HeCd laser ($h\omega_{\text{exc}} = 3.81$ eV) and observe the near band edge emission from 10 K up to RT. At low temperatures the PL of the bound exciton recombination dominates the spectrum, but the PL of the free A exciton and of its phonon replica can also be seen in the spectrum. With higher temperatures the free exciton emission and its phonon replica become dominant. Apart from the recombination of the bound excitons the complete near band edge emission spectrum up to RT has a clear excitonic signature and can be described very well as a sum of the broadened exciton line and its phonon replicas. We fit the temperature dependent spectra with a theoretical model and deduce the temperature dependent band gap and the homogeneous line broadening of the exciton emission. These band gap narrowing data are compared with results of absorption measurements (up to 800 K) and we discuss the behavior of the band gap in respect of different theoretical models (Varshni, Bose-Einstein and a two oscillator model). In addition to these analytic models the band gap narrowing as a function of T is calculated numerically from the phonon spectra, the pressure dependence of the band gap shift, the thermal expansion coefficient and the bulk modulus. All models give a good description of the temperature dependent band gap narrowing with the numerical model being superior in two respects: Firstly, it has a clear physical interpretation and secondly, it has only one free fitting parameter which is the least number of all models.

The homogeneous line broadening is increasing with temperature and can be described by the exciton phonon scattering. At RT the damping factor that determines the broadening is about $\Gamma \approx 22$ meV. This broadening mechanism leads to an increased threshold for stimulated emission. This coupling to phonons sets the effective lower limit of the broadening because at higher excitations densities additional interactions take effect.
The Exciton Polariton Model and Diffusion of Excitons in ZnO Analyzed by Time Dependent Photoluminescence Spectroscopy


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Strong Fröhlich interaction leads to a rapid formation of excitons in zinc oxide (ZnO). Hence exciton dynamics dominates the time evolution of the near band edge photoluminescence (PL) at low temperature. Shortly after excitation above the band gap hot excitons are created by the emission of LO phonons. The exciton distribution then thermalizes to the lattice temperature while the excitons are diffusing out of the excitation spot. Both processes are investigated.

The high quality ZnO bulk sample is of the platelet type and has been grown by a gas transport method [1].

It was excited by \(~100\) fs pulses at 280 nm from a frequency-tripled titanium sapphire laser. The time dependent PL emission spectrum was measured from low temperatures up to 290 K with a combination of spectrometer and streak camera. The spectral (temporal) resolution was 1 meV (5 ps).

Directly after the laser excitation the emission from the free exciton recombination and its phonon replica are visible. The PL from the free exciton decreases faster than its phonon replica. This is due to the diffusion of the excitons from the surface into the sample. The emission of the free exciton from deep within the sample is reabsorbed while the emission of the phonon replica is independent of the depth of the emission source. Light with \(\hbar\omega = X\text{-LO}\) is not absorbed because of the low number of LO phonons present. The diffusion becomes faster with higher temperature due to the greater diffusion constant because of the increasing mean kinetic energy. The decay time of the phonon replicas indicates the lifetime of the whole exciton ensemble while the decay time of the free exciton additional reflects the diffusion process and the escape probability.

A close look at the PL of the free A exciton shows details from the exciton polariton. PL from the upper, intermediate and lower polariton branches is investigated and a relaxation process from the upper to the lower branches can be seen. From these measurements the coupling of the excitons to the acoustic phonons, the splitting of the upper/lower polariton branches and the thermalization speed can be deduced.

Characterization of MBE Grown ZnO on GaAs(111) Substrates

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High quality ZnO epitaxial layers were grown directly on GaAs(111) substrate by plasma assisted MBE [1]. In this paper, we describe the optical and structural properties of ZnO layers grown under different conditions such as beam flux ratio and source shutter opening sequence. ZnO was grown on GaAs(111)B substrate at 420°C. The substrates were chemically etched with 5H2SO4+H2O2+H2O at 60°C, and rinsed in (NH4)2S solution. The grown layers were characterized by low temperature photoluminescence (PL), XRD, RHEED and reciprocal space map (RSM).

All layers were grown epitaxially with orientation relationship of ZnO(0001)//GaAs (111) and ZnO[11-20]//GaAs[01-1], and showed PL spectra dominated by bound exciton lines at 3.330 and 3.360eV with very weak deep level emissions. The relative intensity of the two exciton lines varied with layer thickness and source beam flux ratio. In order to study the effect of source beam flux ratio, a series of samples of a constant thickness grown with the effective O/Zn flux ratios between 0.78 and 3.7 was prepared. The flux ratio was controlled by changing Zn source temperature with constant oxygen supply rate and plasma power. Fig.1 shows excitonic region PL spectra of two samples grown under Zn-rich (O/Zn=0.88) and O-rich (O/Zn=2.2) conditions. The 3.360-eV line is dominant for Zn-rich sample and the 3.330-eV line is dominant for O-rich sample. The c-axis of ZnO layer slightly tilted from the <111> axis of GaAs substrate. The tilting angle and azimuth were measured by observing RSM around the GaAs(111) and ZnO(0002) reflections from various azimuths. The apparent tilt angle $\beta$ observed from azimuth $\alpha$ is given by

$$\beta = \tan^{-1}\left[\sin(\gamma - \alpha)\sin\delta / \cos\delta \right],$$

where $\delta$ and $\gamma$ are tilting angle and tilting azimuth, respectively. Fig.2 shows $\beta$ as a function of $\alpha$. We found that the ZnO c-axis tilted from the GaAs<111> axis by 0.2°~0.3° toward GaAs<1-10> direction for Zn-rich condition or GaAs<2-1-1> direction for O-rich condition.

p-type ZnO and ZnMnO by Oxidation of Zn(Mn)Te Films

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ZnO-based semiconductors with a wide band gap and a large excitonic binding energy hold great promise for future optoelectronic applications. Moreover, Mn doped p-type ZnO is a promising spintronic material \cite{1}. Undoped ZnO is usually n-type, which is associated with native defects and/or residual hydrogen. In contrast, p-type conductivity is difficult to achieve and only a limited number of papers report that p-type is feasible by doping with N or with As, or by co-doping with N and Ga, or by oxidation Zn$_3$N$_2$.

In this communication, we report on the fabrication of p-type ZnO and Zn$_{1-x}$Mn$_x$O films obtained by thermal oxidation of N-doped ZnTe and ZnMnTe layers, respectively. The starting material was grown by MBE, in hydrogen-free atmosphere, either on GaAs with a thick undoped ZnTe buffer, or on bulk ZnTe. Electrical properties of ZnO films were assessed by Hall effect measurements. The microstructure was analysed using XRD, SIMS, and AFM. Also, PL spectra were measured with the excitation of 325nm line of He-Cd laser.

A p-type ZnO with hole concentrations of $\sim$5x10$^{19}$cm$^{-3}$ was obtained for oxidized ZnTe films on GaAs. In the case of ZnTe substrates, the concentration of holes was lower by two orders of magnitude. The incorporation of Mn into ZnO decreased the hole concentration to 10$^{17}$ cm$^{-3}$ for 0.4% of Mn. XRD analysis revealed polycrystalline ZnO with inclusions of metallic Te, most probably due to the fact that sublimation of tellurium is inhibited in the course of the oxidation. The concentration of incorporated nitrogen, as determined by SIMS analysis, varied from 1x10$^{21}$ cm$^{-3}$ at the surface to 3x10$^{20}$ cm$^{-3}$ at ZnO/ZnTe interface. In the samples on GaAs substrates a substantial accumulation of arsenic at the ZnO/ZnTe interface was noticed. The PL spectrum of p-type ZnO:N (see Fig.1) shows three peaks located at 3.360 eV, 3.355 eV and 3.316 eV in agreement with our previous study. We attribute the peaks located at 3.360 eV and 3.355 eV to free exciton and a neutral acceptor-bound exciton A$^{0}$X luminescence, respectively. The third line, at 3.316 eV (N), has been observed by several groups, not only in p-type ZnO but also in weakly n-type ZnO doped with N. All PL peaks decreased in intensity in Mn-doped samples.

Partly supported by grant from the State Committee for Scientific Research PBZ-KBN-044/P03/2001. We acknowledge the support from the Foundation for Polish Science through a Subsidy 8/2003.

Zinc oxide (ZnO) nanowires have recently attracted many research activities because they are considered to be promising building blocks for nanometer-scale optoelectronic devices operating in the blue to UV spectral region. Ensembles of nanowires with diameters of \(\sim 100\) nm are relatively easy to fabricate by the vapour-liquid-solid process. Such ensembles have been characterized with respect to their optical properties in many works. However, few studies of the properties of single wires at low temperatures exist up to now and it is not clear to which extend the ensemble measurements do indeed reflect the properties of single wires. Here, we report systematic investigations of the optical properties of single ZnO nanowires and compare our results with additional measurements performed on the as-grown ensemble.

The nanowires with diameters < 200 nm are grown by a chemical vapor transport and condensation technique on a sapphire substrate. Few wires were dispersed on another sapphire substrate to enable the investigation of the properties of single wires. Additionally, in this way the contribution from ZnO which has not grown as a nanowire is avoided. In Fig. 1, the spectrally resolved photoluminescence (PL) of a single nanowire at low and room temperature is depicted as obtained by using a micro-PL setup with a spatial resolution of \(\sim 1\) \(\mu\)m\(^2\). From our measurements we extract the linewidths of the excitonic resonances in the ensemble and of single wires and compare the temperature and excitation-density dependence.

Since nanowires naturally form an optical cavity their potential application as nanowire nanolasers is one of their most fascinating properties (and has recently been shown by few studies). To get more insight into the microscopic processes which are involved in the lasing process we have performed PL measurements as a function of excitation density (up to 7 MW/cm\(^2\)). In Fig. 2, the PL spectra of an ensemble of nanowires at different excitation densities is depicted. A super-linear increase of the PL intensity is observed \(\sim 20\) meV below the dominant donor-bound exciton resonance. Additional measurements performed with a small ensemble of dispersed nanowires even shows multiple rather narrow emission peaks which evolve on the low-energy side of the broad PL emission at high excitation densities (inset of figure 2). These peaks are attributed to cavity effects which occur in single wires. We systematically analyze these cavity effects as a function of temperature and excitation density.
In recent years, there has been considerable interest in the fabrication of ZnO thin films for a variety of applications including magneto- and spin-electronics. A common approach is the incorporation of transition metal atoms in ZnO. Recent theoretical analysis suggests that Mn-doped ZnO could be ferromagnetic with Curie temperature well above 300 K [1, 2], but the actual origin of ferromagnetism in ZnMnO grown on sapphire remains an issue of debate [3, 4]. We report on our findings concerning magnetic property measurements on Zn$_x$Mn$_{1-x}$O layers grown on sapphire substrates.

Zn$_x$Mn$_{1-x}$O with 2-30 at.% Mn were grown on (0001)- and (11-20)-sapphire using molecular beam epitaxy (MBE). In order to improve the absorption of the substrate for more efficient heating, the back side of the substrates was coated with Ti. The crystal quality of the ZnMnO layers was analysed using HRXRD and TEM and magnetic property investigations were carried out with a Quantum Design SQUID magnetometer and Magnetic Force Microscopy (MFM).

The samples were magnetised in-plane and the field-cooled and zero-field cooled temperature dependence of magnetisation was investigated for temperatures ranging from 4.5 K to 300 K. At first sight, one sample showed a ferromagnetic behaviour with a remnant magnetisation of $10^{-5}$emu. However, further investigations on several samples and chemically cleaned sapphire substrates using SQUID and MFM, coupled with TEM results lead us to the conclusion that our ZnMnO layers show paramagnetic rather than ferromagnetic behaviour. The influence of the substrate on the magnetic property of the whole heteroepitaxial structure has been investigated and the results will be presented in detail. This issue has to be taken into consideration when confirming ferromagnetism in ZnMnO grown on sapphire.

Aqueous Chemical Growth of ZnO Nanostructures

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ZnO is a semiconductor that exhibits exceptional properties. Its bandgap of 3.37 eV and its large exciton binding energy of 60 meV allow optoelectronic applications in the blue and ultraviolet spectral range. A variety of nanostructures can be grown with unique physical properties and potential applications in nanoscale devices.

Various deposition techniques have been reported in the literature to create ZnO nanostructures like metal-organic vapor phase epitaxy (MOVPE), pulsed laser deposition (PLD), molecular beam epitaxy (MBE), radio frequency sputtering or catalyst-assisted vapor phase transport techniques. However, these are rather complicated, expensive and energy-consuming processes using expensive substrates. Aqueous-chemical growth approaches (ACG) are appealing due to mild growth conditions and due to their excellent potential for large-scale production. According to low growth temperatures (T ≤ 95°C) and soft chemical treatment, ACG methods allow for the synthesis of ZnO nanostructures on a large variety of substrates - even on polymer materials.

In this paper we present further improvements on the ACG growth technology. The influence of surface activation on the growth process using nanosized ZnO seedcrystals, photochemical and electrochemical activation was studied in a modified chemical batch reactor. The ACG growth was controlled employing electrical conductivity measurements of the growth solution under in-situ conditions. Various kinds of substrates like (100)- and (111)- Si wafers, sapphire (a-plane, c-plane), SiC, ITO glass and polymer materials were used. Sample characterization was performed with atomic force microscopy (AFM), electron microscopy (SEM/EDX), x-ray diffractometry and cathodo/photoluminescence (CL/PL).

The experiments clearly reveal that activation of the surface plays an important role and offers a possibility to control the morphology and size of the ZnO- nanostructures. Both isolated ZnO nanoflowers or nanobrushes and densely packed nanorod arrays on large surface areas can be grown with the ACG technology. Lithographic techniques were developed to produce a large patterned array of ZnO nanorods as illustrated in Fig. 1. The ZnO nanostructures show hexagonal symmetry with aspect ratios in the order of ten.

Fig. 1. Patterned array of ZnO nanorods grown by ACG on (100)-Si.
Growth of Zinc Oxide Nanostructures on Metal-filled Porous Silicon

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Semiconductor ZnO has a wide band gap of 3.37 eV and a large excitation binding energy of 60 meV and displays excellent piezoelectric and optical properties. In particular, since UV emission at room temperature was demonstrated in ZnO nanowires, one-dimensional nanomaterials have increasingly drawn attention owing to their promising use in ultraviolet-blue light-emitting and lasing devices. The growth of zinc oxide nanostructures on metal-filled porous silicon (PS) has been investigated in this paper.

The PS was formed by electrochemical etching technique. The pore density and dimensions can be determined by the current density and etching time, etc. The deposition of Au, Cu and Zn from HAuCl₄, CuCl₂ and ZnCl₂ solution respectively into the pores of the PS is mainly due to the effect of PS as reducing agent.

Metal catalyzed growth of ZnO nanostructures on the PS was carried out by VLS method. The nanostructures, surface morphology, chemical composition and optical properties of the ZnO nanorods (nanowires, nanobelts) were identified by using XRD (D/max-III), FE-SEM (Philips XL320), TEM (JEM 200CX) and PL (Hitachi F-4500, Japan) AFM respectively.

It was found that the ZnO microstructures on both (100) and (111) PS substrates obtained by using different metal catalyzed growth are all of a hexagonal structure, but of different shapes. For the gold catalyzed growth, ZnO nanorods grown on both (100) and (111) PS substrates are along (0001) orientation and with a hexagonal end face, whose diameter is in a range of 150~350 nm and length up to 3~5 µm. For the Cu (CuO) catalyzed growth, ZnO nanorods grown on the (100) PS substrate are of a quadrangular cross section, whose length was in a range of 2~25 µm, and ZnO nanorods grown on the (111) PS substrate are with a hexagonal end face, whose length is in a range of 2~7 µm. For the Zn catalyzed growth, ZnO nanostructures grown on both (100) and (111) PS substrate are along (0110) orientation and of nanobelt shape, whose breadths were in a range of 50~300 nm and length up to hundreds of micro-meters. The causes for these differences are discussed.

HRTEM lattice fringe images and selected area electron diffraction (SAED) pattern for the typical ZnO nanorods indicate that the nanorods are of a single crystal hexagonal structure without dislocations and stacking faults. PL spectra for all samples are of a similar, rather sharp near band-edge emission band peaked at about 386 nm and a different, rather broad emission band peaked at around 500-540 nm. The reasons for the differences are discussed.

In particular, the study on electrical properties and electroluminescence of the ZnO nanowires is under way. This is carried out using AFM to push a ZnO nanowire onto two special designed electrodes.

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Intrinsic defects are essential for the electrical and optical properties of ZnO. However, there is still a need for clear experimental results on the optical and electrical properties of defects like the oxygen vacancy (V\text{O}) or the Zn intersitial (Zn\text{i}). Recent theoretical calculations indicated that the V\text{O} can be expected to act as a deep double donor with negative U – behaviour, i.e. the 2+/+ recharging level being located above the +/0 level in the bandgap, and the 2+/0 recharging level was calculated to be about 600 meV below the conduction band [1].

We have investigated a set of high purity vapor transport grown ZnO bulk crystals. In the as grown state the slightly Zn-rich crystals are of yellow color, which changes to transparent by post growth annealing treatments in O\text{2} atmosphere. In contrast annealing in Zn atmosphere causes red crystals. The as grown samples show a residual carrier concentration of about $1 \times 10^{16} \text{cm}^{-3}$ which decreases to $10^{14} \text{cm}^{-3}$ for the O\text{2} annealed samples (temperature dependent Hall-measurements). Photoluminescence (PL) and paramagnetic resonance experiments (EPR, ENDOR) identify the residual shallow donors to be Al, Ga, and H. Deep-level-transient-spectroscopy (DLTS) detects the dominant deep donor level at about 530 meV below the conduction band (E4). The deep luminescence is dominated by the 2.45eV emission due to the oxygen vacancy [2]. The O\text{2} annealing suppresses the E4 defect level and the V\text{O}-related emission. The results are consistently explained by the presence of the V\text{O} in the as grown and Zn annealed samples while the O\text{2} annealed samples become stoichiometric. These results are confirmed by low (170 keV) and high energy (2 MeV) electron irradiation of the O\text{2} annealed samples. According to van Vechten [3] the low energy irradiation causes predominantly displacements on the Zn-sublattice, while at high energies Zn- as well as O-ions are displaced. In the 170 keV irradiated sample DLTS shows a strong increase of the E3 level concentration, which we thus would attribute to the Zn\text{i} (the V\text{Zn} is a deep acceptor). In the 2 MeV irradiated sample we find that the E4 concentration increases by more than an order of magnitude. By DLTS experiments with light illumination ($\sim 2$ eV) and short filling pulses (50 ns) it was possible to populate the metastable V\text{O}$^+$ charge state, it is located 140 meV below the conduction band, it is in fair agreement to the theoretical predictions. A configuration coordinate diagram is developed to discuss the electrical and optical properties of the Oxygen vacancy in ZnO.

Influence of Annealing on Semiconducting and Magnetic Properties of Zn$_{1-x}$Mn$_x$O

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The origin of ferromagnetism in ZnMnO is still a question of argument: Is it intrinsic[1,2] or due to some additional or metastable phase [3]. Zn$_{1-x}$Mn$_x$O layers have been grown by MOCVD technique. As precursors- Dimethyl-zinc (DEZ), tertiary-butanol and liquid Tricarbonyl methylcyclopentadienyl Mn have been used. We made growth on 3 type of substrates: synthetic fused silica, “C” and “R” oriented” sapphires.

In the first set of the samples Mn content varies in 0.00 ÷ 0.30 range, while after growing with ZnO buffer layer incorporation of Mn increases up to x=0.32 for silica and x=0.44 for sapphire substrate correspondingly. The 0-20 X-ray diffraction scans of the Zn$_{1-x}$Mn$_x$O films present the wurtzite symmetry structure. The films grown on silica are highly textured, while the layers grown on sapphire substrates are (002) and (110) epitaxially deposited. With the same precursors at T=450$^\circ$ MnO layers with (111) orientation and 0.2$\mu$m growth rate were deposited. All ZnMnO samples, independently of Mn(x) are with n=10$^{18}$ cm$^{-3}$ carrier concentration (Hall-effect) and are antiferromagnetic (EPR measurements) [4].

Pure ZnO and Zn$_{1-x}$Mn$_x$O layers were annealed in hydrogen, oxygen and argon atmospheres at different temperatures. Hydrogen treatment doesn’t change transport properties, while oxygen and argon make Zn$_{1-x}$Mn$_x$O samples insulators. (Different behavior is found for ZnO).

Sample change color from orange to dark green-gray, which is in correlates with dramatic change of EPR signal corresponding to Mn$^{2+}$. XRD spectra reveal existence of cubic phase, with lattice parameters similar to our MnO. EPR and SQUID measurements show the same antiferromagnetic coupling for all annealed layers as for as grown.

Evaluation of Crystal Structure and Photoluminescence for ZnTe Epilayers Grown on a 2° off-oriented GaAs (100) Substrate

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High quality zincblende ZnTe (100) epitaxial layers have been grown on a semi-insulating GaAs (100) substrate by hot-wall epitaxy. The surface topography, the growth rate, and the crystalline were investigated in terms of their growth temperature dependence. It was found that the epitaxial orientation grew inclined to the substrate crystal.

Figure 1 shows the 10 K-PL spectrum for a ZnTe epilayer grown at 470 °C. The near band excitonic emissions are clearly resolved and are very strong and narrow. The deep level emissions of Y-band [1] and oxygen bound exciton (OBE) [2] as shown in the inset are relatively weak. Based on ref.[3], all assigned peaks and their positions were slightly blue-shifted. The 2.3905 eV and 2.3855 eV peaks are emissions of the first excited state of the heavy-hole (X_{2S,hh}) and the light-hole exciton (X_{2S,lh}), respectively. The peaks at 2.3819 eV and 2.3801 eV are the doublet structure of the heavy-hole exciton (X_{1S,hh}), while the ground state emission of the light-hole exciton (X_{1S,lh}) peak is observed at 2.3759 eV. The strong and narrow emission of free excitons indicates that the PL properties and the crystalline quality of the ZnTe epitaxial layer grown on the tilted GaAs substrates are excellent.

The peaks at 2.3740 eV (I_{2A}^{B}) and 2.3709 eV (I_{1A}^{B}) are bound exciton peaks associated with Ga- and As-atoms diffused from the GaAs substrates, respectively, and the peaks at 2.3646 eV (I_{1B}^{C}) and 2.3585 eV (I_{1C}^{C}) are related to the acceptor bound exciton [3].

Figure 1. Typical PL spectrum for a ZnTe/GaAs. The doublet structure of the ground state heavy-hole free exciton (n=1) and the first excited state of the light-hole and heavy-hole free exciton (n=2) are shown. The inset shows the deep level emissions of Y-band and oxygen bound exciton (OBE).

Evidence for Bose Condensation of Microcavity Polaritons

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Bose-Einstein condensation (BEC) is a rare and intriguing physical phenomenon observed at ultra-low temperatures in superconductors, superfluids and atomic gases [1]. Recently, microcavity exciton-polaritons have been proposed as candidates for BEC at very high temperatures, up to 300K [2].

We have studied CdTe/CdMgTe microcavity samples containing 4-16 quantum wells and characterized by a vacuum field Rabi-splitting of 13-26 meV. Electron-hole pairs were excited at T=4K by linearly-polarized light at 1.74 eV provided by a Ti:sapphire laser operating in the pulsed mode (at 80 MHz rate). Spectroscopic imaging in k space as well as near-field spectroscopy show that, above a critical stimulation threshold, polaritons in our microcavities undergo a spontaneous transition to a condensed phase characterized by the massive occupation of the lowest polariton state with in-plane wavevector \(k_//=0\) (see Figs. a-d). The coherence of this quantum state is evidenced by the spectral and angular narrowing of its emission (Figs. e, f). To address the controversial issue of BEC, which is a thermodynamic phase transition, we are currently investigating the polariton condensate formation under nonresonant and quasi-cw excitation. Analysis of the polariton population statistics along the dispersion curve as a function of the excitation power and temperature will be presented.

Figures a to c: 2D images of the far-field polariton photoluminescence (PL) intensity. Vertical and horizontal axes correspond to emission energy and angle, respectively. PL intensity increases from blue to red. Excitation pumping was (in arbitrary units): (a) \(P_0\), (b) \(8.6 P_0\), just below threshold, and (c) \(10 P_0\), just above threshold. (d) Spectrally integrated intensity of the emission from the polariton ground state \(k_//=0\) (\(\theta=0\)) normalized to the pumping power. (e) PL spectra of the ground state, corresponding to pumping powers \(P_0\), 8.6 \(P_0\), and 10 \(P_0\), normalized to the pumping power. (f) Angular profile of the stimulated emission at 1624.9 meV for the highest pumping power 10 \(P_0\).

ZnO Nanorod Heterostructures and Nanodevices

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One-dimensional (1D) semiconductor nanowires and nanorods have attracted increasing interest due to their novel physical properties and diversity for potential electronic and photonic device applications [1]. For 1D nanostructure preparation, a catalyst-assisted vapor-liquid-solid (VLS) method has widely been used since this technique offers an easy and simple method for the synthesis of many kind of 1D semiconductor nanostructures including Si, GaAs, ZnO, and GaN nanowires. However, the catalytic method has several problems in fabrication of high quality nanostructures, due to the use of metal catalysts. At first, the catalyst impurity might be incorporated into nanowires during growth and these unintentionally doped impurities make it difficult to control the intrinsic properties of these materials and are detrimental to device fabrication. In addition, due to the re-alloying of alternating reactants in the metal catalyst during the condensation-precipitation process, compositionally modulated 1D structures with well defined interfaces might be difficult to obtain. In this talk, as an alternating approach, catalyst-free metalorganic vapor phase epitaxy (MOVPE) as a ZnO nanorod growth method would be introduced to minimize both incorporation of unintentional impurity and formation of a mixed interfacial layer, i.e., by utilizing direct adsorption of atoms on the top surface of nanorods [2]. With precise thickness control down to the monolayer level, compositionally modulated nanorod quantum structures can be readily designed within individual nanorods [3]. Moreover, ZnO nanorods grown by this method are aligned vertically and exhibit uniform thickness and length distributions, highly appropriate for a direct integration of 1D nanorod on a device platform to fabricate a unique vertical devices and device arrays. Finally, I briefly describe our recent activities on ZnO nanorod device fabrication and evaluation, including nanorod light emitting devices, field-effect transistors (FETs), Schottky diodes, and logic circuits.

Fig.1 (a) ZnO nanorods, (b) ZnO/ZnMgO nanorod quantum well structures, and (c) nanorod FETs.

Excitons in CdSe/ZnSe Quantum Dots and Exciton-photon Coupling in ZnCdSe/ZnSe Quantum Wells

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CdSe/ZnSe quantum dots have intense emission in the visible region of the spectrum with very strong Coulomb interactions. At the individual quantum dot level, a CdSe/ZnSe quantum dot exhibits pronounced photon anti-bunching. These properties make this material system of great interest for experiments to probe and manipulate a quantum system. However, our experience, and those of other groups, is that the dot density is invariably very high, typically 1000 dots $\mu$m$^{-2}$, making the isolation of the optical response of just one quantum dot very challenging. We present a partial solution to this problem. By performing an in situ annealing step, we show that the majority of dots become heavily alloyed leading to a blue-shift in the emission energy. A small minority however red-shift and we find that these quantum dots are spectrally well separated allowing good discrimination of the emission from individual dots. Neutral excitons in these dots have a massive fine structure splitting, 2.0 meV, leading to strong polarisation selection rules in the exciton and biexciton emission lines.

We present initial attempts to manipulate these quantum states. First, by embedding the quantum dots in a field-effect structure, we are able to control the charge of the exciton. A crucial result is that the pronounced fine structure of the neutral exciton disappears on charging. Remarkably therefore, we are able to control an exchange interaction, in this case between a conduction and a valence electron, simply with a small dc bias applied to the device. Secondly, we present a new concept for fabricating II-VI micro-cavities. By performing an epi-lift off step we can transfer the active part of the heterostructure to a foreign substrate, for instance a dielectric Bragg mirror. We have already demonstrated that this process preserves the excellent optical properties of our material, and that ZnCdSe/ZnSe quantum wells show strong photon-exciton coupling up to 250 K.
CdTe-CdMnTe Quantum Dots
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There is considerable scientific and technological interest in gaining the ability to control and manipulate the spins of electric carriers in semiconductors. In bulk semiconductors as well as semiconductor quantum wells, due to elastic scattering of carriers by phonons and impurities the spin–relaxation times are short – in the order of tens picoseconds. Since in quantum dots (QDs) the carriers are confined in all dimensions such scattering processes are expected to be strongly suppressed resulting in spin-relaxation times of the order of nanoseconds [1].

In this presentation we report recent results of spectroscopy of CdTe and CdMnTe QDs embedded in ZnTe matrix. The investigated structures have been grown by molecular beam epitaxy by Stransky-Krastanow growth mode. Using photoluminescence excitation (PLE) and resonantly excited photoluminescence (PL) techniques, exciton excitation processes have been studied in single QDs and large assembles of QDs. PLE spectra reflect two major mechanisms for carrier excitation – the direct excited-state-ground state transition and longitudinal optical (LO) phonon-assisted absorption directly into the ground states. By combining LO-phonon assisted absorption with circularly polarized excitation, spin-polarized excitons can be photo- excited. For symmetric CdTe QDs at zero magnetic field the spins randomize very rapidly [2]. When the degeneracy is lifted by magnetic field optically created spin-polarized excitons maintain their polarization on a time scale larger than the excitation recombination time. Similar behavior has been found in large ensembles of CdTe QDs.

In the case of QDs containing magnetic Mn ions (CdMnTe) the resonant optical excitation of spin-polarized excitons induces a macroscopic magnetization on Mn system, associated with the formation of exciton magnetic polarons [3]. Due to particular stability of the exciton magnetic polarons in CdMnTe QDs, where the localization of electrons and holes is comparable to the magnetic exchange interaction, the optically induced spin alignment persists to temperatures as high as 160 K [4].

Quantum-confined nanoparticles are being increasingly investigated due to the superior efficiency and tunability of their emission spectra from the ultraviolet to the near infrared. The quantum-nature of an emitting state in a 1D-nanostructure is of fundamental interest. The size-dependent 1D-exciton fine structure defines the eigenstate symmetry, the oscillator strength and the level structure of the exciton ground state. We study the optical properties of excitons in one-dimensional nanostructures at low temperatures by polarization-sensitive photoluminescence spectroscopy of single CdSe(ZnS) core-shell nanorods. The single NR line shape has been determined, and a fine structure is found, which we assign to exchange splitting of a 1D-exciton confined in a cylindrical CdSe nanorod. The measured degree of polarization, the radius-dependent change in ground state symmetry, and the observed increase in photoluminescence decay time with increasing temperature are all explained by the 1D-exciton confinement and exchange interaction [1]. For small nanorod radii \( R < a_B/2 \), an increase in the photoluminescence decay time is found when the temperature increases from 10K to 80K. The observations are explained by a radius-dependent change in the symmetry of the 1D-exciton ground state which transforms from a dark state into bright states below a critical radius of \( R_{\text{crit}} \sim 3.7 \) nm. The engineering of the NC shape increases the dipole oscillator strength for a CdSe NR exciton which opened the way for the experimental observation of the strong coupling regime with semiconductor nanocrystals. We demonstrate a strongly coupled cavity QED system with a CdSe nanocrystal coupled to a single photon mode of a polymer microsphere. The strong exciton-photon coupling is manifested by the observation of a cavity mode splitting of 40 µeV and lifetime measurements of the coupled exciton-photon state [2].

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Calculated fine structure splitting of the 1D-exciton. Optically dark (bright) states are plotted by dotted (solid) curves. The critical radius \( R_{\text{crit}} \) for the symmetry crossing is indicated by an arrow. The inset shows the 1D-exciton ground state energy and the variational parameter representing the exciton spatial extension along the NR axis, versus NR radius [1].
In this paper we present results on further improvements of the recently reported novel approach to zinc oxide Chemical Beam Epitaxy (CBE). Hydrogen peroxide is employed as a very efficient novel oxidant. The ZnO layers with a thickness from 100 nm to 600 nm were grown on c- and a-sapphire using a modified Varian Gen II MBE system. Atomic force microscopy, optical microscopy with Nomarski contrast and scanning electron microscopy were employed for surface morphology analysis. The structural quality of the layers was investigated using X-ray Diffractometry (XRD) and transmission electron microscopy. Electrical properties of the grown ZnO layers were studied by Hall-effect measurements in a standard van-der-Pauw configuration and by CV-measurements. The homogeneity of the samples was investigated by PL-mapping. The measured surface roughness for the best layers is as low as 0.2–0.3 nm rms. XRD measurements of the obtained ZnO layers show excellent quality of the single crystalline ZnO heteroepitaxially grown on sapphire with a MgO buffer layer. The FWHM of the XRD (0002) rocking curves measured for the 2 inch ZnO-on-sapphire wafers is as low as 30 arcsec with a very high lateral homogeneity across the whole wafer. PL-mapping as well as conductivity mapping also show a good uniformity across the 2 inch ZnO-on-sapphire epiwafers. The results indicate that CBE is a suitable technique to fabricate ZnO epilayers and heterostructures of very high structural quality. Due to the extremely high quality of these ZnO/sapphire templates, they can eventually be used as an alternative to high quality ZnO substrates. The influence of the growth conditions on the surface roughness, crystalline quality and electrical parameters of ZnO epilayers as well as the properties of ZnMgO-ZnO quantum well structures will be discussed.
In the development of ZnO-based UV light emitters with ZnO/ZnMgO quantum wells (QWs), one may encounter the problem of quantum confined Stark effect (QCSE) due to piezoelectric polarizations in strained QWs, which decreases the quantum efficiency of light emission from the QWs. This is actually the problem to which the GaN-based light emitters with InGaN/GaN QWs are now facing, and the preparation of non-polar structure such as A-plane or M-plane is suggested and investigated. Consequently, for aiming at ZnO-based light emitters with ultimate efficiency, non-polar ZnO layers are much desirable.

For the above purpose, epitaxial growth behavior of ZnO on M-plane (01-10) and R-plane (01-12) sapphire substrates has been investigated. The growth was done by MOVPE using diethylzinc and nitrous oxide (N2O). The up-to-date results are summarized as follows:

(i) On M-plane sapphire, at higher growth temperature (e.g., 800°C) and/or VI/II ratio (e.g., 1.25×10^5), only ZnO(01-10) (M-plane) was grown. But at much lower growth temperature (e.g., 500°C) and/or VI/II ratio (e.g., 5.6×10^3), not only ZnO(01-10) but also ZnO(01-13) was grown. On the other hand, on R-plane sapphire, at all growth conditions, only ZnO (11-20) (A-plane) was grown.

(ii) In-plane alignment of ZnO on M-plane sapphire was ZnO(11-20)//sapphire(0001), in case of the growth both of ZnO(01-10) and ZnO(01-13). On R-plane sapphire, where ZnO(11-20) was grown, the in-plane alignment was ZnO(0001)//sapphire(01-11).

(iii) Both the ZnO samples on M-plane and R-plane sapphire grown at lower growth temperature and/or VI/II ratio, the ZnO grains preferably extended along the c-axis. This suggests the strong tendency of growing toward the c-axis direction. On the contrary, at higher growth temperature and/or VI/II ratio, they preferably stretched toward the direction perpendicular to the c-axis.

(iv) At higher growth temperature and VI/II ratio (e.g., 800°C and 1.25×10^5), the surface was rough on both M-plane and R-plane sapphire. This is because the ZnO crystal grew toward the direction perpendicular to the c-axis, i.e., the growth occurs not only along the substrate surface but also to the direction vertical to the substrate. On the other hand, with lowering the growth temperature and/or VI/II ratio, the surface morphology became smoother. This was because the ZnO crystal grew preferably along the substrate surface to the c-axis direction rather than to the direction vertical to the substrates.

(v) Interestingly, on R-plane sapphire, very smooth surface was obtained at the low growth temperature and VI/II ratio (e.g. 700°C and 5.6×10^3). Under this condition, ZnO has very strong tendency of growing along the c-axis, which accelerated the lateral growth on the sapphire substrate surface. But on M-plane sapphire at this condition, nanorods tilted by 30° was grown from which the ZnO(01-13) peak of X-ray diffraction was obtained. The formation of these nanorods seems to be due to the growth so that the c-axis becomes perpendicular to the A-plane sapphire, which is inclined by 30° to the M-plane.

Detailed growth behavior will be discussed based on the characterization of initial growth processes.
Large Built-in Electric Fields in c-oriented Wurtzite ZnO/ZnMgO Quantum Well Heterostructures

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ZnO-based quantum wells have attracted much attention in the last few years due to their interesting possibility of combining band gap engineering with large excitonic binding energies. Theoretical predictions indeed suggest that the 60meV-binding energy of excitons in ZnO, the largest among usual semiconductors, could be further doubled in QWs, in agreement with first experimental studies\cite{1}. However, an intriguing feature of the experimental results available until now is that ZnMgO/ZnO QWs do not seem to develop any marked built-in electric field, as it is the case in the neighbouring AlGaN/GaN system due to the non centro-symmetry of the wurtzite structure.

In this communication, we report on the growth, structural properties and electronic structure of fully-strained, c-oriented ZnMgO/ZnO QW heterostructures grown by MBE. Contrary to previous reports, we find evidence of very large built-in polarisation effects in such QWs and values of 0.8 MV cm\textsuperscript{-1} are determined for QWs with Mg content of 20\%.

First we present a detailed study of the growth and structural properties of the investigated samples, as analysed by means of RHEED, X-ray diffraction and TEM. In particular we find that the growth conditions for achieving 2D growth of ZnMgO barrier layers with no cubic insertions have to be strongly modified, as compared to the optimal growth conditions used for growing ZnO.

Second we focus on the electronic properties of the ZnMgO/ZnO QW heterostructures which are studied by means of optical reflectivity, temperature-dependent photoluminescence (PL) and selective photoluminescence. While the emission energies of the narrowest QWs are located above that of the ZnO buffer layer, thicker QWs (L\textsubscript{w} > 3-4 nm) emit at an energy well below. This is a clear manifestation of the quantum confined Stark effect due to the large built-in electric fields in the structures. We note that for very large QWs, red shifts of the order of 400 meV are observed.

Another demonstration of the occurrence of built-in electric fields is given by the energy dependence of the QW emission which varies as a function of the density of photo-generated carriers in the well. Again, the larger effects are observed for wider wells, where the emission energies of some QWs can vary by more than 100 meV depending on the density of photo-generated carriers in the well. Both effects are well accounted for by a simple self-consistent effective mass formalism and estimates of the built-in electric fields are determined.

\[1\] For a review see, T Makino, Y Segawa1, M Kawasaki2 and H Koinuma, Semicond. Sci. Technol. 20 (2005) S78–S91
ZnO is a multifunctional material possessing unique combination of electrical, optical, piezoelectric and acoustical properties with applications such as gas sensors, transparent electrodes, and SAW devices. Compared with other semiconductors, ZnO should compete in the area of opto- and microelectronic devices, because it has higher free exciton binding energy, higher saturation velocity and superior resistance to ionising radiation and high energy particles. The development of ZnO-based p-n junction devices, however, is hindered by difficulty in growing p-type ZnO. So far, mainly heterojunction devices using n-ZnO and comparable p-type wide-gap semiconductors (GaN, NiO, ZnRh2O4) have been shown [1].

We have recently demonstrated that thermal oxidation of Zn-based compounds, namely Zn3N2 or ZnTe, is a viable method of forming p-type ZnO [2, 3]. In this communication we report on fabrication of ZnO p-n homojunctions. We have used p-type ZnTe:N as a starting material and carried out heat treatments in O2 flow at 600°C in order to make p-type ZnO. N-type ZnO was deposited by magnetron sputtering from ZnO target. The thickness of p- and n-type regions was in the range 0.6 - 1 µm. Free carrier concentrations in p- and n-type ZnO were about 1x10^17 cm^-3 and 1x10^18 cm^-3, respectively. Secondary ion mass spectrometry, x-ray diffraction and atomic force microscopy were used to examine the composition, microstructure and surface morphology of ZnO films. The transport properties of p- and n-type ZnO were assessed from Hall effect measurements, while electrical characteristics of p-n junctions were obtained by conventional I-V measurements. Through optimising crucial technological processes such as deposition of low resistivity n-type ZnO, development of ohmic contacts to p-type and to n-type ZnO as well as controlled chemical etching of ZnO we have achieved high quality rectifying p-n junctions. Fig.1 shows I-V characteristics and the schematic cross-section of ZnO-based p-n junction.

Control of ZnO/Al$_2$O$_3$ (11-20) Surface Morphologies Using Plasma Assisted Molecular Beam epitaxy

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Although extensive studies have highlighted the important role of Zn/O flux ratio and the growth temperature on the growth mode and resulting surface structure of ZnO films, which in turn determine their structural, electrical, and optical properties, the development of plasma-assisted molecular-beam epitaxy (PAMBE) growth diagram for ZnO is still under way. Here the characteristic surface morphologies of ZnO grown on Al$_2$O$_3$ (11-20) by PAMBE under various growth conditions have been investigated. Based on in situ reflection high energy electron diffraction (RHEED), we identified four growth regimes, corresponding to the short (1x1), (3x3), (1x1) and spotty RHEED patterns, respectively. The morphology transitions are believed to be association with changes in the growth kinetics caused by variations in the coverage of the ZnO surface by excess Zn or O. The three boundaries appears to be roughly illustrated by Arrhenius relations with the substrate temperature, with activation energies of 1.35eV, 1.97eV and 2.6eV, correspond to the energy of Zn-Zn, Zn-O and O-O bonding energies,[1] respectively. The characteristic morphologies of ZnO films grown within each of the four regimes are investigated using ex situ atomic force microscopy (AFM). The surfaces of Zn-rich films are occupied by nanocrystals of round mound shapes. Films grown at O-rich conditions are with large facet islands of hexagonal bases. For the growth of mild Zn-rich beyond stoichiometry, the RHEED keeps in (3x3) pattern, a smooth surface represented by atomically flat terraces and half unit cell (0.26 nm) high steps (a charge neutral unit of ZnO) is achieved, which shows a low residual carrier concentration of $7.5 \times 10^{17}$ cm$^{-3}$ and high mobility ($\sim 10^3$ cm$^2$/V s), which is comparable to the best value ($\sim 125$ cm$^2$/V s) for ZnO films grown on sapphire $a$-plane (11-20) substrates by radical source molecular-beam epitaxy [2].

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Observation of Zn Vacancies in ZnO

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We have used positron annihilation spectroscopy to study vacancy defects in ZnO crystals grown by various methods. The combination of positron lifetime and Doppler broadening techniques with theoretical calculations provides the means to deduce both the identities and the concentrations of the vacancies. The annihilation characteristics of the Zn vacancy have been determined by studying electron-irradiated ZnO grown by the seeded vapor phase technique [1]. In the same work, the Zn vacancies are shown to be the dominant compensating centers (acceptors) in the nominally undoped (n-type) material grown by that method. The electron irradiation produces vacancies also on the O sublattice [2]. Our results show that Zn vacancies or Zn vacancy related defects are present in as-grown ZnO, irrespective of the growth method. Zn vacancies are observed in undoped ZnO and (Zn,Mn)O grown by chemical vapor transport (CVT). The results show that the introduction of Mn into the material decreases the concentration of other defects observable by positrons, tentatively identified as O vacancies. The Zn vacancies present in undoped ZnO grown by contactless CVT are the dominant negatively charged point defect in the material. Doping the material with As introduces also larger defect complexes involving the Zn vacancy. Hydrothermally grown ZnO contains Zn vacancies and a high concentration of neutral defects with small open volume, likely O vacancies. The Zn vacancies anneal out after annealing at 800 °C, while the O vacancies remain in the material. All the above-mentioned materials are nominally undoped (n-type), and thus the presence of Zn vacancies in as-grown material is natural, since they have the lowest formation energy when the Fermi level is near the conduction band [3]. However, Zn vacancies or defect complexes involving the Zn vacancy are present also in p-type ZnO. Positron results on As-doped ZnO layers grown by an evaporation/sputtering process [4], where the hole concentration is about $4 \times 10^{18}$ cm$^{-3}$ (obtained with As concentration $5 \times 10^{19}$ cm$^{-3}$) indicate that the concentration of Zn vacancy related defects is at least $10^{19}$ cm$^{-3}$ in this material.

Direct Observation of As-related \((e,A^0)\)-emission in ZnO

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We present results from structural and optical characterization of heteroepitaxial grown ZnO doped with arsenic. The samples were grown by metalorganic vapor phase epitaxy on GaN/sapphire templates. After the growth of an optimized ZnO buffer layer (nominally undoped) grown at 450°C a 1 \(\mu\)m thick ZnO layer was grown at 850°C - 900°C using DMZn and N\(_2\)O. This final 1 \(\mu\)m high temperature ZnO layer was doped with arsenic using AsH\(_3\).

In the spatially integrated luminescence spectra \((T=4K)\) the free exciton \(X_A\), the bound exciton lines \(I_0/I_1, I_2/I_3\), and \(I_8\), as well as the 1\(^{st}\) and 2\(^{nd}\) LO phonon replica from \(I_8\) can be easily identified. The TES-\(I_0/I_1\), TES-\(I_2/I_3\) and TES-\(I_8\) line and even the 1\(^{st}\) LO phonon replicas of the TES-\(I_0/I_1\), TES-\(I_2/I_3\) and TES-\(I_8\) line can be observed. The most prominent feature appears almost at the spectral position of TES-\(I_9\): a very intense free-to-bound transition \((e,A^0)\).

The spectral overlap of the TES-\(I_9\) peak with the much more intense \((e,A^0)\) peak is identified by spatially resolved cathodoluminescence (CL) microscopy and is confirmed by temperature dependent PL and CL measurements. We performed temperature dependent CL scans from identical sample position: The \((e,A^0)\) line clearly dominates the local spectrum at individual spots. Here, up to 3 LO phonon replicas of the \((e,A^0)\) are visible. In contrast, the main matrix is dominated by the \(I_8\) emission and also the TES-\(I_0/I_1\), TES-\(I_2/I_3\) and TES-\(I_8\) line are visible here in the matrix at low temperatures. All lines of the matrix shift to lower energies with increasing temperature. In complete contrast, the \((e,A^0)\) peak shifts to higher energies with increasing temperature.

Zeeman investigations will give information about the valence band splitting and the incorporation of donors and acceptors in these doped epilayers.

Fig.1: (a) CL wavelength image of the spectral region of \((e,A^0)\): the spot (green contrast) and the matrix (blue contrast) are visible. (b) Local spectra from the matrix (blue) and the spots (red) at different temperatures.
Characterization of II-VI Semiconductor Surfaces for Photoelectrochemical Conversion of Solar Energy

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Changes of reflectance and photoluminescence spectra CdTe in exciton sphere in dependence on temperature of CdTe with different impurity-defective compositions and concentration of free charge carriers are investigated. New lines are observed on spectra, conditioned by quasi-two-dimensional surface excitons. Two models of quasi-two-dimensional surface excitons of CdTe and ZnO informed by us in [1, 2]. Polarization spectroscopy of reflectance CdTe informed in [3]. Free bulk excitons, bulk excitons connected with neutral donors and acceptors with their LO-phonon repetitions and quasi-two-dimensional surface excitons in temperature sphere 4.2 - 100 K and concentration of free electrons less than $10^{17}$ cm$^{-3}$ are observed on reflectance and photoluminescence spectra. Dependence of spectral lines of quasi-two-dimensional surface excitons on temperature (4.2 - 300 K) and concentration of free charge carriers ($10^{14} - 10^{18}$ cm$^{-3}$) is defined. When temperature of crystal becomes 100 - 300 K and concentration of free electrons - more than $10^{17}$ cm$^{-3}$, contribution of quasi-two-dimensional surface excitons on optical spectra become dominant and for that matter they have to be investigated not only at low, but also at high temperatures. Spectral photosensitivity region of semiconducting photoelectrode extended into IR part of the spectrum through varying the impurity-defective composition of the semiconducting material of photoelectrode. New experimental results on quasi-two-dimensional surface excitons in photoelectrode of CdTe with different impurity-defective compositions from low to room temperatures were presented. The surface states of photoelectrode’s semiconducting material for photoelectrochemical conversion of solar energy were investigated. The results allow getting high efficiency conversion of solar energy.

Registration of x-ray Radiation on Structures ZnS-CdS,
Obtained by a Method of Chemical Pulverization

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One of ways of registration of x-ray radiation is his(its) conversion in visible at the expense of a photoluminescence originating in a semiconductor at absorption of x-ray quanta.

In different devices medical tomography and technical non-destructive testing the systems such as scintillator - hierarchies photodetector are applied, with which help it is possible to transform an optical signal in electrical with the subsequent amplification. The widely used system such as scintillator - photoelectronic multiplying tube (PMT) allows to register radiation radiation in a wide range of energies and intensities. However in a number of cases its application is restricted to disadvantages inherent PMT.

In the present report the results of development the express train - method of manufacturing of system such as «x - luminofor (ZnS)$_x$ (CdS)$_{1-x}$ - photoexplorer CdS» are resulted, on the basis of layers of connections A$_2$B$_6$, received by a method chemical pulverization. The system, received by such method, should consume insignificant capacity, have small dimensions and weight, to raise (increase) reliability and stability of the target characteristics in a wide dynamic range of intensity and energy of x-ray radiation.

On the received layers the researches of optical and photoluminescent properties were carried out (spent). At an irradiation by x-ray radiation layers of a firm solution (ZnS)$_x$ (CdS)$_{1-x}$: CuCl$_2$ Cu, Mn had significant luminescence in blue - green area of a spectrum a strip 400-640 nm.

For experiment the converter such as x - luminofor - photoconductor of film structure (ZnS)$_x$(CdS)$_{1-x}$: Cu, Mn - glass - SnO$_2$ – CdS – In was created.

Using modern methods photolithography on a surface of a glass substrate covered with a conducting translucent layer SnO$_2$ with the help of a special photo mask - of a mask possible to generate numbers (lines) of electrodes, located perpendicularly each other and forming a flat electrode grid from cells by the size 50 $\times$ 50$\mu$m.

On the basis of structure x - luminofor - the photoexplorer, using modern methods of photoengraving is possible to make matrix structure from photosensitive layer CdS and using modern integral engineering, to carry out (spend) scanning the obtained matrix from the obtained photoresistances on x and at under the program from the COMPUTER, and to arrest value of a photocurrent in cells of a matrix, on which the radiation from x - luminescence of a layer, to exhibit x - radiation drops.

The technology, applied by us, allows to create enough effective system «x - luminofor - photoexplorer» on the basis of structure (ZnS)$_x$ (CdS)$_{1-x}$ - glass - SnO$_2$ - CdS - In, which is perspective for problem solving x-ray technical non-destructive testing and medical tomography.
Characterization of II-VI Nanoparticles by Pair Distribution Function

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In this contribution we present the possibilities that the analysis of the pair distribution function (PDF) offers to analyse II-VI nanoparticles. The diffraction pattern of nanoparticles with diameters of less than 4 nm exhibit only few broad maxima. In this sense they resemble the diffraction pattern of amorphous materials. Standard characterisation techniques use the Scherrer equation to estimate particle diameters. Rarely, Rietveld refinement techniques are used. Both method inherently rely on the assumption of a perfectly periodically ordered crystal. These assumptions do not hold, however, for small nanoparticles. The finite particle size and its shape need to be taken into account. Additionally, relaxations due to the large fraction of atoms on the particle surface are important. Finally, nanoparticles often contain large amounts of defects like stacking faults, and twin boundaries. The combination of these substantial deviations from the long range order requires an adequate analysis of the diffraction data.

The Scherrer equation is based on the assumption of a small perfect crystal. The FWHM of the diffraction maxima is interpreted to give the particle diameter. We show that nanoparticles of very different size will yield diffraction pattern with almost identical FWHM. These nanoparticles differ in the amount of defects only.

In this contribution we show the possibilities offered by the pair distribution function. The PDF is obtain from the diffraction data by a sine Fourier transformation of the normalized structure factor. The PDF consists of maxima that represent inter atomic distances. Their height depends on the respective atom types and number of interatomic distances. Contrary to standard techniques, the PDF allows the determination of these interatomic distances without the prior establishment of a structural model. The PDF can be calculated from a structural model that may be based on any internal structure, particle size, particle shape, and defect concentration. A PDF that has been determined from neutron diffraction data can be calculated straightforward from the sine Fourier transformation of the histogram of interatomic distances. To calculate a PDF that has been determined from X-ray data, the q-dependence of the atomic form factor has to be taken into account. We present an exact analytical solution to this issue.

Results will be presented for nanoparticles of CdS, ZnO and CdSe/ZnS core shell particles. The structure of 1.8 nm CdS nanoparticles deviates considerably from that of the cubic zincblende structure of the bulk material. A stacking fault density of 40% requires to describe this material as tetrahedrally bonded network. ZnO and CdSe/ZnS nanoparticles on the other hand contain a very low defect density. Nanoparticles with diameters of approximately 4 nm can still be described as small bulk crystals. Differences between Rietveld refinements and direct modelling of the PDF will be discussed.
Cd$_{1-x}$Zn$_x$Te (x≈4%) is an important semiconductor material needed as substrate in epitaxial growth of top-quality Hg$_{1-y}$Cd$_y$Te infrared detectors and other novel devices. This work aims to review and compare different methods of optical characterization of the quality of these substrates. Basic and simple optical techniques (photoluminescence, transmittance and reflectance) are used to map properties of Cd$_{1-x}$Zn$_x$Te wafers at different temperatures (liquid helium, liquid nitrogen, room temperature). The simplest and the most appreciated information to be obtained is the energy gap value leading directly to the zinc content [1], but other parameters expressing the material quality can be deduced too (linewidths, defects and their rough concentrations).

Liquid helium temperature is needed for high-precision determination of the energy gap of the alloy, however this information can be extracted from spectra of photoluminescence or reflectance even at room temperature. Measurement of transmittance is valuable only for extremely thin samples (≈1 µm) [2]. The use of transmittance on thick samples in practice (for wafer characterization) is questionable as the position of the absorption edge depends on the crystal quality.

Zinc mapping at room temperature faces the fact that the value of energy gap is not known with enough precision. Determination of the energy gap hangs together with its temperature dependence, which has recently been studied recently by simultaneous measurements of photoluminescence and absorption on extremely thin samples [2,3]. We show that the photoluminescence maximum at room temperature lies deep below the band gap energy and cannot be directly linked with neither the free exciton resonance. We demonstrate that zinc concentration mapping is feasible using reflectance (even at room temperature), but its evaluation requires a detailed numerical analysis.


[3] P. Horodyský, R. Grill, P. Hlídek, High temperature photoluminescence in CdTe, to be published
Optical Characterization of Cd$_{1-x-y}$Be$_x$Zn$_y$Se Mixed Crystals

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Among II-VI compound based semiconductors Cd$_{1-x-y}$Be$_x$Zn$_y$Se solid solutions are of particular interest for their potential application in constructing of green lasers, visible LED’s and photodetectors operating in the visible and UV spectral region. There are some literature data concerning reflectivity and luminescence in Cd$_{1-x-y}$Be$_x$Zn$_y$Se thin layers grown on InP [1,2], but the basic crystallographic and optical properties of Cd$_{1-x-y}$Be$_x$Zn$_y$Se bulk solid solutions are only a little known.

This paper deals with investigation of temperature dependence of the near band-edge transitions of a series of wurtzite type Cd$_{1-x-y}$Be$_x$Zn$_y$Se mixed crystals using contactless electroreflectance (CER), photoreflectance (PR) and photoluminescence (PL) in the temperature range of 15 to 450 K. The crystals were grown by the modified high pressure Bridgman method from the melt for 0 < $x$ ≤ 0.15 and 0 < $y$ ≤ 0.30. X-ray investigations show that samples with Be content up to 0.1 are uniform in composition and exhibit one wurtzite phase or wurtzite as a main phase with admixture of another polytypes. The samples with nominal Be content $x > 0.1$, were found to be spatially not uniform in composition. These results well correspond to luminescence data. PL spectra at low temperatures consist of an exciton line positioned in the energy range from 1.906 to 2.422 eV for Cd$_{1-x-y}$Be$_x$Zn$_y$Se with different Be and Zn contents and a second, broader, emission band whose maximum is about 100 meV lower than the exciton luminescence. This emission is thermally quenched completely at temperatures higher than about 100 K and is interpreted as due to recombination of shallow donor-acceptor pairs. In Cd$_{1-x-y}$Be$_x$Zn$_y$Se samples with Zn content equal 0.30 some very weak deep levels emission bands are also observed at energies about 1.9 eV.

The transition energies of the A, B, and C excitons of Cd$_{1-x-y}$Be$_x$Zn$_y$Se are determined via a lineshape fit to the CER and PR spectra. The parameters that describe the temperature dependence of the interband transition energies of the excitonic features are evaluated. The energies corresponding to the exciton emission lines in the luminescence spectra quite well correspond to the transitions energies of A excitons obtained from CER and PR data. The results are compared with that of the zinc-blende Cd$_{1-x-y}$Be$_x$Zn$_y$Se films grown on InP (100) substrates.

Characterization of Be$_x$Cd$_{1-x}$Se Alloys by Contactless Electroreflectance

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Be$_x$Cd$_{1-x}$Se solid solutions are of great interest as they are very promising for construction of full colour visible optical devices due to the large difference in the energy gaps of binary constituents (CdSe: $E_g = 1.78$ eV, BeSe: $E_g = 5.6$ eV). Be$_x$Cd$_{1-x}$Se has been proposed to be used as an active layer material in green semiconductor lasers [1].

In this work single crystal of Be$_{0.075}$Cd$_{0.925}$Se grown by the high pressure modified Bridgman method from the melt and Be$_x$Cd$_{1-x}$Se epilayers on InP substrates grown by the molecular-beam-epitaxy (MBE) have been characterized by the technique of contactless electroreflectance (CER) and photoluminescence (PL). PL spectrum of Be$_{0.075}$Cd$_{0.925}$Se at 38K consists of exciton line (1.956 eV), “edge”- (1.85 eV) and “deep levels”- (1.6 eV) emission bands. The exciton luminescence is observed up to room temperature. In the CER spectra of both Be$_{0.075}$Cd$_{0.925}$Se single crystal and Be$_x$Cd$_{1-x}$Se epilayers, various transitions originating from the band edge and spin-orbital splitting critical points have been observed. A careful analysis of the CER spectra has led to the determination of the band gap energy and the value of spin-orbital splitting to within a few meV. The values of the spin-split off are found to be insensitive to the Be content. The increase of the energy gap with increasing Be content $x$ has been observed and fitted to a quadratic equation: $E_g = 1.78 (1-x) + 5.6x – bx(1-x)$ with a bowing parameter $b = 2.6$ eV.

The Thermodynamic Forecast and Electrochemical Investigation of Oxidation-reduction Reactions in CdTe-electrolyte System


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The interface semiconductor - electrolyte is a basis of many technological operations, which form structure, chemical composition and electronic state of a surface of semiconductor materials.

In this work the thermodynamic forecast and electrochemical investigation of oxidation-reduction reactions, which are possible in systems Cd – H2O, Te – H2O is carried out. On the basis of this results the Purbe diagram for system CdTe – H2O is obtained.

Set, that in the field of cathodic potentials the border of electrochemical stability CdTe transits on a line from $-1.18$ V (pH=1) up to $-1.35$ V (pH=14). The below specified potentials there is a destruction of the semiconductor to transferring of tellurium in gas or in water phases. The surface CdTe thus enrich by cadmium.

The high border of area of stability CdTe in acid solutions is restricted isopotential to a line 0.108 V, and in alkaline solutions - line from 0.108 V (pH = 7.3) up to -0.485 V (pH=14). At higher potentials there is an oxidizing of a surface of the semiconductor, which depending on pH of ambient is accompanied by passing into solution of cadmium as ions Cd$^{2+}$ and HCdTe$^{-2}$, tellurium as ions HTeO$_3^{-}$, TeO$_2^{-}$ and TeO$_2^{2-}$.

Under these conditions on a surface CdTe possible separate and collateral formation of phases CdO, Te$_2$ and Cd(OH)$_2$.

By methods of potentiometry and atomic absorption analysis is shown, that the generalization of results, which are mapped by the Purbe diagram, allows to forecast and to choose optimal compositions of solutions for polishing and selective etching of single crystals CdTe, and also to define conditions of anodic dissolution and oxidation of a surface of this semiconductor.

The stoichiometrical dissolution CdTe is possible only in strongly acid solutions (pH < 0), and at potentials is higher 0.416 V. The shaping on a surface of the semiconductor of films TeO$_2$ and CdO is most probable in area pH 3.0-10.4 in an interval of potentials 0.20-0.35 V. The etch polishing of single crystals CdTe is possible as well is strongly alkaline solutions (pH > 13) at potentials above -0.45 V.

The enrichment of a surface by cadmium takes place at cathodic polarization CdTe ($\phi_k < -1.35$ V) in a wide range pH, and can be technologically utilised at making ohmic contacts to high-ohmic samples of the semiconductor.
The Quality of CdTe Epilayers Grown by MBE Method


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The quality of Cd\textsubscript{x}Hg\textsubscript{1−x}Te (MCT) epitaxial layers for infrared (IR) devices depends strongly on substrate quality especially at using of alternative substrates (buffer CdZnTe layers on GaAs, Si etc.).

We investigated in detail the dependences of full width of half maximum (FWHM) of X-ray rocking curves, surface roughness and morphology defects (mostly voids) of CdTe epilayers grown by MBE on (013)ZnTe/GaAs on growth temperature (T) and a relationship of cadmium (J\textsubscript{Cd}) and tellurium fluxes (J\textsubscript{Te}) K=J\textsubscript{Cd}/J\textsubscript{Te}.

The dependencies of FWHM values, surface roughness and voids had a minimum on ratio K at different T. FWHM values sharply decreases from 1000 arcsec. up to 150÷250 arcsec. at increasing K in interval 0.5÷1 and at further increasing K from 1 up to 28 weakly increases up to 180÷230 arcsec. at T = 280÷315 °C and strongly increases up to over 1000 arcsec. at T=260 °C. We conclude that the optimal growth condition for high quality CdTe epilayers from point of crystal structure perfection is ratio K=5÷7 and growth temperatures T = 280÷295 °C. There is observed the analogous behavior of dependences of surface roughness and morphology defects on K at different growth temperatures. The surface roughness and voids density were less than 2nm and 200÷400 cm\textsuperscript{-2} respectively for CdTe layers grown at optimal condition.

The measurement of high energy electron diffraction and ellipsometric parameters in situ shown that at K= 0.5÷1 CdTe layers were grown by 3D growth and surface morphology became very rough. In this case the diffraction pattern was dotty and ellipsometric parameter Δ was decreased sharply at initial growth stage. We found that CdTe layers were grown through 2D growth mechanism at K > 3 that leads to flat surface slightly roughening with thickness.

The using of CdTe layers on (013)ZnTe/GaAs grown at optimal condition as a substrate allows to grow MCT layers with V-defects density less than 300 – 400 cm\textsuperscript{-2}. Such MCT surface quality gives the possibility to fabricate multi-elements IR detectors with operability over 99 %.
Growth and Optical Properties of Graded Band-gap CdHgTe and CdMnHgTe Structures

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Graded band-gap structures (GBS) of CdHgTe and CdMnHgTe solid solutions were grown by changing of mercury vapour pressure and other technologic parameters using evaporation-condensation-diffusion method modification. CdTe and CdMnTe single crystals were used as substrates. HgTe crystals were the evaporation source.

There were investigated compositional profile of CdHgTe epitaxial films [1] and electrical and photoelectrical properties of CdMnHgTe crystals and films [2]. Optical properties of GBS were studied. They can’t be characterized by one certain absorption coefficient due to their nature [3]. Therefore D(λ) optical density was chosen as corresponding integral characteristic of radiation absorption. By calculations there were determined its values in photon energy region: \(h\nu \leq E_s\), where \(E_s = E_{g\text{min}}\) – on the GBS surface; \(E_s \leq h\nu \leq E_0\), where \(E_0 = E_{g\text{max}}\) – on the substrate surface.

D(λ) optical density for GBS was measured in spectral range of \(\lambda = 0.8 \div 15 \, \mu m\) wavelength. \(E_g\) value changing was determined from spectral characteristics of optical density on absorption edge shift into short-wave region in comparison with CdHgTe and CdMnHgTe absorption edge of homogeneous composition, equal to surface composition of graded band-gap structure. D(λ) spectral dependence obeys the Urbach rule: D(λ) \(\sim \exp(Sh\nu)\) in region of intrinsic absorption edge, where characteristic constant \(S = 20 \div 70\) eV\(^{-1}\) depending on structure thickness and profile. Absorption on free carriers obeys the law: D(λ) \(\sim \lambda^r\), where \(r = 0.85 \div 1.10\) in transparency region. Due to the possibility of thin structure growing, which surface layer represents semi-metal by itself, it is suggested the estimation method of absorption coefficient of semi-metals and gapless semiconductors. Optical density measurements of CdHgTe structure with HgTe on surface allow to estimate HgTe absorption coefficient.

Main Band Parameters Of Multi-Component Solid Solutions
\( \text{Hg}_1-x-y-z\text{A}_x\text{B}_y\text{C}_z\text{Te} \)

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Solid solutions \( \text{Hg}_1-x-x\text{Cd}_x\text{Te} \) offer a number of unique physical and electrooptical properties making such materials attractive for development of IR detectors. But the main disadvantage of HgCdTe is the instability of the material. It was shown theoretically by Sher [1] that this instability is caused by rather large differences between the atomic radii of Cd and Hg. Hence, material stability should increase with introduction of Mn or Zn, since their atomic radius is closer to that of Hg.

Despite the promising character of such materials as \( \text{Hg}_1-x-y-z\text{Cd}_x\text{Mn}_y\text{Te} \) and \( \text{Hg}_1-x-x\text{Cd}_x\text{Zn}_z\text{Te} \), their basic parameters due to the difficulty of obtaining pure and high-quality crystals are not adequately studied. First of all, it is true for the energy gap, intrinsic carrier concentration and effective mass of electrons. Even to a greater extent it refers to \( \text{Hg}_1-x-y-z\text{Cd}_x\text{Mn}_y\text{Zn}_z\text{Te} \), as long as this is absolutely new material for which the above parameters are unknown at all. This paper presents the investigation of the main band parameters of \( \text{Hg}_1-x-y-z\text{A}_x\text{B}_y\text{C}_z\text{Te} \), mentioned above.

The essence of a new calculation method is that multi-component material is represented as a combination of two simpler materials. With the use of this procedure, the formula for energy band, for example, of \( \text{Hg}_1-x-y-z\text{Cd}_x\text{Mn}_y\text{Te} \), will be as follows:

\[
E_g(\text{Hg}_1-x-y-z\text{Cd}_x\text{Mn}_y\text{Te}) = 0.5E_g(\text{Hg}_1-x-z\text{Cd}_x\text{Te}) + 0.5E_g(\text{Hg}_1-x-y\text{Mn}_y\text{Te}).
\] (1)

Calculated by formulae (1), the energy gaps of multi-component semiconductor solid solutions showed a good agreement with the experimental data.

On the base of the investigation an empirical formulae have been proposed for the calculation of energy gap of \( \text{HgCdMnTe} \), \( \text{HgCdZnTe} \) and \( \text{HgCdMnZnTe} \) – a new five-component solid solution.

Based on the results obtained, the intrinsic carrier concentration, the Fermi level position and the effective mass of electrons for materials under study were calculated. The calculations followed the procedure described in [2].

Comparison of the resulting values \( n_i \) with the experiment allows us proposing empirical formula of intrinsic carrier concentration for all the materials considered:

\[
n_i(x, y, z, T) = (A + Bx + Cy + Dz + ET(1 + x + y + z)) \times 10^{14}E_g^{0.75}T^{1.5} \exp(-E_g/2kT),
\] (2)

where \( A, B, C, D, E \) are different for each material.

The effective masses of electrons in nondegenerate and degenerate materials were calculated. It was shown that an increase in the content of manganese and zinc in the solid solution leads to an increase in the effective electron mass and to a decrease in the intrinsic carrier concentration.

Determination of the Thermophysical Parameters of Zn$_{1-x}$Be$_x$Se Mixed Crystals By Means of Photothermal Techniques

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Recently mixed crystals of wide gap II-VI compounds with Be chalcogenides are of particular interest because of their potential applications in constructing of photoelectronic devices operating in visible and UV spectral region. In this context, beside the optical parameters, also thermophysical properties are important. This paper deals with the measurements of thermal parameters of Zn$_{1-x}$Be$_x$Se mixed crystals as grown and annealed in zinc vapour.

Zn$_{1-x}$Be$_x$Se solid solution forms a new class of semiconductors obtained by mixing binary materials with noticeably different shear modulus. Such a mixing induces significant change of physical properties of the material, such as bond polarity, electronic band structure and thermal properties.

Two photothermal methods were used for the investigations of thermal diffusivity of Zn$_{1-x}$Be$_x$Se samples with different content of beryllium: photoacoustic microphone (PAM) and piezoelectric photothermal (PPT). In both methods of detection, the periodical spatial temperature field arises in the sample after the absorption of energy of modulated incident radiation. Taking into account PPT detection, this temperature field causes so called piston and drum effects thanks to the process of thermal expansion of the sample. Piston effect describes a thermal linear expansion of the sample resulting in the periodical changes of the sample thickness, while the drum effect describes the periodical thermoelastic bending of the sample as a result of the temperature gradient in the sample. In the piezoelectric experiments the sum or the difference of these two effects are observed and measured simultaneously, depending on the experimental configuration applied. In this method the change of the sample shape is registered. Photoacoustic microphone technique consists of the measurement of the temperature increase of the sample due to the absorption of radiation, by placing a microphone in a resonant chamber and detecting the changes of the pressure caused by the period change of the temperature at front or at the back of the sample.

For both detections, the thermal parameters were extracted from the phase - frequency domain characteristics. For microphone detection thermal parameters were also evaluated from the amplitude – frequency characteristics. The calculations were performed within a modified Jackson & Amer model [1,2] and Rosencwaig and Gersho [3] models for piezoelectric and microphone detections, respectively. It was found, that the thermal diffusivity increases with increasing of Be content. The usefulness and accuracy of these two methods for determination of thermal parameters of semiconducting materials were discussed.

Long Life Operations over 5000 Hours of BeZnSeTe/MgZnCdSe
Visible Light Emitting Diodes on InP Substrates
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Aging characteristics of visible light emitting diodes (LEDs) fabricated on InP substrates based on BeZnSeTe and MgZnCdSe II-VI materials were investigated. A long lifetime more than 5000 hours was achieved for a yellow (575nm) LED under a high direct current (DC) injection (130A/cm\(^2\)). Compared with precedent ZnCdSe/MgZnSSe LEDs on GaAs, about 1000 times half lifetimes were obtained for same injection current densities. These results indicate high reliability of the BeZnSeTe/MgZnCdSe LEDs.

Be\(_{x}\)Zn\(_{1-x}\)Se\(_y\)Te\(_{1-y}\) possesses direct bandgap energies from 2.1 (590nm) to 2.7 eV (460nm) in the elemental composition range (i.e., x/y from 0/0.54 to 0.3/0.2) under the lattice-matching condition to InP. Including BeSe and BeTe contributes to enhancing the lattice-hardness, which may be effective for lengthening the device lifetime. So far, we have grown and characterized BeZnSeTe quaternaries on InP substrates by MBE[1]. Applying BeZnSeTe with various elemental compositions for active layers, we fabricated visible LEDs to observe yellow-green-to-orange emissions in the wavelength range from 542 to 594 nm.

In this study, aging tests of yellow-light (575nm) LEDs were performed under DC operations at room temperature. The LEDs consisted of 7.5nm-thick BeZnSeTe single quantum well active, MgSe/ZnCdSe superlattice (SL) barrier, MgSe/ZnCdSe SL n-cladding, and MgSe/BeZnTe SL p-cladding layers. Figure 1 shows dependencies of the normalized output on the aging time for various injection current densities from 130 to 497 A/cm\(^2\). A long lifetime operation over 5000 hours was obtained at 130 A/cm\(^2\). Half lifetimes estimated from the aging characteristics are shown as a function of the injection current density in Fig. 2 with the data of ZnCdSe/MgZnSSe LEDs[2] as reference. The half lifetime at 130 A/cm\(^2\) was 5179 hours.

![dependencies of the normalized output on the aging time for various injection current densities](image)

![half lifetimes as a function of the injection current density](image)


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Optical Investigation of Non-equilibrium Carrier Dynamics in Differently Doped VGF-grown ZnTe Single Crystals

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In this study we apply a time-resolved picosecond four-wave mixing technique for investigation of non-equilibrium carrier generation, transport, and recombination in both undoped and differently doped single crystal (100)ZnTe wafers. The undoped ($\rho \sim 10^3 \, \Omega \cdot \text{cm}$), phosphorus (P) doped (hole concentration $p_0 \approx (0.8–2.0) \times 10^{18} \, \text{cm}^{-3}$), and high resistivity ($\rho > 10^5 \, \Omega \cdot \text{cm}$) Ga-doped crystals were grown by the Vertical Gradient Freezing (VGF) method. The samples were excited by light interference pattern created by two ps laser beams, intersecting onto the sample at an angle $\Theta$. The dynamics of the spatially modulated free-carrier pattern, or free carrier grating with period $\Lambda = \lambda / \sin \Theta$, was monitored via diffraction of a delayed probe beam. The carriers were generated by interband transitions, using the 25 ps duration pulses at 500 nm ($h\nu = 2.48 \, \text{eV} > E_g = 2.26 \, \text{eV}$), or by below band-gap excitation at 560 nm ($h\nu = 2.21 \, \text{eV}$) or at 1064 nm ($h\nu = 1.17 \, \text{eV}$).

Near-to-surface excitation of undoped crystal by using $h\nu = 2.48 \, \text{eV}$ revealed a carrier recombination time $\tau_R$ of 120–160 ps, which slightly increased with excitation. In the p-type sample, the linear recombination rate was found more dependent on excitation and provided $\tau_R$ in the 170 to 700 ps range. This difference we attributed to the lower density of trapping centers in p-doped sample, as P is expected to take part in the compensation of native defects in ZnTe [1]. When exciting the entire $\sim 1 \, \text{mm}$ thick crystal with 2.21 eV photons, the kinetics in the p-type ZnTe remained mono-exponential, while the decay time increased up to 0.6–1.1 ns. However, the initial fast component nearly saturated with excitation in the undoped sample, and a slow relaxation tail ($\tau_R \approx 3.3 \, \text{ns}$) became dominant. This behavior indicated a low density of trapping centers in the bulk of the sample, while the presence of a non-saturating kinetics at much higher carrier densities under near-surface excitation conditions points out an inhomogeneous distribution of trapping centers along the [100] direction nearby the crystal surface. The decay kinetics measured at 560 nm in the high-resistivity crystal revealed $\tau_R$ above 6 ns and a bipolar diffusion coefficient $D$ of $\sqrt{1 \, \text{cm}^2/\text{s}}$. The latter value of $D$ and the much higher (13 cm$^2$/s) one measured in the p-doped sample correspond to different non-equilibrium electron-to-hole concentration ratios in present crystals and reflect the electron diffusion in the p-type crystal and the hole diffusion in the undoped and high-resistivity crystals. The slow diffusion observed in high-resistivity ZnTe may be also influenced by carrier drift in the light-created space-charge field [2].

Finally, we used the 1064 nm wavelength to investigate the carrier generation and recombination mechanisms. The measured dependencies of diffraction efficiency on excitation energy revealed various carrier generation mechanisms in the crystals: two-photon absorption in undoped ZnTe, and the photo-ionization of deep-traps at low excitation and two-photon absorption at high one in both p-type and high resistivity crystals.

Influence of Growth Temperature Conditions on Electric Properties of CdTe+Ge Crystals

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Ge-doped CdTe crystals grown by Bridgman method generally had p-type conductivity and became high-resistance when impurity concentration $N_{\text{Ge}} > 2 \div 3 \times 10^{16}$ cm$^{-3}$. These crystals are photosensitive and have the good photorefractive properties. Electroconductivity is determined by shallow acceptor $A$ with ionization energy $E_A = (0.65 \pm 0.05)$ eV. But, it sometimes happens, that at sufficient great Ge content in CdTe the grown crystals have n-type conductivity, determined by the shallow donors. Such material has small specific resistance and $n = 10^{14} \div 10^{15}$ cm$^{-3}$ charge carrier concentration.

Carried out investigations of electric properties dependence on technological regimes of more than 20 grown crystals and annealed samples at different temperatures had allowed to conclude that n-type conductivity appearance was caused by long-term staying of grown crystal at $820 \div 800$ °C temperature during cooling. Such conclusion was confirmed by the special annealing of long p-type CdTe+Ge (l=10 cm) crystal. One end of this crystal was at $T=820-900$°C and the other – at $T=810-700$°C. Crystal part that was at $T>820$°C has changed to n-type due to annealing. These results can’t be explained within the model of Ge impurity incorporation into CdTe lattice, suggested in [1] where acceptors $A$ are connected with $(\text{GeCd} V_{\text{Cd}})^+$ complexes. Unlike, that it took place $(\text{GeTe})^-$ complexes decay and thermodonors generation at $T>820$°C.

It is proposed the model, in which high temperature ($T>850$°C) equilibrium in rapid-cooled samples fixes Ge impurity chiefly in substitution position in $(\text{GeTe})$ tellurium sublattice. $(\text{GeTe})$ defect exhibits as acceptor. At once, $\text{GeCd}$ donors and shallow $(\text{GeCd} V_{\text{Cd}})^+$ acceptors can exist, but $\text{GeTe}^-$ or $\text{GeTe}^+$ acceptors are predominate. Relocalization process of Ge impurity between cadmium and tellurium sublattices according to: $\text{GeCd} + V_{\text{Cd}} \rightarrow \text{GeCd}^+ + \text{VTe}$ takes place in crystal at $T<820$°C. At such reaction it takes place the process when two acceptors disappear and two donors appear, one of which $(\text{VTe})$ must be shallow, that explained the transition into n-type conductivity.

MOVPE Growth Optimization of CdTe Homoepitaxial Layers for p-i-n Diode X-ray Detector Fabrication

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The importance of CdTe for X- and gamma-ray detection is well known in reason of its high stopping power for energetic photons. CdTe detectors have been shown to operate at room temperature, but are limited in size by the material technology, their leakage currents being often too large for advanced X-ray spectrometric applications. CdTe detectors may also show polarisation effects. To overcome some of these drawbacks we are studying the development of new CdTe detectors based on homoepitaxial p-i-n diode structures, where the intrinsic part of the device is a bulk CdTe crystal and the n-/p-doped parts of the diode are grown homoepitaxially.

Aim of this work is to investigate the metalorganic vapour phase epitaxy (MOVPE) of iodine (I) doped n-CdTe layers on detector grade (111)CdTe substrates. Before the epilayer growth an accurate preparation of the (111)B substrate surface was carried out: Br-methanol etch was performed on CdTe substrates to remove scratches and defects from the as-received wafer surface. An in-situ heat-treatment under hydrogen (H\textsubscript{2}) was then performed on the substrates at temperatures varying between 200\textdegree C and 400\textdegree C, to study the desorption of residual oxides from the crystal surface and its effect on epilayer quality. Electronic grade dimethylcadmium (DMCd) and di-isopropyltelluride were used as Cd and Te precursors, respectively, while I doping was realised by means of ethyliodide (EtI). The MOVPE growth of CdTe was performed at 330\textdegree C at atmospheric pressure. An Arrhenius plot of the growth rate versus reciprocal temperature indicates that the growth occurs in kinetics-limited regime. The optimal temperature for the H\textsubscript{2} annealing of the CdTe wafer surface was determined by X-ray surface reflectivity (XSR) measurements and field emission scanning electron microscopy observations performed on the as-grown samples. XSR curves exhibit a different slope of the intensity for angles above the critical angle (\(\theta > \theta_c\)), indicating a different surface roughness for CdTe samples grown on differently annealed substrates. The smoothest epilayer surface was obtained for an annealing temperature \(T_A = 350\textdegree C\). In this case simulation of the experimental XSR curve by using the Parrat recursive formalism and the Nevot-Croce parameter for description of the surface roughness, yields a rms roughness value of \(\sigma = 1.0\text{nm}\).

We further show that the homoepitaxy of the overgrown CdTe layer critically depends on a Cd annealing step performed on the substrate surface immediately before growth. Annealing of the (111)B crystal surface under DMCd flow at 350 \textdegree C allows to improve the subsequently grown epilayer structure and morphology, an effect attributed to the restored 1:1 Cd-to-Te stoichiometry of the wafer surface after Br-methanol etch.

I incorporation is demonstrated by secondary ion mass spectrometry analysis performed on as-grown epilayers. Electrical measurements show a dramatic decrease of the epilayer resistivity for I-doped epilayers, pointing out a relatively good n-doping efficiency of EtI.
Effects of Substrate Temperature upon Photoluminescence and Electrical Properties of ZnTe in Atmospheric Pressure MOVPE Using Tris-dimethylaminophosphorus

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ZnTe is expected as a promising material for optoelectronic devices. As for metalorganic vapor phase epitaxy (MOVPE) of this material, several efforts have been made to attain conductive p-type layer using various dopant materials. We have discovered that tris-dimethylaminophosphorus (TDMAP) is the promising dopant source for MOVPE growth [1], since p-type ZnTe layer with a carrier concentration as high as $8 \times 10^{17}$ cm$^{-3}$ can be obtained with it. We have also studied the effects of the dopant transport rate upon photoluminescence (PL) and electrical properties of the P-doped layers [1]. Substrate temperature is another important factor that determines the P-doped layer quality. Thus, we investigate the role of substrate temperature in these properties of P-doped layers.

The P-doped ZnTe layers were grown by atmospheric pressure MOVPE in almost the same manner as was employed in the previous study [1]. Briefly, dimethylzinc and diethyltelluride were used as source materials while TDMAP as a dopant source. The transport rate for each source was kept at 10 µmol/min, while the dopant transport rate as low as 0.05 µmol/min was used. Hydrogen was employed as a carrier gas. The substrate temperature was varied from 340 to 500°C. We used gallium-doped high-resistive (100) ZnTe substrates in order to facilitate the measurement of the electrical properties of P-doped ZnTe layers. The layers were also characterized by PL measurement.

It was found that the 4K PL spectrum of the P-doped layer is strongly influenced by the substrate temperature. For the layer grown at 340°C, the spectrum is characterized by weak acceptor-related excitonic emission ($I_a$) and relatively strong donor-acceptor pair recombination emission (DAP). When the substrate temperature is increased up to 400°C, the spectrum is characterized by strong $I_a$ together with weak free-to-bound transition emission. At a substrate temperature as high as 500°C, however, the spectrum of the layer is characterized by DAP. Then, some compensation is inevitable for both lower and higher substrate temperature. On the other hand, the carrier concentration of P-doped ZnTe layer increases with the increase of substrate temperature, due to the ease of thermal decomposition of TDMAP.

HgTe Segregation Process in HgCdTe Studied by $E_1$ Reflectance Peak Position

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Long term diffusion processes in Cd$_{1-x}$Hg$_x$Te involving on electronic structure as it is showed in this paper. Measurements of reflectivity and surface characterisation by means of scanning electron microscopy (SEM) were performed for the samples with $x=0.4$ and $x=0.62$. The experiments were repeated after the wet chemical etching. Next, the optical results were compared with the reflectivity spectra obtained 22 years ago using the same samples of investigated material. This paper is dedicated to problem of long time diffusion and role in this process intrinsic defects presented even in good quality HgCdTe crystals. We discuss the observed large changes in the optical spectra on the basis of comparative analysis and SEM results. Both the non-treated samples and the samples after removal of the upper surface layer were measured. The role of the long-time processes of diffusion of defects and their influence on the present form of the fundamental reflectance spectra (FR) of the investigated samples are discussed on the basis of the comparative analysis.

To analyse the changes in the crystalline structure and electron band structure the FR and SEM studies for the two samples Hg$_{0.6}$Cd$_{0.4}$Te and Hg$_{0.34}$Cd$_{0.62}$Te were performed. The results of the FR measurements performed 22 years ago were reported in Ref.1. The optical measurements using the same experimental set-up as in Ref.1: double – beam reflectometer for the specimens that were stored for 22 years at the room conditions have been done. The results of mercury telluride segregation process are mainly streams of new material phase (probably HgTe), surface defects like grains, funnels, vacancies or holes are well seeing in the several hundred enlarged the investigated surface picture given by scanning electron microscope.

The current reflectance profiles differ significantly from the initial spectra for both samples obtained 22 years ago. The recent experimental reflectance curves obtained for Hg$_{0.6}$Cd$_{0.4}$Te and Hg$_{0.34}$Cd$_{0.62}$Te, after a surface etching process, exhibit similar behaviour to cadmium enriched HgCdTe.

The position of the $E_1 + \Delta$ reflectance peak corresponds to binary HgTe in the case of both investigated samples. The measurements of the $E_1$ reflectance peak has proven to be useful tool for mercury telluride segregation in HgCdTe and can be used to determine composition and age of HgCdTe.

Metastabilities in the Electrical Characteristics of Au-CdMnTe Schottky Contacts

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It has been commonly accepted, that in a real Schottky contact, the interface states and bulk traps exist simultaneously. The presence of interface states affects capacitance of the contacts, leading to erroneous interpretation of experimental data. In particular the presence of such states may be responsible for persistent photocapacitance at temperatures as high as the room temperature and it may be recognized as an effect of a metastable defect of a very high barrier for capture. Identification of the photocapacitance origin is therefore of premiere importance for the materials possessing DX centers.

In present paper Schottky Au - Cd_{0.99}Mn_{0.01}T:Ga contacts were studied by the use of the current – voltage, capacitance – voltage measurements and thermally stimulated capacitance (TSCAP) technique. The measurements were performed within a temperature range of 77 K - 400K. Persistent photocapacitance was observed at temperatures as high as 260K. Usually persistent photoeffects related to the metastable DX centers are observed in the material only up to 150K [1,2]. The discrepancy between these observations can be explained assuming the presence of interface states located at or close to the interface between the metal and the semiconductor, separated by a thin interfacial layer. The presence of the interface states has been confirmed by TSCAP studies performed at various reverse bias. Thus, the low temperature (77K-150K) photocapacitance has been attributed to the DX centers whereas that observed at higher temperatures has been linked with the interface states.

Tamm-like Interface States in ZnSe/BeTe Heterostructures: Ellipsometry and Photoluminescence Studying

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In 1949 James firstly expressed an assumption about existence of the interface analogue of well-known surface Tamm states (Tamm levels) \cite{1}. In spite of number of theoretical papers \cite{2,3} in which existence and possible energetic positions of the such “Tamm-like interface states” (IS) was discussed, there is now satisfactory experimental evidence which could indicate that there is a IS in semiconductor heterostructures.

Recent studies of the type-II ZnSe/BeTe periodic heterostructures with nonequivalent interfaces (namely Zn-Te...Be-Se) have revealed natural in-plane optical constants anisotropy of the structures in the spectral range of the spatially direct interband transitions \cite{4}. This effect is due to the local symmetry of the interface separating two zinc-blende substances being lower than the symmetries of the original semiconductors.

In present work spectral dependencies of the in-plane optical anisotropy of undoped periodical ZnSe/BeTe heterostructures with nonequivalent interfaces has been studied by spectroscopic ellipsometry. All measurements were made at low temperatures (77K) using rotating-compensator ellipsometer. Peculiarities of two different types were observed in the spectral range of the band gap. It was found that spectral position of the first type peculiarities is independent on the period of heterostructures. Whereas the second type ones shift to the low energies with decreasing thickness of ZnSe and BeTe layers.

The observed behavior is interpreted in frame of a model, which takes into account existence of the two different types of the Tamm-like interface states. The states of the first type are satellites of the conduction and valence bands and can be considered as electron and hole interface states, correspondingly. The energetic positions of the second type interface states conform to the center of the band gap of the heterostructure, thus being the states of a mixed kind.

One of the prediction of proposed model is a possibility of photoluminescence (PL) caused by optical transitions between electron and hole IS with PL energy being lower than the energy of the spatially indirect optical transitions. Such PL was also observed. PL was excited using pulsed solid state laser emitting at the wavelength 355 nm. At the energies, which is on 300 meV below the energies of the spatially indirect excitonic transitions bright line was observed in the spectra. Spectral position of this line (E = 1.75 eV) is in very good agreement with data, obtained using spectroscopic ellipsometry.

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CdTe in its polycrystalline form is studied for applications where large dimensions are required such as photovoltaics and X-ray imaging. However, compared to its monocrystalline variant, the properties of polycrystalline materials are inherently limited because of the presence of the grain boundaries. For thick layers, the fast deposition processes used such as sublimation also introduce many other structural defects i.e. dislocations, stacking faults and twin boundaries within the grains. All of these structural defects introduce strained areas in their vicinity and/or dangling bonds in their core. As such, they have a negative impact not only on the electronic properties through the formation of deep traps in the gap but also on the transport properties through the formation of barriers because of space charge regions around the defects. It is thus of primary importance to try and compensate for these traps and to passivate the dangling bonds in the structurally imperfect crystal.

We first have undertaken a spectroscopic analysis of the defects present in chlorine doped polycrystalline CdTe by low temperature PhotoLuminescence (PL). It was found that the main compensation processes are in some way similar to what is happening in monocrystalline CdTe:Cl. But a mechanism specific to polycrystalline CdTe:Cl is proposed whereby chlorine atoms compensate impurities, associated to deep levels at around 1.28eV, in the vicinity of the structural defects (e.g. Cottrell atmospheres around dislocations). Interestingly, a bimodal distribution of grain sizes was found, small (5µm) and bigger grains (40µm) involving different compensation complexes respectively between Cl atoms and Cd vacancies and between Cl atoms and extrinsic impurities.

Defect passivation processes were also identified in polycrystalline CdTe:Cl using low temperature CathodoLuminescence (CL) imaging. It was shown that some of the structural defects, namely double positioning boundaries, which appear as non radiative recombination centres in undoped CdTe, are no more visible in doped layers. Cl atoms are thus expected to attach to dangling bonds in the core of these defects in agreement with recent calculations [1].

These interactions between the intentionally introduced dopants and the structural defects, leading to compensation and passivation processes, appear specific of polycrystalline materials and could account for their attractive properties in terms of carrier transport [2], despite the very large density of structural defects.

Phosphor-Doped ZnMgTe Bulk Crystals Grown by Vertical Bridgman Method

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The ternary Zn₁₋ₓMgₓTe mixed crystals are expected as an appropriate material for a cladding layer and a transparent substrate of ZnTe based pure green light-emitting devices, because of the wider band-gap than ZnTe.¹ In the previous studies, we have obtained phosphor-doped ZnTe of good quality by Bridgman method,² which is simple and leads to low cost. Also, we have demonstrated possibility of the fabrication of ZnTe light emitting diodes (LED) by thermally diffusing to these conductive p-type substrates with Al.³ In order to improve the performance of the ZnTe LED, it is significant to investigate conductive p-type Zn₁₋ₓMgₓTe crystals. However, there are few reports on such research. In this study, we have characterized the P-doped Zn₁₋ₓMgₓTe bulk crystal grown by Bridgman method for ZnTe LED application.

P-doped Zn₁₋ₓMgₓTe crystals were grown by vertical Bridgman method. Elemental Zn (6N), Mg (5N), Te (6N) and P (6N) sources were charged into a pyrolitic boron nitride (pBN) crucible of 14 mm inner diameter and 100 mm height. In order to decrease the melting point, a Te-rich growth condition was adopted with 5% deviation from stoichiometry. The typical weight of Te was 24.4 g. The atomic ratio of P to group II elements (Zn and Mg) was 4×10⁻⁴. The crucible containing sources was doubly sealed in a quartz ampoule at a vacuum level of 5×10⁻⁷ Torr. The maximum temperature of the one-zone furnace was set to 1150°C. The crystal growth was started at a lowering speed of 25 mm/day. The grown crystals were characterized by X-ray diffraction, electron probe microanalysis and optical analyses (photoluminescence, reflection and transmission measurements).

Through this experiment, Zn₁₋ₓMgₓTe crystals with Mg composition (x) of 0 to 0.31 were prepared. The PL spectra at 4.2 K were dominated two luminescence peaks, which were assigned to bound exciton emission due to neutral P acceptor and P acceptor related free-to-bound transition emission. These emission peaks shifted towards shorter wavelength with increasing x. The linear increasing relation between the band-gap energy and x was confirmed.

Conductive p-type Zn₁₋ₓMgₓTe crystals for LED application were obtained, although the carrier concentration slightly decreased with increasing x.

Determination of the Lattice Constant of CrS from MnCrS MBE Epitaxial Layers

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We have previously shown that using ZnS as a sulphur source, both MgS [1] and MnS [2] can be grown epitaxially on GaAs substrates in the zinc blende (ZB) structure. Thicknesses in excess of 130nm have been produced before they convert to the rocksalt structure. The method used can be applied to any sulphide containing a metal less volatile than zinc. In this study, we have been attempting to grow CrS. There have been problems with this work because of ambiguity concerning the lattice parameter of ZB CrS, with different calculations [3,4] giving values between 0.504nm and 0.5806nm. Before attempting growth of CrS, the lattice parameter must be accurately determined.

In order to do this, a series of samples with the structure: ZnSe (50nm) / MnCrS (60 second growth) / ZnSe (50nm), were grown with the temperature of the Cr cell varied between 990°C and 1050°C. These samples were analysed using X-ray Interference (XRI) techniques [5] in order to determine the Cr composition and lattice parameter of the ternary compound. Figure 1 shows the 004 XRI experimental and simulated data from the sample grown with a Cr cell temperature of 1000°C. By comparing the XRI results from the full series of samples, an initial value for the lattice constant of CrS has been determined to be 0.5487nm.

In this paper, the method used to calculate the lattice parameter of ZB CrS will be discussed and the limitations of using the XRI technique will also be discussed in detail.

References:

Deep Electron States in Indium-doped Cd$_{0.93}$Mn$_{0.07}$Te - DLTS Study

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Electron traps in indium doped Cd$_{0.93}$Mn$_{0.07}$Te were studied with Deep Level Transient Spectroscopy. Five electron traps labeled by us as E1 to E5 were found. For the traps E1, E2, E3 and E5 energies obtained from Arrhenius plots are equal to 0.23eV, 0.28eV, 0.38eV and 0.65eV, respectively. Electric field enhanced electron emission from the trap E4 was observed and described in terms of the Frenkel-Poole mechanism. Energy activation extrapolated to the zero-electric field intensity for the trap E4 is equal to 0.56eV. Two of the traps observed in the material, E1 and E3, are related to the defects with thermally activated capture cross section of energy barrier for capture equal to 0.14eV and 0.2eV, respectively. Binding energies of related defects are equal to 0.09eV and 0.18eV. Both defects exhibit DX center characteristics. The concentration of the centers were equal about $2\times10^{13}$ cm$^{-3}$. 

The growth and study of semiconductor microcavities are of a great importance due to their potential for a large number of applications. In case of II-VI compounds the microcavities are considered as the possible candidates for manufacturing “polaritonic” devices (e.g. ultra-low threshold lasers) capable of operating at RT. However, the development of molecular beam epitaxy (MBE) technology of ZnSe-based distributed Bragg reflector (DBR) structure is hedged about with serious difficulties because of requirements of growing the whole structure lattice-matched to GaAs and providing simultaneously the large difference in a refractive index between alternative layers.

It has been suggested to use in II-VI DBRs zinc-blende MgS having the lowest refractive index among the II-VI materials nearly lattice-matched to GaAs. Earlier Kruse et al. [1] demonstrated 99% reflectivity in 17-period ZnSe/(ZnSe/MgS) DBR grown by MBE using S-valved cracker cell as a sulphur source. Nevertheless, it should be noted that MBE growth of MgS/ZnSe periodical structure imposes severe restrictions both on the maximum MgS layer thickness, due to known sphalerite-to-rock salt transition, and the whole structure thickness, due to the lattice mismatch between MgS and ZnSe. Employing the ZnS compound as a sulphur source (after Bradford et al. [2]) to grow MgS/ZnSe periodical structure requires additionally a precise adjustment of growth temperature \( T_{\text{sub}} \) and ZnS and Mg flux intensities to provide nearly 100% Mg-Zn exchange interaction in a ZnS film, induced by much stronger Mg-S binding energy as compared to Zn-S one, without Mg precipitation. Moreover, to obtain a reasonable MgS growth rate \( T_{\text{sub}} \) should be kept as low as possible (\( \sim 250^\circ C \)), which is in a contradiction with the favorable growth condition of ZnSe (around 300\(^\circ C \)).

Here we present the MBE growth and studies of novel design II-VI ZnCdSe/(ZnSe/MgS) DBRs with the reflectivity \( R_{\text{max}} \sim 97\% \). The structure was grown pseudomorphically on GaAs substrate at \( T_{\text{sub}} \sim 250^\circ C \), the ZnS was used as a sulphur source. The MgS/ZnSe short-period superlattice (SL) instead of pure MgS layer has been chosen as a low index material, while the ZnCdSe solid alloy with Cd\( \sim 3\% \) instead of commonly used ZnSe has been accepted as a high index material with the aim of both strain compensation and enhancement of refractive index difference in the DBR. The middle of stop band was chosen to correspond to a standard ZnCdSe quantum well wavelength, which is \( \sim 520\text{nm} \). The structure grown has been studied by different characterization techniques (SEM, XRD, reflection measurements), which have indicated good optical and structural characteristics. The period of the composite DBR structure is of \( \sim 110\text{nm} \). The composite multilayer structure consists of 15 periods, having a total thickness of \( \sim 1650\text{nm} \). The periodic structure of both the nested MgS/ZnSe SL and the whole sample is clearly distinguishable in SEM images.

Technological aspects of MBE growth of such structures and their structural and optical properties will be discussed in detail.

Predominant Point Defects in Tellurium Saturated CdTe

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The point defect (PD) structure of CdTe as one of the most used \(A^{II}B^{VI}\) semiconductors (fabrication of \(\gamma\)-ray detectors, infra-red filters and non-linear optical devices) was strongly studied over decades. The PD spectrum in CdTe is very sensitive to the smallest deviations of stoichiometry. There is a consent that the dominant doubly positive charged native donors in the Cd saturation region are Cd \(\text{Cd}^{2+}\) i and \(\text{V}^{2+}\text{Te}\), whereas the situation in Te-saturated CdTe crystals is up to now contradictory.

Experimental results show that at high-temperature defect equilibrium (HTDE) at 300-400°C the hole density does not depend on the Te vapor pressure (\(P_{\text{Te}_2}\)). It means that the potential native acceptor PDs (single negative charged \(\text{V}^{-}\text{Cd}\) and/or \(\text{Te}^{-}\)) do not control the approximated electro-neutrality condition (AENC). Smith [1] explained this fact by supposing the presence of residual impurity acceptors in CdTe crystals, the concentration of the former being predominant in the AENC. Berding [2] calculated from “ab initio” methods the total energies and concentrations of different native PDs and demonstrated respective PD diagrams as functions of deviation from stoichiometry. Her results showed that in the Te saturation region the antisite native donor PD \(\text{Te}^{+}\text{Cd}\) is present in sufficient concentrations and it partly compensates the predominant acceptor \(\text{V}^{-}\text{Cd}\). This results in low hole density and \(P_{\text{Te}_2}\) dependence at 300-400°C, what contradicts experimental results. The same native donor PD proposed Fiederle [3] in order to explain the high-resistivity at room temperature of Cl-doped CdTe grown from Te-saturated melts.

In our experiments CdTe electrical properties at HTDE were studied by high temperature Hall effect measurements using a number of samples of different purity. In the best ones the content of presumably electrically active metallic impurities was not higher than \(10^{15}\) at/cm\(^3\). Si concentration did not exceed the \(10^{17}\) at/cm\(^3\) level. In all samples the hole density at 300-400°C was \(P_{\text{Te}_2}\) independent. These measured values in different samples changed in the \(~(3-6)\cdot10^{16} \text{ cm}^{-3}\) range. A theoretical analysis of the CdTe native PDs structure shows that the concentrations of dominant PDs \(\text{V}^{-}\text{Cd}\) and \(\text{Te}^{+}\text{Cd}\) rise versus \(P_{\text{Te}_2}\) with different slopes, what excludes a possible hole density independence upon \(P_{\text{Te}_2}\). Moreover, computer defect structure simulations indicate that if the \(\text{Te}^{+}\text{Cd}\) native PD concentration is near at \(10^{16}\) cm\(^{-3}\), as supposed by Fiederle, then in electrical measurements at HTDE near Te saturation electronic conductivity will be observed, what is not the case. So, CdTe conductivity under \(P_{\text{Te}_2}\) is nevertheless controlled by residual foreign acceptors. And it is possible to suppose that this acceptor is Oxygen, as was found in [4].

CdTe Native Point Defects under Cd Saturation

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Among A2B6 compounds CdTe is one of the very promising materials for γ-detectors, solar cells, IR and non-linear optic devices fabrication. There are many methods to get the CdTe single crystals for industrial application and often the growth under controlled Cd vapor pressure (P_{Cd}) is used. High temperature annealing also takes place at similar conditions. In all these cases the native point defect (PD) structure forms at high temperature in the cadmium part of the phase diagram. Therefore it is of great importance to make investigations just at high-temperature defect equilibrium (HTDE) under well defined P_{Cd}. Up to now there is a choice of proposed dominant donor defects - Cd^{2+}, V^{2+}_{Te}, Cd^{+} and even Cd_{Te}, but the main ones are the double charged native donors. According to Chern [1] between them up to 800°C dominate V^{2+}_{Te} and at higher temperature - Cd^{2+}.

The aim of our work was: 1) to determine the region of main native PDs existence in undoped CdTe at HTDE under well defined P_{Cd}; 2) to simulate the CdTe PD structure at these conditions.

Undoped CdTe single crystals were grown by the Bridgman method. High-temperature Hall effect measurements in the 700-1170 K temperature range under P_{Cd} were carried out. The classic six-contact Hall-bar method with welded tungsten wires was used.

The investigation of regions where every of these PDs exists consisted in several series of annealings under well defined Cd pressure at 970-1170 K. Since the Cd^{2+} PD is much more mobile than V^{2+}_{Te}, during even a fast cooling, they have time to precipitate. The large decreasing of electron concentration during this process can be an evidence that just these species play the main role. As in experiments [e^-] decreased more than in ~10 times [2], it is possible to suggest Cd^{2+} as the dominant specie at T≥970 K.

Under maximal P_{Cd} value n-type conductivity with an electron concentration about 10^{15} and 7*10^{17} cm^{-3} at 700 and 1170 K respectively was observed. The slope γ=1/3 in P_{Cd} dependencies confirmed that the dominant species are double charge intrinsic donors. The temperature dependencies of [e^-] for isobars P_{Cd}=0.01, 0.1 revealed 2 slopes - ~0.5 eV at lower temperatures and ~0.8 eV at high. It means that at lower temperatures the dominant defects are V^{2+}_{Te}, at higher - Cd^{2+}.

The incorporation energy for both PD was calculated using the Arrhenius equation. It was established that the main intrinsic donor defect at T>930 K is Cd^{2+} with 2.5 eV formation enthalpy. At lower temperatures predominates V^{2+}_{Te} with 1.3 eV formation enthalpy. Defect structure modeling with Kroger’s quasichemical reaction formalism have demonstrated satisfactory agreement with experiment.

Photoluminescence Characterization of Cubic CdS Epilayers

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Cadmium sulfide is a semiconductor with a wide and direct band gap, and it has been studied for heterojunction photovoltaic devices along with other II-VI semiconductor materials [1]. CdS has two structures: a stable hexagonal wurtzite structure and a metastable cubic sphalerite structure. Most studies are on hexagonal CdS whereas those on cubic CdS are rare since the production of high quality cubic CdS is difficult. Cubic CdS epilayers were grown on (100) GaAs substrates by hot-wall epitaxy. The PL characteristics were studied as a function of temperature and excitation power. The strong heavy-hole (HH) free exciton (FE) peak and light-hole (LH) free exciton peak with broad and weak SA emission were observed. The HH and LH FE peak energy are shown as a function of temperature in Figure 1. Below 60 K, there was little change in the peak energy. Above 60 K, it began to decrease and above 150 K it linearly decreased with the increasing temperature. The temperature dependence of the HH FE peak energy was well fitted by the O’Donnell equation [1]. The DAP peak was identified using the excitation power dependence. The temperature dependence of the excitonic peak intensity was demonstrated by using the two-step quenching mechanism. The broadening of FWHM above 60 K explained the phonon interaction. A free to bound transition could be identified with the excitation power dependence.

![Figure 1. The excitonic emission of a cubic CdS epilayer as a function of temperature.](image)

High Efficiency Blue-Violet Optical Modulators of ZnSe/ZnMgSSe Asymmetric Coupled Quantum Wells

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A quantum confined Stark effect (QCSE) of excitonic transition is attracted for optical functional devices such as light modulators, switches or self electro-optic effect devices (SEEDs). In these optical devices, high speed and high efficiency light modulators require a large exciton binding energy where high electric field induced excitonic Stark-effect plays essential role. We have made systematic study on the development of new short wavelength optical modulator using II-VI widegap compounds based quantum wells because of its large exciton binding energy (>20meV).

In this paper we present a high efficiency blue-violet optical modulator consists of ZnSe/ZnMgSSe asymmetric-coupled quantum wells (ACQWs) with modulation efficiency exceeding 50% under room temperature. The new device designed with an electron-resonant type ACQW has revealed a large Stark-shift of 37 meV under room temperature in low electric field condition of $E=480$ kV/cm and very stable device operation.

A: Theoretical Design on Optimum ACQW Structure
A theoretical analysis of optimum ACQW structures under high electric fields is based on the finite element method in the framework of the effective-mass approximation [1]. In this analysis we focused our attention to find the most effective ACQW structure for both a large stark-effect and large $\beta$ value ($\beta=\Delta M^2/E$: variation of transition matrix-elements normalized by electric field strength) under room temperature condition. An important point to achieve this condition is to know optimum polarization-strength (electron-hole displacement) in which excitons in coupled-quantum wells are not dissolved by both high electric field and thermal excitation. We have found one of excellent ACQW structures [ZnSe(6ML) / ZnMgSSe(2ML) / ZnSe(12ML): with very thin ZnMgSSe barrier-width of 2ML]. Here ML represents unit mono-layer width (1ML for ZnSe and ZnMgSSe is 2.83 Å). In this new ACQW structure, very strong coupling of electron wavefunction and large Stark-shift under room temperature are expected.

B: Experimental Evaluation of Stark Shifts and Device Modulation Efficiencies
The ZnSe/ZnMgSSe MQW optical modulators with p-i-n structure diodes including 50 periods ACQWs for active layers are grown on n⁺-GaAs (100) substrates by MBE. Optical absorption spectra under reverse bias conditions were measured in the transmission configuration. High field induced Stark shifts were traced by electro-reflectance (ER) and electro-absorption experiments under low (17K) and room temperature. We have observed large Stark-shifts of 42 and 37 meV under 17K and room temperature, respectively. The large Stark shift under room temperature has proved an effective ACQW structure where excitonic transition effect dominantly contribute without bleaching under room temperature region. The light modulator device fabricated has also exhibited high modulation efficiency of 51% (room temperature) in blue-violet photon incidence (450nm wavelength) under low reverse bias of 28 V. Utilizing high efficiency blue-violet modulator obtained in the present transmission-configuration, the practical wave-guide type light-modulator with intensity-modulation of about 10 dB are found to be realized.
Fig. 1: Schematic device structure of ZnSe/ZnMgSSe asymmetric coupled quantum well (ACQW) optical modulator. Active region of the device is consist of 50 period ACQWs.

Fig. 2: Stark shifts of transition energy between ground quantum levels (E1-HH1) of ZnSe(6ML)/ZnMgSSe(2ML)/ZnMgSSe (12ML) ACQW optical modulator traced by electroreflectance at room temperature and 17K. Broken line represents theoretical transition energy shifts.

Fig. 3: Transmission spectra of the MQW optical modulator of ZnSe(6ML)/ZnMgSSe(2ML)/ZnSe (12ML) ACQW under reverse bias conditions of 0-28V (room temperature). Maximum modulation depth of 51% at the wavelength of 450nm is obtained.

Influence of the Optical Excitation on Properties of CdMnTe Crystals

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The Mn-based diluted magnetic semiconductors have recently received the great attention. It is to note the intense studies of Cd$_{1-x}$Mn$_x$Te solid solution at $x>0.4$ [1]. However, Cd$_{1-x}$Mn$_x$Te crystal demonstrates some properties of interest, e.g. photomemory, also at low manganese concentration in the matrix [2]. As against persistent photoeffect due to the presence of so-called DX-centers observed for many semiconductor compounds and for Cd$_{1-x}$Mn$_x$Te also, we observed the photoconductivity quenching for Cd$_{1-x}$Mn$_x$Te samples with $x=0.08 \div 0.1$.

In the present work, properties of Cd$_{1-x}$Mn$_x$Te semiconductor solid solution under weak and strong optical excitation from the intrinsic absorption region ($h\nu>E_g$) were investigated by the electric and photoelectric measurements in the temperature range between 78$^\circ$ K and 300$^\circ$ K. The temperature quenching of the photoconductivity of Cd$_{1-x}$Mn$_x$Te crystals, which were illuminated by red light ($\sim$2 eV) during cooling was observed. After such operation the increasing of the crystal dark resistance by about order of magnitude was occurred and the sample photosensitivity was dramatically low. It was determined that the partial restoration of the photosensitivity took place only after long-time storage or after ultrasonic annealing. Pulsed ruby laser irradiation ($\lambda=0.694 \mu$m, $\tau_L=20$ns) with under melting threshold energy has resulted in photosensitization of Cd$_{1-x}$Mn$_x$Te crystals and photoconductivity quenching has not been observed.

It is obvious that the photosensitivity of a semiconductor crystal depends on the concentration and state of the recombination centers and the main role in the recombination process is played by the composition and state of the point defect system. Optically induced transformation in the point defect system of Cd$_{1-x}$Mn$_x$Te crystals under weak and strong excitation from the intrinsic absorption region was discussed. It was made the attempt to connect the mechanism of quenching phenomenon with manganese ion photoionization process.

Cooperative Magnetic Phenomena of High-Density Localized Excitons in Semimagnetic Semiconductor CdMnTe

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An exciton magnetic polaron (MP) formed by the exchange interaction of spins between an exciton and surrounding magnetic ions has been studied extensively in semimagnetic semiconductors such as CdMnTe. However, high-density excitation effect of magnetic polarons has not yet been clarified up to now. If one can find the cooperative effect of multi-magnetic polarons, it may lead to macroscopic photo induced ferromagnetism.

In the present study, we have found a new luminescence band which reflects the many body effect of MPs in Cd$_{0.2}$Mn$_{0.8}$Te. By adopting the selective excitation of localized excitons at 2K with a picosecond tunable pulsed laser (OPA), the new luminescence band (denoted by X in Fig.1) appears at the higher energy side of the ordinary MP band only when the excitation energy is below the exciton average energy, and shows the red-shift with increasing the excitation density. The most interesting phenomenon is the magnetic field effect on the X band. By applying rather weak magnetic field (0T to 0.3T), the X band split into several peaks and each peak shows a rapid red-shift with a rate on magnetic field much larger than that of MP band. We consider that such a large magnetic field dependence of the new luminescence band may result from the huge enhancement of internal magnetic field by many body effect. This fact open a possibility of the appearance of macroscopic ferromagnetic domain formed by the cooperation of multi magnetic polarons.

Fig.1. Excitation density variation of the PL spectra of Cd$_{0.2}$Mn$_{0.8}$Te under selective excitation of localized excitons, where the excitation photon energy is 1.920eV. MP and X indicate the exciton magnetic polaron and the new luminescence band, respectively.

Fig.2. Magnetic field variation of PL fine structures of the X band under weak magnetic fields. Excitation energy and density are 1.923eV and 1.6μJ/cm$^2$, respectively.
Non-Linear Thermal Broadening of Exciton Lines in CdTe Self-Organized Quantum Dots

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Micro photoluminescence ($\mu$-PL) is used to study the phonon induced dephasing of the excitons in CdTe self-assembled quantum dots (QD). The samples were self-assembled QDs grown on ZnTe using atomic layer epitaxy, and the density was $\sim$8 x 10$^{10}$ cm$^{-2}$ [1]. Data were acquired by using a microscope objective, which can resolve discrete PL lines from spectrally isolated QDs. PL and $\mu$-PL spectra have been measured at temperatures of 5K < T < 90K. As the temperature increases, the emission peak is redshifted and quenching of the intensity occurs. The full width at half maximum (FWHM) of the exciton line shows a dramatic increase after about 30K due to the exciton-acoustic phonon interaction. The line-shape deviates from a Lorentzian even at relatively low temperatures, and two different structures are observed within the PL emission, namely the zero-phonon line and the phonon sidebands. Although the emission spectra at higher temperatures show high symmetry relative to the zero-phonon line, at lower temperature of up to 30K, there is an observable asymmetry in the line-shape. The low energy side of the phonon sidebands appears to be larger than the high energy side. It is observed that the zero-phonon line of the quantum dot spectrum has a spectral width of about 150$\mu$eV at 5K. The FWHM of the phonon sidebands are a few meV. The zero-phonon line and the sidebands both show non-linear characteristics with respect to temperature. The zero-phonon line disappears above 70K. The theoretical model for the spectra is also calculated for each temperature, and evidence of phonon activity is confirmed.

Similar effects are observed for GaAs QDs, however the rate of increase seems to be smaller than that of CdTe, as the zero-phonon line is more prominent for higher temperatures.

Picosecond Kinetics of Magnetization in Optically Excited (Zn,Mn)Se Quantum Wells

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The interaction of free carriers with magnetic ions in DMS nanostructures may be the basis for ultrafast manipulations with the magnetization. The present work is aimed to monitor the kinetics of the macroscopic incoherent magnetization in longitudinal magnetic field in the DMS quantum wells (QWs) under femtosecond optical excitation, which creates hot electron-hole pairs.

The samples used were five 10-nm-wide Zn₁₋ₓMnₓSe QWs separated by 20 nm nonmagnetic Zn₀.₉₄Be₀.₀₆Se barriers. Three samples with x=0.013; 0.03 and 0.1 have been studied. The DMS QWs were excited at T=1.8 K by a focused (100 µm diameter) beam from a 160 fs doubled (λ=400 nm) linear polarized Ti-sapphire laser with maximum energy per excitation pulse P∼1 nJ. The initial repetition rate (76 MHz) was decreased by a pulse picker in order to have complete relaxation of the magnetization in DMS QWs between the excitation pulses.

To monitor the time evolution of the magnetization we explore the well known giant Zeeman effect and study the time evolution of the relative spectral shift of the exciton photoluminescence (PL) line. This allows monitoring the time evolution of magnetization M(t)=M-∆M(t) (∆M(t)>0, M – equilibrium magnetization). The optical excitation pulse plays two roles (i) of external perturbation for the magnetization decrease and also (ii) of a source for PL excitation.

The transient curves of ∆M(t)/M for two samples with x=0.013 and 0.03 are shown in the figure. The value ∆M(t)/M increases in time and saturates in a time of several hundreds of picoseconds at a value ∆Mₘₐₓ/M, shown by horizontal arrows. The dashed curve shows the PL decay under the same experimental conditions. It is seen that the time constant of the magnetization decrease τₘ=130-180 ps is similar to the PL decay time τₚₗ=160 ps.

We discuss the experimental results analyzing the processes of energy and spin transfer from carriers to Mn²⁺ ions. In order to explain the measured values of ∆M(t)/M and τₘ we propose a model where the energy and spin transfer from a hole to Mn²⁺ ion is governed by the hole relaxation within one Zeeman heavy-hole subband. The model is based on the virtual spin-flip transitions and mixing of heavy-hole and light-hole states.

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Growth and Characterization of Self-assembled CdSe Quantum Dots in MgS Barriers

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A single photon emitter is of high interest with respect to applications in quantum cryptography and quantum computing. The generation of single antibunching photons using semiconductor quantum dots (QDs) was proved in the III-V and the II-VI material system. Up to now, only CdSe QDs showed single photon emission at elevated temperatures of 200 K [1], and by increasing the barrier height around the QDs also room temperature operation is expected. An incorporation of such QDs into a microcavity with high Q-factor could lead to a practical device [2].

For the experiments MgS barriers are chosen, since this material has the highest bandgap available in the II-VI-system (5.5 eV). Self-assembled CdSe QDs have been grown by migration enhanced epitaxy (MEE), i.e. the alternating supply of either Cd or Se interrupted by a pause. All QD samples were grown on GaAs (001) substrates using a 50 nm thick ZnSe buffer layer and a 25 nm thick cap layer. The QD region consists nominally of three layers with the sequence ZnSe (1.4 nm) / CdSe (1.0 nm) / ZnSe (1.4 nm) all deposited by the MEE technique. While the upper ZnSe (1.4 nm) layer covering the CdSe is essential for the formation of the QD structures by a Zn-induced Cd-reorganisation [3], the influence of the lower ZnSe (1.4 nm) layer underneath the CdSe is not well investigated yet.

A pair of samples with two additional 5 nm thick MgS barriers surrounding the QD region and a reference sample without barriers has been prepared. For one of the samples containing the MgS layers the lower ZnSe (1.4 nm) layer was removed, i.e. the CdSe was deposited directly on MgS.

For the following PL measurements we focussed on the emission properties at room temperature (RT) in order to be close to the application. For the excitation a He-Cd-laser emitting at 325 nm (3.82 eV) is used, i.e. the carriers created in the outer ZnSe layers cannot cross the MgS barriers directly (bandgap of 5.5 eV) and have to relax into the QDs by tunneling. The PL spectrum of the reference sample without MgS barriers shows a Gaussian shaped peak with a full-width at half-maximum (FWHM) of 107 meV at RT which is a typical value for this kind of QD ensemble (emission at 2.38 eV / 521 nm). The emission of the sample including the barriers and the ZnSe (1.4 nm) layer below the CdSe is shifted by 240 meV to higher energies (2.62 eV / 473 nm) due to the increased confinement by the MgS barriers. The FWHM of the QD emission peak has a value of 76 meV in this case and is reduced by roughly one third compared to the reference sample. Furthermore, the PL intensity is increased by a factor of three although the relaxation of excited carriers from the outer ZnSe into the QDs has a strongly reduced probability due to the tunneling process.

By contrast, when the lower ZnSe (1.4 nm) layer is removed and the CdSe is deposited directly on the MgS barrier, the luminescence behaviour is drastically modified. Even though a stronger blue-shift is expected due to the further increased confinement, the emission is in fact red-shifted by 180 meV to 2.44 eV (508 nm). An explanation would be a higher Cd incorporation and/or an extended average lateral size of the QDs. A hint for a more inhomogenous size distribution of the QD ensemble is the increase of the FWHM by a factor of two to 149 meV. Nevertheless, this sample has the brightest PL intensity at RT, which is roughly five times higher compared to the reference sample without MgS barriers.

These investigations show the suitability of MgS barriers for increasing the PL efficiency and are an important step on the way to a single photon emitter operating at RT.

Confined Optical Modes in Monolithic ZnSe-based Pillar Microcavities

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Semiconductor microcavities (MCs) which possess a discrete set of confined optical modes are currently a focus of intense research. We report on the successful realization and optical characterization of monolithic II-VI pillar MCs featuring excellent quality factors $Q$ and mode volumes which make them very promising for future applications such as single photon emitters at elevated temperatures or quantum-dot based vertical-cavity surface-emitting lasers in the blue-green spectral region.

The pillar MCs have been fabricated starting from an all-epitaxial planar VCSEL structure grown by molecular beam epitaxy. The VCSEL structure contains a l-cavity in which three ZnCdSSe quantum wells (QWs) are embedded. This cavity is positioned between an 18 period bottom and a 15 period top distributed-Bragg-reflector (DBR) stack. The high-reflective index material of the DBR is made of ZnSSe while the low-index material consists of a short-period MgS/ZnCdSe superlattice. Cylindrically shaped pillars with diameters between 200 nm and $4\,\mu$m were prepared from the VCSEL structure by focused-ion-beam (FIB) etching yielding structures with smooth sidewalls and negligible conicity, compare Fig. 1.

Photoluminescence (PL) measurements were performed on individual pillar structures under cw excitation. At low temperatures (4 K) only emission from fairly localized states of the QWs provides an internal light source revealing the mode structure of the surrounding MC without introducing too much absorption. Series of sharp emission peaks which are blue-shifted with respect to the resonance of the respective planar cavity are observed and attributed to individual transverse modes of the MCs. By imaging spectroscopy the spatial transversal mode structure is investigated showing a simple Gaussian-like intensity profile for the fundamental modes and an increasing number of nodes for higher modes in radial direction. With decreasing diameter of the pillars the energy of the fundamental mode as well as the splitting of the individual modes increases. For the energy position of the modes convincing agreement is obtained with calculations based on an extended transverse matrix method providing the longitudinal and transversal mode structure.

A quality factor of $Q = l/Dl = 3500$ for the individual fundamental mode limited by the $Q$ factor of the respective planar VCSEL is obtained from the PL spectra. This value remains constant for all pillar diameters exceeding $1.5\,\mu$m. For smaller pillars $Q$ decreases because of increasing scattering losses due to residual roughness of the pillar sidewalls. Radiation in transverse direction becomes important, too.

As a figure of merit for our MCs we calculate Purcell factors well above 10 from the measured $Q$ factors and the numerical mode volumes for the smaller pillars. Together with the possibility of straightforward integration of self-assembled CdSe/Zn(S)Se QDs this makes the pillar MCs very promising for the study and application of weak and strong coupling effects.
Optically Pumped Ultraviolet Lasing of BeMgZnSe Based Quantum Well Laser Structures

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BeMgZnSe is a wide bandgap II-VI compound semiconductor with an energy bandgap of $E_g = 2.68-4.72 \text{ eV}$ [1], and a lattice constant of 5.137-5.96 Å. The advantages of this material are as follows; (a) lattice-matched to GaAs, Si and GaP, (b) the bond energy of Be-chalcogenide was strong, and so on. Recently, we have demonstrated the epitaxial growth and photoluminescence at room temperature of high-Be, Mg-content BeMgZnSe with the bandgap of 3.80 eV on the GaP (001) substrate was achieved by introducing the BeZnSe buffer layer in order to suppress the phase separation of BeSe-MgSe [2] and obtain the high quality crystal of Be-MgZnSe. In this report, we demonstrate the optically pumped lasing of BeMgZnSe quantum well (QW) laser structures on GaP (001) substrate at 373 nm for the first time.

Figure 1 shows BeMgZnSe based laser structures that were epitaxially grown on GaP(001) substrate using a molecular beam epitaxy (MBE). The reasons why the BeZnSe buffer layer (BL) was deposited, because of the suppression of the phase separation and the growth of high quality crystal of BeMgZnSe. The compressive strain QW in the BeZnSe active layer was introduced because of increasing the band offset between well and barrier. A KrF excimer laser was used as the pump source.

Figure 2(i) shows the output intensity from the QW laser as a function of excitation power density at 13K. Since the superliner was clearly observed, the lasing was achieved. The threshold power density was 415 kW/cm$^2$. Figure 2(ii) shows the spectra of the edge emission below and above the lasing threshold at four different pumping powers. The narrowing and red-shift were observed. The lasing wavelength was 373 nm. In addition, the lasing was confirmed up to 130K.

From these results, we can believe an important milestone for realizing the UV laser lattice matched to the Si substrate because the defect free GaPN/GaP grown on Si (001) substrate has been achieved [3].

Fig. 1 Schematic model of laser structure

Fig. 2 Laser characteristic

MOVPE Growth and Study of ZnCdSe/ZnSSe MQW Structures for Green VCSELs

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One of the problems in growing of ZnCdSe/ZnSSe MQW structures for green VCSELs by MOVPE in ZnEt₂-CdMe₂-Me₂Se-Et₂S-H₂ system is the Ga penetration into the structure from the GaAs substrate. This occurs when etching the substrate by H₂Se, which appears due to Me₂Se decomposition at growth temperature higher than 390°C. Earlier we found that the optimal temperature for growing the structures with high emission intensity is as high as 425°C. Here we study a possibility to prevent Ga entering while keeping optimal growth temperature.

Growth runs were carried out in a horizontal quartz reactor without substrate rotation with an optical window for in situ multi-wavelength reflectometry control of the MQW structure period, QWs position and surface roughness. As-grown structures were studied by photoreflection, cathodo- and photoluminescence (PL), X-ray diffraction and AFM techniques. Using stepped etching emission uniformity along the structure depth was analyzed.

The deep level emission (580 nm) due to Ga impurity was observed over the distance 2μm into the structure. Efficiency of QW emission drops in this region. Moreover, the growth rate increases with the growth duration that makes hard to keep the structure period. To avoid these drawbacks we studied the growth process at lower temperatures. We found that at a critical temperature of about 390°C the growth rate change drastically. This is shown in Fig. 1a) where the thickness of MQW structure grown at 390°C versus the distance along the surface is presented. It is seen two regions with very different thickness as a result of small temperature variation along the substrate. Fig.1b) shows changing yellow band emission intensity with the structure depth for these regions. It turned out that the region with smaller thickness contains Ga impurity while the other region does not. It means that entering Ga decreases the growth rate.

Based on these results we used a low-temperature thin (about 50 nm) ZnSSe layer as the buffer followed by fast heating up the optimal growth temperature to improve our MQW structure. The microcavity was fabricated on these structures and lasing at λ = 535 nm with 3.2 W output power was achieved in longitudinal pumping by a scanning electron beam at room temperature. The threshold current density was as low as 8 A/cm².

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Energy Spectra of Quasiparticles in Combined Nanosystems: Quantum Dots in Quantum Wires

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The rapid development of the experimental research of nanoheterosystems brought to the existence of rather complicated combined nanoconstructions, containing different spatial combinations of quantum dots, quantum wires and quantum wells. The investigation of such systems is important because of the ability of their utilization in the devices of physical and biomedical electronics [1]. The theoretical investigation of nanoconstructions is only at the beginning due to the problems connected with their mathematical description.

We study the electron, hole and exciton spectra in nanosystems of three types: elliptical quantum wire CdS with the quantum dot HgS (I), two tunnely-bound quantum dots HgS (II) and opened quantum dot in the elliptic wire HgS (III). The potential energy of quasiparticles in the radial plane has the same expression for all types of nanosystems

\[ V(x, y) = \begin{cases} 
0, & x^2/a^2 + y^2/b^2 \leq 1 \\
V_{0\perp}, & x^2/a^2 + y^2/b^2 > 1 
\end{cases} \]

(1)

where \(a\) and \(b\) - the semi widths of ellipses, \(V_{0\perp}\) – potential skip at the interface between the quantum wire and the external medium.

The potential energy of quasiparticles along the cylinder axis has the form

\[ V^I(z) = \begin{cases} 
0, & |z| \leq h/2 \\
V_{0\parallel}, & |z| > h/2 
\end{cases} \]

\[ V^II(z) = \begin{cases} 
0, & d/2 \leq |z| \leq d/2 + h \\
V_{0\parallel}, & |z| < d/2, |z| > d/2 + h 
\end{cases} \]

\[ V^III(z) = \begin{cases} 
0, & \sqrt{h/2} \leq |z| \leq \sqrt{h/2} + d \\
V_{0\parallel}, & \sqrt{h/2} < |z| < \sqrt{h/2} + d 
\end{cases} \]

(2)

where \(V_{0\parallel}\) – potential skip at the interface between the semiconductor media HgS and CdS, \(h\) – quantum dot height, \(d\) – potential barrier width.

The form of the stationary Shrodinger equation allows to separate the radial and axial variables. The radial wave function is obtained as odd and even modified Mathieu functions and the axial one – as a linear combination of exponents.

There are performed the numerical calculations of the electron, hole and exciton energies dependencies on the geometric parameters of nanosystems.

In the limit case of the equal ellipse semi widths it is obtained the spectra of quasiparticles in quantum dots embedded into the cylindrical quantum wire. At the increasing of the relationship between ellipse semi widths one can see the splitting of energy levels for all types of nanosystems. The energies of all levels decrease, reach their minimum and then increase. Herein the energies of odd states are increasing faster than that of the even.

The magnitude of the levels splitting as the function of the barrier thickness separating the quantum dot is calculated for the tunnely-bound quantum dots. The dependencies of quasiparticles lifetimes on the parameters of nanosystems are obtained for the opened quantum dot.

Spectrum of Interface Phonons in Cylindrical Quantum Wires with Quantum Dots Inside

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The modern state of the experimental investigation of nanoheterosystems provides the ability to produce the combined nanoconstructions consisting of quantum dots and wires exhibiting a variety of shapes: rectangle, sphere, cylinder. The theory of phonon spectra in such systems is developed within the dielectric continuum approximation widely applied for the research of confined longitudinal and surface optical modes in low-dimensional crystal structures [1,2].

We consider the nanoconstructions of two types: cylindrical quantum dot embedded into the cylindrical quantum wire placed into the semiconductor medium (I) and cylindrical quantum dot surrounded by two cylindrical anti dots embedded into the cylindrical quantum wire placed into the semiconductor medium (II). The dielectric property is assumed isotropic for all media and the frequencies of transversal and longitudinal optical phonons are known for the bulk analogies of all nanosystem parts. Solving the electrostatic equations it is obtained that the frequencies of confined phonons are equal to the frequencies of bulk LO modes and there are two types of surface modes because the solutions of Laplace equations are different for the top (bottom) ends and for the side walls. They are namely: the side surface optical (SSO) modes and top surface optical (TSO) modes.

The analytical expression for the polarization field of SSO modes in the cylindrical coordinates is chosen to be non decaying along the OZ axis and decaying in the plane perpendicular to it and for the TSO modes — on the contrary. Using the boundary conditions at the side interfaces one can obtain the transcendental equation for the determining of the spectrum of side surface phonons. The corresponding conditions for the top (bottom) interfaces bring to the system of equations for the determining of symmetric and anti symmetric frequencies of top surface phonons.

The numerical calculations are performed for the cylindrical quantum dot CdS embedded into the quantum wire ZnS placed into the massive medium HgS (I). The dependencies of TSO and SSO modes frequencies on the respective quasiwave numbers are obtained for the different geometric sizes of nanosystem parts. It is shown that there are four bands of SSO modes (with different magnetic quantum number) weakly depending on the quasiwave number for the system of type (I) and six bands for the system of type (II). The TSO symmetric and anti symmetric modes frequencies as the functions of two quasiwave numbers are calculated for the both types of nanoconstructions (I,II).

The expression for the Hamiltonian of the free phonon field including the confined LO and two types of surface optical modes is established in the representation of creation and annihilation boson operators. The electron-phonon interaction Hamiltonian is also written as the sum of three terms

\[ H_{e-\text{ph}} = H_{e-\text{LO}} + H_{e-\text{TSO}} + H_{e-\text{SSO}} \]

where the first term describes the electron - LO phonon interaction, the second one - electron - TSO modes interaction and the third - electron - SSO modes interaction.

Cd$_{1-x}$Mn$_x$Te and Cd$_{1-x}$Zn$_x$Te solid solutions are currently the focus of intense research due to an opportunity of improvement of structure and properties of the materials as epitaxial substrates. Treatment of semiconductor surface and its protection till now remains one of the main technological difficulties both in manufacture of semiconductor devices, and in scientific researches. Physical, chemical and mechanical properties of materials very often are determined by a state of surface which formation is insufficiently investigated. Therefore polishing etching is not only one of technological operations during semiconductor devices manufacture, but also precedes study of electrophysical, structural and other properties of the material.

We have carried out studies of solid solutions surface composition and formation evaluating stationary equilibrium in Cd$_{1-x}$Zn$_x$Te - H$_2$O, Cd$_{1-x}$Mn$_x$Te - H$_2$O systems by measurements of electrode potential $\phi$ in various etching compositions. Possible types of equilibrium conditions are investigated by means of construction of Pourbaix diagrams in $\phi$ - pH coordinates. Potential - pH diagrams generalize chemistry of elements solutions and concisely show what ions and molecules are thermodynamically stable against oxidation-reduction reactions depending on pH and $\phi$. It is found that in a form of crystal phases Cd$_{1-x}$Mn$_x$Te and Cd$_{1-x}$Zn$_x$Te solid solutions can exist in all studied pH interval. However, the composition of Cd$_{1-x}$Zn$_x$Te solid solutions surface is more stable against a change of the potential as compared to Cd$_{1-x}$Mn$_x$Te surface. The analysis of Pourbaix diagrams shows, that stoichiometric dissolution of Cd$_{1-x}$Mn$_x$Te and Cd$_{1-x}$Zn$_x$Te solid solutions (the basic feature of polishing etching) is possible in acid (pH $<$ 3) and alkaline solutions (pH $>$ 12). Selective dissolution of solid solutions (on Cd, Zn, Mn) or passivation of their surface by oxidations products is observed in 3 ÷ 12 pH interval. Such products can be oxides and hydroxides of the metals, which constitute solid solutions, as well as tellurium compounds. Dominant effect of Te is caused by the fact that irrespective of medium pH the oxidation reactions in the semiconductor-etchant system with Te participation have higher values of the potential than Cd, Mn, and Zn potentials. In an acid medium polishing etching takes place if their oxidizing potential is at least about 0,416 V. On the other hand in an alkaline medium a role of an oxidizer can play substances which ordinary electrode potential does not exceed $-0,57$ V. Proceeding from the analysis of Pourbaix diagrams an optimum composition of polishing etchant for chemical and mechanical polishing of Cd$_{1-x}$Mn$_x$Te and Cd$_{1-x}$Zn$_x$Te was determined.
Magnetic semiconductors are of interest because of the spin exchange interactions between the magnetic ions and the charge carriers. When a magnetic field $B$ is applied, the spin system formed by the magnetic ions becomes increasingly aligned and, as a result, the charge carriers experience an effective magnetic field $B_{\text{eff}}$ which can be orders of magnitude greater than the applied field itself. The consequent giant enhancement of the $g$-values of conduction band related electrons in dilute magnetic semiconductors is well known and has been studied by a range of magneto-optical techniques, notably by spin-flip Raman (SFR) spectroscopy. In the present work we have used an additional technique, high-frequency (100GHz) optically-detected magnetic resonance (ODMR), to directly investigate electron spin-flip transitions in Cd$_{1-x}$Mn$_x$Te ($x = 0.005$ nominally).

The magnetic resonance condition for conduction band electrons is given by

$$h\nu = g_e\mu_B B_{\text{eff}} = g_e\mu_B (B + B_{\text{ex}})$$

where $g_e = -1.62$ is the $g$-value of conduction band electrons in CdTe, $\mu_B$ is the Bohr magneton and $B_{\text{ex}}$ is the exchange field due to the manganese ions. At the magnetic fields used in our experiments, the manganese magnetization is well below saturation and is a linear function of the applied field. The magnetic resonance condition can thus be written $h\nu = g_{\text{eff}}\mu_BB$, where the effective $g$-value is given by

$$g_{\text{eff}} = g_e - 35\alpha N_0\alpha g_{\text{Mn}}/(12k_b(T + T_0)).$$

Here, $N_0\alpha = -220\text{meV}$ is a measure of the exchange interaction between the Mn ions and the electrons, $g_{\text{Mn}} = 2.00$, and $k_b$ is the Boltzmann constant. Some Mn ions will be paired antiferromagnetically and will thus not contribute to the paramagnetism, causing the effective concentration to be less than $\bar{x}$ and causing the appearance of a Weiss contribution $T_0$ to the temperature $T$. As $x \to 0$, $\bar{x} \to 0$ and $T_0 \to 0$. From SFR experiments we find $\bar{x} = 0.0048$, so that for temperatures below 2K we expect values of $g_{\text{eff}}$ approaching 40.

The ODMR experiments were carried out at 105 GHz under 514 nm Ar$^+$ ion laser excitation. The electron spin-flip signals were detected by monitoring the photoluminescence from donor-acceptor recombination in the region 1.55 eV to 1.48 eV. A notable feature is that the product $g_{\text{eff}}\Delta B$ is a constant (3.5 Tesla, which in energy terms corresponds to 0.2 meV). The implications of this for the mechanisms by which SFR scattering and ODMR are observed will be discussed. A further ODMR signal with a $g$-value of about 5 at 2.1K is also observed and is tentatively ascribed to holes trapped at shallow acceptors. The experiment demonstrates that high frequency ODMR is a suitable method for investigating spintronic materials.
Electron Paramagnetic Resonance of Manganese Ions in Cadmium Telluride
Detected by Coherent Raman Spectroscopy

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Electron paramagnetic resonance (EPR) is a popular way to study semi-magnetic semiconductors. The disadvantages of this technique are its low sensitivity and (in heterostructures) its lack of selectivity. Alternative optical spectroscopic methods such as spin-flip Raman spectroscopy (SFRS) have optical selectivity and better sensitivity but lack the energy resolution of ESR. Coherent Raman-detected ESR spectroscopy (CRESR) incorporates both these methods to give a spectroscopic technique with optical selectivity, good sensitivity and high energy resolution. We report the first application of this technique to a dilute magnetic semiconductor.

We have detected coherent Raman scattering between Mn$^{2+}$ 3d$^5$ spin levels in (Cd,Mn)Te. As with ESR, we observe absorptive and dispersive like components ((a) and (b) in the figure), allowing us to use well established theories to simulate our results. To model these components effectively we must include hyperfine interactions between the Mn$^{2+}$ 3d$^5$ electrons ($S=5/2$) and the Mn nucleus ($I=5/2$), as well as the fine structure Hamiltonian arising from the cubic crystal field. The figure shows how the main features of the CRESR spectrum can be reproduced by six (= 2$I$+1) peaks of equal width, area, and magnetic field separation (illustrated in (c)); for simplicity, the somewhat weaker crystal field effects have not been introduced here, but will also be discussed. The optical resonance conditions of the CRESR signal correspond to the optical resonance conditions of the well-known Mn$^{2+}$ 3d$^5$ “paramagnetic resonance” spin-flip Raman signal. The results provide the first demonstration of the ability of the CRESR technique to probe magnetic ions in semiconductors via resonance with excitonic intermediate states (previous studies have observed $d$-electron signals in resonance with internal ionic transitions in the case of Cr$^{3+}$ in ruby [1], or donor-bound electron signals in resonance with donor-bound excitons in ZnSe [2]). This opens the way to a technique analogous to ESR that may be used to probe magnetic ions and their interaction with band carriers and excitons even in low-dimensional semiconductor heterostructures.

We describe the observation and interpretation of the reflectivity spectra of CdMnTe and ZnSe obtained by a novel form of contactless electroreflectance in which the applied electric field oscillates at a microwave frequency (14 GHz) and a heterodyne technique is used to detect the resulting modulation of the reflected light beam; we term this “microwave-modulated reflectivity” (MMR). The signals appear as an unexpected and strong background during coherent Raman spectroscopy experiments with the apparatus described in [1]. The MMR signals require the presence of a microwave field to be observed but differ significantly from coherent Raman signals; the latter have distinctive absorptive and dispersive line shapes and obey strict microwave resonance conditions (the microwave energy must equal the magnetic field splitting). In contrast, the MMR signals are present over the full range of magnetic field. The coherent Raman spectroscopy technique also involves the low-frequency modulation of the polarisation of the excitation beam, and the polarity of the MMR signal of a given transition is thus found to depend on its polarisation.

MMR has been detected in both (Cd,Mn)Te and ZnSe samples. In bulk CdMnTe ([Mn]~0.005) the resonance of the coherent Raman signal overlaps the MMR signal, as illustrated in the figure. The darker lines show the six calculated optical transitions. The parameters required to calculate these curves have been determined using spin-flip Raman spectroscopy and photoluminescence excitation spectroscopy (PLE). In the case of a ZnSe epilayer, the coherent Raman signal is in resonance with excitons bound to neutral donors, separating it (in energy) from an MMR signal from free excitons. Hence, for ZnSe, we can clearly show the individual magnetic field dependences of both types of signal and can identify the observed MMR signals with the strain-split light- and heavy-hole exciton transitions. We thus show that the non-resonant MMR signals observed in coherent Raman experiments can be identified and can be distinguished from the optically-detected spin resonance signals that are the main point of the technique. Our results show that the MMR effect in fact provides a highly useful tool to determine the nature of the resonant intermediate states involved in the coherent Raman process and represents a promising new technique for magneto-reflectivity studies.

Spatially Inhomogeneous Heating of Spin Subsystem of Mn$^{2+}$ Ions in CdMnTe/CdMgTe SQW

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It has been demonstrated recently that a layer of II-VI diluted magnetic semiconductor (DMS) combined with GaAs based p-i-n LED can be used for effective spin manipulations in spintronics devices [1,2]. These results initiated intensive studies of spin-relaxation processes in DMS structures with 2DEG. It was reported that exchange interaction between 2DEG and Mn$^{2+}$ local spins in DMS systems can lead to heating of spin and free carriers subsystems [3,4], and that spin relaxation processes strongly depend on density of non-equilibrium carriers [5].

In this communication we present results of magneto-optical studies of interactions between Mn$^{2+}$ local spin moments and non-equilibrium 2D electron gas in a single QW structure (8.4 nm wide) of Cd$_{1-x}$Mn$_x$Te/Cd$_{1-y}$Mg$_y$Te ($x=0.01$, $y=0.2$). The studied sample had very wide spacer (300nm) between a QW (Cd$_{1-x}$Mn$_x$Te) and an iodine-doped layer in barrier (Cd$_{1-x}$Mg$_y$Te). The initial density of 2DEG in QW was about 10$^{10}$ cm$^{-2}$. All structures were grown by MBE on GaAs (100) wafers.

We studied magnetic field dependences of excitonic (X) and negatively charged excitonic (X$^-$) photoluminescence (PL) and PL changes under pulsed microwave (MW) pumping (using 60 GHz band). Intensity of photo-excitation was varied from 0.05 to 15 W/cm$^2$. At increased density of photo-excitation we observed heating of the Mn$^{2+}$ spin subsystem. Mn$^{2+}$ spin temperature (ST) increases up to 18 K at excitation density of 15 W/cm$^2$, with lattice temperature of 1.5 K. Difference between Mn$^{2+}$ ST and a lattice temperature decreases with increasing magnetic field. We also observed that the heating is spatially inhomogeneous, due to spatially inhomogeneous distribution of iodine donors in a barrier layer. MW pumping (at Mn$^{2+}$ magnetic resonance conditions) leads to a strong increase of the ST. We observed a nearly total compensation of magnetic field induced red shift of the PL emissions (by 12 meV). This red shift is caused by a giant spin splitting, proportional to the sample magnetization, i.e., we quench sample magnetization by applying microwaves at resonant conditions. In turn, when applied non-resonantly, the microwave pumping induces a small (about 1 meV) red shift of both X and X$^-$ PL lines, observed for magnetic field varied between 0 and 7 T, which we relate to increasing temperature of 2DEG. We measured kinetics of the above effects by applying pulses of microwave power, which enables us to estimate spin-lattice relaxation time of Mn$^{2+}$ spin-system and its dependence on carrier density.

Spin Polarized Carriers in Heavily Chromium Doped ZnSe

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Chromium doped ZnSe is a promising material for spintronics as well as for optoelectronics due to manifested ferromagnetic interaction between curriers and Cr\textsuperscript{2+} ions [1-3] and very efficient tunable laser operation in mid infra red band [4]. Just last purpose initiates a hitch in growth technology of Cr heavily doped ZnSe crystals with excellent optical quality [5]. Our communication report on the magneto-optical studies of PVT grown ZnSe crystals and MBE layers doped by Cr with concentration up to 5\textsuperscript{\times}10\textsuperscript{19} cm\textsuperscript{-3}. In experiments circular polarized spectra of near band gap photoluminescence (PL), absorption and reflection were measured as a function of magnetic field induction in the region of 0-7T. PL was excited by InGaN based laser diode emission with above ZnSe band gap photon energy $\bar{\omega}_{\text{ex}} = 2.98$ eV and power density up to 120 W/cm\textsuperscript{2}. At the temperature range 1.5-20 K strong reflection of free excitons and sharp intensive lines from free (X), donor bound (D\textsuperscript{0},X), acceptor bound (A\textsuperscript{0}, X) excitonic PL and free electron to acceptor (e-A) recombination PL has been observed. Absorption spectra indicate only good structured impurity related tail of fundamental band. At magnetic field only small (about 0.2 meV) diamagnetic shift of position X-line, was observed for free exciton PL and reflection spectra both. Weak circular polarization of bound exciton PL and (A\textsuperscript{0}, X) peak position red shift in magnetic field corresponding to a weak ferroelectric Cr\textsuperscript{2+} (3d\textsuperscript{4}) ion-carrier interaction [3] has been manifested. On the contrary, we observed a very strong rising of $\delta$ - components and quenching of $\delta^+$ components of e-A recombination. Magnetic field dependence of circular polarization rate saturated at magnetic field B=2.5 T with a value up to 90% and has been approximated by Brillouin function for S=5/2. At the spectral range corresponding to shallow acceptor to conductivity band transitions circular polarization of transmitted light i.e. magnetic circular dichroism (MCD) in ZnSe:Cr crystals was observed. Magnetic field dependence of circular polarization rate of e-A recombination exhibits behaviors on chromium concentration, temperature and intensity of photoexcitation.

We discuss two possible scenarios leads to observed spin polarization of nonequilibrium carriers is ZnSe:Cr. First - spin-dependent electron capture to the Cr\textsuperscript{2+} centers and their ionization to Cr\textsuperscript{3+} (3d\textsuperscript{5}) stay. As a result, the spin-up electrons excess could be appear in conductivity band at magnetic field under band to band photoexcitation of ZnSe:Cr. Second - spin polarization of holes, localized at the shallow acceptors, due to exchange with local spin momentum of chromium ions.

Optical Spectroscopy of CdTe/ZnTe Quantum Dot Multilayers


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Growth of quantum dot (QD) bilayer or multilayer structures allows to change electronic and optical spectra of such structures in a controllable manner that gives a possibility to improve the characteristics of QD based optoelectronic devices. Owing to its peculiarities, the CdTe/ZnTe system is of interest to study the effect of multiplayer structure parameters upon the properties of QD structures. We report studies of CdTe/ZnTe QD multilayer structures with different ZnTe spacer layer thicknesses (5 – 50 monolayers). The samples were grown by MBE on GaAs substrates followed by a thick ZnTe buffer layer. We studied the Raman spectra, IR-reflection, and photoluminescence spectra in a wide temperature range.

A new line appears in the Raman spectra of structures with small ZnTe spacer thickness (5 – 10 monolayers). This line was not observed also in Raman spectra of CdTe/ZnTe QD multilayers with thicker spacers grown on thick CdTe buffer layer which were studied earlier [1]. It was shown by theoretical consideration that this line can be caused by a symmetrical vibrational mode of QD pair. We discuss conditions under which a symmetrical vibrational QD mode is active in optical processes. A possibility of this mode to interact with vibrational modes of other QDs is also discussed.

A feature related to vibrational excitation in QDs was observed in IR-reflection spectra along with features related to GaAs substrate and ZnTe buffer and barrier layers. Note that this feature appears already at relatively small number of QD layers.

It has been shown earlier for a set CdTe/ZnTe QD multilayer structures grown on thick CdTe buffer layer that decreasing of spacer thickness affects strongly the emission spectrum and its behavior with temperature increase [2,3]. The QD structure with the thickest ZnTe spacer exhibits a high luminescence efficiency and relatively high value of an activation energy of luminescence quenching (60 meV). An additional luminescence band appears in structures with a small ZnTe spacer thickness. The latter structures exhibit a relatively low luminescence intensity and fast luminescence drop with the temperature increase. For the sample with 5 monolayer spacer, the additional band has a complicated shape. It is interesting to note that the luminescence intensity of this structure with thinnest spacer is higher under quasi-resonant excitation than under above-bandgap excitation. Such results can be explained by the presence of rather intense exciton migration in these QD structures along with decreasing of crystal quality for the samples with small ZnTe spacer thickness.

Suppression of Electron-spin Relaxation Induced by Magnetic Fields in a Cd$_{1-x}$Mn$_x$Te Quantum Well

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Ultrafast spin dynamics of carriers in a semiconductor quantum well (QW) has extensively been studied by transient optical methods. In addition, a diluted magnetic semiconductor (DMS) provides an interesting system in which carriers are interacting with magnetic moments via s, p-d exchange interactions. In the DMS, photo-excited carriers can be fully spin-polarized in magnetic fields and show particular spin relaxation processes accompanying the energy relaxation. The DMS-QW is therefore important as a source of the spin-polarized carriers for semiconductor spintronic devices. However, all of the energy relaxation processes of the spin-polarized carriers have not been systematically understood yet, including spin-polarization, -flip, -migration, -injection, and -relaxation. Therefore, we have developed a circularly polarized pump-probe absorption spectroscopy system using a white light probe, in magnetic fields, which enable us to study sub-pico second transient behaviors of the spin-polarized carriers and exciton in semiconductor QWs [1,2].

We have studied the carrier spin relaxation under magnetic fields in a DMS-QW of Cd$_{0.95}$Mn$_{0.05}$Te, by means of the pump-probe absorption spectroscopy. Dynamical spin-flip processes of the electron and heavy-hole (hh) are clearly shown in time dependences of the circularly polarized differential absorbance after the resonant excitation using a circularly polarized pump pulse. In 0 T, time constants of 17 and 0.4 ps for the electron and hh spin relaxations in the Cd$_{0.95}$Mn$_{0.05}$Te QW are shorter than those of 46 and 1.0 ps in a CdTe QW. It originates from s, p-d exchange interactions between the carriers and Mn spins [3], where the electron-spin relaxation time due to the exchange mechanism is determined as 27 ps, in addition to a Bir-Aronov-Pikus relaxation process that is dominant in the CdTe QW. However, in an intense magnetic field of 5 T, the electron spin relaxation due to the s-d exchange mechanism is found to be strongly suppressed in the Cd$_{0.95}$Mn$_{0.05}$Te QW by magnetic-field-induced pinning of the Mn spins, exhibiting a longer time constant of 29 ps. Here, LO phonons cannot participate the electron-spin relaxation, since the giant Zeeman splitting of the electron is calculated as 17 meV that is smaller than the LO phonon energy. In 3 T, the relaxation time constant is further longer as 41 ps. It can be attributed to limited relaxation passes of the electron spin accompanying the energy relaxation via acoustic phonons, due to reduction of the giant Zeeman splitting of the electron state. The spin dynamics of carriers and the magnetic-field dependence of the electron-spin relaxation will be important for designing a spin-aligner using the DMS-QW for ultrafast spintronic devices.

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Efficient Spin Injection in Self-assembled CdSe Quantum Dots Coupled with a Diluted Magnetic Semiconductor Quantum Well

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Spin injection in semiconductor quantum structures is one of the most important research subjects, because the spin injection is known as a key for realizing semiconductor spintronic devices. The dynamics of the spin injection has been studied in details, in coupled quantum wells (QWs) composed of a spin aligner of diluted magnetic semiconductor (DMS) and a spin detector of non-magnetic well with a proper tunneling barrier, by time-resolved circularly polarized photoluminescence (PL) [1,2]. The spin injection dynamics is quantitatively explained by individual tunneling of a spin-polarized electron and heavy hole (hh). In addition, the spin injection into self-assembled quantum dots (QDs) has recently been reported by using a diffusion process of excitons from the DMS [3]. The spin injection into the QD is very attractive, since spin states of an electron in the QD are widely known as one of the most promising candidates for the material of quantum computing. However, the spin injection into the QD via quantum tunneling is not sufficiently examined yet.

We have studied electron-spin injection from the DMS-QW into self-assembled QDs through a tunneling barrier in the coupled structure. The self-assembled CdSe QDs were grown on the DMS-QW of Zn$_{0.68}$Cd$_{0.22}$Mn$_{0.10}$Se with the thickness of 10 nm, with the tunneling barrier of ZnSe with the thickness of 5 nm. The thickness of the QD layer prior to the dot formation was varied from 1.5 to 5 monolayers in order to control the dot size and thus quantum confinement effects for the carriers. Time-resolved circularly polarized PL was measured in magnetic fields for the coupled structures. The photo-excitation was made above the barrier. As the result, the electron-spin injection from the Zn$_{0.68}$Cd$_{0.22}$Mn$_{0.10}$Se QW into the self-assembled CdSe QDs is demonstrated via LO-phonon-assisted resonant tunneling. The spin injection is experimentally evidenced by the time-resolved circularly polarized PL with the polarization degree up to 40% from the QDs. In addition to this, circularly polarized PL with the lifetime of 3.5 ns is observed, clearly indicating the type-II transition between electrons in the QDs and spin-polarized hh's in the DMS-QW. These PL energies directly indicate that the electron tunneling is assisted by a LO phonon in the CdSe QD. The electron-spin injection time is obtained as short as 20 ps from the rise time of the polarization degree. The fast injection time can be attributed to the tunneling probability of the electron from the DMS-QW side. The electron-spin injection via LO-phonon-assisted resonant tunneling provides the way for an efficient spin injection process into the self-assembled QD exhibiting strong quantum confinement effects.

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Magneto-optical Properties in Hybrid-nanostructures of II-VI Diluted Magnetic Semiconductors with Perpendicular Ferromagnetic Films

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Diluted magnetic semiconductors (DMSs) show remarkable magneto-optical properties, such as, giant Zeeman effects and Faraday rotation. Those properties are very attractive for applications to magneto-optical devices in a visible light region. Also, spin-polarized carriers can be generated in the DMS, which is potentially applicable to a spin aligner in spintronic devices using semiconductors. In those studies, applications of external fields to the DMS are necessary for controlling the spin alignment. Therefore, hybrid structures of the DMS with ferromagnetic materials generating magnetic flux become important, for the purpose of applying efficient local magnetic fields to the DMS nanostructures. We have developed hybrid nanostructures of DMS quantum wells (QWs) with ferromagnetic Co wires [1]. The giant Zeeman effects for excitonic photoluminescence (PL) are also demonstrated due to the field application from the Co wires to the DMS-QW in the Faraday geometry, when the magnetization in the Co is aligned normal to the film plane by external fields [2].

We have studied magneto-optical properties in hybrid nanostructures of DMS-QWs and Co-based ferromagnetic thin films, where we introduce a perpendicular magnetic anisotropy in the Co film in order to align the magnetization normal to the film plane for generating perpendicular magnetic fields to the DMS-QW. A Zn$_{1-x}$Cd$_x$Mn$_y$Se QW was made into wires or dots with the lateral dimensions down to 100 nm and built in the ferromagnetic nanostructures. We used Co/Pt multilayered films indicating a perpendicular anisotropy field of 1.91 T that is higher than an in-plane anisotropy field of 1.76 T. Therefore, the Co magnetization can be aligned perpendicular to the film plane at a zero external field. In the hybrid wire structure using the Co/Pt, the excitonic PL spectrum depends largely on a position of light spot with the diameter of 2 µm for micro-PL measurements. The spectrum width changes from 20 to 32 meV according to the spot position, where the width for the plane QW is 18 meV. In addition, in the hybrid dot structure, the excitonic PL spectrum shows broadening with the width of 25 meV that is almost constant among the measurement position. These increases in the PL spectrum width can be attributed to the giant Zeeman effects of excitons due to the field application from the Co magnetization perpendicular to the film plane, while the circular polarization is not observed in the PL. Magnetic hysteresis measurements reveal significant reduction of the remanent magnetization at 0 T in the Co/Pt film, possibly due to the magnetic domain formation. The domains with opposite directions of the perpendicular magnetization can cancel the circularly polarized PL, since the microscopic magnetic fields with opposite directions are applied to the DMS-QW. The uniform PL-spectrum broadening in the dot structure suggests that the domain size is smaller than 100 nm.

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Luminescence Studies of Heat Treatment Influence on Size Distribution of CdTe Nanocrystals

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Recently, techniques of colloidal chemistry were successfully applied to synthesize semiconductor nanocrystals (NCs), mainly on the basis of II–VI compounds. Due to high photoluminescence quantum yield, II–VI NCs offer a great promise to be used as light emitters, in particular as highly fluorescent markers in biological applications. The emission wavelength may be tuned across the whole visible spectral region, from near-IR to UV, by simply changing NC’s diameter and/or composition. For many applications, nearly monodisperse NCs with a narrow size distribution are required. In some cases, however, a bimodal size distribution of the NCs is preferred.

In this report, possibility of obtaining a bimodal size distribution of CdTe NCs is demonstrated. This can be realized by heat treatment of NCs. We studied CdTe nanocrystals synthesized in aqueous solution at room temperature and stabilized with thioglycolic acid (TGA). The reaction time was adjusted so that the total relative molar concentrations of the constituents [Cd\(^{2+}\)]:[Te\(^{2-}\)]:[TGA] were 1:0.25:2.4 (series A) and 1:0.5:2.4 (series B). After that, aliquots from both series were thermally treated at 100 °C for \(t = 0.5 – 6\) h. Heating influence on size distribution and emission properties of NCs was monitored by measuring room-temperature photoluminescence (PL) spectra.

PL experiments revealed distinct difference between the two series of samples. For series A, heating for \(t = 1 – 2\) h resulted only in low-energy broadening the PL band centered at around 2.4 eV. Prolonged heating (\(t \geq 4\) h) led to appearance of another PL line at 2.2 eV which implies formation of NCs with larger radius. Energy position of this line shifted to the red at increasing heating time and its intensity enhanced relative to the 2.4 eV line. At the same time, energy position of the 2.4 eV line was constant for all heating times applied. Contrary, two PL bands were detected for samples of series B already after a 0.5 h heat treatment. Further increase of heating duration resulted only in a small red-shift of the low-energy band, whereas the intensities ratio of two PL lines remained almost the same.

The difference between the two series of CdTe colloids may be explained by different amount of tellurium in the solutions. Tellurium deficiency in series A results in growth of NCs with poor surface quality. These NCs may be easily dissolved at the following heat treatment and larger particles are formed due to the Ostwald ripening phenomena. Shift of the [Cd\(^{2+}\)]:[Te\(^{2-}\)] ratio towards the stoichiometric one (series B) provides both better surface quality of NCs and conditions for larger particles formation during the synthesis. Higher NCs stability of series B prevents dissolution of smaller particles and the bimodal size distribution remains for the heat treated solutions.
Vertical and lateral alignment of CdSe/Zn(S)Se quantum dots (QDs) is an important issue regarding the device performance of laser diodes emitting in the green and blue spectral range. It is expected that the threshold current density for laser emission can be reduced by using QD lasers instead of quantum well lasers. However, the size distribution of the QDs and composition has to be homogeneous in order to achieve lasing with small emission width. One method to improve the homogeneity of the QDs is to exploit strain driven lateral and vertical ordering effects [1].

In this respect, several samples of five-fold and ten-fold CdSe QD stacks separated by Zn(S)Se spacer layers of different thicknesses (2, 4.5, 8 nm) were grown by molecular beam epitaxy (MBE) on GaAs (001) substrates at a temperature of 280°C. Sulfur was used for strain compensation between the spacer layers and dot layers in order to avoid stacking faults due to the stress accumulation [2]. The samples were investigated by transmission electron microscopy (TEM) and the results were compared with those from grazing incidence small angle X-ray diffraction (GISAXS). TEM specimens were field images using the (220) or the (004) beam were taken in the [110] and [010] zone axis, respectively. The specimens with five-fold stacks separated by 4.5 nm and 2 nm ZnSSe showed strain fields connected to an alignment of the dots in vertical and lateral direction. The mean lateral distance was determined to be 10-13 nm. From plan-view images of the same samples using a (220) dark field imaging condition a lateral distance between 9-11 nm was found. In contrast, the specimen with a Zn(S)Se spacer thickness of 8 nm showed only vertical alignment of the dots. Plan-view images of the five-fold and ten-fold stacks with the same Zn(S)Se spacer layer thickness (4.5 nm) exhibit different angular distributions with respect to lateral ordering of the QDs depending on the number of stacks. The angles between the features are found to be 40° and 50° for the five- and ten-fold stack, respectively. An example is given in Fig.1 where the features due to the strain fields of the enclosed dots are aligned in two directions with an angle of 40°. The cross-section TEM results are in agreement with results from grazing incidence small angle X-ray diffraction (GISAXS) experiments. Both suggest a strain-driven self-organized process [3].

Temperature Dependence of the Photoluminescence from Cd(Se,Te) Quantum Dots in ZnSe Matrix

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It is well-known that coherent CdSe/ZnSe insertions with a nominal thickness in the range of 1-3 monolayer (ML) represent the sheets of CdSe-enriched islands, so-called quantum dots (QDs), incorporated into the body of an alloyed ZnCdSe QW. Previously, we reported the fabrication of inhomogeneous arrays of CdSe QDs with nanometer-scaled sizes and up to 90% Cd content, using the modification of migration enhanced epitaxy (MEE) technique exploiting growth interruptions after each MEE cycle [1]. Just recently we have proposed another approach to fabrication of high-quality structures based on the stressor-controlled self-organization of Cd(Se,Te) QDs in ZnSe, using super-strained CdTe fractional monolayer deposition prior to the CdSe growth. In the paper the temperature dependences (25 – 300 K) of the photoluminescence (PL) and PL excitation (PLE) spectra from the pure CdSe and Cd(Se,Te) QDs are discussed. The non-regular character of the PL energy dependence on the temperature, arising from the non-monotonic behavior of the PL Stokes shift (SS), is registered at low temperatures (see Fig.1 for the MEE case). SS temperature dependence is qualitatively described by the kinetic model of the exciton hopping [2]. Starting from the temperatures of about 100 K, thermalization leads to the decrease of the Stokes shift in accordance with the $-\frac{w^2}{kT}$ law [3], where $w^2$ is a dispersion of the Gaussian-like distribution of states, derived for each sample from the fitting of the PLE spectra by the Gaussian function (see inset in Fig.1). Investigation of the PL temperature behavior in different samples allows us to conclude that both modified MEE and stressor-controlled growth techniques eventually result in the narrower DOS dispersion and higher Cd-content in a CdSe QD array in comparison with a standard MEE or MBE modes. In Cd(Se,Te)/ZnSe heterostructures in addition to the QD-related PL the broad PL band is observed at lower energy. Basing on the excitation power dependence as well as the temperature dependence of PL and PLE we attribute this line to the Te-enriched nanostructures with type II band alignment (see Fig. 2).

Luminescence Properties of ZnSe/CdSe/ZnSe Quantum Dots Fabricated by CdSe Deposition Below the Critical Thickness

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CdSe-based quantum structures, such as quantum wells (QWs) and quantum dots (QDs), have attracted considerable attention for optoelectronic device applications. CdSe dots originate when the CdSe layer exceeds the critical thickness \( t_{cr} \), and this growth mechanism is known as a Stranski-Krastanov mode and the generated dots are called as SK-dots. We report that there is other dot growth mechanism in CdSe dot preparation. We fabricated ZnSe/CdSe/ZnSe structures by using an alternate molecular beam supplying (ALS) method. After terminating ZnSe surface with Zn atom, Se-beam was irradiated at first for 10sec and then Cd beam was irradiated. The Cd irradiation time was varied between 1sec and 10min. As we are interested in the initial stage of CdSe dot generation, we used small ALS cycles of 1 and 2.

In this work, the growth process of ZnSe/CdSe/ZnSe was monitored by in-situ observation of specular spot intensity \( I_{sp} \) in a reflection high energy electron diffraction (RHEED) pattern during CdSe growth, using the ALS method. By investigating the low-temperature photoluminescence (PL) spectra, we studied the generation process of CdSe dots.

In ZnSe/1-ALS CdSe/ZnSe structure (10sec Se- and 1sec Cd-beam irradiation), the PL spectrum shows the single intense peak at 2.792eV with a full width at half maximum (FWHM) of \( \sim 2 \text{meV} \). When the Cd-beam irradiation is extended to 10sec, the PL spectrum presents clear 2 peaks. The intensity of higher energy peak (A) is intense and has narrow FWHM (\( \sim 3 \text{meV} \)), and the intensity of lower energy peak (B) is weak and has rather broad FWHM (\( \sim 10 \text{meV} \)). As the increase of Cd irradiation time, both A-peak and B-peak moved towards lower energy side, and the intensity ratio B-peak to A-peak increased. These PL peaks can be well fitted to 2 Gaussian error functions.

When the CdSe layer is thinner than the \( t_{cr} \) and an ideal atomic layer epitaxy proceeds in ALS growth, no SK-CdSe dots can generate. We conclude both the atomic terraces more than 2ML high and 3D-micro-islands are formed by the beam irradiation of 1-ALS cycle. The former gives rise to SK-dots and the latter 3D micro-islands. The long Cd beam irradiation promotes the SK-dot generation and the short Cd beam irradiation enhances the 3D micro-islands. The 2 mechanisms for dot generation is considered due to that the Se molecular beam is not composed of simple molecules such as Se\(_2\). In this paper, we also discuss the effects of beam interruption during ALS growth on the dot generation.
Optical Properties of Cd(Zn)Se/ZnMgSSe Heterostructures with Fractional QD-like CdSe Insertions at High Excitation Levels

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Recently, we have reported on the investigation of laser properties of the MBE-grown Cd(Zn)Se/ZnMgSSe heterostructures with QD-like CdSe insertions placed into ZnSe quantum wells, embedded in the strained short-period ZnSSe/ZnSe superlattice waveguide [1,2]. Low values of laser threshold \( I_{th}=10^{-15} \, \text{KW/cm}^2 \) have been achieved, and the optical pumping of a green Cd(Zn)Se/ZnMgSSe laser by an optically pumped InGaN/GaN MQW laser has been realized, demonstrating the possibility to create a compact integrated III-V/II-VI-based laser converter emitting in the green region.

In this work, we study the optical properties of these II-VI heterostructures at high levels of optical excitation, which is related mainly to the stability of these structures under impact of the high density of optical radiation. The growth details and the heterostructure design were described elsewhere [1,2]. For excitation, pulsed radiation of a nitrogen laser (\( \lambda=337.1 \, \text{nm}, \tau_p=8 \, \text{ns}, P=20 \, \text{kW} \)) was used. The excitation density \( I_{exc} \) was varied between 5 and 1500 kW/cm².

The general feature of the studied heterostructures with CdSe quantum disks is the stable spectral position of the radiation from the CdSe carrier localization sites with increasing excitation intensity up to the appearance of stimulated emission, while the radiation from the cladding layers exhibit a red shift caused most probably by the heating of these regions absorbing the main portion of exciting radiation.

It has been found that in the lasing regime two concurring processes take place in the structures under study. The first one is the irreversible changes of the spectra, namely the blue shift. The threshold of this process depends on the excitation intensity and on the cavity length, correlating with inherent radiation density in the cavity. Based on this, we claim that the main cause of the changes is the inherent laser radiation rather than the exciting laser light. The high radiation density inside the cavity leads to an interdiffusion of the Zn and Cd atoms between the confinement areas and surrounding barriers, resulting in shallowing of the potential profile, and, thus to the blue shift of radiation. At higher excitation densities (well above laser threshold) one may observe also a reduction of the radiative efficiency. The second process is the increase of radiation intensity during operation caused by the defect annealing. This process turned out to be observed only in a certain interval of the excitation power density levels over the laser threshold. For example, at \( I_{exc}=8I_{th} \) we obtained an increase of the output power by 7 times during the short irradiation time (5 min). The power variation was measured at \( I_{exc}=1.4I_{th} \). At the same time, the threshold value was also decreased by about 15 – 20%. At fixed excitation intensity, the initial increase of the output power is then followed by a decrease, when the density of inherent laser radiation in the cavity becomes higher and the degradation processes prevail.

The relations between the degradation and self-annealing processes in the structures and the ways to achieve a long-term stability of laser operation taking into account the annealing and degradation effects of inherent laser light will be discussed in detail.

Photoluminescence Properties of ZnTeO and ZnSeO Alloys with Dilute O Concentrations

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O substituting Se and Te sites in ZnSe and ZnTe, respectively, attracts electron in the host materials, since electronegativity of O is larger than that of other group VI elements. This property works as an isoelectronic trap and studied well for O in ZnTe\cite{1,2}. Increasing the concentration of isoelectronic traps up to alloy formation with the host material, the interaction of the localized energy level of isoelectronic trap with the energy band of the host material occurs, for example, band gap bowing\cite{3}. The roll of isoelectronic trap to the band gap bowing has been extensively investigated in III-V semiconductors such as N in GaP and in GaAs, while very few were reported for II-VI. In this work, we studied the photoluminescence (PL) of ZnTeO and ZnSeO alloys with dilute O concentrations and show that the influence of O on the PL properties is different for ZnTeO and ZnSeO alloys.

ZnTeO and ZnSeO alloys were grown on GaAs (001) substrates by molecular beam epitaxy (MBE) with a RF-plasma source. The growth temperature was 300 °C. We controlled the O concentrations by O\textsubscript{2} flow rate, while RF power was fixed at 50 W. The thicknesses of epitaxial layers were 600-1000 µm. The O concentrations were obtained by either calculation from the lattice constants measured by X-ray diffractions or secondary ion mass spectroscopy (SIMS). PL spectra were measured mostly at 12 K with a He-Cd laser as an excitation source. The dominant peaks of ZnTe without O were the excitons bound to As (1\textsubscript{As}) and to zinc vacancy (V\textsubscript{Zn}). These near band edge peaks disappeared when O was incorporated. A peak due to the isolated O trap appeared at 1.982 eV (A-line), and sharp emissions from OO-pairs were seen at the lower energy side of A-line. These peaks were followed by their phonon replicas. The energies of these peaks did not change even when the O concentration was increased up to 0.1 %, although the broadening of each peak was recognized. The PL spectra of ZnTeO with dilute O concentrations essentially agree with thus far reported\cite{1,2}. On the other hand, near band edge emissions of ZnSe remained when O was incorporated. The peaks of free exciton (FE), acceptor bound exciton (1\textsubscript{deep}), donor-acceptor pair recombination (DAP), and their phonon replicas shifted to lower energies by 7 meV when the O concentration was 0.015 % (3x10\textsuperscript{18} cm\textsuperscript{-3}). The A-line nor OO-pair recombinations were not observed from ZnSeO. Increasing the O concentration, the peak energies of FE continuously decreased as previously found\cite{3}, and a new peak of bound exciton became dominant at the lower energy side of FE when the O concentration was higher than 0.02 %. The different PL features of ZnTeO and ZnSeO can be related to the larger difference in electronegativities between Te and O compared to that between Se and O.

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Composition Control of ZnSSeO Quaternary Alloys Grown on GaP

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ZnO, ZnS and ZnSe are known as wide bandgap semiconductors for optical devices operated at ultraviolet and blue wavelength region. The largest electronegativity of O among the group VI elements induces large bandgap bowing in ZnSeO and ZnSSeO alloys\cite{1,2}. The bandgap bowing is attractive from the point of bandgap engineering. In order to obtain the advantage of this Zn-VI-O alloy, ZnSSeO quaternary alloy lattice-matched to GaP and Si is expected, since its bandgap energy is estimated to range from infrared to ultraviolet by adjusting group VI compositions. In this study, we investigated the controllability of group VI composition in ZnSSeO quaternary alloy to lattice-matched to GaP and we show the structural and optical properties.

ZnSSeO alloys were grown on GaP (001) substrates by MBE equipped with a RF radical cell. GaAs (001) substrates were also used for the references. Growth temperature was 300 °C. We used ZnS as a S source. The compositions of group VI elements were controlled by supply amount of Se and S sources, while O\textsubscript{2} flow rate and RF power were fixed at 0.1 ccm and 50 W, respectively. ZnSe reference sample of 26.5 % S composition was grown under cell temperatures of Se (T\textsubscript{Se}) and ZnS (T\textsubscript{ZnS}) at 155 °C and 950 °C, respectively.

XRD spectra of all samples revealed single peak from ZnSSeO layers. Together with in-situ RHEED observation, the crystal structure of grown ZnSSeO was found to be zincblende and phase separation was not detected. The lattice constant was able to be matched to GaP when T\textsubscript{Se} and T\textsubscript{ZnS} were 145°C and 950 °C, respectively, as shown in Fig. 1. The O and S compositions of this lattice-matched sample were 10% and 51%, respectively. The lattice constant decreased by increasing T\textsubscript{ZnS} and increased by increasing T\textsubscript{Se}, within the investigated composition range. The decreases of T\textsubscript{ZnS} and T\textsubscript{Se} both resulted in slight increase of O composition. PL spectra measured at 12K showed near band edge emission and the intensities were higher from samples grown on GaP than those on GaAs. The bandgap energy obtained by PR at room temperature almost followed the estimated value taking large bowing into account.

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\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{(004) XRD spectra of ZnSSeO grown with different T\textsubscript{Se} on GaP substrates.}
\end{figure}

Optical and Electrical Properties of ZnO:Ce Layers

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In recent years there has been great interest in the oxide semiconductor ZnO and its ternary alloys for the sake of its good piezoelectric, photoelectric and optical properties. Zinc oxide also exhibits luminescence properties and light sensitivity.

ZnO is a direct band-gap (3.3 eV) II–VI semiconductor material and these layers can be used for applications like surface acoustic wave devices, low-loss optical waveguides, transparent conductive electrodes and varistors for devices like mobile phones. Until now, ZnO thin films have been prepared by a number of techniques such as spray pyrolysis, RF magnetron sputtering, pulsed laser deposition, laser molecular beam epitaxy, sol-gel.

We have studied ZnO:Ce layers deposited by reactive chemical pulverisation spray pyrolysis technique using zinc and cerium chlorides as precursors at temperatures up to 500°C. The temperature dependence (15K-room) of the photoluminescence emission spectra (PL) under continuous excitation (cadmium helium laser) and photoluminescence excitation spectra (PLE) under steady-state conditions have been studied. The thermal quenching of photoluminescence was observed. The photoluminescence spectra of these films have been also studied as a function of doping concentrations. We have also investigated the effect of Ce concentration on the studied structures. Electrical and structural properties of ZnO:Ce layers were studied using Two and Four Probe Method and X-ray diffraction. We observed dependence of conductivity on dopant Ce in ZnO (in temperature interval from 95K, to 380K, and concentration of Ce in ZnO substrate in interval from 0% to 20%) respectively. Our results are showed that dopants Ce have big ascendancy on conductivity in ZnO substrate.

The X-ray diffraction analysis indicates that all films are polycrystalline in nature and clearly shows the appropriate incorporation of Ce atoms in the ZnO films. The carrier concentration ($n$) and mobility ($\mu$) values are estimated by measuring Hall voltage at the temperature range from 77K to 350K. A strong correlation between the structural and electrical properties is observed. The surface morphology characteristics of the films deposited on glass and silicon substrates, as a function of the deposition temperature, will be presented. The dopants impurities, introduced into the ZnO nanostructures, can modulate the local structure and cause the dramatic change which can lead to an increase of their nonlinear optical properties. The chemical composition of the films as determined by energy dispersive spectroscopy is also reported. The ZnO layers display three major PL peaks at 378nm (near-band edge emission peak), 510nm and 650nm. The green emission and red emission are probably associated with the oxygen vacancies and interstitial Zn ions in the ZnO lattice. The influences of Ce concentration on the nonlinear optical properties using THG technique will be presented.

Cr-doped diluted magnetic semiconductors have recently attracted much attention, owing to their ferromagnetism without heavy p-type doping as predicted theoretically [1] and demonstrated experimentally [2]. ZnS has a large bandgap (3.7 eV at RT) and is a host material of efficient visible phosphors. Therefore, ZnCrS is a potential material which provides both optical and magnetic functions. In the previous studies on ZnCrS as materials for diluted magnetic semiconductors [3] or tunable infrared lasers [4], the Cr content was typically small ($x<0.01$ in Zn$_{1-x}$Cr$_x$S) and the crystals often contained poly-type structures. Thus solubility of Cr in ZnS as well as crystal structures of ZnCrS was not fully understood.

In this paper, we present molecular beam epitaxy (MBE) growth and characterization of ZnCrS. We have mainly investigated structural properties of this alloy system grown by the non-equilibrium growth technique, including the dependence of the crystal structure and the lattice constant on the Cr content. We show that zinc blende Zn$_{1-x}$Cr$_x$S layers with the Cr content $x$ of up to 0.015 were epitaxially grown.

ZnCrS layers were grown on (001) GaP substrates by MBE using elemental Zn, Cr and S as source materials. The composition of the layers was evaluated by an electron probe microanalysis and the crystal structure was characterized by a X-ray diffraction (XRD) measurement. The Cr content was controlled by adjusting the Cr cell temperature, and the maximum Cr content $x$ was approximately 0.04 for the Cr cell temperature of 1200 °C which was the highest operating temperature in our MBE system. For the small Cr content, i.e., $x<0.02$, the XRD pattern was similar to that of ZnS epitaxially grown on GaP substrates, suggesting epitaxial growth of zinc blende ZnCrS onto GaP substrates. For the larger Cr content, $x>0.02$, the XRD pattern showed extra diffraction peaks, indicating a phase separation. As for the integrated intensity of the ZnCrS (004) XRD peak, it became weak when the Cr content $x$ exceeded 0.015. From these results, we conclude that zinc blende ZnCrS thin film was epitaxially grown for $x<0.015$. For these single phase zinc-blende crystals, it was found that the lattice constant depends not only on the Cr content but also on the growth conditions. Detailed analyses of these crystals on the structural and magnetic properties will also be presented.

Thermal annealing is one of the most efficient and simple technologies, to improve the quality of ZnO thin films [1]. At present, different sophisticated schemes of thermal annealing arrangement are applied, such as face-to-face annealing [2] and in-situ thermal annealing [3]. For undoped ZnO, annealing in oxygen or ambient atmosphere provides a maximum effect of oxygen in the films resulting in reduction of native point defects. For doped ZnO annealing serves to place impurity ions to lattice sites, creating acceptor centers [4]. Another interesting and desired trend is to obtain highly conductive transparent films for invisible electronics [5]. In this study, we have investigated the influence of thermal annealing on the electrical, structural and morphological properties as well as transparency of Ga-doped ZnO films. Gallium is less reactive and more resistive to oxidation. Ga exhibits a similar atomic radius as Zn compared to the commonly used Al. Zinc oxide thin films, doped by Ga (1%, 3%, 5%, 10% wt) were prepared on Al2O3 (0001), Si/SiO2 and glass by plasma enhanced metalorganic chemical vapor deposition (PEMOCVD) at substrate temperature of 250°C. The samples have been characterized by electrical and optical measurements, XRD and AFM analysis. The resistivity, transmittance, as well as structure and morphology were investigated for as-grown films and compared with results for films annealed in ambient air at 800°C during 2 hours. The transmittance of the films improves after annealing. The intensity of 0002 X-ray diffraction peak is enhanced after annealing procedure because of redistribution of the grains in ZnO polycrystalline films due to increasing the average grain size (preferentially of the grains with orientation 0002, as grains with a lower surface energy). Since PEMOCVD is a non-equilibrium process only a part of the Ga atoms substitute Zn on the lattice sites, while the rest become interstitials. During thermal annealing Ga atoms migrate from interstitials to lattice sites, thus providing additional charge carriers. A correlation between the Ga content and the material properties of the annealed ZnO films will be discussed. The results obtained suggest that the applied thermal annealing procedure does improve electrical, structural and optical properties of ZnO films doped by Ga.

Towards Electrically Pumped Mid Infrared Lasing in ZnCrSe

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Since 1996, when tunable (2.2-2.8 \( \mu \)m) lasing was obtained in ZnSe:Cr crystals by DeLoach and coworkers [1], several groups demonstrated a very efficient laser emission from this material [2,3]. All these groups used resonant pumping of Cr\(^{2+}\) in the region of 1.5-2 \( \mu \)m. This activity was stimulated by a number of very important applications of such lasers in medicine, biochemistry, environmental monitoring, etc. Naturally, it would be important to find a way to obtain laser emission from ZnCrSe under electrical pumping, i.e., to design a tunable laser diode operating in Mid Infrared (MIR) spectral range. In this communication we discuss possibilities to obtain such laser emission from ZnSe:Cr, by exciting Cr\(^{2+}\) intra-shell transition by non-equilibrium carriers.

Recently we demonstrated a stimulated emission from ZnSe:Cr, which was induced by chromium photo-ionization (Cr\(^{2+}\) to Cr\(^{+}\)) [4]. Now we performed detailed investigations of MIR laser emission in chromium doped ZnSe crystals and MBE-grown structures under photo-excitation of non-equilibrium carriers. Stimulated emission was achieved from microchip lasers prepared from PVT-grown ZnSe crystals doped with chromium during a growth process, with Cr concentration from \( 5 \times 10^{18} \) to \( 3 \times 10^{19} \) cm\(^{-3}\), and from MBE-grown ZnCrSe layers grown on (100) GaAs wafers. Cleaved (110) faces of the crystals created Fabri-Perrot type cavity of these microchips, with a typical length of about 2 mm. From MBE-grown samples strips with 1 mm length were cleaved. Transversal pumping of microchips by pulsed OPO system, operating in 430-580 nm spectral range, induced a stimulation emission at 2.45\( \mu \)m, with slope efficiency of more than 20 \%, depending on Cr concentration. We investigated spectral and temporal characteristics of this stimulated emission, which enables us to discuss possible mechanisms of lasing. Our results indicate that MIR laser emission under electrical (injection) pumping is possible in Cr doped wide band gap II-VI semiconductors. Summarizing, in this communication we discuss a possible design of MIR laser diode based on Cr doped II-VI compounds.


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Fabrication of ZnO Quantum Dots Using Silicon Oxide and Rapid Thermal Annealing

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The need for blue and ultraviolet (UV) solid-state emitters and detectors has propelled the investigation of several wide-band-gap semiconducting materials in recent years. ZnO, a II-VI compound, is known to be the brightest emitter among wide-band gap semiconductors. In order to develop high efficiency devices, quantum dots are of great interest owing to their unique optical properties and potential applications for optoelectronic devices. In recent years, nano-structures of ZnO quantum dots (QDs) embedded in some dielectric matrices have been particularly attractive because of the advantage of stabilizing dots and being adoptable to device manufacturing processes. In this study, we report on the fabrication of ZnO QDs embedded in an amorphous silicon oxide layer.

ZnO thin films were grown on Si (001) and c-sapphire substrates at room temperature (RT) by radio-frequency magnetron sputtering. SiO\textsubscript{2} thin films were deposited on the ZnO films by plasma-enhanced chemical vapor deposition. ZnO QDs have been fabricated by the growth of SiO\textsubscript{2}/ZnO films/Si substrate and subsequent rapid-thermal-annealing (RTA) from 450 to 850 °C for 15 s – 3 min in N\textsubscript{2} ambient.

Transmission electron microscopy (TEM) results show that the ZnO QDs 3–7 nm in size are formed and embedded in the amorphous silicon oxide interfacial layer when annealed at 850 °C. Photoluminescence (PL) emission spectra of ZnO films, monitored from 3.360 eV to 3.383 eV, are observed at RT, while PL at 10 K shows broad spectra with a tail up to about 3.5 eV. It was further shown from the PL measurements that the optical properties are improved with increasing annealing temperature and time. The TEM and PL results indicate that the broadening and blue shift of the 10 K PL main peaks are caused by the size effects of the ZnO QDs and hence by the quantum confinement effect.
Self-assembly ZnO Nanorods Growth Using Polymers as Media

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Semiconductor ZnO has a wide band gap of 3.37 eV and a large excitation binding energy of 60 meV and displays excellent piezoelectric and optical properties. In particular, since UV emission at room temperature was demonstrated in ZnO nanowires, one-dimensional nanomaterials have increasingly drawn attention. Many attempts have been made to fabricate ZnO nanowires or nanorods, owing to their promising use in ultraviolet light emitting and lasing devices. A novel process using PVA as self-assembly media for preparing well-aligned crystal ZnO nanorods on a Si (111) substrate without metal catalyst is presented in this paper. The repeat structure unit of the polar polymers, like a chitosan or PVA, has ligands that permit transition metal ion coordination, and has similar capability of complexing along the polymer chain. These properties would automatically generate such a regular structure that the nanoseeds formed by this method are of similar dimensions and are evenly distributed throughout the substrate. In this novel process, zinc ions in the aqueous solution containing Zn(OOCCH3)2, driven by an electrostatic force, were first complexed the OH groups on the PVA chains to synthesize highly regular Zn(OH)2 in an alkali condition, then the Zn(OH)2 transformed into the ZnO at temperature of about 125°C, whose seeding and growing could be adjusted by the size of grids formed with PVA chains determined by the PVA concentration in an aqueous solution, and finally the ZnO nanoseeds grew up into well-oriented nanorods on a Si substrate in zinc and oxygen vapors and the polymer decomposed into carbon backbone grids at temperature of about 210°C that would confine the transverse growth and lead to the orientational growth of ZnO nanorods, whose microstructures can be affected by the temperature of the vapor growth as well as the zinc/oxygen flow rate ratio.

The results of XRD, Raman and FE-SEM indicate that the ZnO nanorods are evenly distributed on the substrate and possess a hexagonal wurtzite structure with preferred c-axis orientation and trend perpendicular to the substrate surface. TEM micrographs of ZnO nanorods show that they have a straight and uniform shape and length of up to about 0.5 – 3 µm, depending on the vapor growth time. Typical HRTEM lattice fringes image and selected area electron diffraction (SAED) pattern reveal that the nanorods possess a single crystal hexagonal structure without dislocations and stacking faults. The image also confirms that the nanorods grow along the [0001] direction. The room temperature PL spectra of the ZnO nanorods exhibit a strong UV emission of about 386 nm and a weak green emission of around 506 nm. They are quite different from those of the metal-catalyzed grown ZnO nanorods reported in the literature. The effects of different synthesis conditions, such as the PVA concentration, the growth temperature, the zinc/oxygen flow rate ratio, and etc. on the microstructures and the optical properties of the ZnO nanorods are discussed.

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Heteroepitaxial structures based on the material system ZnO and Zn$_{1-x}$Mg$_x$O can be used to fabricate ultraviolet light-emitting devices. To this end it is necessary to incorporate a sufficient amount of Mg into ZnO without phase separation and to produce smooth interfaces. We will report on the fabrication of Zn$_{1-x}$Mg$_x$O epilayers as well as ZnO/Zn$_{1-x}$Mg$_x$O quantum well (QW) structures by radical source molecular-beam epitaxy using elemental sources. Zn$_{1-x}$Mg$_x$O was grown at relatively low-temperatures using a-plane sapphire (11-20) as substrate. We revealed that a post-growth annealing of Zn$_{1-x}$Mg$_x$O epilayers at intermediate temperatures yields high-quality layers with very smooth surfaces. The observation of a streaky RHEED pattern typically with a (3x3) reconstruction as well as pronounced oscillations of the specular beam intensity confirm the two-dimensional nature of the films and the smoothness of the surface.

The Zn$_{1-x}$Mg$_x$O layers were characterised ex situ by X-ray diffraction (XRD), atomic force microscopy (AFM) and electron microprobe technique. The optical properties were investigated by transmission and photoluminescence spectroscopy. According to XRD measurements, the $c$- lattice constant decreases linearly with increasing Mg content and reaches a value of 5.143 Å. This is the lowest ever observed $c$- lattice parameter in Zn$_{1-x}$Mg$_x$O epilayers. The optical band gap energy, determined from room temperature transmission measurements, shifts above 4 eV for epilayers with the highest Mg concentration. AFM data yielded a typical value of the root mean square roughness of the Zn$_{1-x}$Mg$_x$O surface after thermal annealing below 0.7 nm for all grown structures.

These results enabled us to fabricate ZnO/Zn$_{1-x}$Mg$_x$O QW structures using Zn$_{1-x}$Mg$_x$O as barrier layers. For the first time, pronounced oscillations of the specular beam intensity could be observed at each interface during formation of the heterostructure (Fig. 1). This confirms the smoothness of the interfaces and gives a means to control precisely the thickness of the QW.

![Fig. 1. RHEED specular beam intensity oscillations recorded at each interface of a QW structure.](image)
Study of Photoluminescence from Annealed Bulk-ZnO Single Crystals

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ZnO is an II-VI compound semiconductor with a wide-bandgap of 3.37eV at room temperature, which has great potential for a variety of commercial applications including substrates, acoustic wave devices, LED, LD and high frequency electronic devices. Since ZnO epilayers have been usually grown on the substrate of Al\textsubscript{2}O\textsubscript{3}, both a large residual strain and structural defects exist in the epilayers. Therefore, it is more suitable to grow the high-quality ZnO homoepilayer on the ZnO substrate. Recently, the hydrothermal method combined with a Pt inner container was applied to grow the large-sized ZnO single crystals with a large size of 50x50x15mm\textsuperscript{3}. The full-width at halfmaximum (FWHM) of X-ray rocking curves for (002) reflections of the ZnO single crystal is 8 arcsec for the hydrothermally grown ZnO single crystal[1]. The speed in developing ZnO homoepitaxy will be accelerated in future. However, the crystal quality of ZnO crystal is determined not only by the growth process, but also by the post-growth treatment. In this paper, we report the influence of thermal annealing on the photoluminescence (PL) properties of bulk-ZnO single crystal. The samples used in the present studies were commercial ZnO(0001) single crystals grown by hydrothermal method. After chemical etching using 20\% HCl at room temperature, the samples were annealed by the rapid thermal anneal system at a temperature in the range of 400-1200°C in O\textsubscript{2}/Vac atmosphere for 60s. The PL spectral measurement was carried out at liquid helium (4.2K). The PL spectrum of as-grown ZnO crystal was dominated by strong emission at 3.360eV due to the radiative recombination bound to neutral donors (D\textsuperscript{0}, X). Although the DoX emission had dominated the PL spectrum in spite of the annealing temperature, the emission line shifted towards lower energy side. On the other hand, the new emission line appeared at 3.330eV with increasing the annealing temperature. These results indicate some unknown defects and/or dislocation are induced by the heat treatment. Their detailed PL and RF spectra will be presented and discussed at the conference.

ZnO has attracted much attention due to the potential for applications in the fields of optoelectronic devices. The intrinsic luminescence of ZnO is in the ultraviolet region and attributed to the recombination of free exciton (FE), and in ZnO crystal involving oxygen vacancies, a broad and green luminescence band is also observed [1]. ZnO crystal in which many oxygen vacancies are introduced at the surface is called ZnO:Zn, which is utilized as a typical green phosphor. In ZnO:Zn, the FE luminescence is hardly observed under photoexcitation at room temperature, since excitons are separated into electrons and holes because of the existence of electron field in the surface depletion layer.

Cathodoluminescence (CL) spectroscopy is one of the techniques to obtain extremely high spatial resolution beyond the optical diffraction limit. Cathodoluminescence means the luminescence from a substance excited by an electron beam. Single particle with nano scale can be spatially resolved in CL measurement due to the high lateral resolution. In addition, the mean penetration depth of incident electrons can be controlled by changing accelerating voltage of electron beam [2]. Electrons with high momentum energy are able to penetrate deeper than photons which penetrate at most to the depth corresponding to the reciprocal of absorption coefficient. Therefore, internal optical properties of substances, which are not detected under photoexcitation, can be examined by means of the CL spectroscopy. In the present work, we measured CL spectra of ZnO:Zn microparticles for various excitation conditions to investigate optical properties at each spatial position of the particle. From the measurement of accelerating voltage dependence of luminescence spectra, influences of the relation between the depletion layer and the excitation depth on the recombination processes of FE are studied. For low accelerating voltage in which the penetration depth of incident electrons is comparable to the reciprocal of absorption coefficient of photons, the green luminescence is dominant and the FE luminescence in the ultraviolet region is hardly observed similar to the case of photoexcitation. On the other hand, the FE luminescence appears for the accelerating voltage in which the penetration depth of incident electrons is several times larger than the reciprocal of absorption coefficient. The luminescence is extremely enhanced under the condition that the penetration depth corresponds to the diameter of the electron-injected ZnO:Zn particle. For the penetration depth beyond the particle diameter, however, the intensity of FE luminescence does not increase with the accelerating voltage. It is found from these results that the width of the depletion layer in the measured ZnO:Zn particle is the order of the reciprocal of absorption coefficient and excitons can be created and recombine radiatively by injecting electrons into the inner region of the particle. The efficiency of the radiative recombination is improved by setting the excitation volume to the particle size.

Effect of GaN Buffer Layers on the Polarity and Properties of ZnO Epilayers Grown on Nitrided c-Al$_2$O$_3$ by MBE

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In the heteroepitaxy of ZnO on c-plane sapphire, we have already reported that the sapphire-nitridation and following deposition of GaN buffer layers are effective on both the suppression of rotation domains and the crystalline quality-improvement of ZnO epilayers. Further, it was found that the deposition conditions of GaN buffer layers such as growth temperature and surface stoichiometry affected the polarity of ZnO epilayers [1].

In this paper, we investigated how the deposition temperatures of the GaN buffer layer affected the polarity of ZnO epilayers and their properties such as structural, optical, and electrical properties. The deposition temperatures of GaN buffer layers were classified into two regions, i.e., low-temperature (LT) at around 650°C and high-temperature (HT) at around 850°C. ZnO epilayers were grown on deeply nitrided c-plane sapphire with LT-GaN and HT-GaN buffer layers by MBE using elemental-Zn and plasma-excited oxygen sources. The epilayer thickness was about 280-450 nm.

Zn-polar ZnO was normally obtained by using the LT-GaN buffer layer. The full width at half maximum (FWHM) values of (002) and (102) $\omega$-scans were 73 and 585 arcsec, respectively. The FWHM values of the O-polar ZnO epilayers grown with the HT-GaN layers were around 140~160 arcsec for (002) and 690~770 arcsec for (102) $\omega$-scans, respectively.

Figures 1 (a) and (b) show typical PL spectra for ZnO epilayers with LT-GaN and HT-GaN buffer layers, respectively. Since the strain in the epilayers affect the position of emission peaks, the phase-shift reflectance spectra between s- and p-polarized light were also analysed to determine the free exciton emission peaks. Further, the strains in the epilayers were also carefully analysed by HR-XRD. The dominant PL peaks were originated from bound excitons and tentatively labelled as donor-bound exciton ($D_0X$) at 3.361 eV and acceptor-bound exciton ($A_0X$) at 3.355 eV, respectively. In this paper, PL spectra observed in ZnO epilayers with different GaN buffer layers are intensively discussed.

Fig. 1 PL spectra of ZnO epilayers grown with (a) LT-GaN and (b) HT-GaN/LT-GaN buffers.

Influence of the Ex-situ and In-situ Annealed Self-buffer Layer on ZnO Films

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ZnO is a very important oxide semiconductor with a direct wide-band-gap (3.37eV) and a high exciton binding energy (∼60meV). It has many interesting applications, especially in blue and ultraviolet light region. In order to obtain high crystal quality ZnO film, many growth techniques such as sputtering, PLD, MBE, MOCVD and so on, have been applied and the influence of buffer layer or annealing on the film has been investigated. For the influence of the ex-situ and in-situ annealed self-buffer layer on ZnO films grown by atmospheric MOCVD method using DEZn, tert-butanol as precursors and H₂ as carrier gas, there is no reports to our knowledge. Here, we present our studies on this problem. Two kinds of self-buffer layer were grown on c-plane sapphire substrates by atmospheric MOCVD method using DEZn, tert-butanol as precursors and H₂ as carrier gas. They were respectively annealed in growth environment and oxygen environment at 600°C for 0.5 hour. After that, ZnO films were grown on them. XRD spectra show that all the films were grown in [002] orientation. Furthermore, the film with a buffer layer annealed in oxygen exhibit much higher crystal quality. Its FWHM of the rocking curve is only 567 arcsec. The Raman scattering spectrum of this sample appears a much stronger E₂ mode peak at 436 cm⁻¹ and its PL spectrum appears a shoulder at 3.367 eV on the higher energy side compared with the sample with the in-situ annealed buffer layer. All above indicate that the self-buffer layer annealed in oxygen can greatly improve the crystal quality of ZnO films grown by atmospheric MOCVD method using DEZn, tert-butanol as precursors and H₂ as carrier gas.
The effect of Oxygen Partial Pressure During p-ZnO Growth on ZnO Homojunction Light Emitting Diode

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To date, p-n heterojunction ZnO light emitting diode (LED) have been successfully fabricated by depositing n-ZnO on other p-type materials such as NiO, Si, GaN, and AlGaN. Although ZnO homojunction LED recently showed rectifying I-V characteristics and electroluminescence (EL) at room temperature, EL emission peak was not from the energy bandgap of ZnO. We inserted the ZnMgO barrier layers between n- and p-ZnO for carrier confinement to increase the radiative recombination efficiency of electron-hole pairs and prevent the recombination of carriers in p-ZnO region. We further investigated the effect of oxygen partial pressure during p-ZnO on the performance of ZnO LED with a size of 300 × 300 µm². The ZnO LEDs showed clear rectification with a threshold voltage of 3.3 V which was in a reasonably good agreement with the bandgap energy of ZnO as shown in Fig 1. The breakdown voltage of about 4 V and a small reverse current of about 10⁻⁶ A were measured. The EL emission was observed at 385 nm with a broad deep-level emission at around 600 nm at an injection current of 40 mA as shown in Fig. 2. The peak at 385 nm was due to the bandedge emission from the ZnO well layer. The ZnO LED with a p-ZnO grown under a higher oxygen partial pressure showed stronger deep level emission as shown in Fig. 2(a). The more intense broad deep-level emission shown in Fig. 2(a) was attributed to the oxygen interstitial defects in the p-ZnO layer. There are two possible reasons. The increase in the deep-level emission indicated that the UV light absorbed in the p-ZnO layer and carriers might overflow into p-ZnO layer via the inserted ZnMgO barrier layer.

![Fig. 1](image1.png)

![Fig. 2](image2.png)
Photoluminescence Spectroscopy of Single Crystalline ZnO-Nanoparticles from the Gasphase

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ZnO nanostructures have attracted great interest because of their wide application potential e.g. in UV optoelectronic devices. A challenge, however, is the preparation of nanoscale material with high crystalline quality, well defined size and good optical properties. E.g. vacancies in the crystal quite often lead to a broad green defect emission band in addition to the near band edge emission [1]. In this work we present photoluminescence measurements on ZnO nanoparticles that were synthesized by chemical vapour synthesis (CVS). It will be shown that the green band can be almost completely suppressed by the right choice of the processing parameters.

As can be seen in Fig. 1 the total intensity of the near band edge emission \( I_B \) strongly increases with sintering temperature [2]. On the other hand for high temperatures the total intensity \( I_D \) of the green emission band decreases and is almost suppressed for temperatures above 500 °C. As both, the crystalline quality and the particle size depends on the sintering temperature, increasing the temperature leads to a variation of the surface to volume ratio which might influence the defect emission. In order to separate these effects, we prepared size selected nanoparticles at a sintering temperature of 900 °C with an average diameter of 10, 20 and 30 nm, respectively. The inset in Fig. 1 reveals that there is no substantial change for \( I_D/I_B \) with particle diameter. Even for particle diameters down to 10 nm almost no defect emission is observed and spherical, single crystalline nanoparticles were obtained [2], emphasizing the high quality preparation route. Temperature and excitation dependent photoluminescence measurements indicate the impact of free and bound exciton recombination on the optical properties of the ZnO nanoparticles.

MOVPE-grown ZnCdSe/ZnSSe Structures for Blue VCSEL with Resonant Periodic Gain

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VCSEL with optical and electron beam pumping can be used as a light source for rear projection television [1]. Another alternative is to use an external cavity mirror to transform a high efficiency GaN-based laser diode into high quality blue laser [2]. For such lasers it is preferable to use thick (5-10 µm) MQW resonant periodic structures which QWs are placed at antinodes of cavity mode being at gain maximum. To obtain blue (455-465 nm) lasers in MQW structures it is necessary to utilize compounds with a wide band gap ($E_g \approx 3.0$ eV). ZnMgSSe matched to GaAs is a suitable material for barrier layers while ZnSSe or ZnSe may be used as the QW material in the blue spectral range. However matched ZnMgSSe with $E_g \approx 3.0$ eV is in the region of its metastable phase and is close to the instability region boundary [3]. The decay of ZnMgSSe solid solution in two or even more phases leads to a significant decrease in the transport of nonequilibrium electrons and holes generated in the ZnMgSSe barrier layers to the QWs and consequently increasing laser threshold. This work studies an alternative way to create blue laser on basis of ZnS$_x$Se$_{1-x}$ with $x = 0.3-0.4$.

ZnCdSe/ZnSSe MQW structures were grown by MOVPE on ZnSSe(001) substrates in a custom built horizontal quartz reactor in hydrogen at atmospheric pressure and $T = 425$ °C using diethylzinc (Et$_2$Zn), dimethylcadmium (CdMe$_2$), diethylsulfide (Et$_2$S) and dimethylselenide (Me$_2$Se) as precursors. The substrates were cut from ZnSSe single crystal grown by physical transport in helium on seed [4]. After cutting, the substrate surface was polished and etched in solution of CrO$_3$ in HCl. The ZnSSe buffer, barrier and top layers were practically matched to the ZnSSe substrate and had thickness of about 0.2 µm. ZnSe or ZnCdSe QW thickness was from 4 to 7 nm. The number of the QWs was up to 40.

Cathodoluminescence of 5 QW structure is presented in Fig. 1. We obtained intense QW emission at RT due to high enough transport of nonequilibrium carriers from the ZnSSe barrier layers into the ZnCdSe QWs. RMS of the surface roughness measured by AFM was about 2 nm. Based on the structure with 30 QWs a microcavity was formed and lasing was studied. Detail characteristics of the ZnSSe substrates, the MQW structures and the laser will be presented.

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Structural and Optical Properties of ZnO Thin Films by Plasma Enhanced Chemical Vapor Deposition

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ZnO thin films were grown by radio frequency plasma enhanced chemical vapor deposition technique on silicon wafers and corning 7059 glass substrates kept at different substrate temperatures ranging from 36 to 400°C with different gas flow ratios. While diethylzinc (DEZ) was used as the source precursor for the preparation of ZnO films, H\textsubscript{2}O and argon were used as oxidizer and carrier gases. Structural and optical properties of these films were investigated using various characterization techniques. X-ray diffraction studies revealed highly oriented films with (002) preferred orientation at a substrate temperature of 300°C with DEZ/H\textsubscript{2}O flow rate ratio 1:4 at 50W of r.f. power. The elemental analysis of the films performed using X-ray photoelectron and Auger electron spectroscopy showed the presence of zinc and oxygen. A textured surface with r.m.s. roughness $\sim$28 nm was observed by atomic force microscopy for the films deposited at 300°C. Optical band-gap was estimated from the transmission spectra recorded by UV-VIS spectrophotometer. A sharp peak at 380 nm in the photoluminescence spectra indicated the UV band-edge transition.
Growth of ZnO by Oxygen Plasma Assisted Pulsed Laser Deposition on Al₂O₃ (0001)

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In recent years considerable research activities have been devoted to the wide bandgap semiconductor ZnO. The revived prospects to use ZnO in (opto-)electronic devices are based on the major advances in thin film epitaxy of this material. Among the various growth techniques, pulsed laser deposition [1] and oxygen plasma assisted molecular beam epitaxy [2] have been shown to yield highly promising epitaxial ZnO layers on c-axis oriented Al₂O₃ substrates. Nevertheless, p-type doping of ZnO films is still an open issue which to date prevents the fabrication of efficient bipolar devices. A pre-requisite on the way to reasonable p-type material is the ability to grow nominally undoped layers with a low residual carrier concentration. Control of Zn/O stoichiometry is crucial in this context. In this work we use a RF oxygen plasma assisted pulsed laser deposition (PA-PLD) process to vary the amount of reactive oxygen species impinging onto the substrate in order to tune the stoichiometry in our ZnO films. We find that the morphological, electrical and optical properties of the grown layers are strongly affected by the RF power.

Our samples have been grown on c-plane Al₂O₃ in a custom built MBE/PLD chamber (base pressure 2×10⁻¹⁰ mbar) by PA-PLD. Sintered ZnO (5N) powder and a KrF excimer laser (λ=248 nm, 2 Hz, 1-2 J/cm²) have been used as target and light source, respectively. The target substrate distance was 10 cm. In contrast to conventional PLD of ZnO we supply oxygen (6N) through a RF plasma source (SVT-Associates) maintaining an oxygen flow of 4 sccm and varied RF powers 0-250 W. Thereby we are able to tune the reactivity of the oxygen species at the substrate while keeping the background oxygen pressure at 2×10⁻⁴ mbar. Samples with a thickness of about 200 nm were grown at substrate temperatures between 650 °C and 700 °C without the use of an optimized buffer process. In-situ RHEED monitoring indicates a 3D growth at the initial stages which transforms to a streaky RHEED pattern after a few minutes of growth. A smooth surface with an rms roughness of 0.6 nm is found for the samples grown at RF powers of 250 W. At lower RF powers the RHEED pattern becomes increasingly spotty indicating 3D growth due to oxygen deficiency. The FWHM of the (0002) rocking curves has been determined by HRXRD and varies between 1100 arcsec (0 W) and 240 arcsec (150 W), indicating reasonable material quality taking into account the absence of an optimized buffer. Room temperature Van der Pauw Hall measurements yield carrier densities around 10¹⁶ cm⁻³ at 250 W and 8×10¹⁸ cm⁻³ at 0 W. Photoluminescence measurements at 50 K exhibit a strong excitonic emission at 3.35 eV which is 10 times more intense in the case of the samples grown at 0 W compared to those grown at 250 W. In the oxygen rich samples clearly visible red luminescence is found at 680 nm indicating the presence of interstitial oxygen. Work aimed at the optimization of the structures by introduction of a buffer layer is in progress.

Spin flip Raman Spectroscopy on Heavily Doped Zn\((1-x)\)Mn\(_x\)Se Layers and Quantum Wells

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For spin-based information technology (spintronics), II-VI dilute magnetic semiconductors (DMS) are very promising materials. Optical methods play an important role as a tool for the analysis of the material properties and for understanding the material systems.

In the center of interest are spin-related phenomena in an external magnetic field, especially for heavily doped samples. For this purpose we apply spin flip Raman spectroscopy from free electrons under resonant excitation at the fundamental band gap. Using two different scattering geometries (forward scattering vs. backward scattering) we can determine material parameters like spin diffusion coefficient \(D_s\) and spin relaxation time \(T_2\).

Our SFRS experiments are performed at \(T=1.6\) K in B-fields up to 7 T. We focus on (Zn,Mn)Se based layers: bulk-like (Be,Zn,Mn)Se epitaxial films with electron concentrations between \(10^{17}\) cm\(^{-3}\) and \(10^{19}\) cm\(^{-3}\) and modulation doped (Be,Zn)Se/(Zn,Mn)Se quantum-wells with a two-dimensional electron gas \((10^9\) cm\(^{-2}\) up to \(10^{11}\) cm\(^{-2}\)). The quantum well widths are between 50 nm and 10 nm. Analysis of the spin flip Raman-signal yields the Mn-concentration, the effective g-factors as well as the effective Mn-temperature. We studied the behavior of conduction band electrons near the metal to insulator transition. Varying the doping level we observed a systematical broadening of SFRS linewidth with increasing electron concentration. Furthermore, the linewidth in backward scattering geometry is significantly higher than in forward scattering. Following theoretical predictions for doped samples, we deduce from this systematics the values of \(D_s\) and \(T_2\). The obtained results agree with electrical characterisations and theoretical predictions [1].

Moreover, investigations of the SFRS peak half width in dependence of the excitation energy show an inhomogeneous broadening, probably induced by Mn concentration fluctuations. Thus, we exploit selective resonance conditions for regions with different Mn content by exciting with different laser energy.

Peculiarities of Defect Formation Processes in ZnSe Crystals with Isovalent Te Impurity

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Isovalent impurities lead to significant increase of temperature and radiation stability of semiconductor. They are also very important for LED and similar applications because of improving intensity of radiation recombination rate. This paper is dedicated to the analysis of doping technology influence on the ensemble of intrinsic defects for zinc selenide crystals and isovalent tellurium impurity. We used the method of quasi-chemical reactions to calculate equilibrium concentration of intrinsic defects. For correct determination of point defect ensemble in the crystals with tellurium impurity the authors carried out pre-calculation of equilibrium concentrations of intrinsic point defects in initial crystals prior to alloying. The latter were obtained by Bridgeman method from the melt of stoichiometric content under noble gas pressure. Our calculation has shown that dominating vacancies for these crystals are positive single-charged selenium vacancies $V_{Se}^+$ and dual-charged negative zinc vacancies $V_{Zn}^{2-}$, as well as their associates. Namely the latter cause orange luminescent spectra at the energies of about 1.9eV which have donor-acceptor nature. It is worth noting that base crystals without impurity featured weak electron conductivity, and experimentally determined concentration of majority carriers are in the good agreement with calculated one. Isovalent tellurium impurity was introduced in two different ways, namely from the vapor phase and during the crystal growth process. Our analysis has shown that in the latter case formation of the defects take place in the following way: tellurium atoms replace selenium ones in anion sub-lattice, pushing them into interstitial states. Simultaneously, additional generation of zinc vacancies in anion sub-lattice takes place. Therefore, main contributions to defect ensemble come from zinc vacancies $V_{Zn}$ together with selenium and zinc atoms occupying interstitial positions in crystalline lattice (Sei and Zni). Single-charged defects create associates of $V_{Zn}^-Zn_i^+$, causing intensive radiation band at the energies of about 1.7eV. Annealing of the sample in saturated zinc vapors resulted in the shift of the band to 1.9eV. Recombination processes taking place in the system for this case involve $Zn_i$ impurity levels. Doping of ZnSe with tellurium from the vapor phase lead to another shift of the effective radiation band to 2.3eV, caused by transitions with participation of single-charged zinc vacancies. Intrinsic defect concentrations obtained from our calculations are in good agreement with experimental data for luminescent and electrophysical parameters and characteristics.
Optoelectronic Properties of Tin-alloyed Zinc Telluride

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Wide-band II-VI compounds are promising for semiconductor and quantum electronics. Unfortunately, these materials feature self-compensation effects which result in their monopolar conductivity, creating obstacles for p-n junction formation. The same is also true for zinc telluride, which usually has p-type conductivity. In this paper we report about creation of n-ZnTe and present investigation results of its main electric and optical properties. Initial zinc telluride crystals were grown by Bridgeman method from stoichiometric composition. Obtained crystals featured weak p-type conductivity at room temperatures. Activation energy of electrically-active acceptor centers, determined from temperature dependence of conductivity, was in the ranges of 0.15-0.20 eV. These values have good correlation with energies corresponding to dual-charged zinc vacations. Inversion of conductivity type was performed by annealing in isothermal conditions. This process was carried out in pumped out (to residual pressure of 0.013 Pa) and sealed quartz tube, containing the surface and alloying amphoteric tin impurity in opposite ends. Surface layers of annealed samples featured electron conductivity, judging from the signs of thermal voltage and rectification over point contact. Temperature investigations of conductivity have shown that for the room temperatures electrically active centers have the activation energy of about 0.15eV. Optical transmission and reflection spectra for energies 1.0-2.3eV measured before and after alloying are practically the same. Most significant changes are observed for irradiative characteristics of the materials studied. Photoluminescence spectra of initial crystals at 300K are formed with a single green band with a maximum at 2.26eV, which is determined by recombination of free carriers. Alloying with tin leads to complete elimination of this band, and to appearing of another anomalously-wide band, located in the red region of the spectrum. Detailed investigations performed using modulated wavelength revealed four sub-bands contributing the photoluminescence spectrum observed. Dominating sub-band is characterized with energy 1.95eV and is caused by donor-acceptor pairs. The latter most probably include tin atoms, replacing main atoms in cation and anion sub-lattices. Defect formation mechanisms are discussed in connection with alloying regimes intending to improve electron conductivity of the material.
Determination of Crystallography Polarity of ZnO Layers

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ZnO-based material is a good candidate for UV region optoelectronic devices due to its large 60 meV excitonic binding energy and bandgap energy of 3.37 eV.

For wurtzite and zincblende crystal structure materials, the lack of a center of inversion symmetry leads to a define polarity along the <0001> and <111> directions. This is typified by the case of ZnO by the Zn polar (0001) and O polar faces (000 ¯1). This leads various differences in, for example, the crystal growth mode, impurity incorporation, piezoelectric and spontaneous polarizations, and surface stability. Recently, several groups have reported a method to control the polarity of ZnO epilayers by modification of the ZnO/sapphire interface. The method of polarity determination used in these studies is very complicated, for example, coaxial impact collision ion scattering spectroscopy (CAISISS), convergent beam electron diffraction (CBED), scanning probe microscopy (SPM).

In this study, the crystallographic polarity of ZnO layers has been determined by X-ray anomalous scattering at the Zn K-edge as well as by acid etching. Zinc and oxygen polar ZnO layers were grown by RS-MBE by changing the MgO buffer thickness [1].

The structure factor of a general (hkl) X-ray reflection is given by

\[ F(hkl) = \sum_j (f_0 + \Delta f' + \Delta f'') \exp[2\pi i(hx_j + ky_j + lz_j)] \]

where \( f_0 \) is the atomic scattering factor, \( \Delta f' \), and \( \Delta f'' \) are anomalous dispersion corrections. For noncentrosymmetric materials, the reflection intensity of (hkl) and (hkl) planes is different when the effects of anomalous dispersion are significant, and Friedel’s law is broken. We used this difference in diffracted intensity near the Zn K-edge at 1.283 Å in ZnO, because the effects of anomalous dispersion are large near Zn K-edge. The intensity of the (0002) and (0002) reflections from ZnO were obtained as a function of \( \lambda \) from the continuous spectrum of a copper tube. We then calculated the reflection intensity ratio \( R = I(0002)/I(0002) \) near Zn K-edge. The measurement was conducted for both faces of bulk ZnO, and for Zn- and O-polar ZnO epilayers. It was found that \( R = 0.83 \) for both ZnO bulk and ZnO epilayers. The measurement value was similar to the calculated one of \( R' = 0.89 \); the agreement between calculated and experimental values was excellent.

The ZnO polarity was also confirmed by diluted hydrochloric acid. It was found that O polar ZnO is etched faster and the etched surface is uniformly rough, on the contrary, hexagonal shaped etch-pits were observed for Zn-polar ZnO. The results were same for both ZnO bulk and ZnO layers, and for simple X-ray method and the destructive etching technique.

We have determined crystallographic polarity not only for ZnO bulk, but also epitaxial ZnO layers by the simple nondestructive method of X-ray anomalous dispersion as well as acid etching.

In-situ Monitoring of ZnO Growth by Metal-Organic Vapor Phase Epitaxy

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Metal-organic vapor phase epitaxy (MOVPE) is a promising method for the fabrication of ZnO-based semiconductor structures. The growth conditions significantly influence the growth modes, resulting in various different nanostructures as well as smooth epilayers\([1]\). Therefore, understanding of growth mechanism of MOVPE is greatly important and required for the control not only of materials properties and doping processes but also of self-assembly growth processes for novel nanostructures. In this presentation, the results of in-situ monitoring during MOVPE growth using diethylzinc (DEZn; \(\text{C}_2\text{H}_5\text{Zn}\)) and nitrous oxide (\(\text{N}_2\text{O}\)) for zinc and oxygen sources, respectively, are to be shown and discussed.

Vapor phase chemical reactions were analyzed by Fourier transform infrared spectroscopy (FT-IR). Careful analyses of FT-IR spectra against the growth parameters have suggested the following model is proposed as the growth mechanism of ZnO in MOVPE.

DEZn dissociation process is found to be like double beta-hydrogen elimination, not the removal of ethyl radical, which occurs over about 300\(^\circ\)C;

\[
\text{(C}_2\text{H}_5\text{Zn}) \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{Zn} + \text{C}_2\text{H}_4,
\]

because the peaks from ethylene and other hydrocarbon species such as ethane and butane were not detected in the FT-IR spectra. On the other hand, \(\text{N}_2\text{O}\) dissociates into \(\text{N}_2\) and \(\text{O}\);

\[
\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}.
\]

This is supported by the fact that although the \(\text{N}_2\text{O}\) peaks in FT-IR spectra are gradually weakened with the temperature increases, additional peaks, for example those from NO besides the \(\text{N}_2\text{O}\) peaks, are not detected.

In the case for the mixture of DEZn and \(\text{N}_2\text{O}\), it was found that \(\text{N}_2\text{O}\) dissociates below 100\(^\circ\)C, while DEZn dissociates over 300\(^\circ\)C. Therefore, it is suggested that DEZn first reacts with \(\text{O}\) generated due to the dissociation of \(\text{N}_2\text{O}\).

\[
\text{(C}_2\text{H}_5\text{Zn}) + \text{O} \rightarrow \text{C}_2\text{H}_5\text{ZnOC}_2\text{H}_5\text{ and C}_2\text{H}_5\text{ZnOC}_2\text{H}_5 + \text{O} \rightarrow \text{(C}_2\text{H}_5\text{O})\text{Zn}.
\]

\[
\text{(C}_2\text{H}_5\text{O})\text{Zn} \text{ generated from DEZn and O seems to react further by beta-hydrogen elimination over about 300\(^\circ\)C:}
\]

\[
\text{(C}_2\text{H}_5\text{O})\text{Zn} \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{C}_2\text{H}_4\text{ and C}_2\text{H}_5\text{OH} \rightarrow \text{Zn(OH)}\text{C}_2\text{H}_4.
\]

It is concluded that \(\text{Zn(OH)}_2\) is the final product of reaction between DEZn and \(\text{N}_2\text{O}\) in the vapor phase, being transferred to the substrate surface.

On the growing surface, \(\text{Zn(OH)}_2\) changes to \(\text{ZnO}\). \(\text{ZnO}\) growth on a- or c-face sapphire occurs either +c or −c direction. In the case of the +c direction growth, \(\text{O}\) atoms in \(\text{Zn(OH)}_2\) bind to \(\text{Zn}\) atoms on the \(\text{ZnO}\) surface. On the other hand, in the case of the −c direction growth, \(\text{Zn}\) atoms in \(\text{Zn(OH)}_2\) bind to \(\text{O}\) atoms on the \(\text{ZnO}\) surface. Then, \(\text{H}_2\text{O}\) molecules are eliminated from \(\text{Zn(OH)}_2\) chemisorbed on the \(\text{ZnO}\) surface;

\[
\text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O}.
\]

Actually, \(\text{H}_2\text{O}\) is detected by FT-IR during the \(\text{ZnO}\) growth, supporting the reaction processes here proposed. Discussions how the above growth processes influence on the material properties and the formation of various nanostructures will be presented at the conference.

\[\text{[1]}\ \text{K. Maejima, M. Ueda, Sz. Fujita and Sg. Fujita, Jpn. J. Appl. Phys. 42, 2600 (2003)\]
Semiconductors exhibiting ferromagnetism above room temperature are indispensable for the future electronics called ‘spintronics’. Up to the present, various combinations of host semiconductors and magnetic elements have been studied as candidates of room-temperature ferromagnetic semiconductors (FMS), but only few have been recognized to exhibit ferromagnetism as an intrinsic properties of the material studied. Cr-doped ZnTe is considered to be one of these rare examples of true FMS; it was reported that ZnTe containing 20% Cr exhibits ferromagnetism around room temperature[1]. However the origin of its ferromagnetism is considered to be different from the carrier-induced mechanism as in Mn-doped III-V semiconductors because (Zn,Cr)Te without carrier doping is almost insulating.

In the present study, we have investigated the effect of additional carrier doping on the magnetic properties of (Zn,Cr)Te, in particular that of n-type doping. Thin films of (Zn,Cr)Te were grown by molecular beam epitaxy (MBE) on GaAs (100) surface. Iodine was added as n-type dopant. Through the structural characterization by x-ray diffraction (XRD) and cross-sectional transmission electron microscope (TEM), it was confirmed that the grown films were epitaxial layers of pure diluted phase without precipitates of other phases than zinc-blende crystal. The magnetization of the grown films were measured by superconducting quantum interference device (SQUID) magnetometer. As a result, it was revealed that the ferromagnetism was enhanced by n-type doping compared to samples without carrier doping. Figure plots the ferromagnetic transition temperature $T_C$ estimated from Arrott plot as a function of Cr composition $x$ for undoped, p-doped, and n-doped samples. As shown in the figure, the ferromagnetism was not observed in p-doped samples. On the other hand, $T_C$ increased sharply in n-doped samples; $T_C$ of the n-doped sample with a Cr composition $x = 0.05$ reached 300K, in contrast to $T_C \sim 15K$ in the undoped counterpart. The significant enhancement of the ferromagnetism by n-doping could be explained qualitatively assuming the double exchange mechanism as an origin of the ferromagnetic interaction. The partially occupied Cr 3d state in the middle of the band-gap is the key to the double exchange interaction between Cr spins[2]. Upon the doping of donor impurities, the Fermi level shifts upward within this localized 3d state, which results in a significant enhancement of the ferromagnetic interaction due to the increase of the electron density in the 3d state.

Fabrication and Characterization of Polycrystalline Bulk ZnO Crystal with Large Grain Size of $\sim 100 \mu m$ by Spark Plasma Sintering

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ZnO is attracting more and more strong interests since the achievement of successful p-type doping and fabrication of pn-junction light-emitting diodes [1] (LEDs). For fabricating the structures of devices such as LEDs, homo-epitaxy processes are much more preferable than those of hetero-epitaxy. Until now single crystalline ZnO bulk crystals for the substrates were prepared by several growth methods such as seeded chemical vapor transport and hydrothermal process, etc. Although the bulk crystal growth of ZnO was much easier and successful compared to the case of GaN, single crystalline ZnO wafers/substrates are still expensive and in particular large size substrates are not easily available.

As for the possibly alternative substrates for the ZnO-based devices, in particular LEDs, polycrystalline ZnO would be used if its grain size is large enough and its conductivity control is possible. It is known that n-type doping of polycrystalline ZnO is easy for very wide range of conductivity and challenging trials for p-type doping are reported by several groups [2]. In this paper, we report our trial to grow polycrystalline ZnO bulk crystals having $\sim 100 \mu m$-level large size grains by using the spark plasma sintering method. Spark plasma sintering is a very attractive method to prepare polycrystalline bulk crystals, because the sintering processes are remarkably enhanced due to the effects of “spark plasma” resulting in a growth of very large grains in a extremely short period at relatively low temperatures compared with those for the conventional hot-press sintering.

We used 5’9 purity ZnO powder with average size of about 0.3-1.0 $\mu m$ as raw materials and investigated how the sintering conditions, such as the sintering temperatures (450 - 1200 C) and their ramping rates (4 -150 C/min), applied pressures (25 - 300 MPa), and sintering periods (15 - 120 mins), affect the properties of sintered ZnO crystals. No additives to enhance the sintering itself were used in this work. The diameter and thickness of the samples were 20 mm and 0.5-1.0 mm, respectively.

It was found that the size of the grains of sintered ZnO bulk crystals ranged from a few to $\sim 100 \mu m$. Further their electrical properties were also found very sensitive to the sintering conditions and varied in the range from 0.07 $\Omega$cm to $\sim 100 k\Omega$cm. The samples were also characterized by HR-XRD mapping, photoluminescence and cathode luminescence etc. and those results will be also reported in this paper.

Finally it will be concluded that the spark plasma sintering method is an attractive way to prepare polycrystalline ZnO bulk crystals possibly applicable as low-cost and large substrates alternative to the single crystalline ZnO bulk crystals/substrates for the application and development of LEDs.

Doping—the intentional introduction of impurities into a material—is fundamental to controlling the properties of bulk semiconductors. The prospect of new technologies has motivated similar efforts to dope semiconductor nanocrystals since their discovery two decades ago. Despite some successes [1–5], many of these efforts have failed, for reasons that remain mysterious. For example, individual Mn atoms can be incorporated into nanocrystals of CdS and ZnSe [3–5], but not into CdSe [6]—despite comparable solubility limits near 50 percent in the bulk crystals. These difficulties have hindered the development of important new materials, including p- and n-type [7], and even magnetic [8], nanocrystals. Such failures have often been attributed to "self-purification," an allegedly intrinsic mechanism in nanocrystals whereby impurities are expelled to the nearby surface. Here we propose a very different view: that doping is controlled instead by the initial adsorption of impurities on the nanocrystal surface during growth. We show that impurity adsorption—and therefore doping efficiency—is determined by two main factors: the crystal structure and equilibrium shape of the nanocrystal. Calculated Mn adsorption energies and equilibrium shapes for several cubic and hexagonal nanocrystals lead to specific doping predictions. These are confirmed by measuring how the Mn concentration in ZnSe varies with nanocrystal size and shape. Finally, we use our predictions to incorporate individual Mn impurities into previously undopable CdSe nanocrystals. This success establishes that earlier difficulties with doping are not intrinsic, and suggests that a variety of doped nanocrystals—for applications from solar cells to spintronics—can be anticipated.

Optical Probing of Interactions in II-VI Semiconductor Structures

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A selection of optical experiments will be reviewed, concerning interactions of carriers and their complexes among themselves, as well as with magnetic ions and photons. In particular exciton-carrier and exciton-exciton interactions, as well as many body effects in quantum wells will be discussed, based on cw and time-resolved experiments. In the field of carrier-magnetic ion interactions, unique opportunities offered by quantum dots containing a single magnetic ion will be analyzed, using results of magnetospectroscopy experiments. Anisotropic electron-hole exchange interaction in quantum dots is known to produce a splitting of the bright exciton state in two components active in perpendicular linear polarizations. This anisotropic exchange splitting is considered to be a major obstacle for generation of entangled photon pairs from a single quantum dot in a biexciton-exciton cascade. Experimental efforts to overcome this obstacle will be discussed, including perspectives to control the anisotropic exchange splitting in excitons, as well as using charged excitons (trions), where no exchange splitting is expected. Experimental testing of single photons and correlated pairs of photons generated by a single quantum dot (by correlated photon counting) will also be presented, providing information on correlation in emission of photons and in their polarizations, as well as on the emission dynamics.

Throughout the range of the reviewed experiments, peculiarities of the II-VI semiconductor systems will be stressed, and compared in particular with those of III-V materials.
Phosphorus-doped p-type ZnO and ZnO LED
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We have successfully grown a phosphorus doped p-type ZnO by RF sputtering and a post annealing process. The influence of Ar/O₂ gas ratio was very crucial on the growth of phosphorus doped p-type ZnO(ZnO:P) thin films during RF sputtering. The p-type ZnO:P thin films have been grown on a c-plane sapphire substrate using an undoped ZnO as a buffer layer under the various Ar/O₂ sputtering gas ratios. The structural, electrical, and optical properties of ZnO:P thin films were significantly depended on the Ar/O₂ sputtering gas ratios. The ZnO:P thin films grown under the Ar/O₂ gas ratio of 1:3 showed a smooth surface and the p-type characteristics after a rapid thermal activation(RTA) activation process. Photoluminescence (PL) properties of p-type ZnO:P thin films also showed an acceptor bound excitonic and phosphorus related peaks. We also report on the characteristics of heterojunction ZnO light-emitting diode (LED) which consists of p-type ZnO:P and n-type GaN:Si layers. The current-voltage (I-V) and electroluminescence(EL) measurements of ZnO LED showed a threshold voltage of 5.4 V and a band-edge emission of 409 nm at room temperature. A p-n homojunction LED of p-ZnO:P/n-ZnO:Ga showed a band edge emission at 380 nm corresponding to the band gap of p-ZnO for the first time. The I-V characteristics of ZnO LED such as the threshold voltage of 3.2V and an ideality factor of 2.5 were very similar to those of GaN LED.
Slow-mode Degradation Mechanism and Its Control in New Bright and Long-lived ZnSe White LEDs

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Phosphor-free ZnSe based white LEDs grown on n-type conductive ZnSe substrate are very unique and attractive devices for practical applications because of all solid-state devices and small operation voltage (2.5V). We present here new bright and long-lived ZnSe white LEDs, developed by controlling so-called “slow-mode degradation” \([1]\) due to high-density microscopic point defect reaction. A systematic study has been made from a viewpoint of microscopic point defect generation and migration in both device active layer (ZnCdSe-ZnSe MQW) and p-type ZnMgSSe cladding layer utilizing DLTS/ICTS, C-V, SSRM (scanning spreading resistance microscope), and EL (electroluminescence)-imaging techniques, coupled with device aging experiments. By careful observation of the slow-mode degradation process, we have found two different degradation stages (first and second stages), caused by quite different microscopic defect species. Major insights on the each degradation stages are summarized as follows:

(A) Slow-mode first-stage due to nitrogen complex deep centers (H0-center)

The first stage of the slow-mode degradation is induced by the active defect generation and long-diffusion of the H0-center (N-complex center in p-type ZnMgSSe cladding layer), forming high density dark-spots in the MQW active layer. Driving force on this defect reaction is efficient electron-hole non-radiative recombination energy, so called REDR reaction. Important properties of this H0-center reaction are: high generation rate under thermal- and/or stress stimulation in their device-fabrication process, and long distant diffusion from p-type cladding layer into active layer under device operation by the REDR effect. We have established a new device-structure and the fabrication process, which can control the first stage of the slow-mode degradation process.

(B) Slow-mode second stage due to carrier compensating donor centers

After controlling H0-center reaction (the first stage), a quite different degradation mode has appeared in very long device-operation time (several 1000 hours) where we have observed no detectable dark spots in the EL-image. This second stage is found to proceed very slowly without any deep hole traps like H0-center. It has been proved that this stage is caused by carrier (hole) removal effect in p-type cladding layer, indicating a new generation of compensating donor-like centers. Gradual but clear decrease in free hole concentration in p-type cladding layer are confirmed by two experiments (DA pair luminescence, and precise SSRM measurement). Detailed nature on this donor-like center generated in p-type cladding layer has not been assigned yet, but we have proved that this donor-like center is produced not by thermal stimulation but by minority carrier injection. This second stage, therefore, can be controlled by the thorough control of carrier (electron) over-flow into p-type cladding layer. Based on these detailed insights on the defect reaction properties, we have established new double cladding i-ZnMgBeSe/p-ZnMgSSe structure ZnSe white LEDs with long device lifetime exceeding 10000 hours under room temperature \([2]\). The improved LEDs reveal very high luminance efficiency (33 lm/W) and superior power efficiency of 16 %.

Inter-dot Spin Exchange Interaction in Coupled II-VI Semiconductor Quantum Dots

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Recently, spin states in quantum dots (QDs) have been proposed as viable candidates for quantum bits in quantum computing. \cite{1} The inter-dot spin exchange interaction in coupled QD structures is then an important phenomenon in order to realize multi-bits gate. We have focused on the double layer QD structures to understand the nature of inter-dot spin exchange interaction. For observing interlayer exchange interaction, we designed coupled asymmetric two-layer QD structures with different bandgap energies. The double layer QD structures were formed by using combination of CdSe and CdZnSe QD layers separated by ZnSe barriers. We observe well-resolved photoluminescence (PL) peaks originating from the two QD layers comprising the double-layer structures, enabling us to identify the PL emissions from each QD family, and to study the influence of one QD layer on the other.

To investigate the spin polarization of carriers in the QDs, we performed polarization-selective magneto-PL experiments by exciting the above structures with unpolarized light, and detecting the PL with either the $\sigma^-$ or the $\sigma^+$ circular polarization. When a magnetic field was applied to the CdSe/CdZnSe double-QD layer, the intensities of the circularly polarized PL peaks corresponding to the CdSe and CdZnSe layers exhibited significant differences, reflecting correspondingly large differences in the degrees of spin polarization of the CdSe and the CdZnSe QDs, in contrast to the PL observed on single-layer CdSe or CdZnSe QD reference structures, both of which showed nearly identical dependence on the field. The behavior observed on the double-layer QD structures was interpreted in terms of anti-parallel spin interaction between carriers localized in coupled QD pairs. Such spin interaction was even more pronounced in double-layer structures in which diluted magnetic semiconductor (DMS) QD layer (either CdMnSe or CdZnMnSe QDs) was used for one of QD layers, reflecting the high potential of magnetic QDs in the context of spin-polarized applications.

\cite{1} D. Loss, and D.P. DiVincenzo, Phys. Rev. A \textbf{57}, 120 (1998).
Semiconductor Nanorod Optical Properties

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There is growing interest in nanometer-scale crystalline semiconductor structures of various shapes, such as nanocrystals, nanorods, and nanowires, created using the "from-the-bottom-up" technological approach. The optical properties of nanorods, however, differ significantly from those of nanocrystals. Compared to nanocrystals, nanorods show higher photoluminescence quantum efficiency, strongly linearly polarized photoluminescence, an increase in the global Stokes shift, and significantly faster carrier relaxation. The size and shape dependence of optical and tunneling gaps measured in CdSe nanorods shows an unexpectedly large difference that cannot be explained by the electron-hole Coulomb correction to the optical gap used for nanocrystals. We have shown theoretically that this difference in optical properties is caused by one-dimensional excitons formed in elongated nanorods. This theory, which takes into account the anisotropy of spatial and dielectric confinement, describes size dependence of interband optical transitions, exciton binding energies, and the fine structure of the ground exciton state [1]. Our results agree well with the size dependence of the energy gap and the photoluminescence polarization degree measured in CdSe nanorods.

Ultrafast Intersubband Optical Switching in II-VI-based Quantum Well for Optical Fiber Communications

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Recently, there is a growing focus on short-wavelength intersubband transitions (ISB-T) in semiconductors quantum wells (QWs), aiming at potential applications for high-bit-rate (above 100Gbits/s) optical fiber communication systems at \(\lambda \sim 1.55\mu m\). An absorption saturation associated with ISBT has ultrafast recovery due to rapid carrier relaxation of sub-ps to a few ps range. This property is a promising candidate to realize all-optical switches and modulators with a bit rate up to \(\sim 1T\) bits/s. To achieve ISBT at \(\lambda \sim 1.55\mu m\), a heterostructure with large conduction band offset (CBO \(\sim 2eV\)) is necessary for use of a deep potential QW. So far, a \(\lambda \sim 1.55\mu m\) ISBT has been reported in InGaAs/AlAs/AlAsSb coupled QWs [1], GaN/Al(Ga)N QWs[2], and our II-VI-based QWs [3,4]. The II-VI-based materials take advantage of their strongly polar nature, regarding the ultrafast switching. As the ISB relaxation is controlled mainly by the Fröhich interaction between electrons and LO phonons, a faster relaxation is expected for a material with higher ionicity. We have employed CdS/ZnSe/BeTe heterostructure [3,4]. Since a CBO in the structure is as large as \(\sim 2.3eV\) for ZnSe/BeTe and \(\sim 3.1eV\) for CdS/BeTe, ISBT absorption as short as \(\lambda \sim 1.55\mu m\) is expected to be easily achievable. We have actually demonstrated \(\lambda \sim 1.55\mu m\) ISBT absorption in (CdS/ZnSe)/BeTe QWs. The QWs consists of Cl-doped CdS/ZnSe well and Be(Mg)Te barrier. Each QW is separated by Zn(Be)Se spacer layer to accommodate strain. In the growth, we found that an insertion of a \(\sim 1\)ML-ZnSe inter-layer between CdS and BeTe is indispensable to keep epitaxial growth in two-dimensional mode [5]. We have also examined ultrafast carrier dynamics associated with ISBT in this heterostructure by use of femtosecond time-resolved pump-probe experiment. The ISBT optical nonlinearity in the wafer sample exhibits sub-ps relaxation time and sub-pJ/\(\mu m^2\) saturation energy, indicating a promising characteristic for high-speed switching [6]. For device applications, a confinement of a light pulse into switching layer with a long distance (\(\sim 1mm\)) using waveguide is important for reducing a net switching energy in the device. We used ZnMgBeSe quaternary as a cladding material, since it can be grown on GaAs substrate with lattice-matched condition as well as with a refractive index lower than core index by 0.1~0.15. We have successfully fabricated high-mesa waveguide with a narrow mesa-width (< 3\(\mu m\)), where TE insertion loss is less than 3dB in the case of lensed-fiber coupling. A high-mesa structure is advantageous for better lateral optical confinement by use of air clad. A current switching extinction ratio in the device is 5.1dB with 10pJ input pulse energy, which indicates the performance much better than nitride-based device, and is comparable to Sb-based III-V device. Device physics associated with further reduction in switching energy will be discussed.

Coherent Control of Excitonic Transitions in II-VI Quantum Wells

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In the past decade the coherent dynamics of excitonic excitations in semiconductors has been a field of intense research because of its importance for the understanding of semiconductor laser dynamics as well as the investigation of fundamental properties of quantum mechanical many-particle systems such as Coulomb-correlation effects. The latter ones manifest themselves especially in non-linear optical signals, and their coherent dynamics can be investigated by different experimental ultrafast-spectroscopy techniques such as pump-and-probe or wave-mixing spectroscopy.

In this presentation, we will focus on the coherent control of excitonic excitations in two-dimensional ZnSe single quantum wells by use of a pair of phase-locked ultrashort laser pulses. The pulses selectively excite the polarization of the heavy-hole exciton-biexciton system which consists of two coupled resonances. At the used temperature of T = 4 K the wide-gap II-VI quantum-well sample allows for a clear spectral separation of the distinct excitonic and biexcitonic signals due to the high Coulomb interaction and large exciton and biexciton binding energies in the semiconductor.

We present results of experimental and theoretical work in which the coherent-control technique has been applied to study the coherent manipulation of excitonic polarization in quantum-well samples as well as the control of center-of-mass quantized exciton-polaritons in heterostructures with an active layer possessing a thickness of about ten times the exciton Bohr radius.

By comparing the results of polarization-selective four- and six-wave-mixing experiments with results obtained by simulations based on a fully microscopic theory we demonstrate the influence of high-order optical non-linearities in the coherent-control signal and discuss their microscopic origins [1,2]. The role of the bound-biexciton state for the occurrence of these non-linearities is analyzed. This naturally leads to the question if and how the optical transition from the excitonic states to the bound-biexciton state (EBT) can be subject to a directed coherent control on ultrashort time scales itself. We will present additional systematic experimental studies and simulations with a simplified phenomenological as well as a fully microscopic theory which clearly demonstrate that in pulse-transmission and four-wave-mixing experiments the EBT can be coherently manipulated for certain sequences of the excitation pulses [3,4].

The high-quality ZnSe quantum-well samples have been kindly provided by the groups of W. Faschinger (Würzburg) and D. Hommel (Bremen). The microscopic simulations have been performed by V. M. Axt and T. Kuhn (Münster).

Zinc oxide (ZnO) has become an interesting and potential candidate for ultraviolet (UV) light emitters due to the increasing demands for short wavelength light emitting diode (LED), because ZnO has its characteristic features that include a large bandgap energy of 3.27 eV, a large exciton binding energy of 60 meV, and band gap engineering. [1,2] We report on the ZnO homojunction LED using a ZnMgO barrier layer, which was grown by radio-frequency (rf) sputtering deposition on $c$-Al$_2$O$_3$. The ZnMgO layer was used as a barrier material to improve the efficiency of LED by confining carriers in the active region. The LED with size of a 300 $\times$ 300 $\mu$m$^2$ showed clear rectification with a turn-on voltage of 3.2 V which is in a reasonable agreement with the bandgap energy of ZnO as shown in Fig. 1. Figure 1(a) shows $I$–$V$ characteristic from the homojunction LED with a 300 nm thick $p$-ZnO film, which has high series resistance of 22.0$\Omega$ presumably due to the poor current spreading, compared to that with a 400 nm thick $p$-ZnO which shows a series resistance of 12.8$\Omega$ as shown in Fig. 1(b). High breakdown voltage of about 9 V and a small reverse current of about $10^{-6}$ A were also observed. EL emission was observed at 378 nm with a broad deep-level emission at an injection current of 40 mA as shown in Fig. 2. The peak at 378 nm is believed to be the emission from the ZnO well layer. The broad deep-level emission at around 600 nm is believed to the various defects in the $p$-ZnO layer. The ratio of bandedge and deep level emission is higher in the LED with a 300 nm thick $p$-ZnO film [Fig. 2(a)] than in the LED with a 400 nm thick $p$-ZnO film [Fig. 2(b)]. This result can be attributed to the absorption of UV light emitted from the well layer in the $p$-ZnO layer.
Strong Heavy-hole – Light-hole Mixing in CdZnSe Quantum Dots
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Semiconductor quantum dots grown by molecular beam epitaxy are known to differ considerably from the ideal picture of an isotropic “dot” structure. The growth direction defines the $z$-axis along which the quantum dots (QDs) are much thinner, and even the $xy$ in-plane symmetry is frequently lifted due to the QD’s shape or the influence of strain. The in-plane anisotropy is well-known to split the exciton line into a radiative doublet due to exchange interaction. It also mixes heavy-hole (hh) and light-hole (lh) states. A strong hh-lh mixing can lead to unequal intensities of the two components of the doublet [1]. To measure this mixing in a rather direct way, we use the trion transition of single QDs under magnetic field in transverse geometry (Voigt configuration). We choose to study QDs formed with the CdSe/ZnSe material system, which is non-intentionally $n$ doped so that most of the QDs are negatively charged. After deposition of the CdSe layer on the ZnSe barrier, the QD formation is induced either by thermal annealing or by deposition/desorption of amorphous Se [2]. We find in the present study that the hh-lh mixing can greatly vary from QD to QD, reaching values much larger than those reported very recently [3].

The negative trion momentum is only determined by the hole spin. No Zeeman splitting is expected for pure heavy holes in Voigt geometry. So, without hh-lh mixing, only two transitions are expected for the trion under magnetic field, corresponding to the two spin states of the excess electron which remains in the QD after trion recombination. The presence of hh-lh mixing however results in a non-zero value of the in-plane hole g-factor. Consequently, in the general case the trion splits into four lines under magnetic field [3]. Additionally, by depolarizing the QD emission to rule out the polarization dependence of our detection, we observe intensity differences between the two inner and the two outer lines of the trion quartet. We attribute this to another consequence of the hh-lh mixing. By studying several trions under magnetic field, we indeed find a correlation between the g-factors and the intensity differences between inner and outer lines. For some of the trions, the inner doublet is close to the outer doublet, and all lines have nearly the same intensity, indicating a small hh-lh mixing similar to previous observations [3]. Other trions however show well separated doublets together with large intensity differences and thus strong hh-lh mixing. Trions with a triplet structure due to a twofold degenerated center line (even at 11 T) have also been found, revealing hole g-factors as large as electron ones. This strong hh-lh mixing is an indication for weakly strained QDs, where the lh states are not well separated from the hh states anymore. Such a week strain may arise from a large size of the QDs, a certain Zn content inside the dots and/or defects generated next to the dots, which seems to be confirmed by preliminary structural investigations on our samples.

Stimulated Emission from ZnO Nanorods and ZnO/ZnMgO Quantum Wells


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The large band gap semiconductor zinc oxide (ZnO) is of significant interest for optoelectronic application in the ultraviolet. We report here on investigations of stimulated emission in one and two dimensional waveguide structures.

First we study ZnO nanorods whose fabrication process is template assisted and involves gold nanodisk arrays obtained by using a gold membrane. The membrane itself is a replica of an amorphous aluminum oxide membrane as a deposition mask, and subsequent site-specific growth of ZnO. This leads to a long range ordered array of ZnO nanorods with a narrow size distribution centered at 300 nm and a typical height of 1.5 µm, i.e., an aspect ratio of 5. Photoluminescence spectra (PL) were obtained using a time-resolved confocal micro-PL system (spatial resolution: <500 nm, temporal resolution: 5 ps). A frequency doubled Ti:Sapphire laser was used which delivers ~100 fs pulses at 3.49 eV with an average power of up to 100 mW. The sample is mounted in a He flow cryostat for temperature dependent measurements.

At low excitation conditions the emission is dominated by recombination of free and bound excitons with little deep defect luminescence that is usually attributed to oxygen vacancies. The excellent crystalline quality is reflected in an unaltered peak position of the A-exciton compared to the bulk value and in the formation of three phonon replica at elevated temperatures. The luminescence under high excitation conditions is compared to an epitaxal layer sample where the coherent optical feedback can easily be modeled numerically as well as derived from reflection measurements. In the case of the epitaxal layer strongly nonlinear emission is observed only in the spectral range associated with exciton-exciton scattering (P-band). In contrast to that in the case of nanorods stimulated emission can be observed over the whole gain spectrum depending on the exact excitation conditions and the position. This nanorod sample is also compared with nanorods grown by MOVPE, a different process where no gold is present. No P-band emission is found in these structures which have a smaller diameter of only 50 nm. To illuminate the influence of the aspect ratio and the presence/absence of gold layers finite element calculations of the electromagnetic field distribution inside the nanorods are carried out.

As an example of a two-dimensional waveguide structure time resolved PL measurements of a ZnO/ZnMgO quantum well feature prominent emission from biexciton recombination. Due to quantum confinement the emission from the ZnO well is shifted to higher energy with respect to bulk material and the formation of biexcitons is enhanced. This leads to stimulated emission origination from recombination of biexcitons rather than from the P-band as in epitaxal layers.
Cyclotron Resonance in II-VI Semiconductors at THz Region

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Cyclotron resonance (CR) is an excellent method for obtaining effective mass of semiconductors directly, and the effective masses of most high quality semiconductors were already determined by using this method. CR experiments for the low dimensional systems (quantum wells or quantum dots) have been performed recently, and various significant phenomena, such as the mass or spin-split cyclotron resonance, confinement effect and plasmon-phonon coupling effect, have been found out through the detailed measurements at the wide range of the photon energy.

II-VI compounds are polar materials, and hence they are good candidate for studying the polaron effect since they have larger electron-LO phonon interaction caused by an ionic crystal character. However, in most wide gap II-VI semiconductors, it was hard to satisfy the resonant condition ($\omega_c \tau > 1$) owing to their low electron or hole mobility. Thus the CR experiment in most II-VI semiconductors was difficult to perform at the GHz region (low magnetic field) even at low temperatures.

Recent developments of high magnetic field technology enable us to observe the clear CR even in low mobility crystals at the THz region [1]. Moreover, the progress of epitaxial growth techniques make it possible to study the quantum Hall effect in II-VI semiconductors recently [2], and hence detailed CR experiments can be carried out even in 2 dimensional electron gas systems (2DEGs) of II-VI diluted magnetic semiconductors.

In this paper, we will discuss the electron CR in II-VI semiconductors (ZnO, ZnS, ZnSe, CdS, CdSe, CdTe) and Cd$_{1-x}$Mn$_x$Te/CdMgTe 2DEGs at the wide range of THz frequency, and thereby the bare effective mass and the electron-LO phonon coupling constants have been determined by the comparison with calculation results of a polaron perturbation theory. In CdTe/CdMgTe 2DEGs, the CR measurements are performed in details with the use of a FT-IR, and the sudden variation of the effective mass at the integer filling factors is clearly observed. In CdMnTe 2DEGs, the drastic narrowing of the CR width is found below a saturation magnetic field of the magnetization of Mn ions. This result suggests that the drastic variation of the electron mobility occurs with changing the magnetization of Mn ions, and hence the spin scattering between the 2DEGs and Mn ions should be considered for interpreting the anomalous feature in the semi magnetic samples.

High Sensitive Ultraviolet PIN Photodiodes of ZnSSe n+-i-p Structure / p+-GaAs substrate grown by MBE

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High sensitive and stable ultra-violet PIN photodiodes of ZnSSe n+-i-p structure on p+-GaAs substrates are developed by MBE growth. The short wavelength photodiodes are grown on p-type (100) GaAs by MBE utilizing an optimized “hetero-interface super-lattice (SLE) buffer” consists of ZnTe-ZnSe MQW, by which a large energy barrier (> 1 eV) for hole ohmic conduction is overcome. In this study we have focused our attention to improve the ZnSSe n+-i-p structure so as to obtain high ultra-violet sensitivities (~300 nm wavelength). Major technical points improved are following: (i) theoretical design and its practical growth of very thin interface SLE, and (ii) to form highly doped and extremely thin n+-ZnSSe window layer (N_d - N_a > 1x10^19 cm^-3, W_D ≤ 250Å). The first point is related to control (or absorb) high density of macroscopic defects (dislocations/stacking faults generated in hetero-interface), which leads to control low dark currents under high field operation, and the second concerns with marked improvement on ultra-violet sensitivity.

A: Theoretical analysis on extremely thin interface SLE and its fabrication

Careful design of ZnTe-ZnSe tunneling interface super-lattice on p-type GaAs is carried out by Schrödinger’s and Poisson’s equations in self-consistency using finite elemental method. Required conditions for the SLE design are to find an optimum SLE with very thin super-lattice structure with total thickness below 116Å (= critical value for the coherent MBE growth), and to achieve complete hole ohmic-conduction by resonant tunneling. In this analysis we have established an optimum interface SLE structure: 5 periods of p-type ZnTe layers with each different thickness of 5W, 4W,3W,2W and W from p-type GaAs side: here W (= 0.6Å) represents base-width of p+-ZnTe QW, and p-ZnSe barrier width is fixed to 21.4Å. Using this interface SLE, practical n+-i-p structure PIN photodiodes are developed. It is found that the thin interface SLE (116Å) acts as an efficient buffer to absorb high density of macroscopic defects, by which we have achieved very small dark leakage currents below sub pA/mm² under 10V operation condition. Complete ohmic hole-conduction in p-type hetero-structure of GaAs-ZnSe is confirmed in forward I-V characteristics (built-in voltage =2V).

B: Characteristics of ZnSSe n+-i-p structure PIN photodiodes on p+-GaAs.

The ZnSSe n+-i-p structure PIN photodiodes covered by Al2O3 anti-reflection coating with extremely thin n+ window (≥ 250Å) has revealed high ultra-violet sensitivities of 0.12 A/W for 300nm wavelength (external quantum efficiecy ξ_ex =50 %), and also exhibited very high blue-violet sensitivities of 0.24 A/W for 400nm wavelength (external quantum efficiency ξ_ex =75 %). Here marked improvement in the ultra-violet sensitivities is not only due to the transparent thin window effects, but also to a contribution from higher energy valence band effect (spin-orbit spit-off valence band: E_0 + Δ_0). These results have proved an excellent short wavelength PIN photodiodes on the present new hetero-structure, and a large potential toward its practical application.
Fig. 1. ZnSSe Ultraviolet n⁺-i-p structure PIN photodiode on p⁺-GaAs substrate with optimized interface SLE.

Fig. 2. Current-voltage characteristics of (a) ZnSSe-PIN/p⁺-GaAs with interface SLE, in comparison with (b) ZnSSe-PIN/p⁺-GaAs without interface SLE and (c) ZnSSe-PIN/n⁺-GaAs.

Fig. 3. Improved dark current characteristics of n⁺-i-p structure PIN on p⁺-GaAs in comparison with conventional ZnSSe PINs on n⁺-GaAs, GaN based PIN and Si-PIN. Dark current of ZnSSe PIN on p⁺-GaAs is suppressed below sub pA/mm².

Fig. 4. Spectrum sensitivities of the n⁺-i-p structure ZnSSe PIN on p⁺-GaAs, ZnSSe on n⁺-GaAs and Si PIN for ultraviolet. ZnSSe PIN on p⁺-GaAs with AR coating exhibits large external quantum efficiency > 50% at ultraviolet wavelength of 300nm.

Local Electrical and Optical Properties of ZnO Layers Co-doped with Nitrogen and Arsenic


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Despite of a lot of activities it has been established that doping of ZnO layers only with nitrogen provides non-reproducible and unstable p-type conductivity. We will show that these difficulties may be overcome by simultaneous doping with nitrogen and arsenic. The samples under study were grown by metalorganic vapor phase epitaxy in a two-step growth process on GaN on sapphire templates. After the growth of a ~300 nm thick ZnO layer deposited at 450°C using DMZn and tert-butanol a high temperature ZnO layer was grown at 850°C-900°C using DMZn and N₂O. For doping experiments, the high temperature layer was doped with arsenic using AsH₃ and nitrogen using unsymmetrical-dimethylhydrazine. For electrical characterization we performed conventional macroscopic C-V-analysis as well as scanning capacitance microscopy (SCM). This latter SCM method bases on the atomic force microscopy setup and measures the local carrier concentration via the local C-V-curves with submicroscopic spatial resolution. As a result we found in SCM that all samples exhibit a so-called mixed conductivity instead of uniform carrier concentration and conductivity type. That means, they typically contain more or less largely extended p-type domains disturbed by local n-type regions. A comparison between topography and SCM signal revealed, that most of the n-type features are related to structural layer defects. A systematic variation of the growth parameters was performed and will be discussed in terms of the electrical data. Furthermore, the optical characteristics of these co-doped samples were analyzed by spatially resolved cathodoluminescence and photoluminescence measurements. Here, we observed in the p-type regions only orange luminescence at about 1.77 eV, but almost no near band edge luminescence. In contrast, n-type domains exhibit rich excitonic features in the near band gap region.
Yellow-green Lasing Operations of ZnCdTe/MgZnSeTe Laser Diodes on ZnTe Substrates

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We have succeeded in yellow-green lasing operations of ZnCdTe/MgZnSeTe laser diodes (LDs) fabricated on ZnTe substrates for the first time.

High-quality ZnTe substrates with low defect density have been developed[1], which has triggered a new evolution of ZnTe-based II-VI materials such as ZnCdTe and MgZnSeTe for yellow-to-green LDs and LEDs. To date crystal growth and characterization of these materials on ZnTe substrates have been reported[2]. Yellow-to-green LEDs have been fabricated[3-6]. Especially we have developed a novel ZnTe/CdSe superlattice (SL) n-contact structures to make a low-resistance ohmic contact[3]. Refractive indices of these materials have been systematically evaluated, which was utilized for waveguide design of LD structures[6]. Based on these results, ZnCdSe/MgZnCdSe LDs were fabricated in this study.

The LDs consisting of ZnCdTe single QW active (10nm) sandwiched by ZnTe barriers (50nm), MgZnSeTe/ZnTe SL optical confinement (100nm), and n- and p-MgZnSeTe cladding layers were grown on p-ZnTe substrates by MBE. The n- and p-type dopants were Cl and radical N, respectively. The LD wafer was fabricated to be 16-μm-wide contact stripe geometry. The n- and p-side contacts were made by evaporating Au. After the wafer was cleaved to LD chips with cavity lengths from 300 to 1000 μm, the LDs were characterized under single pulse current injection drives. The light output was detected by photo-multiplier, and the emission spectra were measured using the CCD array detector. Figure 1 and 2 show typical injection current density versus light output (I-L) characteristics and emission spectra at 100 K. In Fig. 1, the threshold current density was 2.8 kA/cm². Yellow-green lasing emissions at 564 nm were observed. The lasing operations were obtained up to 170 K.

![Figure 1: I-L characteristics of ZnCdTe/MgZnSeTe LDs at 100 K.](image1)

![Figure 2: Emission spectra of ZnCdTe/MgZnSeTe LDs at 100 K.](image2)

Study of ZnCdSe/ZnCdMgSe Multi-Quantum Well Structures Prepared by Molecular Beam Epitaxy

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Multi-Quantum Well (MQW) structures made from II-VI semiconductors have important applications in Quantum-Well-Infrared-Photodetectors (QWIPs) and Quantum Cascade Lasers (QCLs) due to their widely adjustable bandgaps. Devices, such as QWIPs operating at 3\(\sim\)5\(\mu\)m atmosphere window, and QCLs for optical fiber applications (1.55\(\mu\)m), require MQW systems with larger band discontinuity than that achieved in currently well-studied III-V As-based systems. A II-VI semiconductor material system recently investigated in our lab, ZnCdSe/ZnCdMgSe MQWs, meets this requirement. According to our recent research accomplishments, contactless electroreflectance (CER) has been used to determine the conduction band offset (CBO) of ZnCdSe/ZnCdMgSe system. For Zn\(_{0.5}\)Cd\(_{0.5}\)Se/Zn\(_{0.29}\)Cd\(_{0.71}\)Mg\(_{0.47}\)Se single QW the CBO has been estimated as 590meV [1] and for the limit composition of this lattice-matched system, Zn\(_{0.5}\)Cd\(_{0.5}\)Se/Zn\(_{0.13}\)Mg\(_{0.87}\)Se, the CBO has been estimated to be as large as 1.12eV [2].

In this work, a series of high quality Zn\(_{0.5}\)Cd\(_{0.5}\)Se/Zn\(_{0.15}\)Cd\(_{0.25}\)Mg\(_{0.60}\)Se MQWs with different QW thicknesses have been grown on InP substrates by MBE method. The quaternary bandgap for these samples was controlled at \(\sim\)3.1eV. The MQWs were characterized by X-ray Diffraction (XRD) and Photoluminescence (PL) measurements. Well-shaped satellite peaks were observed in XRD data showing the high quality and abrupt interfaces of the superlattices. The periods of these superlattices calculated from the X-ray data are very close to the designed values. Strong and sharp interband photoluminescence was observed for all the MQWs samples. The E1-H1 interband transition energies of these MQWs agree well with theoretical prediction. All experimental data show that the grown Zn\(_{0.5}\)Cd\(_{0.5}\)Se/Zn\(_{0.15}\)Cd\(_{0.25}\)Mg\(_{0.60}\)Se MQWs are lattice-matched and have high material quality. Doping of the QW layers by n-type dopants, which is needed to investigate the IR absorption, has also been accomplished. Calculations were made to estimate the intersubband transition energies, which are in the range of 3\(\sim\)5\(\mu\)m. CER measurements were performed to verify our predictions. Optical absorption and photocurrent measurements will be used to study intersubband transitions of the MQWs, and further explore their application in IR devices.

Exciton Polaritons in Cubic Semiconductors in Magnetic Fields

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Magneto-reflectivity spectra taken from CdTe and ZnSe-based heterostructures containing a wide quantum well have been studied. It has been found that the magnitude of the exciton Zeeman splitting grows more than in 10 times with the increase of the number of the quantization level. As the number of size quantization level \( N \) is in a relation to the magnitude of the exciton wave vector \( K \), the observed effect means the growth of the exciton magnetic moment with the increase of its kinetic energy.

We studied CdTe and ZnSe QW heterostructures. The structures were grown by molecular-beam epitaxy on (100) substrates (GaAs in case of ZnSe and ZnCdTe in case of CdTe-based structures). The structures contained a QW with QW width varied from 50nm to 200nm. Reflectivity spectra from these structures have been studied in magnetic fields at normal incidence in Faraday geometry.

The interference structure located energetically higher than the exciton resonance frequency \( \hbar \omega_0 \) has been observed in the spectra. The appearance of this structure is due to the size quantization of the exciton as a whole in the QW if the QW width is much larger than the \( a_B \) – the exciton Bohr radius (\( a_B = 3 \)nm in ZnSe and \( a_B = 6 \)nm in CdTe). In our samples we observed the even interference features only because of better overlap of the even exciton and photon eigenmodes that are defined by the design of the structure.

Presence of this interference feature allows us to reconstruct the polariton dispersion curves using the interference condition \( KL = \pi N \), where \( K \) is the exciton wave-vector, \( L \) is QW width, \( N \) is the number of the quantized level [1]. We observed up to 10 polariton quantized levels in our samples.

In applied magnetic fields in Faraday geometry we have found that the values of Zeeman splitting increase with increasing of the number \( N \). This means that the exciton magnetic moment or the exciton \( g \)-factor increases with increase its \( K \) vector. We have found that the \( g \)-factor grows more than in 10 times in the range where the interference picture is observed.

We also found that for the structure grown in (110) direction the Zeeman splitting is the same for all the quantized levels. This fact directly indicates that the effect should be connected with features of the energy band-structure. The very similar effect was observed in CdTe and ZnSe-based QW structures and also in GaAs wide QWs. We explain this effect by the contribution of cubic \( K \)-terms into the exciton \( g \)-factor in zinc blend type semiconductors.

An empirical formula for the \( K \)-vector dependence of the exciton \( g \)-factor has been deduced:

\[
geff = g_0 + cK a_B^2 / (1 + (Ka_B)^2) .
\]

Structural and Optical Properties of Cd$_{1-x}$Dy$_x$Te (0≤x≤0.05) Crystals

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A wide application of both pure and doped single crystals of cadmium telluride and solid solutions on its basis is currently interfered by a number of thermo-dynamical and technological factors occurring in growth process (vapor pressures of the components, crystallization and cooling rate, impurity segregation coefficient etc.), which appear to influence dramatically the physical properties of the obtained material.

The analysis of the results obtained on the CdTe:4f (Eu, Gd, Dy) single crystals proves the impurity of Dy to cause the most significant influence on magneto-optical phenomena [1]. Namely, Faraday rotation in the CdTe:Dy crystals exceeds one observed in CdTe:Mn, with doping impurity concentrations of $N_{\text{Dy}}=N_{\text{Mn}}=10^{20}$ cm$^{-3}$. Investigation of the solid solution existence range in the CdTe-DyTe system is of a practical interest since in such crystals one may expect an emerging of giant Faraday rotation.

In this paper the results of the electron-microscopic, structural and optical properties of the Cd$_{1-x}$Dy$_x$Te (0.005≤x≤0.05) crystals are presented. Crystals for investigations were grown via the vertical Bridgman method at the rate of 0.1 cm/h with the temperature gradient equaling 20-25 K/cm.

The results of electron-microscopic investigations indicate that the isolation of the other phase occurs in the upper part of the crystal with composition of x≥0.005. The observed inclusions differ in shape and extension. Their length is up to ∼50 µm and the width ranges from 8-10 µm to 30-35 µm. EDAX analysis of the inclusions testified the isolated phase to be a compound of Dy$_2$Te$_3$.

The increase in composition changes a nature of inclusions and their distribution along the grown crystal. In this case inclusions are distributed almost in parallel and dark areas of different shape and extension, which adjoin to them, appear. EDAX analysis provides evidence of the inclusions distributed in parallel to correspond to the phase of Dy$_2$Te$_3$, whereas the dark areas are attributed to DyTe.

The linearly changes in lattice parameter for the Cd$_{1-x}$Dy$_x$Te crystals with x up to x=0.01 points out the formation of solid solutions in the given composition range.

Modifications of absorption spectra with photon energy for the samples with composition of x≤0.01 are of the same character. A band gap width $E_g$ established from the $\alpha^2=\beta(h\nu)$ dependence for the investigated range of composition amounts to $E_g=1.445-1.448$ eV, that is 0.057-0.06 eV less than that of CdTe ($E_g=1.505$ eV) at the same temperature.

It has been found, that Dy within the limits of its solubility of (1-3)$\cdot 10^{20}$ cm$^{-3}$ changes $E_g$ of CdTe only by 0.057-0.06 eV, while with further increase in the Dy content the $E_g$ value suffers no modification.

Laser modification of semiconductor is the perspective method for creation of modern functional elements for opto- and microelectronics. Possibility of locally influence on surface of micro sizes region, high rapidity heating and mobility of laser beam control in the laser modification method makes it more attractive. However, influence of powerful radiation might accompanied by undesirable effects associated with generation of point and extended defects, non-uniform heating and formation of periodical structures of surface relief. In particularly critical presence of defects is influenced on properties of micro- and nanosize crystal materials. Namely such size elements are used in modern electronics. To choose optimal regime of laser treatment of materials is necessary for clear understanding of mechanisms of generation, interaction and accumulation of structural defects. In accordance with this we investigated forming of nanostructures on CdTe crystal’s surface in dependence on irradiation dose and power density of laser radiation under one-shot irradiation.

In this paper we present our results on the pulse laser irradiation effect on (111) surface of CdTe crystals. Nominally undoped single crystals were grown by the vacuum vapor phase method. Density of dislocations was about $\sim 10^2$ cm$^{-2}$. Multimode Q-switched ruby laser was used as a source of single pulses with $2 \cdot 10^{-8}$ s duration.

The atom-force microscopy investigation shows that the initial crystals surface is atomically smooth, but after irradiation nanostructures appear. Character of distribution and sizes of structures depend on as laser irradiation doze so and power density of single laser pulse. It is shown, that formation the thin film of Te, generation the point defects and their following clustering take place on surfaces depending on dose of the irradiation. At the same time the formation both of large-scale (0.1-1 µm) and small-scale ($\sim$10-100 nm) nanostructures on CdTe surface are observed. Optimum modes of formation of uniformly distributed nanostructures with minimum lateral sizes and period 100 nm on surfaces of the CdTe crystals depend on power density of the laser radiation. Their periodicity appears only in one of crystallographic directions. In this case Fourier-spectra analysis shows that the first stage – self I organization–selection of lattices on period and partial angular self-organization process are passed.

Experimental results are explained in the framework of the model supposing self-organization of defects and formation of ordered nanostructures on (111) surface of p-CdTe crystals due to the generation of some critical concentration of point defects and their clustering under laser irradiation.
Vapour Growth of II-VI Single Crystals Doped by Transition Metals for Mid-infrared Lasers

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Transition metal doped II-VI crystals are perspective materials for mid-infrared lasers. Usually to obtain such doped crystals a two-stage technology method is used. It includes the growth of the pure crystal preferably from vapour phase and doping of it by thermal diffusion from the solid metal layer coated previously on the crystal surface. Doping directly during vapour growth process is more perspective to obtain uniformly doped crystals with low defect concentration. However this way is realized with difficulty because of considerable difference in saturated vapour pressures of the crystal and the doping material. In this work we demonstrate that this difficulty may be overcome. Characteristics of the lasers created on basis of the grown crystals are presented also.

The growth technology used was close to the technology developed earlier for growth of solid solution II-VI single crystals [1]. The growth was performed by seeded physical (or chemical with hydrogen) vapour transport from two separate sources containing a II-VI polycrystalline compound and a dopant respectively. A transition-metal chalcogenide was used as the dopant. Change of doping level was carried out by changing the growth temperature and/or the design of the sources. As a result the ZnSe:Cr, ZnSe:Fe, ZnSe:Co, ZnSe:Ni, CdSe:Cr, ZnTe:Cr, ZnS:Fe and ZnS:Mn single crystals with doping level up to $10^{19}$ cm\textsuperscript{-3} were obtained. Uniformity of doped crystals was high enough. The concentration of doping impurity changed at the most two times along the crystal diameter of 50 mm and height of 15 mm.

Grown ZnSe:Cr single crystals with [Cr] $= 5 \times 10^{18}$ cm\textsuperscript{-3} were successfully used as active elements in IR lasers. Under optical pumping by emission of Co:MgF\textsubscript{2} laser ($\lambda = 1.67 \mu\text{m}$) the laser action at 2.45 $\mu\text{m}$ wavelength with high quantum efficiency of 87\% was achieved. Upper limit of the crystal absorption at laser wavelength without taking into account other losses of the cavity was as small as 0.07 cm\textsuperscript{-1}. It evidences high quality of obtained crystals. The intracavity laser spectroscopy performance of the Cr\textsuperscript{2+}:ZnSe laser was investigated. Several CO absorption lines appearing near 2.4 $\mu\text{m}$ were used to study the spectral dynamics of intracavity absorption in the Cr\textsuperscript{2+}:ZnSe laser. It was found that the absorption signal exhibits linear growth with the time of laser generation at least up to 235 $\mu$s, which corresponds to the effective absorption path length of 70 km.

Lasing at wavelength of about 4 $\mu\text{m}$ was realized also on grown ZnSe:Fe single crystals. Laser efficiencies were determined for temperatures ranging from 80 to 260 K. Output energy of 130 mJ and quantum efficiency of 60\% were obtained at 80 K. With a CaF\textsubscript{2} prism, the Fe\textsuperscript{2+}:ZnSe laser was tuned from 3.8 to 4.4 $\mu\text{m}$ at 80 K with output energy up to 80 mJ.

Study of Electrical Properties of II-VI-based Distributed Bragg Reflectors

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An approach for a monolithic II-IV-based vertical-cavity surface-emitting laser (VCSEL) with green emission at room temperature has been developed by our group [1]. Such devices show a better coupling behaviour in fibres especially in data transmission using plastic optical fibres (POFs). These fibres have their absorption minimum around 560 nm. The key technology toward an electrically pumped device in this respect is the realization of high reflectivity Bragg-mirrors with sufficient conductivity in vertical direction.

Distributed Bragg-reflectors (DBRs) were grown on a GaAs(001)-substrate. They consist of alternating layers of materials of high and low refractive index. The high-index material is a ZnSSe layer using sulfur to achieve lattice matching to the substrate. The low-index material is made of a short period MgS/ZnSe or MgS/ZnCdSe superlattice (SL). This is lattice matched by varying the layer-thickness of the ZnSe or the Cd amount in ZnCdSe, respectively. The maximum reflectivity of the DBR used for this device can be tuned from 480 nm to 600 nm. These DBRs were grown p- or n-doped using nitrogen-plasma for p-doping and chlorine for the n-doping.

Current-voltage-characteristics were measured for DBRs with different numbers of Bragg-pairs. A sufficient conductivity of n-doped DBRs has been achieved. The conductivity depends strongly on the period and composition of the MgS/Zn(Cd)Se-SL. A DBR with 6 periods shows a current density of $10^4$ A/cm$^2$ at 1 V while a DBR with 12 periods needs 4.5 V to achieve this value.

Optical pumped VCSELs show a laser-threshold fifty-times lower than edge-emitters [2]. If this reduction is comparable to electrical operation the achieved current densities are in the order of magnitude needed for lasing. The p-doped DBRs show a higher resistance with carrier-densities of low $10^{16}$ cm$^{-3}$ and are unlikely to be used in VCSELs. The optical properties are not affected by the doping. A n-DBR with 12 periods shows a reflectivity of 97%, a p-doped sample with 17 periods reaches 99%.

Considering these results the most promising approach is a VCSEL-structure consisting of no p-doped DBRs. This leads to configurations with either tunnel-junction (TJ) and two n-doped DBRs or top-side undoped DBRs combined with upper current injection near the active region. Results of these approaches will be discussed at the end.

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Strain Effects in Multi-layer CdS/ZnS Nanocrystals

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Chemically synthesized semiconductor nanocrystals have been recently intensively investigated due to their potential applications as efficient fluorescent markers, biomarkers, quantum dot lasers and building blocks for future quantum computers. They can be synthesized as multi-shell structures (most usually quasi-spherical or tetrahedral), being built of several concentric layers of different semiconducting materials, with the shell thickness controlled down to a single monolayer. This gives a possibility to tailor the energy structure of such systems, to a large extent. Electronic and optical properties of multi-shell nanocrystals have been investigated theoretically within the multi-band kp and tight-binding approaches. No strain effects have been studies so far in chemically synthesized multi-shell nanocrystals. Here we formulate an empirical tight-binding theory, supplemented by the valence force field approach to account for the effects of strain that appear due to the lattice mismatch at the interfaces separating neighboring semiconductor layers. We show how the strain effects modify the electronic properties of multi-shell CdS/ZnS nanocrystals. We study the dependence of the strain field on the quantum dot geometry. We investigate also the effects of strain in artificial molecules built of two strongly coupled nanocrystals.
Growth and Characterisation of Cd$_{1-x-y}$Zn$_x$Be$_y$Se Crystals by Spectroscopic Ellipsometry and Luminescence

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Cd$_{1-x-y}$Be$_x$Zn$_y$Se mixed crystals are interesting semiconductors as they can be used for constructing of green lasers, visible LED's and photodetectors operating in the visible and UV spectral region. The study of optical properties is very useful in establishing composition for the fabrication of full-colour visible optical devices. In optical studies the response of a homogeneous material to an applied electromagnetic field is determined by the frequency-dependent complex dielectric function $\tilde{\varepsilon}$. Using dielectric function or complex refractive index $\tilde{n}$, the absorption coefficient $\alpha(\omega)$ can be calculated. In this work we used spectroscopic ellipsometry (SE) in order to determine the spectral dependence of $\tilde{\varepsilon}$ of Cd$_{1-x-y}$Zn$_x$Be$_y$Se crystals in the UV and visible range. In this range of energy the photoluminescence (PL) and ellipsometric investigations are complementary to each other. The investigated crystals with composition $0 < x \leq 0.15$ and $0 < y \leq 0.30$ were grown from the melt by high pressure Bridgman method. X-ray investigations show that samples with Be content up to 0.1 are uniform in composition and consist mainly one wurtzite phase.

Ellipsometric spectra were measured at room temperature in the photon energy range 0.75-6.5 eV for samples with optic axis (c-axis) perpendicular to the air-sample interface. The results represent an approximation of the optical properties in a direction perpendicular to the c-axis ($E_c$), because at the angles of incidence considered both polarisations of the incoming light probe mainly the direction perpendicular to the c-axis. The structure in $\tilde{\varepsilon}$, originating from singularities in the joint density of states, was identified as $E_0(A)$, $E_0(C)$, $E_1(A)$, $E_1(B)$, $E_1(C)$ and $E_2$ threshold energies, comparable to relevant interband transitions for hexagonal CdSe. The dispersion of the refractive index of the alloys was modelled using a Sellmeier-type relation to fit $n^2(E)$ in the photon energy range below the fundamental energy-gap.

Photoluminescence spectra were measured in the energy range from 3.2eV to 1.5 eV at temperatures from 38K to room temperature. For investigated Cd$_{1-x-y}$Zn$_x$Be$_y$Se samples with Be content lower than $y=0.15$ the PL spectrum at low temperatures exhibits exciton emission, so called “edge luminescence” due to recombination of shallow donor-acceptor pairs and weak band associated with deep levels. The values of fundamental and exciton band-gap energies estimated from ellipsometric and photoluminescence measurements are in good agreement.
Effect of Indium Doping on Structural, Electrical and Optical Properties of CdTe Thin Films

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CdTe with a direct bandgap is one of the most promising semiconductor material for thin film solar cells. Thin films of CdTe were grown by thermal evaporation onto glass substrates kept at temperature in the range of 200-300°C under a vacuum of $5 \times 10^{-6}$ torr. The distance between the source and substrate was low (5-7 cm) as compared to conventional distance (20-30 cm). The films were deposited with different indium doping typically between 2-10 wt % at substrate temperature of 250°C. X-ray diffraction showed <111> orientation for undoped and In-doped films. A significant effect of substrate temperature and In-doping on structural and electrical properties of films had been observed. The films doped with 5% indium were found to have d.c. conductivity $\sim 5.8 \times 10^{-2}$ ohm$^{-1}$ cm$^{-1}$ and Hall-mobility $\sim 2.5 \times 10^2$ cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature with a grain size of 21 nm. Optical properties of CdTe were also investigated and the band gap of films was found as 1.55 eV for undoped and 1.63 eV for 5% In-doped.
Point Defects Control in II-VI Semiconductors by Laser Driven Shock Waves

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Our experiments focus on laser driven shock waves (LSW) generated at room temperature by nanosecond laser irradiation pulses to study their influence on point defects, extended defects such as dislocations and macroinhomogeneities and the properties of semiconductor-dielectric interface.

We have studied the LSW impact on the defect system in narrow-gap HgCdTe alloys and proposed the mechanism to explain this impact in the following way: the Frenkel pairs are formed, while the native point defects acquire the energy sufficient to migrate in the semiconductor volume \cite{1}. It was established that the strongest influence was in the crystals with higher initial point defects density and especially in those with macroscopic inhomogeneities (inclusions, interfaces etc.). The proposed mechanism causes the material parameters to change in one of two dominant ways depending upon the LSW processing mode. (i) Single pulse mode results in the low temperature shock wave annealing of present point defects (these are mainly mercury vacancies in HgCdTe) that causes HgCdTe alloys to tend to p-n conversion. (ii) Multi-spike pulse mode results in the low temperature shock wave annealing of emerged point defects (these are mainly interstitial mercury in HgCdTe) that causes n-p conversion in HgCdTe alloys.

The influence of LSW on HgCdTe / CdTe films having huge amount of inhomogeneities have been studied \cite{2}. Under the high pressure gradient affect the decomposition of precipitates takes place in solids resulting from effective LSW scattering at the matrix – inclusion interface. Besides, inclusion atoms diffuse against the concentration gradient due to the LSW strain field thus redistributing in the material volume. Thus the dissipation of inclusions and ordering of native and impurity defects structure takes place in solids resulting from point defects diffusion in the LSW strain field.

Our research demonstrated the shock wave treatment as an effective non-thermal technique to process the anodic oxide – HgCdTe interface \cite{3}. The experiments show that LSW has a dual influence upon the interface, i.e. on the one hand the fixed positive charge tends to approach a particular value which seems equilibrium, but on the other hand the electron concentration in the n-type layer having emerged after annealing decrease by an order of magnitude. These phenomena are caused by the anodic oxide-HgCdTe interface rebuilt and the changed properties of Hg source at the interface in particular.

Besides, the possibility of LSW stimulated diffusion of group I metals into HgCdTe at room temperature is revealed.


Influence of a Pulse Laser Irradiation on the Charge Transfer Mechanisms in Pt(Al,Au)-CdTe Structures with a Schottky Barrier

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The electronic properties of the metal - semiconductor contacts (MES) on a basis CdTe and its solid solutions Cd$_x$Zn$_{1-x}$Te, Cd$_x$Mn$_{1-x}$Te are well interpreted by model generation - recombination charge transfer mechanism through deep levels in the area of a space charge of contact [1]. In this work the features of I-V and C-V characteristics and parameters MES with a Schottky barrier modification at laser activation of interphase interaction on the boundary metal - A$_2$B$_6$ semiconductor in a solid phase is investigated experimentally. Set parameters of optimization of modes of a pulse laser irradiation (PLI) for correction of phase composition and structure under surface layer of the semiconductor, and, accordingly, characteristics and parameters of contacts [2].

As object of investigations have utillized MES, obtained by thermal deposition of a thin film of metal (Al, Pt, Au) or chemical precipitation Au from a solution H[AuCl$_4$]·4H$_2$O on a surface of polished chips CdTe doped by atoms of arsenic or chlorine. PLI was carried out in a mode of single-pulses by intensity $I_0=0.01-20$ MW/cm$^2$ and duration $\tau = 2 - 4$ ms, on wavelength $\lambda = 1.06$ microns. Investigation of morphology of a surface and cross having chopped off MES carried out with the help of optical and scanning electronic microscopy (SEM). I-V and the C-V characteristics of MES measured at temperatures from 77 up to 350 K. Investigations of a I-V and the C-V characteristics display, that the barrier properties of MES are influenced by presence of local inserts of a phase of tellurium in a space charge of contact. The phase composition and allocation of inserts in the area of potential energy barrier by method of a X-ray diffraction microanalysis were explored. Visualization of local electric fields near interface of MES confirms change of a spatial distribution of potential in transition area owing to PLI. It results the basic charge transfer mechanism in structures is changes. The dependences log $I = f (1/T)$ and value of height of potential energy barrier calculated for low-temperature area testify confirms this idea. The investigation of surface morphology of both structure of a metal film and chips after etching of metal has shown, that at particular modes of an irradiation there are structural - phase change on an interface and the diminution of structural defects concentration of a semiconductor substrate is observed. The parameters of barrier structures thus are improved.

Off-stoichiometry Determination of II-VI Bulk Crystals

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Many physical properties of semiconductors depend on the deviation from the ideal stoichiometry of the real crystals. This is because the off-stoichiometry directly influences the density of both the point defects and the complexes of point defects and impurities. However, the available characterization techniques for the determination of the deviation from stoichiometry are usually not accurate enough. For example, in the case of II-VI materials, the previously reported technique (x-rays fluorescence, titration and coulometry) can hardly detect deviations lower than 0.1 moles% [1]. This sensitivity is clearly unsatisfactory, because the maximum width of the existence region for II-VI compounds is in the 0.01 moles% range.

Some of the authors have recently demonstrated that it is possible to determine the off-stoichiometry of CdTe samples with a sensitivity in the $10^{-4}$ moles% range by using an accurate analysis of the vapor partial pressures in equilibrium with the samples at high temperatures [2]. The partial vapor pressures are determined by means of the vapor optical absorption at the wavelengths of a HeCd laser source. The high brilliance, the pointing stability and the low divergence of the laser source make the optical bench alignment easy and the measurement procedure highly reproducible [3].

In this work it will be shown: i) the calibration curves for the partial pressure measurements of the different gas species involved ii) the equations adopted for the determination of the sample composition by using the partial pressure data iii) the experimental determination of the composition in the case of CdTe, CdZnTe, ZnTe, CdS, CdSe, ZnS and ZnSe crystals. Moreover, it will be demonstrated that by changing the sample mass to the ampoule volume ratio it is possible to determine the composition of both large deviated crystals and close to stoichiometry crystals with a sensitivity of about $10^{-4}$ moles%.

Defect Formation in CdTe in the Act of Laser-Induced Doping and Producing of Nuclear Radiation Detectors

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High-resistivity CdTe:Cl crystals are widely used for nuclear detectors. However, the resistivity ($\sim 10^9 \Omega \text{cm}$) of commercial CdTe is not high enough to achieve a low leakage current. Therefore, CdTe detectors have been usually fabricated as a diode. Laser procedure has been successfully used for doping and producing CdTe diode structures [1-3]. Laser-induced incorporation of In atoms can suppress dopant self-compensation and provide heavy doping of CdTe with a high carrier concentration ($\sim 10^{19} \text{cm}^{-3}$). However, the doping of CdTe can be accompanied by the spontaneous formation of native point defects or dopant complexes [1]. Moreover, extended defects can be generated in the act of cutting of the doped CdTe wafers.

First of all, structure defects affect a leakage current of detectors. We used $p$-like CdTe:Cl wafers of size $5 \times 5 \times 0.5$ mm$^3$. An In film was evaporated on (111)B-face. For doping of a surface layer, the samples were subjected to irradiation from the In-coated side with KrF excimer laser pulses. The In film was not completely evaporated under irradiation and it served as an electrode. A thin Au electrode was evaporated on (111)A-face. A shallow built-in $p$-$n$ junction at the In-CdTe interface arose and a Schottky barrier at the Au-CdTe contact was formed [2]. Finally, detectors were cut into $0.8 \times 2$ mm$^2$ pieces and tested by measuring the $I$-$V$ characteristics in the dark at 300 K, including time dependences of the leakage current at an applied reverse bias of 100 V (gold negative).

$I$-$V$ characteristics of In/CdTe/Au diodes showed a high forward current and low reverse currents which differed in their magnitude and shape. The lowest leakage current density of among the detectors was 1 nA/cm$^2$ and such detectors showed high spectral resolution quality [3]. All time dependences of the leakage currents can be distinguished as three types (Fig.). Type I is caused by uncompensated point defects in CdTe. Type II is associated with the current-stimulated transformation of the CdTe structure at the In-CdTe interface. Type III is attributed to the influence of the local potential fluctuations, induced by elastic deformations, on carrier generation and recombination as well as interaction of point defects with dislocations.

The defect formation in CdTe has been discussed and charge transport processes in the fabricated Au/CdTe/In diodes have been analyzed.

Influence of Defects on Phonon and Vibrational Spectra of Hydrogenated CdTe

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The high resistive CdTe is a base material for nuclear particle detectors while the presence of oxygen leads to a decrease of resistivity as well as that of the most important parameter for detectors: the $\mu \tau$ multiplication, where $\mu$ is the electron mobility and $\tau$ is the electron life time [1]. The presence of oxygen impurity is highly destructive of quality of the obtained crystals and, in turn, of their application usefulness [2]. To remove oxygen impurity, ultra-pure hydrogen is used. As already reported in our last few papers, we are able to remove oxygen from materials containing tellurium, i.e., CdTe, CdZnTe, and ZnTe [3-5]. Hydrogenation is a technological process that can purify the basic material from oxygen mainly associated to the formation of cadmium and telluride oxide compounds incorporated in CdTe lattice. The crucial point of technology is controlling of the amount of hydrogen introduced into the crystal. It has been found that a hydrogen atom localized in the crystal lattice introduces energy states into the energy gap [3]. At the same time, large amounts of introduced hydrogen can cause degradation of the obtained crystals (it concerns tellurium compound).

The analysis of the physical properties of CdTe monocrystals with different level of hydrogenation is a challenging task for research and applications.

We shall present complete MIR and FIR experimental data obtained using synchrotron radiation for special prepared CdTe-monocrystals with different level of hydrogenation. A statistical approach for a quantitative analysis of FIR measurements, based on the strained tetrahedra model, that considers extrinsic point defects in CdTe will be applied as well as the possible positions of hydrogen atoms in crystalline lattice will be presented using MIR spectral data.

Evidence of a Soft Optical Mode Driven by a Zero-gap State in HgCdTe and HgZnTe Alloys


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Lattice vibrations are very sensitive to the nearest neighbors, and thus probe the crystal structure on a small scale of the order of a lattice constant. The study of electron-phonon coupling permits to determine the long-range part of inter-atomic interaction. The influence of the electron system on the phonon spectrum of crystals is most conveniently investigated in narrow-gap semiconductor alloys of II-VI type. In some of these alloys (HgCdTe, HgZnTe), under certain conditions, a zero-gap state is realized, followed by band inversion. In order to study the effect of band inversion on the phonon spectra of HgCdTe and HgZnTe alloys we have choused the alloy samples with compositions close to the zero-gap point: $Hg_{0.115}Cd_{0.885}Te$ and $Hg_{0.1}Zn_{0.9}Te$. The fine-tuning of the exact zero-gap state we are interested to investigated may be achieved by changing the sample temperature well characterized thin crystals. The theory predicts an optical mode softening and other anomalous effects in this region [1].

For MCT alloy we measured the $Hg_{0.885}Cd_{0.115}Te$ sample with the band crossing point at approximately 230 K. Measurements were performed using a BRUKER Fourier interferometer at the National Laboratory at Frascati. A conventional Hg-lamp and synchrotron radiation sources were used alternatively. We measured Far-infrared reflectivity spectra in the temperature range 80 – 300 K. The oscillator parameters were determined by sequential application of Kramers-Kronig and dispersion analysis. Near the temperature of band crossing (230 K) a minimum is observed in temperature dependence of TO frequency of HgTe- and CdTe-like phonons. We emphasise here that this investigation is the first optical studies of the electron-phonon coupling in zero-gap state of a semiconductor crystal

Anisotropy of the Oriented Mono-crystalline ZnCdTe Phonon Spectra

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Oriented (110) (ZCT) mono-crystals have attracted considerable interest for their practical applications. In our previous work [1] we measured the reflectivity spectra of several compositions ZCT at 300K. It is necessary to note that measurements were performed for the perfect ZCT crystals samples without twins and Te-excess obtained by use of a special PVT technology [2]. Using the synchrotron radiation, as a source of FIR, enabled us to obtain a significant advantage in the spectral resolution (was about 1 cm⁻¹).

The influence of orientations is considered in literature. In the zinc-blende structure of ZCT, [3], Te (Zn) has 4 Zn (Te) neighbours at about 2.65 Å and 12 Te (Zn) neighbours at about 4.27 Å. For small amounts of Cd doping (x=0.05), the Te–Te (Zn–Zn) pairs have the same bond length while the Te–Zn pairs show substantial increases in the bond length and the disorder values compared with the ZnTe crystal. These observations suggest that at x = 0.05 the crystalline structure slightly expands along the direction of the Te–Zn bond and shrinks in the direction perpendicular to the bond. The expansion is expected to occur along the (111) direction because atoms are stacked with an ABAB pattern along the (111) direction in the zinc-blende structure, although we cannot disregard the possibility of an expansion in other directions.

There were carry out the FIR reflectivity measurements for samples ZnₓCd₁₋ₓTe, x= 0.056, x=0.28 from surfaces of (111) as well as (110) orientation at 20K in polarised light. A conventional Hg-lamp and synchrotron radiation sources were used alternatively. The results confirm the existence of differences in the phonon spectra of ZnCdTe solid solutions, for distinct crystal planes: (111) and (110).

Conductivity Switching Effect in CdZnTe Films

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A great deal of work has been done on the application of ferroelectric materials to microelectronics including dynamical random access memory and nonvolatile memory devices. The most widely studied materials are perovskite oxides, among which Pb(ZrTi)O$_3$ has been successfully applied to ferroelectric memories [1]. However, degradations such as fatigue, imprint, and retention have been a serious problem for the fabrication of nonvolatile memory devices.

The bulk CdZnTe was suggested by Weil at all. [2] to exhibit ferroelectric properties. It seems that required condition for ferroelectricity in II-VI materials is that the substitutional atoms have to be of appreciably different size from that of the host atoms they replace. Marbeuf at all [3] in their theoretical considerations on CdZnTe alloys give the hypothesis that ferroelectricity is connected with rhombohedral distortion of cubic zincblende (ZB) structure. Recently ferroelectricity has been observed in CdZnS, CdZnSe [2,4]. The main advantage of II – VI compounds is their crystal structure which better matches Si, and the fact that most of them are nonoxides.

The subject of our work was to study the conductivity switching effect in thin epitaxial layers of CdZnTe grown by MBE. CdZnTe films of different thickness (0.7 – 2) µm. and composition (0.04- 0.20) were grown on Si, Si/Au at low temperatures, 200-260 C and on GaAs substrates at temperatures of 270-350 C. The layers were characterized by X-ray diffraction (XRD) and current – voltage (I-V) measurements.

The XRD measurements indicate a polycrystalline growth of ZB CdZnTe in the case of films grown on Si and Si/Au substrates - rhombohedral distortion of the cubic unit cell was not observed. The CdZnTe layers grown on GaAs (001) substrate are single crystal with (111) ZB planes parallel to the plane of growth. The ZB unit cell being under small tensile strain (caused by thermal mismatch between the layer and substrate material) is rhombohedrally distorted.

The study of I-V characteristics were made of on metal – CdZnTe - metal structure; one contact being Schottky barrier and other - ohmic. The structure in high resistivity state after application of about +3V impulse switches to low resistivity state. The action of negative impulse restore the previous state. The image of I-V switching is presented on fig.1.

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Two Dimensional Electron Gas in a HgCdTe-based Heterojunction

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A 2DEG has been observed earlier at the surface of HgCdTe alloys. [1] However, to our knowledge, a 2DEG has not been observed in a HgCdTe based heterojunction. 2DEGs in HgTe based quantum wells have been extensively investigated. [2] Those systems are characterized by a very large Rashba effect [3] and high carrier mobilities up to 6.0x10⁵Vs/cm². In addition Mn can be substitutionally incorporated in the system which leads to a large Zeeman splitting due to the large g factor. [4] Electron concentration in HgTe quantum wells can be tuned over a wide range by applying voltage to a top gate contact. However it has proven difficult to completely deplete the quantum well which for example is necessary for gate controlled quantum point contacts. This could be possible in a triangular potential at a heterojunction.

We have found evidence for the formation of a two dimensional electron gas (2DEG) at the interface of a Hg₀.₈Cd₀.₂Te/Hg₀.₃Cd₀.₇Te heterojunction grown by molecular beam epitaxy (MBE). In transport measurements moderately distinct Shubnikov-de-Haas oscillations and Hall plateaus have been observed. The modulation doped Hg₀.₃Cd₀.₇Te/Hg₀.₈Cd₀.₂Te heterojunctions were grown by MBE on (001) CdZnTe substrates. On this structure an eight terminal Hall bar has been defined by standard lithography and etching procedures. The electrical contacts were fabricated by thermal indium bonding. Transport measurements were done at liquid helium temperature of 4.2K and at 1.6K and at magnetic fields up to 7 Tesla.

MBE Growth of ZnSe/MgCdS and ZnCdS/MgCdS Superlattices for UV-A Sensors

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The application of visible blind UV-A sensors was extensively studied for wide bandgap II-VI compound epitaxial layers. ZnMgCdS quaternary alloys as well as ZnCdS/MgCdS superlattices are II-VI compound systems which exhibit the room temperature bandgap corresponding to the UV-A region (about 3 eV). In this study, ZnSe/MgCdS superlattices were employed and compared with the properties of ZnMgCdS based materials. Binary material, ZnSe, would show easier controllability of physical properties than ternary alloy ZnCdS. UV-A sensors were grown using those three material systems, and device characteristics were compared.

ZnSe/MgCdS superlattices as well as ZnMgCdS and ZnCdS/MgCdS were grown on semi insulating (001) oriented GaAs substrates by MBE. Prior to the nucleation of the superlattices, ZnSe layers were grown to improve the surface smoothness and to avoid the defect formation associated with the reaction between the S beam and the GaAs surface. Several sample structures were grown on homoepitaxial GaAs layers.

Figure 1 compares low temperature photoluminescence (PL) spectra of a ZnSe/MgCdS superlattice sample and a ZnCdS/MgCdS superlattice sample. PL exhibited that sharp luminescence peaks were observed at around band edge region. PL intensities of ZnCdS/MgCdS superlattices were stronger than those of ZnSe/MgCdS superlattices. The PL peak position could be controlled by changing the layer thickness and the alloy composition. The PL peak positions agreed well with theoretically predicted values.

Au electrodes were deposited and the photo-responsivity was characterized using the metal-semiconductor-metal (MSM) structure. The sensitivity exhibited about 5.0 x 10^{-4} A/W only at around 400 nm very small responsivity was observed at the visible region. The ON-OFF ratio of the sensor was about 5.0 x 10^{2} for all material systems.

It was confirmed that ZnSe/MgCdS superlattices, ZnCdS/ZnMgS superlattices, and ZnMgCdS ternary alloy material were applicable to visible blind UV-A sensors.

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Effect of Surface Treatment on Properties of ZnTe LED Fabricated by Al Thermal Diffusion

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ZnTe is expected as a promising material for a variety of optoelectronic devices such as pure green light emitting devices because of its direct transition band gap of 2.26 eV at room temperature. Although p-type ZnTe was obtained easily, the growth of n-type material was difficult due to the so-called self-compensation effect and the incorporation of residual impurities. Recently, Sato et al. have overcome the problems and fabricated pn-junction LED by Al diffusion technique using high-quality bulk crystals grown by a vertical gradient freezing method [1]. We have also fabricated a ZnTe LED by Al diffusion using Bridgman-grown substrates, and observed the pure-green electroluminescence (EL) at room temperature [2]. In the thermal diffusion, it is important to control the interface of Al and ZnTe substrate since the interface would influence the diffusion property. In this study, we have investigated the effect of the surface treatment before Al deposition on the properties of ZnTe LED fabricated by the thermal diffusion of Al.

p-type ZnTe was used as the substrates. We have attempted three kinds of substrate treatments: (1) wet cleaning using organic solvents and a Br-methanol solution for the etching, (2) in-situ thermal cleaning after wet cleaning, and (3) in-situ H radical cleaning after wet cleaning. The surface crystallinity of the ZnTe was monitored using reflection high-energy electron diffraction (RHEED). Then, Al film was deposited on the substrate, and the Al thermal diffusion was carried out as reported previously [2]. After the thermal diffusion, an electroless Pd was deposited on the back surface to fabricate the LED.

In the case of the wet cleaning, the ring pattern was observed in RHEED measurement, indicating that the surface of ZnTe was poly-crystalline due to the presence of native oxides or contaminations. The LED fabricated by using this process showed a rectification behavior of pn-junction diode with a turn-on voltage of 2-4 V in I-V characteristics, and the electroluminescence (EL) was seen in the LED with low turn-on voltage. On the other hand, the spot pattern was observed in the case of in-situ thermal or H radical cleaning, indicating that the clean surface of ZnTe was obtained. However, the I-V characteristics of the LED fabricated on them showed a very large series resistance, and the EL was not observed. This means a resistivity of the diffusion layer is very high, probably due to the formation of a heavily Al doped layer resulting from the Al diffusion through a clean interface. The reason why the properties of LED fabricated using wet cleaning were better than others is considered to be due to the fact that the presence of a poly-crystalline layer at the interface prevent the ZnTe from a heavy Al doping. Based on these results, we have attempted to control the interface by inserting an oxide layer on a clean surface of ZnTe intentionally in the next. As a consequence, we have found that the Al concentration in the diffusion layer can be controlled by changing the thickness of the oxide layer. The LED performance was improved significantly by optimizing the Al concentration.

Percolation Model for Long Wave Phonons in random Zincblende Alloys: from II-VI’s to III-V’s

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It is admitted that the $q\sim 0$ phonons from random $\Lambda_{1-x}B_xC$ mixed crystals comply with the 1-bond-1-mode behavior, as envisaged by the well-known modified-random-element iso-displacement (MREI) model. This is based on a description of the mixed crystals in terms of the virtual crystal approximation (VCA), i.e. of an ideal effective medium that is perfectly homogeneous at the local scale. While the VCA seems appropriate for the description of physical properties that are integral in character, such as the band gap or the lattice constant, our view is that it is not valid for phonons, because these are local properties. Therefore their basic understanding should require detailed insight upon the topology of the substituting species, which falls into the scope of the percolation site theory.1

Precisely in the recent years we have developed an empirical percolation model for the $q\sim 0$ phonons in random zincblende mixed crystals. Most our attention was focused on (Zn,Be)-chalcogenides. Indeed these open the class of mixed crystals with a large contrast in the bond stiffness and percolation effects in vibrational spectra, that address directly the bond constant, are expected to be exacerbated in such contrasted systems. In the percolation model the $\Lambda_{1-x}B_xC$ mixed crystals are described at each composition in terms of composite systems made of the randomly-formed $A$-rich and $B$-rich regions. This brings naturally a 1bond-2mode behavior which discriminates between vibrations in the statistically-formed $A$- and $B$-rich regions. In particular the model takes into account the ‘fractal-normal’ transition which accompanies the ‘dispersion-continuum’ topology transition at the corresponding bond percolation thresholds, i.e. $x_{BC}\sim 0.19$ (B-rich region) and $x_{AC}\sim 0.81$ (A-rich region). We emphasize that there is no additional input with respect to the MREI model.

In this work we start from a detailed description of the percolation model for transverse optical (TO) and longitudinal optical (LO) $q\sim 0$ phonons related to the stiff Be-Se bond in the pioneer mixed crystal ZnSe-BeSe, that could be achieved only recently,2 and derive a simplified version of the percolation model that can be applied to usual zincblende mixed crystals, i.e. with no contrast between the bond stiffness. This is tested with GaAs-InAs, taken here as a typical challenging system. The much debated multi-phonon behavior of this III-V alloy over the last twenty years is accordingly re-examined, with such success. The discussion is supported by full contour modeling of the Raman lineshapes, and ab initio calculations of the internal tensions in the ZnBeSe alloy.3

Growth of Boron-Doped ZnTe Homoepitaxial Layer by Metalorganic Vapor Phase Epitaxy

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ZnTe is expected as a promising material for pure green light emitting diodes and laser diodes, since it has a direct transition band gap of 2.26 eV at room temperature. However, conductive n-type ZnTe is still difficult to be obtained except for aluminum doping [1-3]. As for metalorganic vapor phase epitaxy (MOVPE), which is a promising growth technique for mass production, so far, several efforts have been made to attain n-type ZnTe using a variety of dopant sources. However, there have been no reports on boron (B) doping on ZnTe.

In this study, we have investigated the growth of B-doped ZnTe layer on the (100) ZnTe substrate by atmospheric pressure MOVPE using triethylboron (TEB). Dimethylzinc (DMZn) and diethyltelluride (DETe) were used as Zn and Te sources, respectively. Hydrogen was employed as a carrier gas. The substrate temperature and the total flow rate of carrier gas were kept at 380°C and 308 sccm, respectively, which provide an optimal condition for preparing undoped homoepitaxial ZnTe layer of good quality. Typical transport rates of DMZn and DETe were 10 and 30 µmol/min, respectively. In order to determine the B-related level in B-doped homoepitaxial ZnTe layer, photoluminescence (PL) measurement was performed. The PL spectrum at 4.2 K of undoped ZnTe layer exhibited a strong free excitonic emission (FE), its longitudinal optical phonon replicas (FE-LO) and very weak excitonic peak (Ia) attributed to an emission from exciton bound to neutral acceptors such as Na.3) The introduction of the dopant induced the considerable change in the PL spectra even in the case of a low transport rate of 0.1 µmol/min. Excitonic emission bound to neutral donor with shallow level and donor-acceptor pair (DAP) recombination emission were emerged by adding the TEB dopant source, which indicates the incorporation of B into ZnTe as a donor impurity. The PL intensity of the DAP drastically decreased with increasing the temperature (5∼160 K) due to thermal quenching. From fitting analysis for temperature dependence of the PL intensity of DAP recombination, based on a two-step quenching mechanism, 4) the value of donor level was estimated to be ∼20 meV. This value agrees well with one obtained from relationship between PL intensity and the excitation intensity.

Abnormal Surface Oxidation in High Resistivity Poly-CdZnTe

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High resistivity poly-CdZnTe (polycrystalline CdZnTe) is an attractive material for large area X-ray detector especially in medical applications, due to its high atomic number, low electron-hole pair creation energy, high mobility, and chemical stability. In our previous research, we reported the deposition process of high resistivity ($1 \times 10^{10} \Omega$ cm) poly-Cd$_{0.96}$Zn$_{0.04}$Te:Cl layers (150 µm thick) by thermal evaporation method, its characterization and the detailed procedure to reduce leakage current by Schottky barrier formation.[1,2]

To decrease the carrier recombination at surface and grain boundary and the crosstalk between electrodes, we tried to oxidize poly-CdZnTe using different KOH and H$_2$O$_2$ concentrations and treatment time (maximum 1 hour) at 60°C after 2% Br-MeOH etching. In the AES (Auger electron spectroscopy) measurement, very thin mixture of elemental Te and TeO$_2$ or CdTeO$_3$ layers were found in oxidized samples as reported earlier but, unlike that of single CdTe or CdZnTe which shows fast surface oxidation, the poly-CdZnTe samples kept in the air for 1 hour (i.e. air kept samples) after Br-MeOH did not showed oxidation layers. The gold electrode was formed by thermal evaporation and it showed nearly ohmic contact properties. The leakage current of all the samples was about 90nA/cm$^2$ at 40 V. All the measurement was done at room temperature. In the photoconductive decay measurement [3] of oxidized and kept in air samples, poly-CdZnTe exhibits nearly same photoconductive decay properties regardless of existence of oxidation layer as shown figure 1.

In this paper, we tried to exploit the mechanism of oxidation process in poly-CdZnTe samples.

Figure 1. Photoconductive decay signal of as-etched (kept in air for 1 hour), KOH and H$_2$O$_2$ solutions treated samples. Excitation source was 612nm laser diode.

Ferroelectricity in (Cd,Zn)Te was first observed in 1989 [1], with the electric polarization oriented in the [111] direction. Since then, the effect has been observed in other II-VI alloys, such as (Cd,Mn)Te and (Cd,Zn)S. Electric characterization revealed a clear hysteresis in the polarization-voltage dependence [2]. Due to the presence of switching effects these materials are considered in future applications in microelectronics including dynamical random access memory and nonvolatile memory devices. Despite the well-established experimental results, the mechanism of ferroelectricity in (Cd,Zn)Te is not understood.

We investigate possible sources of the electric polarization in (Cd,Zn)Te using ab-initio calculations based on the Local Density Approximation and atomic pseudopotentials. We employ the code developed in Trieste and Bologna (ww.pwscf.org) that uses plane waves as the basis set. (Cd,Zn)Te alloy is lattice mismatched, which according to our calculations induces its instability with respect to segregation and formation of fluctuations with the varying chemical composition. The presence of fluctuations may generate two effects. The first one is the possible formation of nanoinclusions with the wurtzite structure. The hexagonal symmetry of such inclusions allows for the presence of spontaneous electric polarization together with piezoelectric effects, which may be enhanced by the difference of lattice constant induced by the fluctuations of the chemical composition. The second effect consists in the formation of metastable configurations of host atoms that are similar to the DX-like configurations of dopants. These configurations are characterized by breaking of one of the four bonds with nearest neighbors, and they depend on the neighbors’ chemical identity.

Far Infrared Selective Absorption in Uniformly Iodine Doped MBE CdTe/CdMgTe Quantum Well – with no Energetic Scaling

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The properties of shallow donors in 2D systems were intensively investigated in selectively doped GaAs/GaAlAs structures, where one observes a strong dependence of the donor binding energy on its position in the structure. Similar experiments, based on magnetophotoconductivity measurements in the Far Infrared (FIR), based on Zeeman’s splitting of the levels in the external magnetic field, done on CdTe/CdMgTe single quantum well, uniformly doped with iodine, showed the same relation in II-VI 2D systems.

On the contrary to the $\delta$-doped 2D samples, for the case of uniform doping, the additional features of the system have to be considered in order to understand obtained results. For the CdTe/CdMgTe quantum well, the measured photoconductivity ($PC(B)$) spectra exhibit relatively broad, nonsymmetrical lines due to intra-impurity transitions. The spectra recorded for different photon energies (between 2.2 and 17.6meV), exhibit maxims for the same magnetic fields. They do not obey the Zeeman’s rule of proportionality between energy level splitting and $B$. For the investigated system, we report observation on the measured $PC(B)$ spectra two lines (a strong one at $\sim 2$ T and a very weak - at $\sim 4.5$ T - see Fig.). The range of transition energies, when lines are visible, corresponds to the energy width of a quasi-continuum of intra-impurity transitions present in the sample. The presence of this continuum is due to homogeneous doping with iodine donors in the region of quantum well and barriers, which results in uniform distribution of donors, giving the full spectrum of available intra-donor transition energies. The theory explaining the surprising lack of energetic scaling is basing on the presence of local potential fluctuations in the sample, which do localize electrons and mentioned continuum of available shallow donor states, were presented elsewhere.

On the base of line positions in magnetic field we can estimate the spatial size of fluctuations in the investigated system – about 35nm for line visible at $\sim 2$ T, and $\sim 24$ nm for the line at $\sim 4.5$ T. We are able to identify the location of donors, which do contribute to the observed signal. The results are discussed in terms of mentioned theory.

All presented results were done on 200meV deep in the conduction band and 16nm wide CdTe/Cd$_{0.8}$Mg$_{0.2}$Te quantum well doped uniformly with iodine in the well and in the barriers at the level of $\sim 10^{16}$cm$^{-3}$ (below Mott transition in CdTe). The samples were obtained by MBE method on the semiinsulating GaAs substrate with 8µm buffer layer of undoped CdTe.
The New Method to Analyse of the Photoluminescence Spectra of CdS$_{1-x}$Se$_x$ Solid Solutions

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The photoluminescence spectra (PL) of solid solutions (SS) are strongly influenced by compositional disorder, which generates localized electron states in the band gap. In PL exciting spectra (PLE) and selective excited PL are revealed a fine structure of the spectra due to specific manifestation of separated localized states. This fact allows to study the contribution of localized excitons with certain localisation energies in radiative recombination of solid solution.

In the present work is reported about systematic study of selective excited PL and PLE spectra for CdS$_{1-x}$Se$_x$ crystals. CdS$_{1-x}$Se$_x$ crystals were grown by means a sublimation method at 950 C. Registration of the PLE spectra was performed at 4.2 K, the PL spectra at 4.2. The energy of the registration varied over the spectral range of the first phonon replica with 2 meV steps.

In PLE spectra registered at energies in the range of first LO phonon replica observed narrow peaks. The narrow peaks are formed by the radiative recombination with an emitting of LO phonon from localized states belonging to a certain narrow part of the DOS tail. The intensity of the peak in the PLE spectrum is proportional a contribution of the excitons with the certain localisation energy in the radiation recombination with LO phonon emitting. The dependence of the amplitude of the peaks on their energy position ($A(E)$) is a spectral distribution of contributions of the exciton localized states in the PL within the first LO phonon replicas range. An analytic expression for $A(E)$ is build on a base of the expression describing PL intensity of localized excitons. The PL is proportional to both the absorption coefficient ($\alpha(E)$) and the relative population of the states ($P(E)$): $I(E) \sim \alpha(E) P(E)$. A selection of an analytic expression for $I(E)$ depends on both the type of the and parameters of function of density of the states (DOS) and processes of energy transfer by DOS tail. To obtain this information is performed systematic study of selective exciting PL spectra and PLE spectra at fixing of registration energies within nonphonon line. This study alloyed to reveal the limit to linear approximation for the relative population of the states function using for diluted SS.

It is showed that the PL of localized excitons for SS with significant concentration of both anion components can be described by the following expression:

$$A(E) = a[e^{\exp(-E/E_{ME})}d\exp(-2\exp(-E/E_{ME})/d)] + \exp(-E/E_{ME})/d\exp(-3.037\exp(-(E-E_{ME})/d))]$$

where $E_{ME}$ – a mobility edge (the energy separate isolated localized states from others), $d$ – a parameter depending on the width of the tail carrying in the PL considerable contribution. This parameters are the best fitting parameters for a describing the experimental $A(E)$ by expression (1). An analysis of selective exciting PL spectra performing with expression (1) allows to separate resonance and relaxation parts in a range of phonon replicas. The PL spectra of CdS$_{1-x}$Se$_x$ SS with hexagonal structure and with co-existence of regions with hexagonal structure and structure with stacking faults [1] were analyzed by means expression (1).

Observations of the triplet trion states were reported in a number of publications devoted to the studies of modulation-doped quantum wells based on ZnSe [1], GaAs [2] and CdTe [3]. However theoretical calculations show that the optical transitions into the triplet states are forbidden. Thus the question “why are the triplet states of the trion observed?” remained unclear.

In the present work we studied modulation-doped CdTe/(Cd_{0.7}Mg_{0.3})Te QW structures containing a 2DEG with electron density varying from $n_e < 10^{10}$ up to $10^{12}$ cm$^{-2}$ with a 100 Å single quantum well (QW) grown on GaAs (100) substrates and were $\delta$-doped in the barriers at 100 Å distance from the QW. We studied photoluminescence (PL) and reflectivity spectra of these structures in the magnetic field up to 45T.

In the PL spectra of the sample with $n_e = 3 \times 10^{10}$ cm$^{-2}$ in low magnetic fields the lines of the exciton and singlet trion state were observed. In magnetic fields higher than 25T in the vicinity of the crossing of the upper Zeeman component of the trion and the lower Zeeman component of the exciton a new line appeared. In reflectivity spectra this line was not observed which allows us to attribute the observed PL line to the optically dark triplet trion state. The binding energy of the this triplet state increased in magnetic fields from 0 to 3 meV in the field of 45T, which is in correlation with theoretical calculations for the binding energy of dark triplet state.

In magnetic fields starting from 35T both in reflectivity and PL spectra a bright triplet trion state was observed. Its binding energy amounted to about 1 meV in 45T magnetic field.

The observation of the dark triplet trion state in the PL was explained by the preferable population of exactly this triplet trion state meanwhile the formation of the singlet trion states is suppressed in the magnetic field at low temperatures.

The singlet trion states are formed when the electron from the lower Zeeman sublevel becomes bound with the exciton from the upper Zeeman sublevel or when the electron from the upper Zeeman sublevel binds with the exciton from the lower Zeeman sublevel. In the first case the formation of the singlet state is suppressed due to the depletion of the exciton Zeeman sublevel, in the second case – due to the depletion of the electron Zeeman sublevel. On the contrary, the observed triplet state is formed by electron and exciton both from the lower Zeeman sublevels. Thus the formation of the this dark triplet state becomes preferable in the magnetic field at low temperatures, which leads to observable luminescence from this state despite the fact that the oscillator strength of such transition is very low.

A model calculation using the system of the kinetic equations describing the PL of the exciton-trion system was performed. The calculated dependences of the intensities of all the spectral lines on the magnetic field were close to the experimental.

Optical Detection of a Spin Accumulation in a CdTe Quantum Well

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New electronic devices for future information technologies may use the spin of carriers. This upcoming domain, spintronics, seems very promising to improve nowadays possibilities: spin transistors for instance. Understand spin carrier behaviour in various structures will allow big advances for this new field.

Tunnelling between 2 ferromagnetic (FM) layers has been widely studied with metals showing spin dependent transport. Spin polarised currents in those structures (FM/non magnetic (NM)/FM) induces a spin accumulation in the anti-parallel magnetic configuration, leading to a separation ($\Delta \mu$) of the electrochemical potential of spin up and down. In metallic structures, this separation is only of a few $\mu$eV [1] due to the high density of carriers in the NM layer. In order to increase $\Delta \mu$, the use of diluted magnetic SC as spin polarizer seems promising. Another advantage would be the possibility to optically probe these structures. In III-V SC, an indirect electric measurement with a GaAs quantum well (QW) embedded into 2 GaMnAs DMS layers showed a separation around tens of meV [2]. II-VI SC have also been used for spin devices [3].

Figure 1: Sample.

Figure 2: CdMnTe aligner Zeeman splitting

Our sample consists of a CdMnTe spin aligner, a CdMg$_{30}$Te barrier and a CdTe QW where spins are accumulated (fig.1). The CdMnTe layer presents a high spin polarisation at low temperature under magnetic field due to giant Zeeman effect. We reached a Zeeman splitting of 90 meV (fig.2) high enough to consider a total polarisation of electrons. Samples are grown by Molecular Beam Epitaxy and Al/Au contacts made under ultra high vacuum. N-doped contact layers showed perfect ohmic contacts at 7K.

Further investigations to detect spin accumulation are needed. Then, new perspectives would be opened: samples with FM electrodes (p-doped CdMnTe) in order to switch from parallel to anti parallel configurations, optical control of spin accumulation and size dependent phenomena with narrower etching process.

Investigation of Spin - Injection into InAs Based LED’s

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We have investigated electroluminescence and current-voltage (I-V) characteristics of both magnetic and non-magnetic InAs-based light-emitting-diodes (LED’s). An n-type (Cd,Mn)Se layer is used to spin-polarize electrons, which are injected into an InAs quantum well. For comparison, nominally identical non-magnetic structures, with the n-type (Cd,Mn)Se injector replaced by n-type CdSe, were also investigated to elucidate the inherent band structure and spin-orbit interaction effects on the circularly polarized emission. Measurements of circularly polarized electroluminescence of the top emitting LED’s were performed in magnetic fields up to 10T at low temperatures. Measurements were made with samples immersed in liquid helium to minimize lattice-heating effects of the injection current. The spectra were obtained with a Fourier Transform Spectrometer equipped with a 77 K InSb photodiode detector. The observed circular polarization degree of the magnetic structures shows a maximum of about 10% at 3.5T and decreases for higher magnetic fields. The non-magnetic structure also shows a maximum of comparable magnitude, but the signal-to-noise is considerably worse due to decreased emission. In this case the observed polarization is attributed to the complex nature of the valence band and the participation of both heavy and light holes in the wide InAs layers. We will discuss the origin of the observed luminescence features based on their dependence on temperature, injection current and magnetic field, as well as the relationship of the circular polarization properties to the injected spin polarization.
Epitaxial Quantum Dots from Immiscible II-VI/IV-VI Material Combinations

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The shape and the compositions of self assembled quantum dots from the commonly used group III-V and group IV material heterosystems are strongly modified during overgrowth, due to intermixing between the dot and the host materials. This intermixing can be avoided, when immiscible material combinations are used for heteroepitaxial growth, such as IV-VI compounds, crystallizing in the cubic rock-salt structure (rs), embedded in zinc-blende (zb) II-VI host crystals. For a demonstration of immiscible, epitaxially self-organized quantum dots we choose the combination PbTe(rs)/CdTe(zb). It offers several advantages: (a) almost perfect matching of the cubic lattice constants, (b) growth on epiready GaAs substrates, (c) large quantum confinement, and (d) small nonradiative Auger recombination in PbTe.

The sample preparation is done in two steps: First, at substrate temperatures of 250 °C, 5 nm thick PbTe quantum wells are grown on CdTe/GaAs pseudosubstrates and covered by 50 nm thick capping layers. Subsequently, the quantum dot formation is induced by thermal annealing at temperatures up to 350 °C. This allows the minimization of the PbTe/CdTe interface energy by a rearrangement of the PbTe from the quantum well into an array of regularly shaped, highly faceted, quantum dots. By high resolution transmission electron microscopy, the quantum dot shape is found to be approximately that of a small rhombicuboctahedron with a diameter of about 25 nm. These quantum dots show abrupt interfaces and intense room temperature photoluminescence in the mid-infrared, in spite of the different lattice structures of the quantum dots and the host materials. This makes them very promising for the development of efficient quantum dot devices emitting in the mid-infrared.

Fig. 1: (a) Transmission electron micrograph of a strongly faceted PbTe quantum dot in a CdTe matrix. (b) Room temperature photoluminescence spectra of a PbTe/CdTe heterostructure for various annealing temperatures. The peak at 2.9 \textmu m wavelength is caused by the initially grown quantum well while the peak at 3.2 \textmu m wavelength is ascribed to the quantum dots, which are formed during thermal annealing.
Electrical Manifestation of Ferromagnetic Ordering in Phosphorus-doped Semimagnetic Semiconductor Zn_{1-x}Mn_xTe

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Recently, we have found that annealing of Zn_{1-x}Mn_xTe crystals doped with phosphorus to a level of $5 \times 10^{19}$ atoms/cm$^3$ under high pressure of nitrogen gas allows us to obtain Zn_{1-x}Mn_xTe:P with the hole concentration ($p$) as high as $4.8 \times 10^{18}$ cm$^{-3}$ for $x = 0.03$. This concentration is comparable to the Mott critical density for ZnTe, $N_C \approx 1 \times 10^{19}$ cm$^{-3}$. In this communication, we report the results of the Hall effect, resistivity, and magnetic susceptibility measurements for Zn_{1-x}Mn_xTe with the value of $p$ close to the $N_C$. We found that in the annealed Zn_{1-x}Mn_xTe:P samples with $p(300K) = (4.8 - 7.8) \times 10^{18}$ cm$^{-3}$, the acceptor binding energy ($E_A$) increases at temperatures lower than 6 and 25 K for Mn molar fraction $x = 0.01$ and 0.03, respectively. Simultaneously, the increase in $E_A$ is accompanied by the change in the Curie–Weiss temperature ($T_{C-W}$) sign from negative to positive, and by the large negative magnetoresistance: $\rho(0,1.3K)/\rho(6T,1.3K) > 10^3$. No such behavior was detected for the as-grown Zn_{0.97}Mn_{0.03}Te:P with $p = 2 \times 10^{18}$ cm$^{-3}$ or ZnTe:P with $p = 9.8 \times 10^{18}$ cm$^{-3}$.

Zn_{1-x}Mn_xTe crystals ($0 \leq x \leq 0.09$) were grown by the high pressure Bridgman method and were subjected to post-growth high pressure annealing in nitrogen atmosphere. To investigate the effects of the annealing on the net $p$, $E_A$, and $T_{C-W}$ the Hall effect, resistivity, and magnetic susceptibility measurements were carried out as a function of temperature. We have found that the electrical resistivity of the ZnTe:P sample with $p = 9.8 \times 10^{18}$ cm$^{-3}$ exhibits a metallic behavior, showing practically no change in the temperature range from 300 to 1.3 K. In contrast, the electrical resistivity of the Zn_{1-x}Mn_xTe samples exhibits an insulating behavior. In particular, the resistivity of the as-grown Zn_{0.97}Mn_{0.03}Te sample is characterized by a negative $T_{C-W} = -2.5$ K, reflecting the antiferromagnetic nature of Mn–Mn coupling. However, both the annealed Zn_{0.97}Mn_{0.03}Te with $p = 4.8 \times 10^{18}$ cm$^{-3}$ and Zn_{0.99}Mn_{0.01}Te with $p = 7.8 \times 10^{18}$ cm$^{-3}$ and $\mu = 40$ cm$^2$/Vs exhibit weaker temperature dependence of the resistivity and show that the $E_A$ increases on lowering temperature.

We have found that in the annealed Zn_{0.97}Mn_{0.03}Te sample $E_A$ increases from 0.003 eV for $T > 25$ K to 0.009 eV for $T < 25$ K, at the same time the $T_{C-W}$ reaches $+2.5$ K indicating the carrier-mediated ferromagnetic exchange interaction between Mn$^{2+}$ ions; and for Zn_{0.99}Mn_{0.01}Te, $E_A$ increases from 0.0009 eV for $T > 6$ to 0.0016 eV for $T < 6$ K, and $T_{C-W}$ reaches $\sim +0.8$ K. Evidently, the increase in $E_A$ is closely connected with the ferromagnetic ordering in both the annealed samples. We have developed a theoretical model taking into account the magnetic contribution to $E_A$. The calculated temperature dependence of the resistivity well describes the experimental data as shown in the Figure, and gives a value of $T_{C-W}$ close to that determined from the magnetic measurement.

In conclusion, the increase in $E_A$ revealed from the resistivity measurements can be regarded as an electrical manifestation of the ferromagnetic ordering in Zn_{1-x}Mn_xTe:P.
Structural and Optical Properties of CdSe/ZnSe Nanostructures Grown by MBE on Virtual Si/Ge Substrates

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Growth of self-assembled II–VI quantum dots (QDs) on Si/SiGe substrates is of crucial importance for the integration of optoelectronic devices with the mainstream silicon-based technology. This work is devoted to growth, TEM, X-ray and PL characterization such CdSe/ZnSe QD structures. The samples were grown by molecular beam epitaxy on Si(001)/Ge(001) virtual substrates. They consisted of one or five periods of CdSe QDs with nominal thickness of 1-4 monolayers with ZnSe spacer layer thickness of about 20 nm. Reference samples were grown on conventionally used GaAs(100) substrates. The results of TEM and X-ray measurements showed that high-quality ZnSe layers as well as CdSe QD arrays embedded in ZnSe barriers could be grown on Si/Ge virtual substrates.

It has been established that the QD structures grown on different substrates exhibit comparable high luminescence efficiency at low temperatures. Two peaks were observed in the luminescence spectrum of some samples grown on GaAs as well as Si/Ge substrates. They are attributed to the emission from two types CdSe islands (QDs) between which there is no efficient exciton transfer. This is confirmed by presence of these two luminescence lines in the emission spectrum up to room temperature. The slowest luminescence quenching with the temperature increase was displayed by a structure grown on Si(100)/Ge virtual substrate. The activation energy of luminescence quenching for this structure exceeds 120 meV. In summary, we have shown that using of Si(001)/Ge(001) virtual substrates is promising for the growth of CdSe/ZnSe QD structures with high luminescence efficiency.
The Effects of In Situ Annealing on CdSe Quantum Dots Grown by ALE

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The growth mechanism for CdSe Quantum Dots (QD) has been the subject of much debate. Transition from 2D to 3D growth occurs gradually in the CdSe/ZnSe system suggesting that the mechanism is more complex than Stranski-Krastanow (SK) growth alone [1]. Oswald Ripening (OR) has been observed in the CdSe/ZnSe system [2]. The theory is well understood but less is known about the influence of strain on island stability, size and spatial distribution. TEM studies have revealed the presence of two types of dots; SK dots and Strain Modified (SM) islands [3].

At Heriot-Watt we have observed differences in the PL spectra between as-grown CdSe QD and samples subjected to an annealing step before the cap deposition. Separation of the emission energies of two types of dots, attributed to the annealing of the dot layer, has been observed in PL spectra [4]. The energies of the SM and SK dots overlap in as-grown samples. Additional studies have been carried out into the effect of the dot annealing procedure, in order to further understand the result. A series of samples, containing CdSe layers grown by ALE with identical thicknesses (Fig. 1) has been grown with annealing times of 3 to 13mins. PL data (Fig. 2) obtained from the series of samples shows that as the annealing time is increased so the emission energy increases.

The effect of annealing on the distribution of QD sizes and densities measured by AFM and the corresponding changes in PL intensities will be discussed.

Quantum dots (QDs), frequently referred to as artificial atoms, attract much fundamental and practical interest. Experiments presented here were carried out on self-assembled CdSe/ZnSe QDs grown on (001) GaAs substrate by molecular beam epitaxy. Photoluminescence (PL) was excited by a dye-laser which allowed us to change excitation energy continuously, exciting either in the ZnSe barrier or directly in the CdSe dots. Sample orientation was controlled by a stepping motor with accuracy better than 1°.

A feature specific to self-assembled QDs is their extremely anisotropy. Because of their elongated shapes and the strain field around the dots, the point-group symmetry of such QDs reduces to $C_{2v}$ or even below, resulting in an anisotropic exchange splitting of the radiative excitonic doublet [1]. As a consequence the PL turns out to be linearly polarized with the polarization axis along [110]. Low symmetry of QDs manifests itself in the existence of the second harmonic with respect to sample rotation around the growth direction. Application of a magnetic field in Voigt geometry additionally leads to the appearance of the zeroth and the fourth harmonics [2]. Moreover, we found a symmetry enhancement of QD emission, induced by an in-plane magnetic field. At some compensation field, $B_c$, the amplitude of the second harmonic becomes exactly zero and the fourth harmonic dominates. This implies symmetrization of QD optical response counter-intuitive to the intrinsic low symmetry of the QDs.

We also found circular-to-linear polarization conversion, similar to that reported for superlattices [3]. In the case of CdSe/ZnSe QDs the conversion occurs in zero magnetic field, owing to anisotropic exchange splitting under quasi-resonant excitation. In order to separately separate the exciting and emitted lights, the PL was detected at phonon replica. The circular polarization of the emitted light reveals opposite signs for excitation-polarizations along [100] and [010] directions, and becomes zero when linear polarization of the exciting light is set to [110] axis. Under circularly-polarized excitation the polarization axis of the linearly polarized PL rotates from [110] towards [100] or [010] directions. Such a behavior is qualitatively explained in terms of pseudospin formalism.

Nanosecond Spin Memory of Electrons in CdTe/CdMgTe Quantum Wells

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Long spin memory of free carriers is essential for spin-based devices. It is relevant for II–VI materials where efficient spin injection has been demonstrated [1]. We report on the electron spin relaxation time \( \tau_s \) in CdTe quantum wells (QWs) which are as long as from 1 to 16 ns. We exploit two different optical techniques to study spin dynamics in an 80 Å-wide CdTe/CdMgTe QWs with a two dimensional electron gas (2DEG) of density \( n_e = 8 \times 10^{10} \) cm\(^{-2}\). Signals given in the figure were detected on the resonance energy of the negatively charged exciton (trion) at a temperature of 1.7 K and in magnetic field oriented along the QW plane.

(i) The Hanle curve of the optical orientation signal measured under cw excitation is given in panel (a). The appearance in CdTe QW was similar to the one reported for GaAs QWs [2]. Due to the spin dependent formation of the trion the polarization of both exciton and trion is linked to that of a 2DEG. Electron spin relaxation time \( \tau_s = 16 \) ns was evaluated from the characteristic magnetic field \( B_{1/2} = 0.45 \) mT.

(ii) The time-resolved pump&probe Kerr rotation technique with 1-ps pulses was used to measure electron spin beats as shown in panel (b). Electron spin relaxation time \( \tau_s = 1 \) ns was evaluated from the beat amplitude decay. It is interesting that the spin relaxation times obtained by two methods differ by an order of magnitude. Our current explanation is that in optical orientation experiments contribution of localized electrons dominates, while the Kerr signal all electrons are contributing.

High-efficiency Low-threshold Optically-pumped Green Laser with Single CdSe Quantum-disk-sheet Active Region

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High power semiconductor lasers of green spectral region (500-550 nm) are of great demand for numerous applications, like projection television, local optical communications, laser location and navigation, underwater communications etc. Although ZnCdSe/ZnMgSSe laser diodes revealed enhanced optical degradation due to the metastable nature of N-acceptors [1], undoped ZnSe-based laser heterostructures pumped by electron or optical beams show much better degradation stability and high enough quantum efficiency [2]. The need of compact laser devices, like e-beam pumped lasers using micro-guns [3] or a blue-violet to green optical converters exploiting a III-nitride laser for pumping a II-VI active laser element [4], imposes strong limitations on threshold characteristics of the II-VI laser chip. II-VI laser heterostructures with CdSe quantum-disk-sheet (QDS) active region embedded in a short-period superlattice (SL) waveguide [2,4] can meet the requirements of low threshold, high quantum efficiency and high output power simultaneously, owing to a purposeful design modification.

In this paper we report on the studies of structural, photoluminescence and laser characteristics of the molecular-beam-epitaxy (MBE) grown Cd(Zn)Se/ZnMgSSe optically-pumped laser heterostructures of a modified design. The modification concerns both the CdSe QDS active region and overall structure design. The CdSe QDS is fabricated by the multi-cycle migration enhanced epitaxy (MEE) technique to achieve narrower lateral size distribution and higher Cd content of CdSe quantum disks [5]. The laser structure design comprises: a Zn\textsubscript{0.86}Mg\textsubscript{0.14}S\textsubscript{0.21}Se\textsubscript{0.79} bottom cladding layer of increased thickness (above 1 \textmu m) and energy gap (2.98 eV at 300K) to prevent the optical mode leakage to a GaAs substrate, a wider gap ZnMgS/MgSe strained SL at the cladding-substrate interface to prevent carrier escape to the GaAs substrate, a 0.23 \textmu m-thick ZnS\textsubscript{0.15}Se\textsubscript{0.85}/ZnSe SL asymmetric waveguide with the CdSe QDS/ZnSe QW active region shifted by 50 nm from its center to the bottom cladding, i.e. to the optical mode maximum, and a top 50-nm ZnMgSSe cladding layer to avoid generated carrier loss at the surface. A 337.1 nm wavelength of the N\textsubscript{2}-laser (8 ns, 10\textsuperscript{3} Hz) was used for excitation. As a result, minimum laser threshold, maximum external quantum efficiency and maximal output power of 4.8 kW/cm\textsuperscript{2}, 32\%, and 21 W from both facets, respectively, have been achieved at 300K. The laser structure shows internal loss as small as 1-2 cm\textsuperscript{-1}. Simultaneously, transmission electron microscopy reveals a noticeable density of extended defects generated within the body of the ZnMgSSe cladding layer, presumably due to the onset of phase separation processes at high Mg and S content. Optimization of the growth of the thick cladding, providing an additional room for improvement of laser characteristics, is under the current study.

Influence of CdTe Sub-Monolayer Stressor on CdSe Quantum Dot Self-Organization in ZnSe

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Cd(Zn)Se/ZnSe-based nanostructures still remain the most suitable semiconductor materials for fabrication of both optically and electron-beam pumped lasers emitting in the green spectral region. Using of quantum dots (QD) instead of quantum wells as an active region of such devices leads to better laser performance [1]. Therefore, fabrication of optically active up to RT self-organized CdSe QD with the higher density, narrower size distribution and higher Cd content is still of a great importance. An efficient way to control the QD self-organization has been found to be a pre-deposition of strongly lattice-mismatch fractional monolayer (FM)-stressor onto the matrix surface before the deposition of the QD material. The FM-stressor forms much denser array of small islands serving as nuclei for the accumulation of the QD material. This method has been proposed for the first time and experimentally realized during studies of type-II CdSe/BeTe QD system [2], resulting in a $10^{12}$ cm$^{-2}$ surface density of CdSe QDs.

In this paper we report on the attempt to apply the stressor-controlled QD fabrication technique to the conventional CdSe/ZnSe nanostructures. Super-strained CdTe FM having a ~14% lattice mismatch with ZnSe and grown on top of the Te-stabilized ZnSe surface prior to deposition of CdSe has been used as a stressor. The grown structures are studied by x-ray diffraction (XRD), transmission-electron microscopy (TEM), photoluminescence (PL) and PL excitation in comparison with conventional CdSe/ZnSe QDs obtained by a migration enhanced epitaxy (MEE) technique. Two structures of the similar design comprising a single 2-monolayer (ML) CdSe QD sheet in the ZnSe matrix have been grown by molecular beam epitaxy (MBE). They differed in the CdSe deposition technique. The CdSe insertion of reference structure (A) was grown directly on ZnSe by the modified MEE [3]. In structure B, the initial ZnSe surface was stabilized consequently under Zn and Te fluxes to form the Te-terminated surface. After that a preliminarily calibrated CdTe FM was deposited in a conventional MBE mode as a stressor. The actual design of structure B is ZnSe/0.4ML-ZnTe/0.2ML-CdTe/2ML-CdSe/ZnSe and that of reference structure A is ZnSe/2ML-CdSe/ZnSe. The nominal thicknesses of CdSe insertion as well as of ZnTe and CdTe FMs employed in the structures have been evaluated from a semi-kinematic simulation of XRD $\Theta$-2$\Theta$ rocking curves of three superlattices (ZnSe/CdSe, ZnSe/ZnTe and ZnSe/ZnTe/CdTe) grown using the same regimes. The dominant PL line in low-temperature PL spectrum of structure B is 150 meV-shifted down in energy as compared to the CdSe PL line in structure A. It can be explained by the CdSe redistribution during the growth and the increased Cd content in CdSe QDs accumulated on the CdTe stressor nuclei. Dark-field TEM cross-section image of CdSe/ZnSe SL structure with CdSe insertions grown as in structure A resembles the typical morphology of 2ML CdSe in ZnSe with the onset of formation of flat CdSe-rich islands, while the SL with CdSe insertions grown as in structure B displays appearance of sharp isolated QDs of higher density.

In order to manipulate the local distribution of charge carriers in a semiconductor electric fields applied by a metal gate are nowadays routinely used. In the same way, one should be able to employ magnetic fields originating from microscopic ferromagnets to locally control the spin state of the semiconductor’s charge carriers. The realization of such a “magnetic gate” is of great interest to the research field of spintronics.

In our approach, the stray field of a ferromagnet is used to induce locally a Zeeman splitting of the spin states in the semiconductor. Since in conventional semiconductors the g-factor and hence the energy splitting is small we use a dilute magnetic semiconductor quantum well (ZnCdMnSe/ZnSe) with an effective g-factor of up to 700. On top of the semiconductor ferromagnetic Cobalt and Dysprosium dot, wire and antidot structures with lateral dimensions down to 200 nm were prepared by electron beam lithography and lift-off technique. In order to get optical access directly beneath the ferromagnets, the opaque substrate was removed from some samples by mechanical polishing and wet-chemical etching.

To characterize the samples we employed magneto-micro-photoluminescence spectroscopy, which offers a spatial resolution of less than 1 μm at temperatures of 4K and magnetic fields of up to 5T. The impact of the fringe field on the semiconductor’s charge carriers is evidenced by a spatial modulation of the spin dependent bandgap [1,2]. This results in a spatial variation of the spin distribution and therefore the optical polarization degree. In the figure, the polarization degree is shown as a function of external magnetic field in the absence and the presence of a 600 nm antidot structure. The magnetic field is applied perpendicular to the sample surface and the photoluminescence is collected from the semiconductor through the apertures of the antidot field. With increasing magnetic field we obtain a pronounced spin polarization of the charge carriers. Since the stray field from the antidots is oriented opposite to the external field a weakening of the overall magnetic field and therefore a reduced polarization degree is observed in the antidot structure with respect to the reference. This clearly demonstrates the ability to obtain a lateral spin control in a diluted magnetic semiconductor by nanostructured ferromagnets.

[1] H. Schömig et al. J. Appl. Phys. 95, 7411 (2004);
Monitoring Atomic Intermixing in Single Self Assembled ZnCdSe Quantum Dots

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The formation of self assembled quantum dots (QDs) is mediated by an interplay of different microscopic material transport processes, driven by the strain accumulated in highly mismatched layers during the growth of semiconductor heterostructures. It is well known that intermixing of atoms occurs during the assembly of QDs and overgrowth, which in turn results in size and composition fluctuations of the QDs. Thermal treatment during and after growth of QDs has been found to enhance sometimes their spectral quality \cite{1} attributed to a reduction of tensile stress \cite{2} and homogenization of dots sizes. However, most diffusion effects are reported on dot ensembles for which the spectral emission broadening hampers detailed investigations of single excitons.

We report the intermixing of the atomic species, studied by probing the excitonic photoluminescence (PL) emission of single QDs. The evolution of the luminescence, both for single and an ensemble of dots, was monitored as a function of the time and temperature of annealing. To resolve single-dot emission lines, mesas, with sizes down to 50nm, were fabricated by electron beam lithography and wet chemical etching. The mesas were thermally treated for 30 s with comparably low annealing temperatures ranging from 100°C to 240°C. By estimating the electron-hole ground state energies after every annealing step, it was possible to evaluate the diffusion lengths and the activation energies for the QDs under investigation. It is found that for different exciton (X) lines, the observed blue shifts vary significantly, which is ascribed to different activation energies of the Cd-Zn interdiffusion process. Fig.1 shows the thermal evolution of the PL spectra for both exciton and biexciton emissions for an investigated mesa. A typical variation of the emission energy shifts as a function of the diffusion lengths, obtained from our calculations is shown in Fig.2. We present a model to evaluate the activation energy and diffusion length from a single QD emission line and also discuss how the TA-induced QD-potential alteration, influences multiexciton emission. Actually, in some mesas enhanced biexciton formation is found for annealing temperatures larger than 180°C, which is interpreted in terms of larger QD dimensions.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{Fig.1}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2}
\caption{Fig.2}
\end{figure}

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Internal Laser Parameters and Optical Properties of CdSe Quantum Dot Lasers of Different Design

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II-VI-based laser heterostructures emitting in the green spectral region are still promising for filling the gap between blue and red regions covered by III-V compounds, because of the lack of a significant progress in penetration of III-V-based devices into the green area. In this work, we investigate optically pumped lasers based on the Cd(Zn)Se/ZnMgSSe heterostructures of a different design of both an active region and a waveguide, grown by the molecular beam epitaxy (MBE). In some samples, the multi-cycle migration enhanced epitaxy (MEE) was used for the formation of CdSe quantum dots (QD) instead of conventional MBE. Samples with both symmetrical and asymmetrical waveguide design, with and without a ZnMgSSe top cladding layer were studied. The waveguides were designed based on the calculations of the optical field distribution within a multilayer waveguide using the plane-wave approach. The samples were excited by the radiation of a pulsed N₂ laser (λ=337.1 nm, τ₀=8 ns, P=40 kW), and a CW HeCd laser (λ=325 and 441.6 nm, P=30 and 1 mW, respectively), as well as by the monochromatized radiation of a Xenon lamp. PL spectra at excitation densities between 0.01 mW/cm² and 500 kW/cm², PLE spectra as well as reflection spectra were recorded at T=77 and 300 K. Laser thresholds were measured in the temperature range from 300 K up to 500 K. The values of threshold and differential quantum efficiency were measured as functions of the cavity length.

The PLE spectra of the structures with the symmetrical waveguides show a well pronounced maximum in the region of 440-457 nm which corresponds to the absorption of radiation in the strained-layer superlattice forming the guiding layer. The efficiency of the excitation via ZnMgSSe top cladding layer is low, most probably due to the potential fluctuations created by the compositional variations of the quaternary compound. The half-width of PL spectrum is lower, and its intensity is higher for the structures with asymmetrical waveguide design without ZnMgSSe top cladding layer and with CdSe QD grown by MEE.

The measurements of laser characteristics showed that the symmetrical design of the waveguide together with the fabrication of QD by MBE yield the estimated values of the characteristic gain Γ₀ of 66 cm⁻¹, the internal quantum efficiency ηᵢ of 13-17%, the maximal external quantum efficiency ηₒ of 12%, and internal losses αᵢ of about 5-15 cm⁻¹. In the structures with asymmetrical waveguides and MEE-produced QD these values are Γ₀ ~69 cm⁻¹, ηᵢ ~36-42%, ηₒ ~32%, and αᵢ ~1-3 cm⁻¹. It was shown from calculations and measurements of the spectral-angular distributions of the output radiation that in all cases lasing takes place on the fundamental mode independently of the waveguide design. The relations between the PL and lasing parameters from one side and the heterostructure design and carrier transport peculiarities from the other side will be discussed in detail to define possible ways of further improvement of laser thresholds and characteristic temperatures.
Spin polarized transport through magnetic resonant tunneling diodes (RTDs) with magnetic ZnMnSe quantum wells has been previously demonstrated [1], with applied bias voltage used to control spin selection of the transmitted electrons. The potential use of the RTDs for spin detection, however, needs further investigation. Here, we report on the growth, characterization and modeling of resonant tunneling structures with magnetic injector.

The all II-VI RTDs were grown by molecular beam epitaxy, processed into pillars of 100x100 microns and investigated in transport studies at low temperatures and high magnetic fields. The figure shows the magnetic field dependence of the current-voltage characteristic of a sample with a 6% manganese injector. A resonant peak is seen at 50 mV accompanied by its phonon replica just above 100 mV. A dramatic increase in the amplitude of the resonance peak, along with a slight shift in peak position, is observed with increasing external magnetic field. Our modeling shows that both the increase in amplitude and peak position shifts can be attributed to a change in conduction band energy of the injector region resulting from the giant Zeeman splitting in the dilute magnetic semiconductor. The influence of the spin polarization in the injector on the transport characteristic of the RTD is described in terms of resonant tunneling and changes in the local density of states in the dilute magnetic semiconductor. Growth details, spin-transport and simulation will be discussed.

On Peculiarities of the Exciton-Longitudinal Phonon Coupling in CdSe/ZnSe Quantum Dots

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Quantum dots (QDs) are the interesting objects to study phonon coupling with carriers or excitons. This caused by the fact of the variability of the coupling strength in QDs \cite{Nguyen2004} and opportunity to investigate the phonons along the whole energy branch. Experiments presented here were carried out on self-assembled CdSe/ZnSe QDs grown on (001) GaAs substrate by molecular beam epitaxy. CdSe QD’s were formed by depositing 1 monolayer on a ZnSe surface. Such QDs have the energy level of the exciton ground state rather close to the ZnSe barrier being just 200 meV below. In the samples selected for the study the energy splitting between the exciton ground and excited states was equal to the integer number of the longitudinal phonons energy in ZnSe that makes possible to analyze exciton-LO phonon coupling under the double resonance condition.

Photoluminescence (PL) and PL excitation measurements were performed. PL was excited by dye-laser allowing us to change excitation energy continuously from ZnSe barrier down to exciton ground state in the CdSe dots. For the linearly polarized excitation the polarization degree of the PL (optical alignment) was analyzed as well. To be able to monitor modification of the PL spectra under continuous variation of the excitation energy a CCD camera was used as a detector.

PL spectra demonstrate strong alternation of the PL band profile when excitation energy fits the double resonance condition. The full width on a half maximum of the PL band decreases from 35 meV (for non resonant excitation) to 12 meV. Moreover additional features appear on the higher energy side from the main phonon replica. This additional structure manifests more pronounced in PLE spectra, where LO phonon assisted absorption appears as a broad band with a complicated structure. To explain the observation we assume that due to the strong 3D localization of the excitons it is possible them to interact with phonons of any wave vector. In this case the width of the band corresponds to the difference of the minimal and maximal energy on the LO phonon branch. The resonances like features within the LO absorption band are related to the specific points of the LO-branch. By using the experimental data we were able to reconstruct the LO phonon dispersion within the Brillouin zone.

By analyzing the signal of the optical alignment as a function of the excited energy we were able to compare the exciton relaxation time under the different regime of the coupling with LO phonons.

Comparative Study of Self-assembled CdSe/ZnSe Dots Grown by Variants of Conventional MBE


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Epitaxial quantum dots (QDs) of CdSe on ZnSe, which do not grow in the classical Stranski-Krastanow mode, can however, be realized by certain variants of the conventional MBE process. In this work we investigate CdSe islands grown by (a) conventional MBE at 300°C, (b) a combination of MBE growth of a 2-dimensional CdSe layer at 230°C and subsequent in-situ annealing under Se flux to 310-340°C [1], and (c) a similar MBE growth as in (b), combined with deposition of an amorphous Se layer at room temperature and its subsequent re-desorption at 280-300°C [2]. We compare the morphology, composition, and luminescence of a series of QD samples, with varying CdSe coverages, grown by the aforesaid methods. The CdSe coverages were precisely calibrated using X-ray interferometry, a technique, which also established the absence of desorption during growth or annealing for all three methods. While inconspicuous for methods (a) and (b), RHEED shows a transition from a streaky (after CdSe growth) to a spotty (after desorption of Se layer) pattern in method (c), even for 1 monolayer (ML) CdSe coverage. In AFM images we observe a layer like morphology (roughness ~1.5 nm) for method (a), but separated dot-like features, 2-4 nm high, for method (b). The features are more pronounced (6-7 nm high), and also with a bimodal size distribution, in case of method (c). (See Fig. (a), (b), and (c), respectively (700 nm x 700 nm)). Replacing Se- by Te-amorphous layer enables the growth of S-K like dots as high as 12-14 nm but of similar lateral dimensions. By microscopic PL on mesa structures, the dot densities measured for methods (a) and (b) are 1x10^{12} cm^{-2}, and 6x10^{10} cm^{-2}, respectively, the later value in good agreement with that obtained from AFM images. The PL efficiency is high for all three methods. The exciton energy decreases linearly down to 2.35 eV for 4 ML CdSe in methods (a) and (b). The decrease is however more gradual for method (c), despite more pronounced dot formation. In all three methods, we observed the prevalence of intermixing, to varying extents, during both growth and annealing. A blue shift of the PL energies with increasing annealing temperatures in method (b) substantiated the observation. Also in Raman spectroscopy, vibrational modes of ternary (Zn,Cd)Se, redshifted with respect to the ZnSe LO phonon were observed. The redshift increases with CdSe coverage, up to 8.5 cm^{-1} for nominally 4ML CdSe. We discuss in detail these observations, along with the effects of varying growth and annealing parameters, taking intermixing, strain relaxation, and formation of misfit dislocations into account.


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Growth and Vertical Correlation of CdSe Stacked Quantum Dots on ZnCdMgSe Barriers Varying Spacer Thickness and Mg Content

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The promising characteristics of optical or optoelectronic devices with quantum dots (QDs) in the active layer (such as lower laser threshold, reduced temperature dependence threshold...) have generated fervent interest in their growth and electronic properties of these nanostructures. Using QDs instead of quantum wells in the active region of II-VI based devices is also expected to decrease the device-induced degradation effects that currently limit II-VI devices. Even though high-quality, dislocation-free single layers of QDs and stacked or multi-QDs layers (MQDs) have been fabricated by self assembly (SA) using molecular beam epitaxy (MBE) technique in different systems and these have been integrated into device structures, there are still some engineering disadvantages, such as control in the location, density, size and shape of SAQDs that influence the optical properties and applications of these nanostructures. Recently, attempts to solve problems such as spatial distribution (lateral and vertical distribution), uniformity in size (height and lateral size) and shape of QDs have been reported. Some methods used are seeding of QDs, patterned substrates, or correlated stacked MQDs. Among these, the use of MQDs offers, in addition, the possibility of controlling the polarization of the light emitted by the QDs layers, which plays a significant role for some devices applications such as surface-emitting and edge-emitting lasers.

In this work, two sets of structures having thirty MQDs layers of CdSe SAQDs were grown with different Mg content in the ZnCdMgSe, the first with 34 % of MgSe (2.737 eV) and the second with 63 % (3.065 eV). The 150nm-InGaAs buffer and bottom ZnCdMgSe barrier layers were grown following the procedure described elsewhere \cite{1}. Samples for photoluminescence (PL) studies were capped with ZnCdMgSe followed by a 54 Å-thick CdSe layer grown to protect Mg from oxidation. Uncapped structures were also grown. Microstructural and optical properties of the CdSe MQD layers separated by ZnCdMgSe spacers have been studied using PL, contactless-electroreflectance and atomic force microscopy measurements. Vertical coupling of CdSe MQDs is obtained by varying the ZnCdMgSe spacer thickness and/or their Mg content. The PL peak position of the QDs depends on the Mg content of the ZnCdMgSe barrier. Samples with properties intermediate between those of totally coupled MQDs and uncoupled ones were also grown. Power dependence studies demonstrated that the PL peak associated with coupled QDs depends on the excitation power while the PL peak of the uncoupled ones remains invariable. Linearly polarized PL studies were carried out to analyze the luminescence originating from the QDs. Results show that for edge emission, polarization is mostly TM for the case of coupled QDs, indicating QDs exciton delocalization along the growth axis and TE polarized for the uncoupled QDs, as it is expected due to the QDs shape anisotropy. For the surface configuration, PL emission was slightly TE polarized for the coupled QDs while it is slightly TM polarized for the uncoupled case, suggesting a kind of surface organization.

Deposition of II-VI semiconductor structures on GaMnAs offers the possibility of combining magnetooptical properties of diluted magnetic semiconductors with the GaMnAs ferromagnetism. In this communication we present results of preliminary studies aiming to accomplish this goal, namely MBE growth of single layers of CdTe and MnTe on GaMnAs(100) epilayers. The successful MBE growth of CdTe and MnTe on GaMnAs was achieved, using GaMnAs layers with thick, protective amorphous arsenic capping. 10 – 100 nm thick Ga$_{0.95}$Mn$_{0.05}$As layers were grown in the separate MBE system, located at MAX-lab, Lund University, Sweden. They were capped with 200 – 300 nm thick amorphous As layers directly after the MBE growth, taken out of the vacuum system and transferred (in air) to the II-VI MBE system. Arsenic capping was desorbed by heating a sample to 250 – 300 °C during 1 – 2h. It was verified by SQUID magnetometry that the heating process did not decompose GaMnAs ternary alloy; the samples were still ferromagnetic after the heat treatment, and further deposition of CdTe or MnTe. After desorption of a protective As capping GaMnAs surface was identical to the surface of as-grown GaMnAs. Reflection high energy electron diffraction (RHEED) showed smooth (1x2) reconstructed surface with high intensity specular spot. The MBE growth of both CdTe and MnTe on such a surface always resulted in (111) oriented layer, which was verified by RHEED and X-ray diffraction measurements. The (100) orientation could however be achieved by use of a very thin (5 - 10 nm) ZnTe buffer. The CdTe and MnTe MBE growth, as analyzed by RHEED, started with the fast strain relaxation within the growing epilayer, identified as a slight decrease of a distance between the diffraction streaks. Depending on the particular sample the MBE growth proceeded either in a layer-by-layer mode with smooth epilayer surface and no visible transition from 2D to 3D growth mode, or exhibited 3D islanding at the GaMnAs/II-VI interface and subsequent smoothing with increasing II-VI layer thickness. In the case of MnTe layers we have observed an interesting anisotropy between two in-plane directions, parallel to [0-11] and [011] azimuths of the GaAs(100) substrate. This anisotropy was manifested by the presence of deep, elongated trenches parallel to the [011] direction on the GaAs(100) surface. The MnTe surface between the trenches was atomically flat, as showed both by 2D RHEED features and AFM images revealing surface roughness at the level of a single molecular layer. The MnTe/GaMnAs system is expected to exhibit interesting magnetic properties due to the interactions between antiferromagnetic MnTe and ferromagnetic GaMnAs. This may bring new possibilities in construction of the prototype GaMnAs based spintronic devices.
Growth and Optical Property Characterizations of ZnTe:(Al, N) Layers
Using a Co-doping Technique

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The attainment of high and activated n-doping levels for ZnTe remains difficult. In part, this is due to the relatively deep donor levels allocated for the preferred dopants. To overcome dopant compensation, the co-doping concept introduces two oppositely polar atoms at the same time in a 2:1 ratio, forming metastable three-atom complexes located at adjacent crystal sites. Hence, a donor-acceptor-donor (D-A-D) complex is formed for n-doping. Their introduction into the editorially grown layers raises the dopant activation levels and lowers the layer resistivity from values obtainable from their respective single acceptor or donor dopant [1]. In this study, co-doped ZnTe:(Al, N) layers were grown by MBE and their optical and electrical properties were studied.

Fig 1. Low temperature PL spectra of ZnTe:(Al, N) layers

The ZnTe:(Al, N) layers were grown on (001) oriented ZnTe substrates. The substrate surface oxide was removed by the atomic hydrogen irradiation. The calibrated substrate temperature was fixed at 320°C, and 6N-purity aluminum and RF plasma excited nitrogen were used as dopant sources. In order to introduce the D-A-D complex into the crystal, a modified planar doping technique was employed. Between the formation of undoped ZnTe layers (about 3.6 nm), Zn beam exposure, Al and N beam exposure, followed by Te beam exposure were performed. Figure 1 summarizes low temperature photoluminescence (PL) spectra of ZnTe: (Al,N) layers with various Al cell temperatures. The spectrum from an ZnTe: (Al,N) layers (T_{Al}:830°C) showed two kind of donor-acceptor (D-A) emissions around 2.330∼2.335eV. It probably suggests that each dopant formed its own D-A pair in this temperature range. In the high Al-cell temperature regime (T_{Al}:755∼855°C), the D-A emission peak moved to low energy as the Al-cell temperature increases. The increase of Al-cell temperature has encouraged N-dopant to activate. ZnTe: (Al, N) layers grown with T_{Al}:820 or 755°C showed hole concentration of around 2 × 10^{18}cm^{-3}. At other Al-cell temperature, the observed resistivity was high implying that Al and N dopants have compensated each other.

It was confirmed that the co-doping technique was a useful technique for the control of carrier concentration in ZnTe, but minimization of nitrogen doping level would be required to achieve highly doped n-ZnTe layers.

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Electroreflectance Spectroscopy in Self-assembled Quantum Dots

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Modulated electroreflectance spectroscopy $\Delta R/R$ of semiconductor self-assembled quantum dots is investigated. The structure is modeled as dots with lens shape geometry and circular cross section. A microscopic description of the electroreflectance spectrum and optical response in terms of an external electric field ($F$) and lens geometry have been considered. The field and lens symmetry dependence of all experimental parameters involved in the $\Delta R/R$ spectrum have been considered. Using the effective mass formalism the energies and the electronic states as a function of $F$ and dot parameters are calculated. Also, in the framework of the strongly confined regime general expressions for the excitonic binding energies are reported. Optical selection rules are derived in the cases of the light wave vector perpendicular and parallel to $F$. Calculations show good agreement with measurements recently performed on CdSe/ZnSe when statistical distribution on size is considered, explaining the main observed characteristic in the electroreflectance spectra.
Formation of CdO Dots on Atomically Flat ZnO Surfaces

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ZnO and related oxide materials have large exciton binding energies and the corresponding large oscillator strengths. Enhancement of excitonic properties is expected in quantum structures such as quantum dots and wires, and higher-performance lasers and/or single-photon-based quantum information processing devices are expected with these distinguished features in oxide-based quantum structures. Open-shaped ZnO dots and wires have been actively studied recently, however formation of heterostructure quantum dots will be essentially important for future applications. The most promising candidates of the materials system will be Cd(Zn)O dots/ZnO or ZnO dots/ZnMgO. However there have been no reports or studies of CdO-based quantum structures.

In this paper, formation of CdO dots is reported on atomically flat ZnO substrate surfaces. Alignment of the CdO dots along the surface atomic step edges is also demonstrated. ZnO substrates with Zn-polar (0001) surfaces were thermally annealed at 1000°C in air for 1 hour and clear surface terraces and steps were observed with atomic force microscope (AFM). CdO was grown at the temperature of 200°C with metalorganic molecular-beam epitaxy (MOMBE). Dimethyl-Cd (DMCd) with the beam equivalent pressure (BEP) of 1.0x10⁻⁴ Torr was supplied with a pulsed mode for the duration of 5s followed by 20s pause with simultaneous continuous supply of H₂O with BEP of 0.3x10⁻⁴ Torr, which resulted in the growth rate of 0.2Å/cycle.

A CdO layer was grown with 70 above cycles. The grown CdO layer surface remained streaky in reflection high-energy electron diffraction (RHEED) measurements. However AFM measurements of the CdO surface showed that some minute grooves were formed on the terrace surfaces. After thermal annealing up to 650°C for 30min, it was possible to form CdO dots structures as shown in Fig. 1. The dots were typically ~6nm in height and ~60nm in diameter. The alignment of the CdO dots along the surface atomic step edges as well as the grooves formed on the “CdO wetting layer” will be clear. The details will be discussed during the conference.

Fig. 1. AFM image of CdO dots grown on ZnO Zn-polar (0001) surface. The alignment of the CdO dots along the surface atomic step edge will be clear especially in the expanded view. Dots are also aligned along surface grooves formed on the terrace surfaces.
Morphology of CdSe/ZnSe Quantum Dots Grown by MBE

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The features of CdSe/ZnSe quantum dots (QDs) grown by molecular beam epitaxy at 280°C are studied by transmission electron microscopy (TEM), atomic force microscopy (AFM) and photoluminescence (PL). The epitaxial structures consist of a single layer of CdSe islands sandwiched between two 40 nm thick ZnSe layers grown on a [100]-oriented GaAs substrate. CdSe islands are formed as a result of strain relaxation in 3 ML of CdSe pseudomorphically deposited on ZnSe. The 6\% lattice mismatch between CdSe and ZnSe leads to a well known 2D-3D transition of the sample surface which is evidenced by a spotty RHEED pattern during growth and by UHV-AFM images taken before deposition of the ZnSe capping layer (fig 1). After encapsulation, samples were investigated in cross section by high resolution electron microscopy as well as Z-contrast microscopy (fig 2). Surprisingly, we did not observe any reminiscence of CdSe islands pointing to the surface, as observed by AFM, but we noticed the presence of flat Cd-rich islands, about 50 nm long and 8 nm high, originating from the wetting layer and pointing to the substrate. This post-growth diffusion of cadmium into the first ZnSe barrier leaves the interface between the QD layer and the second ZnSe barrier perfectly flat.

The image analysis shows that the Cd concentration is much lower in the center of the islands than at the outskirts. The core contains 30–40\% Zn and the shell consists of almost pure CdSe. Both size and composition are consistent with the \(~\text{2.35 eV}\) PL energy that we measured. Moreover the unexpected QD morphology with Cd-rich outskirts can explain why the PL decay time depends on the samples because the confinement of holes in the QD edges makes the electron-hole overlap very sensitive to QD size.

Fig 1: Atomic force microscopy of CdSe islands on ZnSe before deposition of a ZnSe capping layer.

Fig 2: Z-contrast microscopy of CdSe/ZnSe quantum dots grown on a GaAs substrate.
Spin Waves and Exchange Interactions in Hexagonal MnTe

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The hexagonal structure of NiAs type is the stable phase of the natural MnTe. This semiconductor exhibits antiferromagnetic properties up to about $T = 310$ K, resulting from superexchange interactions. Single MnTe crystals were obtained a long time ago but the information on magnetic interactions in this material is still very limited. In particular, the values of the exchange integrals describing the magnetic properties of MnTe are not known. A single paper [1] used Raman scattering data to propose an estimate of the three first integrals and the resulting magnon dispersions. The first neutron scattering study devoted to magnons in MnTe was reported very recently in [2], the results of recent elastic scattering measurements can be found in [2-4].

The bulk single crystal of hexagonal MnTe used in the present study was grown by the physical vapour transport method. The magnon dispersion has been determined at low temperature ($T = 10$ K) along five principal directions of the Brillouin zone. Some experimental data were also taken at higher temperatures, in order to get an overview of the evolution of the magnon stiffness. From the measured magnon branches, the values of exchange integrals have been determined, using a theoretical description based on a Heisenberg Hamiltonian. To obtain a correct description of the experimental dispersion we have to take into account four exchange integrals.

MnTe is the first magnetic semiconductor for which as much as eight various exchange integrals were determined (previously, four for the zinc blende phase [5] and, at present, four for the hexagonal phase). Due to such a unique opportunity, the angular and distance dependence of the superexchange in this material is now within reach.

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Band Structure of Mn/ZnTe – an Angle-resolved Photoemission Study

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ZnMnTe, a well known semimagnetic semiconductor, attracts renewed interest since theoretical considerations showed that free carrier-induced ferromagnetism may occur in II-VI compounds \cite{1} and effective spin injection from ZnMnTe to non-magnetic semiconductor was demonstrated \cite{2}. The band structure of ZnMnTe, in particular distribution of Mn 3d states, is an important piece of information for description of interaction between magnetic ions. Thus, it is crucial for understanding the magnetic properties of the material.

We report on the results of band structure study of the Mn/ZnTe system prepared in situ by deposition of submonolayer amounts of Mn on the ZnTe(110) surface. Making use of this method, previously developed and tested for other II-VI compounds \cite{3}, we obtain a thin subsurface layer of Mn-doped crystal, due to reaction of deposited Mn atoms with the surface of the substrate. Therefore, we could study ZnTe and ZnMnTe for the same sample and under the same experimental conditions. This made comparison of the results more reliable and enabled us to reveal the Mn 3d contribution to the valence band structure.

The angle-resolved photoemission experiments were performed in the 15-30 eV photon energy range at the F2.2 beamline at HASYLAB, Hamburg (Germany). The radiation was linearly polarized, the angle of incidence - 45°. Mn was deposited from an effusion cell. The deposition process was divided into four stages by 0.2 ML. The energy distribution curves were acquired for normal emission mode as well as for off-normal configuration (for two nonequivalent directions). Thus, the band structure was mapped along (110) (normal to the surface) and (110), (001) (parallel to the surface).

The changes in the band structure of the system caused by contribution of Mn 3d states could be observed, in spite of the low photoemission cross section for Mn 3d at photon energies suitable for angle-resolved experiments. Mn deposition resulted in noticeable energy shifts and/or changes in relative intensities of spectral features, even after the first step of deposition. In particular, additional emission was detected at the binding energies of about 2.4 and 4.5 eV below the Fermi level, for higher emission angles (i.e. for states lying away from the center of the Brillouin zone). The results were compared with photoemission spectra calculated for the model diluted magnetic semiconductor – CdMnTe \cite{4}.

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\begin{thebibliography}{9}
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Anisotropic Magnetic Properties of Zn$_{1-x}$Co$_x$O Thin Films Grown by Pulsed Laser Deposition

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ZnO-based diluted magnetic oxide, in which Zn is partially substituted by transition metals (TM), is expected to be utilized in the future electronics called ‘spintronics’. Since the theoretical prediction of the ferromagnetism of TM-doped ZnO above room temperature[1], a considerable number of experimental studies have been reported, in particular on Co- or V-doped ZnO, but it has not yet been settled whether these materials are really ferromagnetic or not. In relation to this critical issue about ferromagnetism, anisotropic magnetic properties were also reported in Co-doped ZnO[2]. The anisotropy in the magnetism is considered to be important in the understanding of the electronic state of a transition metal substituting the Zn site. In the present work, we investigated the anisotropy in magnetic and magneto-transport properties of Zn$_{1-x}$Co$_x$O grown by pulsed laser deposition (PLD) technique.

Zn$_{1-x}$Co$_x$O thin films with $x = 0.05, 0.1$ and $0.15$ were grown on sapphire (0001) substrates by PLD using frequency-tripled Nd-YAG laser ($\lambda = 355$nm). The magnetization of the grown films were measured using superconducting quantum interference device (SQUID) magnetometer with magnetic fields applied either parallel ($H$//ab) or perpendicular ($H$//c) to the film plane. The magneto-transport measurements were performed both in the longitudinal ($H$//I//ab) or transverse ($H$//I//ab) configurations. Figure 1 shows the magnetization curve at 5K of Zn$_{0.9}$Co$_{0.1}$O with an electron concentration at room temperature of $3.5'10^{18}$cm$^{-3}$. In the measurement, a hysteretic behavior was not observed down to our lowest temperature of 2K, which suggests that the sample studied here was not ferromagnetic. As shown in the figure, the magnetization under magnetic fields parallel to the plane ($H$//ab) was larger than that under perpendicular magnetic fields ($H$//c). Figure 2 shows the magnetoresistance (MR) of the same sample at 4.2K in the three different configurations. At low field region, positive MR was observed in all the configurations, which is attributed to the effect of the Zeeman splitting on the quantum correction of the electron-electron interaction. As shown in the figure, the magnitude of the positive MR was larger under in-plane fields ($H$//ab) than that under perpendicular fields ($H$//c). This is considered to be due to a larger Zeeman splitting under in-plane fields. This anisotropic MR is consistent with the anisotropy in the magnetization in Fig. 1, with a larger magnitude in the same field direction. The origin of the observed anisotropy will be discussed.

Effect of Atomic-Hydrogen Irradiation on Epitaxy and Properties of ZnO Layers Grown by Molecular Beam Epitaxy

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Recently, p-type ZnO layers were successfully grown by N-doping and the fabrication of ZnO p-n junction LED was achieved [1]. However, the N-doping of ZnO is still a difficult problem and the hole carrier concentration of N-doped p-type ZnO is not good enough for high performance LEDs in commercial use-level. This is due to high residual electron concentration in nominally-undoped ZnO films and low doping efficiency of nitrogen as well.

Hydrogen is a possible candidate for the residual donors in as-grown "high-purity" ZnO films due to the presence of residual hydrogens and/or hydrogen-including molecules such as water vapor and hydro-carbons even in the quite clean growth ambient such as UHV-MBE system. On the other hand, it is known that the presence/irradiation of atomic hydrogens on the growth front surface is effective to enhance the surface migration of adsorbed species resulting in an improved crystallinity and atomically smooth surface. Furthermore, it may be possible to improve the N-doping efficiency by using the co-doping of nitrogen and hydrogen.

In this paper, we investigated the effects of atomic-hydrogen irradiation on the epitaxy process and properties of ZnO epilayers grown on c-plane sapphire by molecular beam epitaxy. The atomic hydrogen was provided by cracking hydrogen molecules using efficient catalytic effects on the hot-tungsten filament. The pressure of hydrogen was varied from 1.6×10⁻⁷ to 1.0×10⁻⁵ Torr. About 2 – 5 % of hydrogen molecules were cracked into atomic hydrogen in this work. The sapphire substrate was deeply nitrided after thermal cleaning and followed by the deposition of a low temperature ZnO buffer layer on it. Then ZnO epilayer was grown at 750°C. The ZnO layers were controlled to be Zn-polar in this work. The epilayers were characterized by AFM, HR-XRD, Hall, FTIR, and low temperature HR-PL measurements.

First, it was found that the irradiation of atomic hydrogen affected in all aspects of ZnO epitaxy including its properties. In particular, the carrier concentration and PL properties were drastically affected; the residual electron concentration of 2.2×10¹⁷ cm⁻³ in the non-doped sample was increased to 1.3×10¹⁸ cm⁻³ after the hydrogen doping. The PL spectrum at 14 K of non-doped ZnO was dominated by D°X emission at 3.363 eV accompanied with slightly weak free exciton emission at 3.374 eV and D°X emission at 3.358 eV. In the case of hydrogen-doped ZnO samples, the PL spectra were all dominated by D°X emission at 3.358 eV and its intensity increased with doping by 200 times stronger than that of non-doped one. Further, the growth rate of ZnO films was gradually decreased by 13 % with the increase of hydrogen pressure. The surface morphology changed form typical Zn-polar surface with pits to grain-like top surface. In comparison to non-doped ZnO film, the crystalline quality measured by XRD was improved by the atomic hydrogen exposure in the hydrogen pressure less than 5.0×10⁻⁶ Torr. With the increase of hydrogen pressure, the FWHM values of (002) and (102)ω-scans are decreased first and then increased.

In summary, our results indicated that the hydrogen had large effect on properties of ZnO film, while hydrogen impurity and/or hydrogen-related complexes acted as an effective shallow donor in ZnO film.

ZnO Crystals for Substrates in Micro and Optoelectronic Applications

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Effective sublimation and diffusive transport of crystal components are necessary for growth of single crystals. The crystallization front is morphologically stable if the partial pressure ratios of the vapours are at optimum, and if the gradients of partial pressures of the growing species meet the stability criteria. The axial dimension of crystal grown from the vapour is always small. Reports about success of the hydrothermal method make the impression of poor perspective for vapour grown ZnO crystals for production of substrates for micro and optoelectronic applications. However, our last results prove, that the method of ZnO crystal growth from the vapour has a big potential, which may soon lead to a development of effective low-cost production. This optimistic opinion results from a simplicity of the growth system and the following findings: (1) the problem of single nucleation can be solved by the method of Low Supersaturation Nucleation \cite{1}, (2) the morphological stability of the crystallization front can be maintained during the entire growth run, using modified temperature profile, (3) low-cost silica glass ampoule can be used, if the method of contactless growth is applied, (4) the steady transport conditions can be effectively maintained by a system of steady supply of hydrogen. What makes the vapour growth system superior to the hydrothermal method is the growth in the environment of only one additional element (hydrogen), as opposed to multielement mineralizers (LiOH, KOH) applied in the hydrothermal method.

Fig.1. Two-side polished ZnO substrates

Zinc oxide crystals were grown in modified system by the CVT Contactless Crystal Growth Method \cite{1}. The temperature field was modified as compared to previous reports, in order to make application of longer ampoules and powdered source material feasible, similar to growth of other II-VI compounds. Using the longer ampoules and a sapphire pedestal, 2.5cm diameter crystals were grown with no contact with the ampoule wall. The largest grains yield 0.5 cm\textsuperscript{2} single crystal substrates. The usual structural quality of these substrates was not fully satisfactory, represented by FWHM exceeding 60 arcsec. However, areas characterized with FWHM as low as 29 arcsec were also found. The electrical properties of these substrates were similar to those reported previously \cite{1}, and were dependent on the partial pressure of zinc and on the dopant used.

\cite{1} Krzysztof Grasza and Andrzej Mycielski, \textit{phys.stat.sol (c)} 2, 1115 (2005)
ZnO is a promising alternative to GaN for a wide variety of electronic and optoelectronic applications but still lacks reproducible and stable p-type doping. We developed a two step growth process for ZnO on GaN templates and achieve high quality ZnO layers with background carrier concentrations below $10^{16} \text{ cm}^{-3}$ which makes them interesting for p-type doping experiments. For acceptor doping we have investigated several group-V sources as NH$_3$, UDMHy, NO, PH$_3$, and AsH$_3$. Some of these sources induce N or As related acceptor levels as determined by photoluminescence measurements, however, no p-type conductivity is achieved by them. We will discuss possible ways to achieve p-type conductivity by doping with group-V elements.
Photoluminescence Recombination Centers in ZnO Crystals

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Photoluminescence (PL) spectroscopy in the band-edge emission region is one of the most versatile techniques to study in detail the lattice defects in semiconductors. There have been many PL studies of ZnO. Particularly, Mayer et al. recently reported results on the comprehensive study on the PL properties in ZnO [1]. However, details of the lattice defects responsible for the PL emission peaks in ZnO are still controversial.

We have been studying the PL properties of ZnO crystals as functions of (i) sample growth methods and conditions, (ii) doping elements, (iii) measurement temperature, and (iv) excitation laser power. As the results, we have identified the lattice defects responsible for recombination centers of some typical PL emission peaks in ZnO as summarized in Table I.

<table>
<thead>
<tr>
<th>Peak Name</th>
<th>Photon Energy (eV)</th>
<th>Lattice Defects</th>
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<tbody>
<tr>
<td>I₃</td>
<td>3.3657</td>
<td>Intrinsic defects</td>
</tr>
<tr>
<td>I₅/₆</td>
<td>3.3604</td>
<td>Donor impurities such as aluminum</td>
</tr>
<tr>
<td>I₈</td>
<td>3.3596</td>
<td>Donor impurities such as aluminum</td>
</tr>
<tr>
<td>I₉</td>
<td>3.3565</td>
<td>Defects related to the incorporation of acceptor impurities</td>
</tr>
<tr>
<td>G</td>
<td>3.3327</td>
<td>Intrinsic defects</td>
</tr>
</tbody>
</table>

Our identification of peak I₅/₆ is in agreement with that in Ref. 1, which has established a good PL fingerprint for aluminium impurity in ZnO. Also, our identification of peak G is in agreement with that in Ref. 1, where the extended lattice defects such as dislocation loops are argued as the origin of the peak, since dislocation loops are intrinsic defects.

On the other hand, our identification of peak I₉ is not in agreement with that in Ref. 1, where gallium is argued as the origin of the peak. However, we have observed in some samples that the origins of peaks I₅/₆ and I₈ are strongly related each other. Our identification of peak I₉ is also not in agreement with that in Ref. 1, where residual indium is argued as the origin of the peak. However, we have observed the strong enhancement of the peak I₉ in samples grown by MBE and doped with phosphorus, which is expected to be an acceptor in ZnO. Therefore, we think that the identification of the origins of the peaks I₈ and I₉ needs to be discussed further.

Direct Evidence of Impurity Related Free-to-Bound Transition in ZnO

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We present a comprehensive analysis of the optical properties of a nominally undoped, i.e. n-conducting ZnO epitaxial layer by means of temperature dependent photoluminescence (PL) and scanning cathodoluminescence (CL) microscopy. The thick ZnO epi-layer under study was grown by metal organic chemical vapor phase epitaxy on a GaN / sapphire template. A 0.3 µm thick optimized ZnO buffer was first deposited at 450°C and in situ annealed for 4 min at 900°C inside the reactor. The final nominally 8 µm thick ZnO layer was subsequently grown at 900°C.

At low temperatures (T=4K) the spatially averaged luminescence spectrum (PL and integral CL) is dominated by the impurity bound exciton I\(_8\). The free exciton FX, the bound excitons I\(_0\)/I\(_1\), I\(_2\)/I\(_3\), and I\(_9\), as well as the LO phonon replica of I\(_8\) can be identified. Additionally, the two electron satellites (TES) of I\(_8\) and I\(_9\) are also visible in the near band gap region. All lines are 0.7 meV red shifted with respect to their fully relaxed position known from bulk crystals indicating minor tensile strain. At 4K the TES I\(_8\) and TES I\(_9\) line are well separated and easy to identify.

At elevated temperatures (e.g. T = 40K) a new broad peak shows up precisely at the spectral position of the TES I\(_8\) peak. This line exhibits a pronounced high energy Boltzman tail and up to 5 LO phonon replica at the low energy side. With increasing temperature this line together with it’s LO replicas become dominant. Due to its temperature dependence of intensity and spectral shift we assign this line to free-to-bound transition (e,A\(_0\)). The spectral position of (e,A\(_0\)) with E = 3.307eV gives an acceptor binding energy of about 130meV, which is in the range of the expected value of the elective mass acceptor in ZnO (static dielectric constant ε ≃ 7 and hole polaron mass m\(^*\)\(_h\) ≃ 0.7m\(_0\)). Magneto-optical investigations supports the incorporation of shallow acceptors in this sample.

Highly spatially resolved CL of planar regions as well as at surface defects (e.g. hexagonal craters) evidence the microscopic complementary behavior of FX and (e,A\(_0\)). In particular at the facets of hexagonal craters an enhanced (e,A\(_0\)) emission is found. This strongly suggests an acceptor accumulation in the vicinity of the morphological defects.

![Fig.1: Temperature dependent PL spectra: the free-to-bound transition (e,A\(_0\)) becomes dominant at higher temperatures.](image-url)
Wide band gap II-VI semiconductor materials containing Mg, such as Zn$_x$Mg$_{1-x}$Se, are of considerable interest for the fabrication of optoelectronic devices because their bandgaps range from 2.75 to 3.7 eV, which allows us to reach higher bandgap values than those available from currently used II-VI materials [1]. A series of high crystalline quality zincblende Zn$_x$Mg$_{1-x}$Se alloys was grown lattice matched to InP (001) substrates by molecular beam epitaxy. The use of InP as a substrate allows us to optimize the materials quality of the high Mg content compositions, since near lattice matching to this substrate is achieved with as much as $\sim 87\%$ Mg concentration. This alloy has a bandgap of 3.6 eV at 77K. The crystalline quality was assessed by X-ray diffraction techniques. The band gap energies of the alloys were determined using photoluminescence measurements and were plotted as a function of Mg concentration. A linear dependence between the band gap and the Mg concentration was observed for the entire range and, from the extrapolation of our experimental data, the bandgap of zincblende MgSe was determined to be 3.74 eV [2]. Using Zn$_x$Mg$_{1-x}$Se as a barrier layer we have grown several Zn$_x$Cd$_{1-x}$Se/Zn$_x$Mg$_{1-x}$Se single quantum well (QW) structures. These samples exhibited emission that ranges form the near-UV, throughout the visible range of the spectrum. The dependency of the QW emission with QW layer thickness was modeled using a finite barrier model. Finally, using a modulated spectroscopic technique known as contactless electroreflectance, a very large conduction band offset for this QW structure, of $\sim 1.12$ eV, was estimated. This result makes this a very promising material for applications in the fabrication of intersubband devices such as quantum cascade lasers with short wavelengths ($1.55 \, \mu\text{m}$) as needed for ultra fast optical communications.


Epitaxial Growth and Luminescence Properties of Thin Films and Quantum Wells of Partially Ordered Zn\(_{0.5+y}\)Cd\(_{0.5-y}\)Se alloys

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Traveling along the [001] direction of a zincblende binary compound one finds cation and anion atoms in alternate layers. In the case of Zn\(_{1-x}\)Cd\(_x\)Se ternary alloys we will find Se layers alternating with Zn\(_{1-x}\)Cd\(_x\) layers; the cation fcc sublattice consists of a random distribution of Cd an Zn atoms and most of the optical, structural and electronic properties are correctly described by the virtual crystal a approximation (VCA). In the particular case of Zn\(_{0.5}\)Cd\(_{0.5}\)Se we will find in each cationic (001) layer the same amount (in average) of Zn and Cd atoms. However, we can build another ternary alloy with the same chemical composition but with a different crystalline order along the [001] direction, only Cd or Zn atoms in each cation layer with the sequence Zn-Se-Cd-Se..., i.e., a Zn\(_{0.5}\)Cd\(_{0.5}\)Se ordered alloy, or more properly, the ordered ZnCdSe\(_2\) tetragonal semiconductor. Changes in the material properties due to changes in symmetry and short range order, such as band gap reduction, valence band splitting, polarization dependence of optical transitions, changes in vibrational spectrum and others may be expected; the VCA approach cannot be employed to describe the ordered Zn\(_{0.5}\)Cd\(_{0.5}\)Se alloy [1, 2]. In this work, we present the results of our current efforts towards the growth by atomic layer epitaxy (ALE) of films and quantum wells (QWs) of the ordered Zn\(_{0.5}\)Cd\(_{0.5}\)Se alloy. In principle, the alternate deposition of CdSe and ZnSe monolayers (ML) by ALE could be expected to produce the ordered alloy, however, due to the unavoidable Zn-Cd chemical interaction, that results in the substitution of Cd atoms by Zn atoms and then the desorption of Cd atoms [3], the Cd content is lower than 0.5 and the resulting alloy presents a composition Zn\(_{0.5+y}\)Cd\(_{0.5-y}\)Se where y can be as high as 0.2. In order to minimize the effects of the thermally activated Zn-Cd interaction we have grown QWs at relatively low substrate temperatures (\(\sim 220^\circ\)C) and reduced the exposure times to Zn during the Zn-Se ALE cycles. The samples have been characterized by low temperature photoluminescence (PL) and we have observed that, at lower substrate temperatures and lower exposure times to the Zn effusion cell flux, we are closer to the nominal Zn\(_{0.5}\)Cd\(_{0.5}\)Se alloy composition; however, the excitonic emission of the QWs broadens indicating a increase in alloy disorder and structural defects caused by the reduced diffusion at the surface of the impinging atoms. A comparison of the electronic band structure of the ordered and disordered alloys will be presented and the degree of disorder of the samples will be described in terms of an order parameter.

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Magnetoresistance Measurements of n-type ZnO:Al and Zn$_{1-x}$Mn$_x$O:Al Thin Films

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Effects of spin-orbit coupling and s-d exchange interaction are probed by magnetoresistance measurements carried out down to 50 mK on ZnO and Zn$_{1-x}$Mn$_x$O with $x = 3$ and 7%. The films were obtained by laser ablation and doped with Al to electron concentration $\sim 10^{20}$ cm$^{-3}$. A quantitative description of the data for ZnO:Al in terms of weak-localization theory makes it possible to determine the coupling constant $\lambda_{so} = (4.4 \pm 0.4) \times 10^{-11}$ eV cm of the kp Hamiltonian for the wurzite structure, $H_{so} = \lambda_{so}c(s \times k)$. A complex and large magnetoresistance of Zn$_{1-x}$Mn$_x$O:Al is interpreted in terms of the influence of the s-d spin-splitting and magnetic polaron formation on the disorder-modified electron-electron interactions. It is suggested that the proposed model explains the origin of magnetoresistance observed recently in many magnetic oxide systems.

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Magnetic Anisotropy of Co$^{2+}$ in ZnO

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Recent theoretical predictions of the ferromagnetic phase with a critical temperature going up to the room temperature in diluted magnetic semiconductors made by K. Sato and H. Katayama-Yoshida [1] have renewed the interest of ZnO:MT (MT=Co, Mn, Cr, etc...) . The highest critical temperature of 320K was predicted on the basis of LDA for ZnO:Co system. As far as epitaxial layers are concerned, the samples of ZnO:Co are usually fabricated by sputtering, PLD, MBE, and MOCVD techniques but show controversial magnetical properties.

In this communication, we present details of MBE fabrication, structural and magnetic properties characterizations of Zn$_{1-x}$Co$_x$O epitaxial thin films grown by plasma-assisted MBE with Co concentration varying from x=0.003 to x=0.005. The sample thicknesses are around 1µm. 2D growth is achieved for growth temperature of 560°C, i.e. 50°C higher than the optimal growth temperature used for ZnO, resulting in streaky RHEED patterns. For this range of Co composition, the rocking curve FWHMs are in the range of $\omega$~0.15 deg along (002), (-105) and (105). The low $\omega$ values measured both for (-105) and (105), as well as their similarity, indicate a large column diameter, close to 1µm. The conductivity of the films is n-type, with residual carrier concentrations $n_e < 1 \times 10^{18}$ cm$^{-3}$, a doping level well bellow the Mott transition.

EPR EMX Bruker spectrometer was used to collect the spectra in X-band and in the temperature range between 4K and 300K. The detected EPR signal is constituted by a single distorted Lorentzian with varying line width $\Delta H$. We have found a strong anisotropy of EPR line position when varying the magnetic field orientation. The extracted g factor and $\Delta H$ values are $g_{||}=2.22(3)$ and $\Delta H_{pp}=130G$ for $H \parallel c$, and $g_{\perp, eff}= 4.53(8)$ and $\Delta H_{pp}=70G$ for $H \perp c$. This g-factor anisotropy is due to the trigonal distortion characteristic of the ZnO wurtzite structure and is described by a term $DS^2$ in the spin Hamiltonian of Co$^{2+}$ with $D=2.7$ cm$^{-1}$.

Another evidence of strong magnetic anisotropy of Co$^{2+}$ in ZnO comes from the studies of magnetic properties. It is found that a field dependence of the magnetization at fixed temperature, $M(H)$, shows anisotropy of an 'easy plane' type. As expected $M(H)$ is not explained by classical Brillouin function and the temperature dependence of the magnetic susceptibility presents a strong deviation from the Curie law. We have succeeded in description of the Co$^{2+}$ behaviour (both static and dynamic) in the framework of a simple statistical model based on spin Hamiltonian of Co$^{2+}$.

We have developped a theoretical model of Co$^{2+}$ in the diamagnetic ZnO lattice using the crystal field approach. This model gives us the possibility to describe the fine structure of the $^4F$ level taking into account the spin-orbit coupling and Zeeman effect. It also allows us to introduce the effect of ionic anisotropy on $^4A_2$ level due to spin-orbit coupling. We have calculated numerically using the Macfarlane approach [2] the values of $D=2$ cm$^{-1}$ and g-factor: $g_{||}=2.24(2)$ and $g_{\perp}=2.27(7)$ using 5 parameters: $B=760$ cm$^{-1}$, $D_{q}=400$ cm$^{-1}$, $v=-120$ cm$^{-1}$, $v'= -320$ cm$^{-1}$ and $\lambda= -143.3$ cm$^{-1}$.

Photoluminescence Properties of ZnO Single Crystals with Polar and Non-polar Faces

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Photoluminescence (PL) was measured for ZnO single crystals with polar and non-polar faces. PL spectra of ZnO single crystals depended on polarity of ZnO single crystals. An emission due to neutral-donor-bound excitons (D₀X) was dominantly observed on all surfaces of ZnO single crystals. An emission due to ionized-donor-bound excitons (D⁺X) was observed on the O-face but not on the Zn-face.

ZnO has been investigated for application to UV-LED and -LD due to its direct wide band gap of 3.37 eV and large excitonic binding energy of 60 meV. It has recently been shown that homoepitaxial ZnO films have several advantageous compared with ZnO films grown on sapphire substrates [1] and that qualities of homoepitaxial ZnO films depend on the polarity of ZnO single crystals. In this report, we describe in detail the PL properties of ZnO single crystals with polar faces and non-polar faces.

Bulk single crystals of ZnO were grown by a hydrothermal method [2]. Several c-plane crystals with polarity surfaces were obtained by slicing both +c and −c sectors of one ZnO crystal. An a-plane and an m-plane with non-polarity surfaces were sliced from +c sectors of the same bulk. The excitation source was a He-Cd laser (325 nm). Figure 1 shows PL spectra of the Zn-face and O-face of a c-plane ZnO crystal at 4.2 K. A dominant emission observed at 3.361 eV can be assigned to D₀X. The full-width at half-maximum (FWHM) of the D₀X emission of the specimens sliced from the +c sector was smaller than that of the specimens sliced from the −c sector, indicating that high-quality crystals were grown in the +c sector. Again, emission assigned to D⁺X was observed at 3.366 eV on the O-face, but the emission was not observed on the Zn-face and the emission was weak on the a- and m-planes of ZnO. These results indicate that D⁺X emission originated from surface levels due to oxygen.

It is thought that the density of ionized donors at the O-face of the c-plane is larger than that at the Zn-face because the surface state density for electrons of the O-face is higher than that for electrons of the Zn-face, and D⁺X emission was therefore observed at the O-face.

In conclusion, PL emissions of ZnO crystals differed of the O-face and Zn-face. This suggests that PL measurement is useful for determining the polarity of a ZnO crystal.

Applicability of ZnO Single Crystals for Ultraviolet Sensors

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Photoconductivity of ZnO single crystals for ultraviolet (UV) light was measured. O-faces of ZnO single crystals showed higher photocurrents and wider spectral response compared to those of Zn-faces.

UV sensors using wide band gap semiconductors have advantages because wide band gap semiconductors are insensitive to visible light. ZnO is an attractive material for a UV sensor because of its direct wide band gap of 3.37 eV. However, preparation of a highly sensitive UV sensor using ZnO single crystals or films has been difficult, because it is difficult to obtain ZnO single crystal and films of high quality. Recently, large ZnO single crystals with high quality and high resistivity and with low densities of intrinsic defects and impurities have been successfully grown by a hydrothermal method [1].

In this report, we describe photoconductivity of ZnO single crystals grown by the hydrothermal method for UV light and show that ZnO single crystals are advantageous for use in ultraviolet sensors. ZnO substrates of 0.5 mm in thickness were sliced parallel to the c-plane or a-plane from a ZnO single crystal. The c-plane has polarity, one side of the plane having an O-face and the other side having a Zn-face. However, the a-plane does not have polarity. Both sides of the ZnO substrates were polished by a CMP technique. Al electrodes with gaps of about 1 mm were deposited on the surfaces of the ZnO substrates by the vacuum evaporation method. Spectral responses of photocurrent of the ZnO substrate were measured using an Xe-arc lamp and diffraction grating.

The spectral sensitive characteristics differed greatly depending on the face of the substrate that was irradiated. Figure 1 shows the normalized spectral response curves of photocurrents on the O-face (a) and Zn-face (b) of a c-plane substrate and on the a-plane (c) of ZnO single crystals. All samples showed photo response in a wavelength shorter than the absorption edge of ZnO. The O-face also showed a strong response in a wavelength region shorter than 300 nm, but the Zn-face showed only a weak response in that region. The O-face also showed a high photocurrent, whereas the photocurrent of the Zn-face was very low. It is thought that band bending at the surface regions of ZnO crystals is large at the O-face but small at the Zn-face, because the surface state density for electrons of the O-face was higher than that for electrons of the Zn-face and, therefore, carriers generated at the surface region by UV light were effectively separated at the O-face region before recombination.

In conclusion, ZnO single crystals are suitable for use in highly efficient photo-sensors for a wide range of UV spectra, and the O-face of ZnO is advantageous compared to the Zn-face. The difference between photo responses of the O-face and Zn-face is also useful to determining the polarity of a ZnO crystal.

Correlation of Micro-structure and Optical Properties of MgZnO/ZnO/MgZnO Quantum Wells

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A direct correlation of structural and optical properties of a MgZnO/ZnO/MgZnO quantum well is observed on a microscopic scale using highly spatially, spectrally and time resolved cathodoluminescence (CL).

The sample under study was grown by metalorganic vapor-phase epitaxy on GaN/sapphire template at a growth temperature of 600°C. A ZnO buffer was included to improve the quality of the structure. Diethylzinc (DEZn), bis(methylcyclopentadienyl)magnesium (MeCp\textsubscript{2}Mg), and nitrous oxide were used as the zinc, magnesium (Mg), and oxygen precursors, respectively. First, a 300-nm-thick Mg\textsubscript{0.06}Zn\textsubscript{0.94}O epilayer was grown as barrier material. Then, a 2 nm thick ZnO single quantum well (SQW) was grown followed by the 50 nm thick final Mg\textsubscript{0.06}Zn\textsubscript{0.94}O barrier layer. Further details of the growth are given elsewhere [1].

The low temperature spectrum (T=4.2K) is dominated by three spectral bands originating from the ZnO buffer (E=3.356eV), the 2 nm thick MgZnO/ZnO/MgZnO SQW (E=3.383eV) and the Mg\textsubscript{0.06}Zn\textsubscript{0.94}O barrier (E=3.450eV). The spectral position of the MgZnO barrier peak is in agreement with the CL spectrum of a thick MgZnO epitaxial reference layer with [Mg] = 6%. Both, the emission band from the SQW structure, as well as from the Mg\textsubscript{0.06}Zn\textsubscript{0.94}O barrier, consist of two peaks each.

The excitation and the temperature dependence are investigated: No spectral shift with excitation density is found. However, the intensity ratio of the two respective spectral lines strongly changes. While the intensity of the high energy MgZnO peak exhibits an almost perfectly linear dependency on excitation density the low energy peak increases superlinear with excitation. Identical dependencies are found for the two peaks from the ZnO-SQW.

Morphological features of the layers directly correlate with the local spectral CL emission characteristic on a microscopic scale. While the high energy peak of MgZnO buffer and of the SQW exhibit an almost homogeneous lateral distribution, the emission of the low energy peak of the MgZnO barrier, as well as, of the SQW vanishes completely at local surface defects.

A cross sectional CL spectrum linescan of the sample structure gives access to the vertical transport, diffusion and capture of carriers in an MgZnO/ZnO/MgZnO quantum well. The rise in the quantum well intensity exhibits an ambipolar diffusion length of excitons recombining in the SQW of $L_{\text{diff}} = 140$nm.

Spectral-time-resolved measurements directly evidence the transient competition between two different recombination channels in the SQW, as well as, in the MgZnO barriers, respectively.

Magneto-Optical Spectroscopy of Zn$_{1-x}$Co$_x$O Epilayers

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We have studied MBE grown Zn$_{1-x}$Co$_x$O epilayers by magneto-optical spectroscopy. We determined the impact of the Co$^{2+}$ ions on the reflectivity, transmission and photoluminescence spectra of the host semiconductor (ZnO). We observed sharp lines related to $^4$A$_2$ $^2$E intra-ionic Co$^{2+}$ transitions. The intensity of the intra-ionic absorption was calibrated and used as a sensitive tool to determine the Co concentration. The positions and intensities of the transmission and photoluminescence lines were also used to determine the values of the parameters describing the isolated Co ions, such as the in plane magnetic anisotropy and the g-factor of $S=3/2$ cobalt spins. We show that, the absorption intensity in a magnetic field is governed by the thermal occupation of Co ions spin levels and is directly related to the magnetization.

Excitonic transitions observed in reflectivity (Fig. 1) were used to estimate the spin-carrier exchange integrals. The direct observation of the excitonic Zeeman splitting was possible for diluted samples with Co concentration from 0.1% to 0.5%. The excitonic Zeeman splitting observed under magnetic field was found to be proportional to the magnetization calculated by taking into account the spin anisotropy. The value of $N_0$ ($\alpha-\beta$) is about 0.4 eV. The Zeeman splitting has almost the same magnitude for the two visible excitons A and B, but it has an opposite signs. This is a consequence of the small coupling between the B and C excitons, due to the small value of in plane spin orbit parameter ($\Delta_3$). It is much smaller than the difference of B and C exciton energies ($\Delta_1 - \Delta_2$).

In samples with a high Co concentration (up to 11%), the magnetic circular dichroism (MCD) near the energy gap was measured. Despite confirmed presence of Co pairs, the magnetic field dependence of MCD was found to be proportional to the magnetization calculated for isolated magnetic ions. We have also studied magneto-optical properties of Zn$_{1-x}$Co$_x$O quantum well with barriers made of Zn$_{1-y}$Mg$_y$O. We discuss magnetic circular dichroism of excitonic transitions.

Fig. 1. Reflectivity of Zn$_{1-x}$Co$_x$O (left figure) is compared with reflectivity of ZnO (right figure). Presence of Co ions enhance magneto-optical effects near energy gap due to s,p,d interactions.
Raman Scattering on Mn or Co Doped ZnO Crystals

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Transition metal impurities doped ZnO is one of the diluted magnetic semiconductors, which has been proposed as a possible candidate for exhibiting a ferromagnetic order at room temperature [1]. While recent reports on the properties of such mixed crystals indicated the presence of a ferromagnetic interaction at room temperature, some other demonstrated a clear proof of an antiferromagnetic behavior. According to present knowledge, the magnetic properties of these semiconductors strongly depend on the conditions during the crystal growth. Nevertheless, the transition metals doped ZnO is still considered as a promising material for future spintronics applications.

The goal of the present work was to observe new vibration modes resulting from the presence of the impurities. The ZnO:Mn and ZnO:Co crystals in the bulk form, containing up to a few percent of the transition metal were grown at the Institute of Physics of the Polish Academy of Sciences in Warsaw by a chemical vapour transport method. Pure bulk ZnO crystals were grown for comparison using the same technique. The Raman spectra were collected at room temperature and at about 15 K using several Ar\textsuperscript{+} and Kr\textsuperscript{+} laser lines in the visible spectral range. The Raman spectra on both pure and doped ZnO samples were collected for the wave numbers from zero to 800 cm\textsuperscript{-1} with a spectral resolution better than 1 cm\textsuperscript{-1}.

The comparison of the Raman spectra taken on pure ZnO, ZnO:Mn, and ZnO:Co demonstrated for the doped samples a presence of some new peaks situated in the frequency range of the ZnO polar modes. The frequency of these peaks almost did not depend on the nature of the impurity. A possible identification of observed new modes is discussed in term of vibrational band modes.

This work was supported in part by the Center of Excellence of the European Union CEPHEUS (Contract No G1MA-CT-2002-04017), by the ACI NR0095 NANODYNE from the French Ministry of National Education and Research, and by the research grant No PBZ/KBN/044/P03/2001 from the State Committee for Scientific Research (Poland).

In this work we investigated ZnO films grown on GaAs substrates by Pulsed Laser Deposition. Using this approach Ryu [1] claimed to produce p-doping in thin ZnO layers by inter-diffusion. Subsequently, various authors have employed As in p doping of ZnO [2-4]. The subject has become controversial, however, with some failing to reproduce the same results under comparable deposition conditions [5], others suggesting that the “p doping” signal originates in a ZnAs interfacial compound, and others suggesting that As cannot be the acceptor itself, but that it facilitates p-doping by opening up the structure such that subsequent oxygen annealing will create Zn vacancy acceptors around the As impurity [6]. Furthermore, other reports suggest that ZnO layers (usually hcp wurtzite) can exhibit Zinc Blende structure when grown on GaAs substrates [7].

In this work we grew ZnO films grown on GaAs substrates by Pulsed Laser Deposition in order to investigate these phenomena. The impact of a subsequent post-annealing in molecular oxygen, was also studied because it has been claimed to activate the p doping in the ZnO layer [1]. Samples were investigated using techniques including X-ray diffraction, Atomic Force Microscopy, Raman Spectroscopy, Rutherford Backscattering Spectrometry, Electrochemical C-V Profiling, UV Photoluminescence, Scanning Electron Microscopy and Low Temperature Hall Measurements. Preliminary work revealed that the issue is indeed complex, in that high quality 2D growth is difficult to achieve, a new interfacial compound may have been formed and the photoluminescent response of the samples appears to evolve over time.

Growth, Structural and Optical Properties of A-plane ZnO Epilayers Grown by Plasma-Assisted MBE

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Until recently the growth, structural and optical analysis of ZnO materials have been performed predominantly for crystals and thin films oriented along the c-axis. However, non-polar surfaces are of particular interest because the built-in electric fields (both piezo and pyro-electric components) developed along the c-axis in the wurtzite structure, are oriented perpendicular to the growth axis. As a result, it is expected that quantum well structures with no screening of the exciton binding energies could be grown on such orientations. In this communication, we report a detailed investigation of epitaxial growth, as well as structural and optical properties of A-plane orientated ZnO epilayers grown by MBE.

1 µm-thick ZnO films were grown in the temperature range of 400-550°C. Prior to growth, the R-plane (01-12) sapphire substrates were thermally cleaned and subsequently exposed to oxygen plasma. Streaky RHEED patterns could be maintained throughout the growth, albeit a slight modulation for the [1-100] azimuth. Such anisotropy is also observed, and quantified, using ex-situ measurements such as AFM, X-ray diffraction and transmission electron microscopy (TEM). Detailed results will be presented.

Regarding the electronic structure of the films, the A and B free excitons are observed in the reflectivity spectra for the (E $\perp$ c) polarisation, while the C free exciton is only detected for the (E $\parallel$ c) polarisation. A large blue shift ($\geq$ 20meV) of the excitonic transitions is observed as compared to c-orientated ZnO films. This large shift in the energy gap indicates that a large strain is induced within the ZnO films, in agreement with X-ray data.

PL spectra were recorded for both the (E $\perp$ c) and (E $\parallel$ c) polarisations respectively, and displayed a number of well resolved features associated with free and bound excitons, as well as lower energy bands. The full width at half maximum of the these $I_2$ lines is in the order of 1.5 meV. In addition, we also note that the bound exciton emission in the PL spectra appeared less sensitive to the selection rules. This was not the case for the free excitons, the emission of which strongly polarised. The lower energy bands were studied using polarisation- and polarisation-dependent spectroscopy as well as selective PL. They are found to originate from the superimposition of free exciton phonon replica along with the recombination of carriers localised at structural defects. An investigation into the exact nature of these defects is currently under investigation.
Fast and Invisible ZnO based Thin Film Transistors
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Transparent electronics are nowadays an emerging technology for the next generation of optoelectronic devices. Oxide semiconductors are very interesting materials because they combine simultaneously high/low conductivity with high visual transparency and have been widely used in a variety of applications (e.g. antistatic coatings, touch display panels, solar cells, flat panel displays, heaters, defrosters, optical coatings, among others). Transparent oxide semiconductor based transistors have recently been proposed using as active channel non-doped ZnO [1,2]. One of the main advantages exhibited by these transistors lies on the magnitude of the electron channel mobility leading to higher drive currents and faster device operating speeds. The mobility reported in the literature is ranging from 0.2 to 7 cm²/Vs with an on/off current ratio from 10⁵ to 10⁷ and a threshold voltage between -1 and 15 V. To date, ZnO channel ayers have been deposited using substrate heating or submitted to post thermal annealing in order to increase, mainly the crystallinity of the ZnO layer and so the film’s mobility.

The main advantage of using ZnO deals with the fact that it is possible to growth at/near room temperature high quality polycrystalline zinc oxide, which is a particular advantage for electronic drivers, where the response speed is of major importance. Besides that, since ZnO is a wide band gap material, it is transparent in the visible region of the spectra and therefore, also less light sensitive. TFTs based on a-Si:H technology present some limitations like: light sensitivity and light degradation accompanied with a low mobility (<$2cm²/Vs). On the other hand, the poly-silicon TFTs in spite exhibiting a high mobility ($50≤μ≤500cm²/Vs$) their opacity limits the aperture ratio for active matrix arrays. Apart from that, if flexible substrates based on polymers are intended to be used, the processing temperature is also a quite limiting factor. The figure displays the input and output characteristics of the developed ZnO based TFTs, exhibiting a channel mobility of 27 cm²/Vs, a gate voltage swing of 1.39 V/decade and an on/off ratio $>10⁷$. The ZnO-TFT present an average optical transmission (including the glass substrate) of 80 % in the visible part of the spectrum.


Typical ZnO-TFT output characteristics, with the channel layer deposited at room temperature by rf magnetron sputtering produced at FCT-UNL.
Mobile Donors in Undoped ZnO

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Some shallow donors, which could migrate in crystal lattice at respectively low (about 400K) temperatures, were earlier supposed to be present in ZnO crystals [1,2]. In the present work, the direct evidence has been obtained that such mobile donors exist indeed.

Nominally undoped ZnO single crystals grown by a vapor-phase technique have been investigated. The crystals were colorless and transparent needles with hexagonal cross section 0.2-0.4 mm² and 10-15 mm in length. To reveal mobile donors a method based on the drift of charged defects in external electric field was used [3]. The redistribution of shallow donors along the sample was monitored by the intensity of donor-bound exciton luminescence band $I_D$. Exciton luminescence was excited by N₂ laser ($\lambda=337$nm) at 77K. After the action of direct electric field at $T=500$-800K the density of donors responsible for $I_D$ band was found to decrease near the anode and to increase near the cathode. It was shown that mobile donors influenced not only electrical, but also optical and luminescent characteristics of ZnO crystals and could cause the instability of these characteristics.

The nature of mobile donors has been discussed.

Electronic Properties of Zn-polar ZnO/Ga-polar GaN Heterointerfaces

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Electrical properties of ZnO/GaN heterostructures are investigated by capacitance-voltage (C-V) measurement. It is found that two-dimensional electrons are accumulated at the ZnO/GaN heterointerface due to both type-II band offset and spontaneous polarization. ZnO/GaN heterostructures are fabricated on Ga-polar GaN templates by plasma-assisted molecular-beam epitaxy. GaN templates used in this work are predeposited by metal-organic chemical vapor deposition on (0001) Al$_2$O$_3$ substrates. The typical electron concentration of GaN templates is $2 \times 10^{18}$ cm$^{-3}$. Prior to ZnO growth, Zn beams are exposed onto the GaN templates to prevent oxidation, which is required to grow Zn-polar ZnO layers. Then, low-temperature ZnO buffer is grown at 500 °C on GaN templates, followed by high-temperature annealing at 800 °C. Subsequently, ZnO layers are grown at 700 °C. Finally, N-doped ZnO capping layers are grown at 300 °C for the formation of Schottky contacts. The thickness of ZnO and ZnO:N layers are 1000 nm and 10 nm, respectively. Au electrodes are deposited on ZnO surface to fabricate Schottky contacts, while In electrodes are deposited on GaN epitaxial layers to form Ohmic contacts.

Capacitance voltage characteristics show a large plateau region, which extends as wide as 6.5 V. Such anomalous C-V characteristics are interpreted in terms of MOS like electronic state of the ZnO/GaN interface. The C-V measurements indeed show the accumulation of high density of electrons as high as $4.5 \times 10^{18}$ cm$^{-3}$ at the ZnO/GaN heterointerface. Such large density of two-dimensional electron accumulation is due to the type-II large conduction-band discontinuity and the spontaneous polarization field. The build-up of electron concentration at the ZnO/GaN heterointerface should be compared with $3 \times 10^{17}$ cm$^{-3}$ in Al$_{0.5}$Ga$_{0.7}$As/GaAs heterointerfaces and $3 \times 10^{17}$ cm$^{-3}$ in In$_{0.5}$Ga$_{0.5}$P/GaAs heterointerfaces. It is suggested that the ZnO/GaN heterostructure is very promising for the application to heterojunction transistors.
There is currently widespread interest in the development of novel semiconductors which are ferromagnetic above room temperature. Much of this work has been stimulated by predictions of high temperature ferromagnetism in $p$-type semiconductors doped with Mn [1]. For ZnO above room temperature $T_C$ has been predicted, providing simultaneous incorporation of 5% of Mn and $3 \times 10^{20}$ holes per cm$^3$ can be achieved. Despite the $p$-type doping, the other big issue in preparation of ZnO:Mn films is avoiding inhomogeneous distribution of Mn ions, their clustering and the presence of foreign phases of various Mn oxides. Zn-MnO samples grown by standard high-temperature methods ($T > 700^\circ C$) are found to exhibit clustering and contain inclusions of magnetic Mn oxides. The unique feature of our growth method (atomic layer epitaxy (ALE)/atomic layer deposition (ALD)) is that precursors are introduced sequentially into the growth chamber. This allows using a wide range of reaction precursors including those with relatively low evaporation temperatures, i.e., low temperature (LT) growth ($T < 500^\circ C$) is achievable. In the present study we applied two types of organic Mn precursors [Mn(thd) and Mn(acac)] and organic zinc precursor [Zn(CH$_3$COO)$_2$]. Growth orientation of LT ZnO films strongly depends on a lattice mismatch between ZnO and a substrate. In the consequence, we obtained monocrystalline ZnO films on GaN/Al$_2$O$_3$ and polycrystalline films on Al$_2$O$_3$, Si and lime glass. LT doping with Mn affects film crystallinity. All LT ZnMnO films are polycrystalline. Mn doping affects also growth mode. ZnMnO films have privileged orientation either with $c$ axis parallel to the substrate or with $c$ axis perpendicular in other samples. The latter growth mode was always observed in undoped ZnO films.

Magnetic properties of these films are investigated by SQUID magnetometry. We find that at high temperatures, both types of samples exhibit nearly-paramagnetic behaviour from which Mn concentration of approximately 5% and negative Curie-Weiss temperature can be inferred. Below $\sim 100$ K these layers exhibit distinctively different magnetic properties. In samples prepared from Mn(acac)$_3$ a signal from magnetically ordered spinel Mn$_3$O$_4$ dominates that of ZnMnO. Interestingly, measurements of pure Mn(acac)$_3$ precursor yield qualitatively the same, but relatively much weaker, low temperature behaviour. It is therefore natural to assume that during growth, magnetically ordered Mn$_3$O$_4$ grains are transferred from the precursor to the layers with efficiency exceeding by far that of Mn incorporation. Contrary to the previous case, Mn(thd)$_3$ originating ZnMnO shows only weak zero-field-cooled/field cooled difference which can be attributed to small superparamagnetic component. Since we do not detect these in pure Mn(thd)$_3$ precursor, this deviation from paramagnetic behaviour are attributed to (Mn$_{1-x}$Zn$_x$)$_2$O$_3$ ‘broken’ antiferromagnetic precipitations.

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A High-Resolution Electron Microscopy study of Mg$_x$Zn$_{1-x}$O Films Grown on MgO/c-sapphire

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Much interest has recently been shown in Mg$_x$Zn$_{1-x}$O alloys films as a promising candidate for ZnO band gap engineering (from 3.37 eV for ZnO to 7.8 eV for MgO). It has also been found to be a suitable material for the barrier layers of Zn/MgZnO super lattices due to its wider band gap. Mg$_x$Zn$_{1-x}$O layers can possess two different crystal structure of rock-salt cubic and hexagonal wurtzite as a result of Mg content difference. Reports show that crystal structure, and crystal quality of Mg$_x$Zn$_{1-x}$O layers can be affected by growth technique and growth condition. Crystal structure and orientation of substrate or buffer layer also play an important role in the mentioned aspect. [1,2]

In this study we will report on microstructure of Mg$_x$Zn$_{1-x}$O films grown on MgO/c-sapphire by P-MBE. Cross sectional specimens of three layers with rock salt, wurtzite, and mixed crystal structure were studied by high-resolution transmission electron microscopy (HREM). Selected area diffraction pattern (SADP) and Fast Fourier Transform (FFT) were also employed to analyze the samples. The results indicate the growth of cubic MgZnO along the [111] direction with 180° rotation twin about [111]. HREM micrograph of wurtzite MgZnO confirmed that initial stage of the growth starts with a cubic structure and then changes to the more stable [0002]-oriented wurtzite phase. Therefore by introducing a thin MgO buffer layer, growth of Mg$_x$Zn$_{1-x}$O-rock salt structure with low Mg concentration is feasible. The overlap region of cubic and wurtzite structure in sample with mixed structure was also studied and the detail of the results will be presented in this paper.

Catalyst-free Vapour Phase Transport Growth of ZnO on Different Substrates

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ZnO is a very promising wide band gap semiconductor with a great potential for applications in micro-, opto- and magnetoelectronics. Various deposition techniques have been reported in the literature to fabricate ZnO layers and nanostructures: metal-organic vapor phase epitaxy (MOVPE), pulsed laser deposition (PLD), molecular beam epitaxy (MBE), radio frequency sputtering or catalyst-assisted vapor phase transport techniques.

In the present paper we report on further development of the ZnO vapour transport growth technology. We develop this approach without implementation of a catalyst (in the literature Au is mostly used as a catalyst). The influence of gas flows, pressure in the reactor and temperature on the growth process in a modified vapour transport reactor was investigated. Employed growth temperatures were in the range from 300\textdegree{}C to 1100\textdegree{}C. Various aspects of ZnO layer growth on different substrates such as silicon, sapphire, silicon carbide and polymer material are discussed and compared. Optical microscopy, atomic force microscopy, scanning electron microscopy, x-ray diffractometry and photoluminescence were employed for characterisation of the obtained samples.

The developed VPE growth approach is very attractive due to flexible growth conditions, low cost and thus excellent potential for large-scale production. Due to the possibility of low growth temperatures (T as low as 300\textdegree{}C), VPE allows growth of ZnO layers and nanostructures on different types of substrates including polymer materials. The PL spectrum of ZnO layer grown on a plastic wafer is shown on Fig. 1. The ZnO layer on the plastic wafer was further patterned for further device applications.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1}
\caption{PL spectrum of ZnO deposited on a plastic substrate.}
\end{figure}
Homoeptaxial Growth of High-quality ZnO Layers by Molecular Beam Epitaxy

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High-quality ZnO substrates are now commercially available. Nevertheless, the line-width of X-ray diffraction (XRD) curves of homoepitaxial layers often exhibits a broader value than ZnO substrates. This can be ascribed to the surface finish of ZnO substrates, which is still far from a satisfactory level for epitaxial growth. In order to improve surface properties of ZnO substrates, we propose high-temperature annealing of ZnO substrates, which has indeed improved both surface smoothness and crystal quality as evaluated by XRD, atomic force microscopy (AFM), and photoluminescence (PL).

ZnO crystals used in this study are grown by hydrothermal technique and either mechanically or chemo-mechanically polished. ZnO substrates are annealed at various temperatures under oxygen ambient. Before annealing, the FWHM values of (0002), (0004), (0006), (10-11) peaks of a mechanically polished substrate are 56.9, 36.7, 29.9, 171.7 arcsec, respectively. The FWHM of low incident angle peak is wider than high incident angle peak, indicating that the surface has a damage layer caused by mechanical polishing. After annealing, the FWHM of these diffraction peaks are reduced to 13.0, 12.2, 12.6, 16.6 arcsec, respectively. In consistent with the improvement of crystal quality, low-temperature PL spectra of the annealed substrates show well-resolved dominant exciton emission lines with negligibly low deep-level emission. Although any surface steps are not apparent with some scratches and pits resulting from mechanical polishing before annealing as indicated by AFM observation, well-aligned surface steps with bilayer step height of 0.52 nm are formed. Such smooth surface on an atomic level should offer an ideal template for the growth of ZnO layers. We have indeed succeeded in growing high-quality ZnO layers with the same or even smaller XRD FWHM than that of annealed ZnO substrates.
ZnO Polar Surfaces Investigated by Scanning Probe Microscopies, AES and LEED

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ZnO based Diluted Magnetic Semiconductors (DMS) are very promising materials in the field of room temperature spintronics [1]. Even though room temperature ferromagnetism was already demonstrated for (Zn,Mn)O and (Zn,Co)O, the mechanisms underlying this behaviour are still under speculations.

The present study aims to characterize (Zn,X)O (where X is a ferromagnetic element) DMS using Spin Polarised Scanning Tunneling Microscopy (SP-STM). Nevertheless atomically flat surfaces of these materials are still a concern. Indeed (Zn,X)O single crystals are not yet available and the roughness of MOCVD or MBE grown epilayers does not allow atomic scale STM characterization.

This work focuses on the characterization of hydrothermally grown ZnO(0001) and ZnO (000-1) single crystals by using Atomic Force Microscopy (AFM), Low Energy Electron Diffraction (LEED), Auger Electron Spectroscopy (AES) and Scanning Tunneling Microscopy (STM).

The thickness of the surface fluid layer, due to air exposure of the samples, was measured by AFM and a chemical cleaning procedure was set up in order to remove this layer. Under Ultra High Vacuum (UHV), repeated cycles of Ar ions sputtering followed by annealing resulted in clean surfaces and crystalline surfaces (see LEED pattern in Figure 1). Finally, STM images revealed atomically flat triangular surfaces (see Figure 2) and various aspects related to electron tunneling on this wide bandgap, poorly conductive material were investigated.

Figure 1: LEED pattern. $E_p = 101\ eV$.  
Figure 2: $0.5\mu m \times 0.5\ \mu m$ STM image.

Optical Properties of ZnO Nanorods and Nanowire

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ZnO nanowire have promising potential applications in the blue and ultraviolet (UV) frequency range. We report continuous-wave and time-resolved optical spectroscopy of ZnO nanorods of varying diameters grown by MOVPE, under varying thermodynamical conditions. We discuss the influence of these conditions and of the different spectral components. Generally, photoluminescence spectra are dominated by strong excitonic contribution related to a series defect-bound excitons and to their two-electron satellites. The relative intensities of various contributions and of the lower-lying donor-acceptor band appear to be strongly dependent of the grown conditions and of the diameter of the nano-structures.
Converting ZnO into p-Type

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We report on a conversion of ZnO into p-type by nitrogen doping and a demonstration of blue light emitting diode based on ZnO p-n junctions. Behind the success, much effort has been paid to make non-doped ZnO as perfect as possible. We have marked records of the mobility (400cm²/Vs@300K and >5,000cm²/Vs@100K) and exciton radiative recombination lifetime (>2.5ns@300K), both of which surpass to the values achieved in world-best bulk single crystals. The residual electron concentration is as low as 10¹⁵cm⁻³ with keeping such high quality properties. The use of ScAlMgO₄ substrate and proper buffer layer make it possible to grow such thin films in a persistent layer-by-layer growth mode in pulsed laser deposition [1].

Another trick was to incorporate nitrogen with high concentration (10²⁰cm⁻³) with keeping such high crystalline quality by using “repeated temperature modulation technique” [2]. In this process, we repeated 15m of nitrogen doped ZnO growth at 400°C, rapid rump of temperature to 1000°C, and additional growth of 1nm ZnO at the high temperature for making several hundreds nm thick films. The films show clear and reproducible p-type conduction as revealed by Hall effect with a hole concentration of 10¹⁶-10¹⁷cm⁻³ and an activation energy of 100meV. We observed 420nm emission upon forward bias current drive for p-i-n junctions. The radiative recombination in the p-type ZnO by the electron injection into that layer seems to dominate.

As future challenges, we pursue higher hole concentration (> 10¹⁸cm⁻³), doping of (MgZn)O into p-type and the use of ZnO single crystal substrates with aiming at practical devices.

High-Temperature Defect Study of Tellurium-Enriched CdTe

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The properties of native and extrinsic point defects (PDs) in Te-rich CdTe are of fundamental importance for the electric characteristics and practical application of such material in the Gamma- and x-ray detector industry. Contrary to the extrinsic PDs, which control electric properties of CdTe at room or lower temperatures, native PDs vanish fast during the quenching of annealed sample due to their strong reactivity and a fast diffusion. Therefore, the identification of native PDs at low temperature is very complicated. The high-temperature in-situ measurements give the only possibility of a credible study of native PDs.

In this paper we report on high-temperature study of thermodynamic properties of native defects and their interactions with extrinsic defects including self-compensation, defect reactions, complex formation, and Te precipitation in Te-enriched undoped and doped CdTe. Quasi-chemical formalism is used to evaluate both defect equilibrium at the high temperature annealing and defect evolution during the cooling down to the room temperature. We show that the cooling mode significantly influences the room temperature electric properties. The proper thermal treatment can be conveniently used for the optimization of electric properties and for a preparation of the semi-insulating detector grade material with a deep level doping below the limit $10^{13}$ cm$^{-3}$ demanded in the detector industry. The simulations are based on a realistic defect model, which accords with the high temperature transport data and pressure-temperature-composition phase diagram [1].

The explored method is successfully applied for the evaluation of the high-temperature (100-800°C) in-situ conductivity and Hall effect measurements performed on undoped, Ge-doped and In-doped Te-rich CdTe single crystals grown by the Bridgman method. Assuming local defect equilibrium, the experimental data are fit both above 600°C, where the transport properties are determined by native point defects, and below 600°C, where extrinsic impurities start to dominate.

III-V/II-VI Heterovalent Double Quantum Wells

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Most of semiconductor device heterostructures used at present are isovalent, i.e. they involve compounds of only one chemical group. Heterovalent structures including compounds of different groups can provide additional advantages, integrating useful properties of chemically different materials. Recently we have proposed the concept of heterovalent resonant-tunneling structures, where a III-V quantum well (QW) (GaAs/AlGaAs) and a II-VI diluted magnetic semiconductor (DMS) QW (ZnCdMnSe/ZnSe) are electronically coupled through a thin barrier containing a heterovalent interface AlGaAs/ZnSe [1]. In principle, such hybrid III-V/II-VI heterostructures can combine the magnetically tunable spin-dependent confining potential in the II-VI DMS part and many useful properties of the nonmagnetic III-V part, such as high electron mobility, relatively slow electron spin relaxation, and well-developed growth technology. The proposed design has pursued two purposes. Firstly, when the electron levels in the two QWs are in resonance, efficient inter-well mixing of the electron states drastically enhances the electron penetration from the nonmagnetic QW into the DMS QW and vice versa. Under these conditions, application of a relatively weak external magnetic field results in a giant Zeeman splitting of both mixed electronic states and hence in the efficient spin polarization of electrons and excitons in the nonmagnetic III-V QW. Furthermore, an exciton in the GaAs/AlGaAs QW placed in the vicinity of the AlGaAs/ZnSe junction can be considered as a sensitive indicator of both local electric fields and disorder induced by the heterovalent interface, since these factors affect the position and width of the exciton resonance. Therefore optical excitonic spectroscopy applied to such samples gives valuable information about the interface microstructure.

In this paper we report on the molecular beam epitaxy and magneto-optical studies of a number of GaAs/AlGaAs/ZnSe/ZnCdMnSe heterovalent double-QW structures with varied widths of the involved GaAs/AlGaAs QW. The comparative studies of temperature-dependent photoluminescence in different samples have provided an insight into the nature of the exciton localization potential induced by the heterovalent interface. It was found that the presence of the heterovalent junction manifests itself in an additional inhomogeneous broadening of the QW excitonic resonance, resulting most probably from random variation of the interface chemical composition. The resonant inter-well electronic coupling was observed in the sample with a specific width of the GaAs/AlGaAs QW (3.4 nm). The resonant conditions result in drastic renormalization of the effective g factor of the exciton in the GaAs QW. The sign of the g-factor changes and its absolute value increases by more than one order of magnitude as compared to the reference isolated GaAs/AlGaAs single QW. The exciton linewidth in this structure is quite moderate (∼25 meV), which reflects a relatively small probability of the electron to be found under the resonance conditions in the vicinity of the noticeably disordered heterovalent interface. These studies indicate practical applicability of the heterovalent QW structures, provided the structure design and fabrication technology are carefully optimized.

Spectroscopic Studies of Ferromagnetic (Cd,Mn)Te Quantum Wells

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Modulation-doped (Cd,Mn)Te quantum wells form a model system for the study of carrier-induced ferromagnetism. They are mostly investigated by magnetooptic techniques. Photoluminescence spectra in the presence of a spin-polarized two-dimensional hole gas are better understood now [1], up to the point that it can help us to elucidate several properties of magnetic phase in a quantum well.

At low spin splitting, the photoluminescence is due to a singlet state which exhibits much of the properties of a charged exciton. It is observed in both $\sigma^+$ and $\sigma^-$ polarizations, and the observed splitting does not depend directly on the carrier density. It is a good measure of the local magnetization. At large spin splitting, the singlet state is destabilized and the photoluminescence spectra exhibit a double-peaked line similar to band-to-band luminescence, with a width which increases with the carrier density.

In a micro-PL study, the local carrier density can thus be deduced from the width of the double peak, and the local spin density from the field-induced shift, while the zero-field $\sigma^+/$$\sigma^-$ splitting measures the local spontaneous magnetization. The result is a map of the spontaneous magnetization, which shows a strong correlation with the map of carrier density, while the spin-density fluctuations are too small to play a role [2].

The properties of domains in the ordered phase were studied through time-resolved photoluminescence. In particular, measurements after a short pulse of magnetic field allow us to study the magnetization relaxation. It is faster than 20 ns in the paramagnetic state [3], and increases up to 2 $\mu$s at temperatures below $T_C$. We show that this relaxation corresponds to the dynamics of the ferromagnetic domains.

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