Optically anisotropic media: Computed polarization in terms of the Stokes vector $\vec{S}$ for a cavity photon mode of an anisotropic microcavity depending on the in-plane momentum $\vec{k}_{||}$ in the entire hemisphere. An optically uniaxial cavity medium with positive birefringence is assumed. The optic axis is aligned in the cavity plane and vertical in the plot. Color represents the $S_3$ component (circular polarization), arrows depict the projection of the Stokes vector in the $S_1$-$S_2$ plane (linear polarization). The positions of exceptional points (pure circular polarization) are marked by the white dots.

Background image: Cross-section electron microscopy image of an $m$-plane oriented anisotropic ZnO/(Mg,Zn)O microcavity.

TCO 2017.
Felix Bloch Institute for Solid State Physics

Linnéstraße 5
D-04103 Leipzig, Germany

Phone: +49 341 97-32650
Fax: +49 341 97-32668
WWW: https://www.physgeo.uni-leipzig.de/en/fakultaet/institutebereiche/felix-bloch-institute/
Preface

We are happy to present our latest research with this report and hope that you enjoy going through it. Among others, you will find novel results on exceptional points in optically anisotropic bulk materials and planar microcavities, lasing in nanostructures and electrical properties of amorphous oxides. Copper iodide was found to exhibit by far the largest figure of merit for p-type transparent conductors. Our work has also been featured on a couple of journal covers.

A particularly interesting feature of anisotropic (biaxial) optical materials is the occurrence of singular axes. For such axis only one polarization eigenmode exists. We have investigated such phenomenon in monoclinic gallia bulk crystals. This represents the first data on the spectral dispersion of the angular position of singular axes. We have put particular effort on the correct modeling of transmission and reflection in the vicinity of singular axes. A related phenomenon are the polarization properties of anisotropic microcavities, i.e. cavities where the optic axis of the uniaxial cavity medium (e.g. GaN or ZnO) is inclined with respect to the mirror normal. Such medium turns out to be 'effectively' optically biaxial and the eigenmodes are generally elliptically polarized. For further details see Section 1.16.

A number of thrilling results have been obtained for amorphous oxides, namely ZTO (zinc-tin-oxide) and ZON (zinc-oxynitride), offering rather large electron mobilities. Using the composition-spread approach to combinatorial deposition, we could optimize the cation-ratio for ZTO and have realized quite good Schottky diodes. Expect further results for integrated circuits based on this technology.

From the many other results in this report I like to draw your attention to the
experimental determination of the non-linear optical deformation potential of ZnO, determined from luminescence experiments on bent ZnO micro-wires (see Section 1.12).

We are largely indebted to our funding agencies in particular Deutsche Forschungsgemeinschaft (DFG). We are grateful for the continued funding of Sonderforschungsbereich SFB 762 "Functionality of Oxide Interfaces" that has been renewed (2016–2019) and our project on nanowire heterostructures in the Forschergruppe FOR 1616 "Nanowire Optoelectronics" which was extended for the second funding period (2015–2018). A project on flexible oxide electronics has started in the new DFG SPP FFlexCom (SPP 1796). The work of our students and researchers together with our academic and industrial partners near and far was fruitful and enjoyable and thus it is with pleasure that the semiconductor physics group presents their progress report.

Leipzig,  
August 2017  

Marius Grundmann
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Structure and Staff of the Semiconductor Physics Group

Prof. Dr. Marius Grundmann

Secretary
Anja Heck
Birgit Wendisch

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Monika Hahn
Dipl.-Ing. Holger Hochmuth
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PD Dr. Rainer Pickenhain
Prof. Dr. Bernd Rheinländer (retired)
Dr. Rüdiger Schmidt-Grund
Dr. Chris Sturm
Dr. Holger von Wenckstern
Dr. Chang Yang

PhD candidates
Sofie Bitter, M.Sc.
Stefan Hohenberger, M.Sc.
Marcus Jenderka, M.Sc.
Robert Karsthofer, M.Sc.
Max Kneiß, M.Sc.
Abdurashid Mavlonov, M.Sc.
Tom Michalsky, M.Sc.
Dipl.-Phys. Stefan Müller
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Peter Schlupp, M.Sc.
Alexander Shkurmanov, M.Sc.
Daniel Splith, M.Sc.
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Lukas Trefflich, M.Sc.
Haoming Wei, M.Sc.
Marcel Wille, M.Sc.
Zhang Zhipeng, M.Sc.
Vitaly Zviagin, M.Sc.

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Philipp Bischoff
Raffael Deichsel
Oliver Herrfurth
Rebecca Hölldobler
Tanja Jawinski
Florian Jung
Evgeny Krüger
Oliver Lahr
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Ahsan Rasheed
Laurenz Thyen
Benjamin Wehr
Anna Werner
Report of the Semiconductor Physics Group
1.1 Semi-transparent ZnO-based UV solar cells: Analysis of electrical loss mechanisms

R. Karsthof, H. von Wenckstern, M. Grundmann

Transparent solar cells open new fields of application for photovoltaics, such as energy harvesting on glass facades and windows, or autonomously powered mobile devices via display-integrated solar cells. In general, such devices could convert any surface into a photovoltaic power source without having an impact on the appearance of the latter. We recently reported on the successful fabrication of a semi-transparent, UV-active heterojunction solar cell, based on a pulsed laser deposition (PLD) grown zinc oxide (ZnO) absorber and a DC-magnetron sputtered nickel oxide (NiO) front contact, exhibiting a power conversion efficiency of 3.1 % with respect to the ultraviolet part of the sunlight, and 0.1 % with regard to the complete solar spectrum [1]. Although already showing superior performance in comparison with other transparent solar cells presented in scientific literature, our devices suffer from a pronounced deformation of the current-voltage characteristics under illumination. This results in lower photovoltaic performance than could be expected in a model assuming ideal superposition of (dark) injection and photocurrents, affecting open-circuit voltage $V_{oc}$, short-circuit current density $j_{sc}$, and fill factor $f$ of the solar cell.

In this work, we have investigated the loss mechanisms causing this behavior in more detail [2]. For this purpose, we compared three different ZnO-based diode structures that can all be employed as semi-transparent UV solar cells. All three device types had the same design with respect to the back contact and absorber components: a 180 nm thick Al-doped ZnO layer was grown on $a$-plane oriented sapphire substrates, serving as back electrode; subsequently, a 1 µm thick, nominally undoped ZnO layer was deposited on top. The growth method for both layers was PLD, the substrate temperature was kept at 670 °C, the oxygen partial pressure was 0.02 mbar. The first diode type was identical to the one presented in Ref. [1], possessing a 16 nm thick sputtered $p^+$-NiO front contact. For the second type, a 100 nm thick PLD-grown $p$-NiO front contact was used instead, which was deposited at room temperature and at an oxygen partial pressure of 0.1 mbar. In both cases, a 3 nm thin Au capping layer was DC-magnetron sputter-deposited on top of the NiO to ensure uniform current extraction over the entire contact area. The third one employed a Schottky-type front contact made from reactively sputtered platinum oxide (PtO$_y$) [3].

All three device types exhibit good current rectification properties with rectification ratio of more than six orders of magnitude at ±2 V, and ideality factor of around 2 for the NiO contacts and close to 1 for the Schottky structure, in accordance with theory (Fig. 1.1(a)). Under illumination with light from a solar simulator, the diodes show comparatively distinct photovoltaic action, with the PLD-grown NiO producing the highest $V_{oc}$ values of 530 mV, while the largest $j_{sc}$ of 0.61 mA/cm$^2$ is obtained with PtO$_y$ Schottky front contacts (Fig. 1.1(b)). For the NiO-based structures, the UV power conversion efficiency is slightly above 3 %, while the Schottky type gives around 4 %.

When the characteristics obtained under dark and illuminated conditions are compared, a significant light-induced deformation of the curves can be seen in all three cases – in particular, a strong bowing in the fourth quadrant (photovoltaic mode), respons-
Figure 1.1: Comparison of current density-voltage (jV) characteristics of the three solar cell types using a PLD-grown NiO, DC-magnetron sputtered (ms) NiO or DC-magnetron sputtered PtO$_x$ Schottky front contact. (a) in the dark (semilog scale), (b) dark and illuminated conditions, linear current density scale.

ible for a low fill factor, and an intersection of the dark and illuminated characteristics (referred to as cross-over) close to $V_{oc}$ which is indicated by the arrows in Fig. 1.1(b). It can be concluded that the superposition principle described above is violated in all solar cell types. Especially the cross-over behavior can only be understood when an enhancing effect of the impinging light flux on the injection current is taken into account. For the case of Schottky diodes, this effect has already been described in the literature for GaN-based Schottky diodes [4] and can be assigned to trapping of photo-generated holes at the semiconductor-metal interface, reducing the built-in voltage of the junction. For the NiO-based devices, we propose a model involving an optically activated recombination channel at the NiO-ZnO interface. Electronic defect states localized at this interface provide means for carrier transport, also in the dark state, as was shown in an earlier publication [5]. Without illumination, however, this recombination is rather slow. Within the framework of our model, this is due to the fact that the rate with which an electron, once trapped at an interface defect site, is re-emitted, is low compared to the capture rate for following injected electrons, such that at higher injection levels, most of the defect states are occupied and cannot contribute to recombination. Under illumination, this situation changes because the defects are depopulated by optically enhanced emission. This will increase current flow evoked by injection, but recombination of photo-generated carriers crossing the NiO-ZnO interface as well. The latter can be seen in the data of the spectrally resolved photocurrent (more specifically, external quantum efficiency, QE). In Fig. 1.2 the QE curves for the three device types are shown under two different conditions: one is obtained by monochromatic excitation only, the other is measured while the sample is simultaneously illuminated with white light from the solar simulator (corresponding to the situation applicable to the illuminated jV measurement), referred to as white light biasing.

It can also be seen that the drop of the QE above the ZnO band gap energy ($\approx 3.3$ eV) is mostly determined by absorption in the respective front contact material, as shown by the transmission (T) data plotted alongside with the QE data in Fig. 1.2. In the case of Schottky type front contacts, the light bias does not lead to differences in the measured QE within the range of measurement errors. For the NiO-based solar
cells, however, a large drop of the QE is produced in this case, independent of the photon energy, and most pronounced for PLD-grown NiO where the values are approximately halved under illumination. This supports our hypothesis that interface recombination rates are enhanced by strong illumination with white light. Since the effect is not present in the Schottky device, it can be concluded that it is not related to the ZnO layer itself. To look into the light-induced recombination processes in more detail, we studied the voltage-dependent photocurrent collection of the solar cell with the PLD-NiO, where the differences in the QE where most prominent, following the procedure described in Ref. [1]. The analysis was, again, performed under both weak monochromatic excitation close to the ZnO band gap energy and under intense white (solar) light illumination, and the results were compared. By using an analytical model for the collection probability, taking into account both recombination processes within the space charge region (SCR) in the ZnO and at the NiO-ZnO interface, the data could be fitted, which yielded low collection probabilities (around 50 % at short-circuit) due to high interface recombination for strong white light. In the case of weak monochromatic illumination, the collection efficiencies were significantly higher (83 % at $V = 0$ V), and losses were mostly determined by SCR recombination. These findings further support our hypothesis of an optically activated interface recombination channel.

Figure 1.2: External quantum efficiency data for the three investigated solar cell types under monochromatic and white light biased conditions, measured at short-circuit, and optical transmission of the respective front contact materials

1.2 Influence of Cation Composition on Material Properties of Amorphous Zinc-Tin-Oxide Thin Films

S. Bitter, P. Schlupp, H. von Wenckstern, M. Grundmann

The possibility of room temperature deposition makes amorphous zinc-tin-oxide (ZTO) an ideal candidate for flexible, large-area, and cost-efficient devices [1]. It consists of the non-toxic and naturally abundant elements zinc and tin. The influence of the composition on electrical and optical properties of ZTO has been reported for a few discrete cation ratios only [2, 3]. Besides the chemical composition, the oxygen pressure during growth has a strong influence on ZTO material properties as reported for e.g. pulsed laser deposition [4].

We discuss the electrical and optical properties of amorphous ZTO in dependence on the cation composition for a wide composition range and oxygen growth pressures of 0.025 and 0.030 mbar.

The ZTO thin films were deposited by a continuous composition spread (CCS) approach for PLD [5]. For that, a segmented ceramic target is rotated synchronously with a 50 × 50 mm² glass substrate. Additionally, an offset of 24 mm between the normal on the center of the substrate and the normal on the center of the target was chosen to achieve the composition gradient. Here, we present electrical properties for ZTO thin films with compositions between 0.08 and 0.82 Zn/(Zn+Sn).

![Figure 1.3](image-url)

**Figure 1.3:** (a) Resistivity $\rho$ determined by Hall effect measurements for different deposition pressures and targets, which can be seen in different composition ranges. These values were compared to thin films deposited from single composition targets (SCT). (b) Absorption edge for a deposition pressure of 0.03 mbar and different targets (I: segmented target with a pure SnO₂ and pure ZnO half, II: Halves with Zn/Sn ratios of 1:2 and 2:1).

Targets with different zinc to tin ratios in the segments were used to achieve larger or smaller composition gradients. Targets with a pure zinc oxide and tin oxide segment
resulted in thin films with a wide composition range but also a high droplet density on the thin films. The droplet density could be reduced by choosing the compositions of the target segments as 1:2 and 2:1 ZnO:SnO₂. The 50 × 50 mm² samples were investigated by energy dispersive X-ray analysis to map the composition. Subsequently, the samples were divided into 5 mm wide stripes which were then broken into 5 × 5 mm² pieces for the investigation of the electrical properties by Hall effect measurements. The resistivity and absorption edge of the thin films are depicted in Figure 1.3 in dependence on the zinc to tin ratio. The measured values for the CCS samples were compared to those of thin films deposited from standard, single composition PLD targets and a good agreement was observed.

A tuning of the free carrier density from 2 × 10¹⁶ cm⁻³ to 1 × 10²⁰ cm⁻³ is possible with this approach, while the smallest measured resistivity of 5.9 × 10⁻⁵ Ωm was found for 0.13 Zn/(Zn+Sn) and a deposition pressure of 0.025 mbar O₂ [6]. The absorption edge varied between 1.8 and 3 eV and increased with increasing zinc content. A further tuning of the thin film properties is possible by a variation of the deposition pressure [4]. This wide range of properties allows the fabrication of optimized devices based on this compound. All-amorphous pn-heterojunctions have been reported for 0.3 Zn/(Zn+Sn) already [7][8].


1.3 Schottky barrier diodes based on room temperature fabricated zinc tin oxide thin films

P. Schlupp, H. von Wenckstern, M. Grundmann

Low temperature fabrication of semiconductors is desirable not only because of the low costs. It also enables the use of thermally unstable but flexible substrates. Unfortunately, most semiconducting materials require a good crystalline quality and with that a high fabrication temperature in order to fulfill the requirements for most applications. Amorphous oxide semiconductors (AOS) are materials which do not underlay this contradiction. Due to their electronic structure, they exhibit good electric properties in the disordered amorphous phase [1]. Zinc tin oxide (ZTO) is a promising AOS because it consists of naturally abundant materials only. Electron mobility of 12 cm²V⁻¹s⁻¹ was reported while the conductivity is controllable varying the fabrication parameter [2, 3]. Schottky barrier diodes are a viable option to create rectifying contacts on semiconductor thin films and are a prerequisite for space charge region spectroscopic methods like capacitance-voltage (CV) and thermal admittance spectroscopy (TAS). They can
also be used as gate contact in metal semiconductor field effect transistors (MESFET). We report on Schottky diodes using platinum metal contacts. In figure 1.4a the current density-voltage characteristics of two diodes on one and the same thin film are depicted. The grey line represents a Pt/ZTO Schottky contact. Since the leakage current is more than $10^{-3}$ A cm$^{-2}$ at -1.5 V and increases exponentially with increasing voltage tunneling is most likely responsible for the high leakage current. To decrease it, a thin semi-insulating ZTO layer was introduced at the platinum/ZTO interface. This reduces the leakage current of about four orders of magnitude (black line figure 1.4a). Both diodes were investigated by capacitance-voltage and thermal admittance spectroscopy. The net doping density was calculated from the CV data and is depicted in figure 1.4b. The values are between $10^{17}$ and $10^{18}$ cm$^{-3}$. A slight decrease to the surface is observed.

From TAS $G/\omega$ vs. $T$ is obtained and depicted in figure 1.5. Both diodes show two peaks in $G/\omega$ shifting with the temperature as the probing frequency is increased. These peaks correspond to defect states in the material. The deep defect is located 215 – 220 meV below the conduction band minimum. The calculated capture cross sections are $1 \times 10^{-14}$ and $1.7 \times 10^{-14}$ cm$^2$ for the diodes without and with semi-insulating ZTO layer, respectively. This is a rather high value indicating a rather large defect. Undercoordinated cation pairs are known to form deep defects [4] and are candidates for the deep defect observed. The shallow defect is within the freeze-out regime. Therefore the method of Pautrat et al. is applied for evaluation [5]. For that we assume that scattering at potential barriers, located at the conduction band minimum due to the different cations, is the dominant scattering mechanism in the freeze-out temperature regime [6]. Assuming a potential height of 10 to 20 meV an activation energy of 15-27 meV is obtained. Further investigations are necessary in order to obtain information about the microscopic nature of the shallow defect.

The work was supported by the ESF(SAB 100124929) and Leipzig School of Natural Science (BuildMoNa).

Figure 1.5: Temperature dependence of $G/\omega$ for the both diodes. The peaks shifting with the temperature indicating two defect levels.


1.4 Chemical bonding states of rf-sputtered amorphous zinc oxynitride thin films


*Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Fakultät für Chemie und Mineralogie, Universität Leipzig

Recently, amorphous zinc oxynitride (a-ZnON) has attracted much attention as active channel material for high-performance thin-film transistors with superior field-effect mobilities [1]. However, the electrical properties of room-temperature deposited thin films depend significantly on the anion content and are also affected by moderate annealing temperatures [2]. Additionally, chemical stability is a remaining issue for reliable device production.

In order to understand changes in electrical properties, we have investigated the chemical bonding states of as-deposited, annealed and aged ZnON thin films by means of X-ray photoelectron spectroscopy (XPS). The surface sensitive XPS measurements were performed in UHV ($< 5 \times 10^{-9}$ mbar) using Al K$_\alpha$ radiation ($h\nu = 1486.7$ eV). The C 1s line attributed to aliphatic carbon with a binding energy of 285 eV has been used to calibrate the spectrometer. The ZnON thin films were radio-frequency sputtered at room temperature from a metallic zinc target in a reactive atmosphere consisting of Ar, N$_2$ and O$_2$ at a total gas pressure of $4 \times 10^{-3}$ mbar. XPS measurements were performed directly after thin film deposition (as-dep.) and repeated after two weeks.
Table 1.1: Electrical properties determined by Hall effect measurements: electrical conductivity $\sigma$, electron concentration $n$ and Hall mobility $\mu$.

<table>
<thead>
<tr>
<th></th>
<th>$\sigma$ (S/cm)</th>
<th>$n$ ($\text{cm}^{-3}$)</th>
<th>$\mu$ (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-dep.</td>
<td>39.4</td>
<td>$5.3 \times 10^{18}$</td>
<td>46</td>
</tr>
<tr>
<td>after 5 months</td>
<td>61.0</td>
<td>$7.3 \times 10^{18}$</td>
<td>52</td>
</tr>
<tr>
<td>annealed</td>
<td>299.4</td>
<td>$3.4 \times 10^{19}$</td>
<td>55</td>
</tr>
<tr>
<td>after 5 months</td>
<td>295.3</td>
<td>$3.3 \times 10^{19}$</td>
<td>56</td>
</tr>
</tbody>
</table>

(aged). Additionally, XPS spectra of an aged (5 months) thin film, which was annealed directly after thin film deposition, were obtained for comparison. The annealing was performed for 1h in N$_2$ atmosphere at about 200 °C. X-ray diffraction measurements confirmed that the investigated ZnON thin films are X-ray amorphous.

The annealed as well as the aged ZnON thin film reveal an increased conductivity compared to the as-deposited films. This increase is due to an increased electron concentration as well as mobility, as indicated by means of Hall effect measurements (Tab. 1.1). While the change in carrier concentration is more pronounced for the annealed thin films, their electrical properties remain stable over months.

As indicated by XPS, only the as-deposited ZnON thin film appears to contain a few Zn–N bonds at the surface (Fig. 1.6(a) and 1.6(g)). After two weeks air exposure the Zn–N peak is reduced owing to a decreased nitrogen content (Fig. 1.6(h)). The annealed ZnON thin film also show a decreased Zn–N peak intensity compared to the as-deposited film (Fig. 1.6(i)). Besides, the Zn–O peak becomes more pronounced and the peak attributed to absorbed oxygen species is significantly reduced as a result of annealing (Fig. 1.6(f)).

In summary, the altered electrical properties of aged ZnON thin films can be attributed to nitrogen loss. Presumably, additional doping owing to adsorbed species from ambient is present. Annealing cannot prevent nitrogen loss from the surface, but the resulting ZnO surface is more stable against adsorption, which leads to improved long-term stability of ZnON thin films.


1.5 Electronic defects in In$_2$O$_3$ and In$_2$O$_3$:Mg thin films on r-plane sapphire

D. Splith, F. Schmidt, S. Müller, H. von Wencstern, M. Grundmann

In$_2$O$_3$ is a material mostly known in its highly conducting, tin-doped form, being used as a transparent conducting oxide, e.g. as an electrode in displays or in thin film solar cells or as a contact layer in touch screens. However, interest in the semiconducting properties of In$_2$O$_3$ arose in the last years. Recently, first rectifying diodes using Schottky contacts (SCs) [1] as well as $pn$-heterojunctions [2] were realized on In$_2$O$_3$ thin films on yttria-stabilized zirconia substrates. Since In$_2$O$_3$ tends to form a surface electron
In this study we investigated electronic defects in nominally undoped and Mg-doped In$_2$O$_3$ thin films grown by pulsed laser deposition on $r$-plane sapphire using thermal admittance spectroscopy (TAS) and deep-level transient spectroscopy (DLTS) [4].

From Hall-effect measurements, the influence of the Mg-doping on the free charge carrier density was investigated. Nominally undoped In$_2$O$_3$ shows a high free electron concentration above $1 \times 10^{19}$ cm$^{-3}$. Since Mg acts as an acceptor in In$_2$O$_3$, the free carrier concentration is reduced with increasing Mg content. In order to obtain SCs with low series resistance for defect spectroscopy, the Mg-doped or nominally undoped thin films were grown on top of a highly conducting Sn-doped In$_2$O$_3$ layer, acting as a back contact layer. In Fig. 1.7 (a) the IV characteristics of reactively sputtered Pt-SCs fabricated on such samples are shown for different Mg contents. The performance of these SCs strongly depends on the Mg content: while almost no rectification can be observed on samples without Mg-doping, rectification ratios of 570 were observed on the sample with 1 wt.% MgO.

TAS and DLTS measurements were performed for the nominally undoped sample
and a 1 wt.% MgO-doped thin film. For the sample without Mg doping, one defect is visible in the TAS measurement. The position of the peak was determined for different measurement frequencies and plotted in an Arrhenius diagram depicted in Fig. 1.7 (b) (open symbols labeled E2). For the Mg-doped sample, two defects were found (solid symbols labeled E2 and E1). Unfortunately, DLTS measurements on the nominally undoped sample are not possible due to the high reverse current. For the Mg-doped sample, the DLTS measurement shows three defects, which are also depicted in the Arrhenius plot (solid symbols labeled E3, E4 and E5). From a linear fit we can determine the thermal activation energy $E_t$ as well as the apparent capture cross-sections $\sigma_n$, which are summarized in Table 1.2. Due to the similar defect parameters of E2 in both samples, we assume that this is the same defect. E1 is only visible in the Mg-doped sample, possible candidates for this defect are therefore interstitials of Mg or In. However, further investigations are necessary in order to clarify the chemical nature of this defect and the other defects observed.


Table 1.2: Parameters of the defects found in the Mg-doped and nominally undoped sample by TAS and DLTS measurements

<table>
<thead>
<tr>
<th>defect</th>
<th>MgO (wt.%)</th>
<th>method</th>
<th>$E_t$ (meV)</th>
<th>$\sigma_n$ (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>1.0</td>
<td>TAS</td>
<td>91</td>
<td>$4.6 \cdot 10^{-18}$</td>
</tr>
<tr>
<td>E2</td>
<td>0.0</td>
<td>TAS</td>
<td>189</td>
<td>$1.7 \cdot 10^{-16}$</td>
</tr>
<tr>
<td>E2</td>
<td>1.0</td>
<td>TAS</td>
<td>204</td>
<td>$4.6 \cdot 10^{-16}$</td>
</tr>
<tr>
<td>E3</td>
<td>1.0</td>
<td>DLTS</td>
<td>283</td>
<td>$4.9 \cdot 10^{-13}$</td>
</tr>
<tr>
<td>E4</td>
<td>1.0</td>
<td>DLTS</td>
<td>405</td>
<td>$1.9 \cdot 10^{-13}$</td>
</tr>
<tr>
<td>E5</td>
<td>1.0</td>
<td>DLTS</td>
<td>569</td>
<td>$4.2 \cdot 10^{-11}$</td>
</tr>
</tbody>
</table>

Figure 1.7: (a) current density - voltage characteristic of reactively sputtered Pt-SCs on In$_2$O$_3$ thin films with different Mg content. (b) Arrhenius-plot of all defects found in Mg-doped (solid symbols) and nominally undoped (open symbols) In$_2$O$_3$ thin films by either TAS (gray area) or DLTS measurements.
1.6 Room-temperature domain-epitaxy of p-type transparent conductive semiconductor copper iodide thin films for transparent CuI/ZnO heterojunctions

C. Yang, M. Kneiß, M. Lorenz, M. Grundmann

Over the last decade transparent conductive materials (TCMs) had a dramatic increase in interest in the field of optoelectronics. Most attention has been paid to n-type wide bandgap semiconductors including In$_2$O$_3$, SnO$_2$, ZnO, TiO$_2$ and their doped versions. However, the lack of suitable p-type TCMs has been the main obstacle in front of either passivate or active electronic applications. Copper iodide in the zincblende ground-state phase ($\gamma$-CuI) has p-type conductivity with a high Hall mobility (>40 cm$^2$/V$\cdot$s$^{-1}$ in bulk), a wide band gap (3.1 eV) with a direct band structure, and a large exciton binding energy (62 meV). These advantageous properties make it one of the most promising p-type TCMs [1].

It is a challenge to grow epitaxial thin films of CuI due to the lack of lattice-matched substrates. Here, we report the room-temperature heteroepitaxial growth of CuI on various substrates by reactive sputtering technique [2]. In such heteroepitaxial growth the formation of rotation domains is observed and hereby systematically investigated in accordance with existing theoretical study of domain-epitaxy [2, 3]. The rotational symmetries of the substrates used in this study are $n = 2, 3, 4$ and $6$, namely for a-sapphire [Al$_2$O$_3$(1120)], NaCl(111), NaCl(001), c-sapphire [Al$_2$O$_3$(0001)], respectively. As depicted in Fig. 1.8 (a), the heteroepitaxial relationships can be deduced as CuI[$\bar{1}$10](111) || Al$_2$O$_3$(0001)(1120), CuI<112>(111) || NaCl[112](111), CuI<112>(111) || NaCl[110](001), and CuI<112>(111) || Al$_2$O$_3$(1110)(0001). The formation of these different rotation domains can be explained using atomic configurations as sketched in Fig. 1.8 (b).

**Figure 1.8:** (a) Schematic alignment and (b) atomic configurations of CuI crystallites epitaxially grown on NaCl and sapphire substrates. In (b) blue sphere: cation of substrate material; grey sphere: Anion of substrate material; red sphere: I$^-$ of CuI epilayer.
The controllable epitaxy of CuI thin films allows for the combination of p-type CuI with suitable n-type TCMs with the purpose to fabricate epitaxial thin film heterojunctions. Such heterostructures have superior properties to structures without or with weakly ordered in-plane orientation. Based on these results, bipolar heterodiodes were fabricated from epitaxial p-CuI/n-ZnO on a-sapphire heterostructures, as shown in Fig. 1.9. The obtained epitaxial thin film heterojunction of p-CuI(111)/n-ZnO(00.1) exhibits a high rectification up to $2 \times 10^9$ ($\pm 2$ V), a 100-fold improvement compared to diodes with disordered interfaces [2, 4]. This value presents by far the highest rectification of crystalline diodes involving oxide semiconductors. The low growth temperature (room temperature) and the use of sputtering technique make it a facile way to produce large area CuI epilayers for applications in transparent electronics.

**Figure 1.9:** (a) Schematic of the CuI/ZnO diode structure, (c) photograph of CuI/ZnO bilayer on a-sapphire substrate, and (b) Current density vs. voltage characteristic of CuI/ZnO diode. The inset depicts the characteristics of the fitted multiple barriers near the kink region. Black arrow: kink at 0.6 V probably related to inhomogeneous diode properties. Grey arrow: voltage sweeping direction.

1.7 Boosting the Figure of Merit of p-Type Transparent Conductors: Degenerate Copper Iodide Thin Film Synthesized at Room Temperature

C. Yang, M. Kneiß, M. Lorenz, M. Grundmann

Transparent conductors (TCs) are well known for their wide use in passive electronic applications, such as transparent electrodes for solar cells, flat-panel displays and light emitting diodes. However, the lack of high-performance p-type TCs has been the main obstacle for both passive and active electronic applications. A high-conductivity, high optical transmittance material with corresponding low-temperature synthesis techniques is desired for practical use.

In this study, we overcome the challenge in achieving simultaneously high conductivity and transparency for p-type TCs by developing the degenerate wide bandgap semiconductor CuI. We propose industrially applicable techniques including room-temperature physical deposition by reactive sputtering for thin film growth and iodine-doping of CuI. The obtained degenerate CuI polycrystalline thin films exhibit record high p-type conductivity of $156 \text{ S/cm}$ for undoped CuI and $283 \text{ S/cm}$ for I-doped CuI. At the same time, the films appear clear and exhibit a high transmission of 60–85% in the visible spectral range. In Fig. 1.10 we summarize the electrical conductivity ($\sigma$)
and visible transmittance ($T_{\text{vis}}$) (i.e. the transmittance averaged over the visible spectral range 400–800 nm) for CuI thin films as well as for other TCs. For the purpose of achieving simultaneously high $\sigma$ and $T_{\text{vis}}$, there is obviously a huge gap between p- and n-type TCs. It is now filled by CuI. For a high $T_{\text{vis}} > 70\%$, our p-type CuI thin films exhibit a very high conductivity, two or three orders of magnitude higher than that of any other p-type TC of such transparency.

The realization of such simultaneously high conductivity and transparency boosts the figure of merit (FOM) of a p-type TC. As shown in Fig. 1.11, the FOM for p-type TCs has improved over the years from 1996 until now. Except for CuI, the FOM for most p-type TCs is lower than 200 M$\Omega^{-1}$ unless sacrificing their transmittance below 50%. In contrast, the as-deposited CuI in this study shows an FOM about 50 times higher, up to 9500 M$\Omega^{-1}$, while providing a high $T_{\text{vis}}$ above 70%. This FOM value can be further doubled to 17000 M$\Omega^{-1}$ without affecting the transparency by iodine doping. These results demonstrate the superior TC performance of our CuI thin films with respect to all measures. The CuI reported here exhibits significantly higher FOM (10 times) compared to previously reported CuI and p-type ZnO, and even 100 times greater compared to any other p-type TC.

![Graphical representation of FOM over time for p-type TCs with $T_{\text{vis}} > 30\%$.](image)

**Figure 1.11:** Graphical representation of FOM over time for p-type TCs with $T_{\text{vis}} > 30\%$.

Our results underscore the great potential of CuI applied as p-type transparent electrodes [1]. It is also compatible with many other n-type TCs for active device structures, such as transparent CuI/ZnO bipolar diodes [2]. Besides diodes, CuI/n-
type TC tunneling contacts also appear attractive and could be a further direction of research. The sputtering technique at room temperature used here can be upscaled for applications of CuI in transparent electronics. These results may motivate further systematic studies of CuI as one of the most promising p-type TCs [3].


1.8 Exchange bias in LaNiO$_3$ / LaMnO$_3$ superlattices

H.M. Wei, J. Barzola-Quicia*, T. Höche†, C. Patzig†, M. Lorenz, and M. Grundmann

*Division of Superconductivity and Magnetism, Institute für Experimentelle Physik II, Universität Leipzig
†Center for Applied Microstructure Diagnostics, Fraunhofer-Institut für Mikrostruktur von Werkstoffen und Systemen, Halle/S.

The exchange bias (EB), exhibiting a shift of the center of the magnetic loop along the magnetic field axis, has tremendous utility in magnetic recording, magnetic tunnel junctions, and giant magnetoresistance sensors [1]. For a long time, it has been known in many different systems containing interfaces between ferromagnetic and antiferromagnetic materials [2]. Recently, we observed an unexpected EB effect in superlattices (SLs) composed of layers of paramagnetic LaNiO$_3$ (LNO) and ferromagnetic LaMnO$_3$ (LMO). The SLs are grown by PLD with structure of LMO$_n$+[LNO$_m$/LMO$_n$]$_l$ SLs ($m$ and $n$ indicate the number of unit cells, respectively, thereafter referred to as $[m/n]_l$). The stacking periodicity is repeated $l$ times to adjust the total SL thickness. Two kinds of SrTiO$_3$ (STO) single crystals with orientations of (001) and (111) are used as substrates.

Fig. 1.12 (a) and (b) display AFM images of [2/2]$_6$ SLs deposited on STO (001) and STO (111) substrates, respectively. The SLs show monolayer terraces with low roughness of 0.095 nm for (001) and 0.1115 nm for (111). The steps height are 0.39 nm and 0.22 nm, corresponding to one unit cell for (001) and (111) orientation, respectively. The in-plane epitaxial relationship between SLs and substrates is analyzed by X-ray diffraction (XRD) reciprocal space map (RSM). Taking the [8/2]$_{10}$ SL, for example, the in-plane lattice match can be deduced from the vertical alignment of the SL and substrate peaks as shown in Fig. 1.12 (c). In addition, the SL period can be calculated from the distance between two adjacent satellite peaks. More accurate structural parameters are obtained by high-resolution transmission electron microscopy (TEM). As shown in Fig. 1.12 (d), 10 double layers LNO/LMO with thickness of about 3 nm were confirmed, corresponding to the designed (111)-oriented [7/7]$_{10}$ SL structure. The inter-planar spacing along the growth direction is 0.22 nm, whose value is equal to the steps height of one unit cell measured by AFM. The in-plane lattice parameter of SL is about 0.27 nm, further confirming the lattice match between SL and substrate.

The magnetic properties of SLs are measured using superconducting quantum interference device (SQUID) and double checked by the vibrating sample magnetometer.
Figure 1.12: AFM images of $[2/2]_6$ LNO/LMO SLs deposited on (a) STO (001) and (b) STO (111) substrates. (c) XRD RSM with indicated reflection of $[8/2]_{10}$ SL grown along (001) orientation. (d) TEM image of the $[7/7]_{10}$ SL grown on STO (111) substrate.

Figure 1.13: (a) Magnetic hysteresis loops at 2 K for the (111)-oriented $[7/7]_{13}$ SL after field-cooling at two different fields $\mu_0 H_{FC} = \pm 1$ T. (b) Hysteresis loops for the (001)-oriented $[5/5]_{10}$ SL at different constant temperatures after cooling the sample with a field of +1 T. (c) Magnetic moment versus temperature of (111)-oriented SL in the ZFC and FC states at a field of 0.2 T. The inset is $dM/dT$ versus temperature of FC curve.

of a physical property measurement system (PPMS-9) from Quantum Design, Inc. Fig. 1.13 (a) presents hysteresis loops of (111)-oriented SL at 2 K after field-cooling from room temperature in the presence of $\pm 1$ T fields. The shift of the hysteresis loops along the magnetic field axis is clearly visible. This behavior is a classic signature of EB effect. Different from the previous study by Gibert et al. [3], the EB is also present in the (001)-oriented SL with a clear shift of the hysteresis loops at different measured temperatures as shown in Fig. 1.13 (b). In order to further understand the EB effect, temperature-dependent zero-field-cooling (ZFC) and field-cooling (FC) magnetization measurements have been performed. As shown in Fig. 1.13 (c), the ZFC and FC curves
show different behavior at low temperatures, suggesting that the sample contains two magnetic phases with different magnetocrystalline anisotropy [4]. Since the difference in the magnetic moment measured in ZFC and FC sequences was insignificant in LMO/LaAlO$_3$ SLs, we conclude that the EB observed in LNO/LMO SLs is related to the interfaces between the two components. In addition, the Curie temperature of SL was obtained to be 90 K from the minimum of the $dM/dT$ curve as shown in the inset of Fig. 1.13 (c). If we define the characteristic Néel temperature ($T_N$) where the ZFC magnetic moment shows a maximum, a temperature of 10 K was obtained.

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1.9 Effect of Bi-content and Gd-doping on the multiferroic properties of BaTiO$_3$-BiFeO$_3$ superlattices

S. Hohenberger, M. Lorenz, V. Lazenka*, K. Temst*, M. Grundmann

*Institute for Nuclear and Radiation Physics, KU Leuven, Belgium

Periodic thin film multilayers of BaTiO$_3$ (BTO) and BiFeO$_3$ (BFO) show vastly increased magnetoelectric (ME) coupling, compared to single phase materials [1]. These layered epitaxial thin films combine the ferroelectric BTO and the only known single phase room temperature multiferroic BFO. Our previous work suggests that the exceptionally large ME voltage coefficients of up to 49 V/cmOe at 300°C in these films is linked to epitaxial strain at the interfaces [2]. However, the exact origin of the magnetoelectric coupling mechanism still requires further investigation. Additionally, the ferroelectric and magnetic performance of these films have to be improved to pave the way for practical applications.

In single phase films of BFO, a common route is to enrich the Bi-content in the ablation target to account for the inherent volatility of Bi [3] and thus reduce the defect density and reduce leakage current. In another approach, substituting Bi in BFO with rare earth ions such as La, Nd, or Gd has been shown [4] to increase the saturation magnetization and decrease the roughness of single phase Bi$_{1-x}$RE$_x$O$_3$ films deposited on STO.

Samples consisting of 15 double layers of 15 nm BTO and 5 nm - 50 nm BFO were fabricated by pulsed laser deposition on un-doped and Nb-doped, (001)-oriented SrTiO$_3$ (STO) single-crystal substrates at 650°C and 0.25 mbar oxygen partial pressure. The substrates were etched and annealed prior to deposition, creating TiO$_2$-terminated,
single unit-cell stepped surfaces. The composition of the BFO films was varied by altering the proportions of Bi₂O₃, Gd₂O₃, and Fe₂O₃ powders used in the target synthesis, yielding the nominal compositions Bi₁.₁FeO₃ and Bi₀.₉₅Gd₀.₀₅FeO₃.

X-ray diffraction experiments show the high crystalline quality of the deposited films. As depicted in the reciprocal space maps (RSM) in fig. 1.14, superlattice fringe peaks are clearly visible to seventh order and higher, indicating sharp, coherent interfaces. Furthermore, RSM measurements in the vicinity of asymmetric substrate peaks (not shown here) indicate a relaxed growth of the superlattices with respect to the substrates. Fig. 1.15 (a) highlights the pronounced enhancement of the magnetic properties of BTO-BFO superlattices by Gd-doping. While at room temperature the superlattice with Bi₁.₁FeO₃ saturates at 1.₅ emu/cm³, the sample with Bi₀.₉₅Gd₀.₀₅FeO₃ shows an enhanced saturation magnetization of 2.₂ emu/cm³. Whereas the highest difference in magnetic saturation was measured in samples with large BFO thickness relative to the BTO thickness, samples with low BFO thickness showed the both the largest values and most pronounced differences for the ME voltage coefficients. Depicted in fig. 1.15 (b) are temperature-dependent measurements of the ME voltage coefficients of two such samples with low BFO thickness, with the Bi₁.₁FeO₃ sample reaching 3₄ V/cmOe at 300 K, and the Bi₀.₉₅Gd₀.₀₅FeO₃ sample reaching 5₁ V/cmOe.

**Figure 1.14:** Reciprocal space maps around the (001) STO substrate peak of superlattices 1₅×BaTiO₃ and (a) Bi₁.₁FeO₃ and (b) Bi₀.₉₅Gd₀.₀₅FeO₃. The inserted superlattice periodicities \( d_{SL} \) were calculated from the spacing of the fringe peaks.

In summary, high quality multiferroic superlattices of BTO and BFO were fabricated on STO single crystalline substrates. Variation of the Bi content and doping with Gd were shown to be promising approaches to further push the boundaries of magneto-electric coupling in composite multiferroic materials.

Figure 1.15: (a) Room temperature magnetic hysteresis measurements of two superlattices with high BFO layer thickness; (b) T-dependent ME voltage coefficient measurements of two superlattices with low BFO layer thickness. BTO layer thickness is kept constant at ca. 15 nm for all samples.

1.10 Optical properties of CuI-based inorganic-organic hybrid materials

L. Trefflich, G. Benndorf, M. Wille, R. Schmidt-Grund, H. Krautscheid*, M. Grundmann

*Institut für Anorganische Chemie, Universität Leipzig, Johannisallee 29, 04310 Leipzig, Germany

Figure 1.16: a) Photoluminescence spectrum of Cu$_2$I$_2$(3 – pc)$_4$ shows spectrally broad emission around 550 nm, which results in bright orange light clearly visible to the naked eye (b). c) Timeresolved photoluminescence spectroscopy shows a decay time of around 10 µs as well as a monoexponential decay in the time range up to 50 µs.

In recent years, a lot of research has been done in the field of phosphors for white light generation. However, nearly all of them suffer from doping with rare-earth elements [1], which can be problematic because of their environment unfriendly mining and possible supply issues. A promising replacement are CuI-based lighting phosphors due to their
optical tunability, facile synthesis and high quantum yield of up to 95% [2]. We studied the optical as well as electrical properties of (CuI)-based inorganic-organic hybrid materials for application in rare earth free white light LEDs and electrically driven inorganic-organic solid state lasers. Therefore we deposited approximately 170 nm thin films of Cu$_2$I$_2$(3- pc)$_4$ (3- pc means 3-Picoline) via spincoating on Si + SiO$_2$ and c-plane sapphire substrates and investigated their optical properties as well as temporal dynamics using photoluminescence spectroscopy. We found spectrally broad photoluminescence emission around 550 nm resulting in intense orange visible light emission (Figure 1.16). This luminescence is most likely caused by recombination of electrons and holes in the LUMO and HOMO bands respectively [3]. The luminescence shows a monoexponential decay with a decay time of around 10 µs. This is roughly two orders of magnitude shorter than the lifetime of currently used phosphores [4], demonstrating the applicational potential of this material class.


1.11 Growth kinetics of ZnO nanowires grown by pulsed laser deposition

A. Shkurmanov, C. Sturm, H. Hochmuth, M. Grundmann

The exploitation of ZnO nanostructures such as nanowires (NWs) for devices is already demonstrated for a wide variety of applications as light emitters, electromechanical resonators, pressure and 3D imaging sensors. However, the functionality of these devices depends strongly on the NW geometrical characteristics [1]. For instance, thick NWs with a diameter of few µm are preferred for applications which are based on compression, e.g. caused by an externally applied pressure, whereas thin NWs with a diameter of a few nm offer a large surface-to-volume ratio, making them interesting for bending sensitive applications [2, 3]. Thus the understanding of the growth kinetics in order to control the shape of the NWs is important [4].

In order to investigate the growth process of ZnO NWs by using undoped ZnO seed layers and a growth temperature of $T \approx 950$ °C, we fabricated a series of NWs which differ in the amount of deposited ZnO material. This was achieved by varying the number of laser pulses from 3000 to 36 000. The first 3000 pulses are responsible for the growth of the pyramidal nucleation seeds. For larger pulse numbers the growth of the NWs is then obtained on top of the seeds. The NW aspect ratio and diameter are presented in Fig. 1.17 as a function of the laser pulse number. For the applied pulses in the range of 3000–9000 (regime I), the length of the NWs increases whereas the NW diameter remains almost constant. A larger number of laser pulses in the range of 9000–12 000 (regime II) leads to an increase of the length and decrease of the diameter. When 12 000–24 000 (regime III) pulses were applied, the length and the diameter increases and decreases further, respectively, but at a lower rate. For larger number of laser pulses (over 24 000 pulses, regime IV) we observe that in some cases of growth, the diameter increases whereas the length decreases with number of pulses.
Figure 1.17: Median values of aspect ratio (a) and diameter (b) of nanowires, grown on pure ZnO layer, as functions of number of laser pulses. First 3000 pulses corresponds to the formation of ZnO seeds for further growth of nanowires. A scheme of the NW growth by interaction of three flows of the ZnO particles (c).

The observed behavior of the NW developing might be caused by interaction of three flows of particles (Fig. 1.17c) [4]. The first one ($f_1$), the flow of the deposited particles on the seed layer, is responsible for formation the nucleation seeds. The second flow ($f_2$) is a movement of the particles on the facets of the NW and responsible for the length and diameter developing. The third ($f_3$) is a constant flow of particles which are deposited from the target to the substrate and arrive directly to the NW facets.


1.12 Non-linear optical deformation potentials in uniaxially strained ZnO microwires

C. Sturm, M. Wille, J. Lenzner, S. Khujanov, M. Grundmann

ZnO microwires are interesting building blocks for the realization of low dimensional devices, e.g. pressure sensors with high spatial resolution [1]. The presence of strain leads to a change of the electrical and optical properties, especially the band gap energy. It can be exploited in order to tune the emission properties, therefore the optical deformation potentials were investigated in the last years in detail (e.g. Ref. [2]). However, these investigations are mainly limited to small strain values and only linear optical deformation potentials were reported.

For the determination of the optical non-linear deformation potential, we fabricated ZnO microwires with diameters in the range $d = 1.5−7.3\, \mu m$ by vapour phase transport method. Selected microwires were transferred onto a Si substrate and bent. By doing so we induced an uniaxial strain of up to $±2.9\%$. The optical properties of these bent microwires were investigated by cathodoluminescence spectroscopy at $T = 10\, K$. Exemplary emission spectra are shown in Fig. 1.18(a,b) for two microwires with a diameter of $d = 1.5\, \mu m$ and $d = 7.3\, \mu m$. The presence of the rich mode structure, which
Figure 1.18: Cathodoluminescence spectra of linescans across the wires perpendicular to the wire c-axis for bent microwires with a diameter of (a) $d = 1.5 \mu m$ and (b) $d = 7.3 \mu m$. The vertical dashed lines in (a) depict exemplarily the spectral positions of two modes. (c) Shift of the emission energy as a function of the strain ($\varepsilon$) determined at the tensile and compressive strained edges of the microwires of different diameters and different bending radii. The red dashed and solid lines represent the fit by a polynomial of the first and second order, respectively.

is observable for the thin microwire, we attribute to the fact that in these microwires the photon density of states is not monotonically increasing and exhibit minima and maxima at certain energies. At these energies the recombination of the excited charge carriers is suppressed or rather enhanced, similar to the Purcell effect in resonators. For the thick microwires, the photon density of states is almost increasing with energy and thus the Purcell effect is less pronounced.

The change in the emission energy as a function of induced strain for different microwire diameters is shown in Fig. 1.18c. At the compressive and tensile strained edge of the microwire the photon density of states is less modified with regard to the free space such that the emission spectrum resembles almost the gain spectrum of the material [3]. We thus consider only the emission from these two edges by applying scans along the wire covering positions with different bending radii. Note, the energy shift determined by this method is in excellent agreement with that, which can be obtained from linescans across the thick wire from the tensile to the compressive strained edge [3]. For small strain values ($|\varepsilon| < 1.5\%$), we observe a almost linear dependence of the emission energy on the applied strain. This is in agreement with our previous experiments [4]. However, for larger strain values, a non-linear energy shift is observable and its magnitude depends on the sign, i.e. tensile and compressive, of the strain. In order to deduce the optical deformation potentials we described the observed energy shift by a polynomial of second order, i.e. $\Delta E = D_1 \varepsilon + D_2 \varepsilon^2$. The linear and non-linear optical deformation potentials are then determined to be $D_1 = (-2.50 \pm 0.05) eV$ and $D_2 = (-15.0 \pm 0.5) eV$, respectively. This agrees very well with those which are deduced from theoretical calculations [5]. In this publication, optical deformation potentials were determined to be $D_1 = -2.2 eV \ldots -4.1 eV$ and $D_2 = -6.7 eV \ldots -19.2 eV$, depending on the applied method.

1.13 Growth and characterisation of MgO/TiN superlattices


*Nanomaterialien und Nanoanalytik, Center für Angewandte Mikrostrukturdagnostik CAM, Fraunhofer-Institut für Mikrostruktur von Werkstoffen und Systemen IMWS, Walter-Hülse-Straße 1, 06120 Halle, Germany

We investigated the growth and structural properties of MgO/TiN-based multilayers and superlattices with a lattice periodicity of a few nanometers. Planar periodic nanostructures comprising of a plasmonic and a dielectric component are expected to exhibit a hyperbolic dispersion, i.e. different signs for the effective dielectric functions in the direction of layer growth $\epsilon_\perp$ and in the layer plane $\epsilon_\parallel$. These materials are referred to as hyperbolic metamaterials [1]. Such structures, with titanium nitride as plasmonic component, have already been realised by Naik et al. [2].

Single layers of titanium nitride and magnesium oxide were ablated on MgO(100)-substrates with a miscut of less than 0.1° from sintered targets in an argon atmosphere using pulsed laser deposition (PLD). TiN single layers with high crystalline quality have been successfully fabricated in our group by M. Bonholzer et al. [3]. The growth was monitored in-situ by reflection high-energy electron diffraction (RHEED). From the RHEED oscillations and diffraction patterns, the thickness of the layers and the growth mode were derived, respectively. RHEED oscillations were observable up to a total lattice thickness of approximately 110 nm with single layer thicknesses of TiN and MgO layers of approx. 10 nm, indicating a Frank-van-der-Merwe growth mode (Fig. 1.19(a),(b)).

Superlattices were grown with a number of three to ten layer pairs of titanium nitride and magnesium oxide. X-ray reflectivity (XRR), X-ray diffraction $2\theta-\omega$ scans and reciprocal space maps revealed homogeneous layer thicknesses and an epitaxial growth of the multilayer samples, as well as a small amount of tungsten, originating from impurities in the sintered TiN-targets (Fig. 1.19(c)). By modeling the XRR data, the layer thicknesses of individual layers in the superlattice were determined and this information was used to achieve a uniform layer thickness. High-resolution transmission electron microscopy, high-resolution scanning electron microscopy (HRSTEM), scanning electron microscopy-energy-dispersive X-ray spectroscopy and nanobeam diffraction studies have been performed, yielding very smooth interfaces and a almost perfect crystal structure throughout the entire layer stack (Fig. 1.19(d)).

Ellipsometry was applied to both, single- and multilayers, in order to judge the quality of their optical properties. For the optical figure of merit (FOM) of the TiN layers, defined by $FOM = -\epsilon' / \epsilon''$, where $\epsilon'$ and $\epsilon''$ are the real and the imaginary part of the dielectric function, we reached up to now $FOM = 4$. Current research is focused on improving the optical properties of the TiN films in order to beat the best values.
Figure 1.19: a) and b): RHEED oscillations during the growth of the first and the eleventh single layer in a MgO/TiN-superlattice structure, respectively. From the number of the intensity maxima, the thickness of the layers was calculated. c): XRD $2\theta$-ω-scans with different diffraction peaks. The unlabeled peaks are the $K\beta_2$, $L\alpha_1$, $L\alpha_2$, $K\alpha_1$ and $K\alpha_2$-peaks of the (200) and (400)-orientation of the superlattice respectively. Data is presented for three samples with different number of layer pairs as indicated in the graphs. d): High-angle annular dark-field imaging (HAADF) HRSTEM image of a TiN/MgO superlattice on MgO(100)-substrate with seven layers of MgO and one layer of TiN (measured at the CAM of the IMWS in Halle).

Known from literature ($FOM = 4$ [1]). This should be achieved by a systematic study of the dependence of the optical properties on growth parameters during PLD.


1.14 Model dielectric function analysis of normal and inverse Spinel Ferrites in relation to their magnetic and structural properties

V. Zviagin, P. Huth*, Y. Kumar, I. Lorite, M. Bonholzer, A. Setzer, K. Fleischer †, R. De-necke,* P. Esquinazi, M. Grundmann, R. Schmidt-Grund

*Universität Leipzig, Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Linnéstr. 2, Germany.
†School of Physics, Trinity College Dublin, Dublin 2, Ireland
Transition metal spinel oxides have played a vital role in technologically advancing the semiconductor industry and continue to do so as a result of their versatile application potential, namely high-frequency and high-power applications, detectors, sensors, microwave and spintronic devices [1]. With a chemical formula $AB_2O_4$, spinel ferrites have $(A_2B^3_x +_{1−x})[(A^2_x +_{1−x})B_3^3 +_{x}]O_2^{−4}$ ion distribution where $x$ is the inversion parameter and tetrahedral and octahedral crystal lattice sites are denoted by parentheses and square brackets, respectively. Depending on the choice of A and B elements as well as growth parameters, namely temperature and pressure, synthesis of normal, disordered and inverse spinel structures with variable magnetic and electronic properties is possible. It is only recently that spectroscopic methods have been applied to investigate mechanisms responsible for the mentioned tuneable magnetic properties in $ZnFe_2O_4$ (ZFO) [2]. The model dielectric function (MDF) was obtained by spectroscopic ellipsometry in a wide spectral range $(0.5−8.5)$ eV. From the MDF, we were able to determine the possible cation occupancy as well as the degree of inversion in ZFO and $Fe_3O_4$ (FFO) spinel ferrites based on the electronic transitions assigned from literature and give an explanation for the magnetic response measured by superconducting quantum interference device (SQUID) [3, 4]. Although optical properties of magnetite have been thoroughly investigated, the controversy over the validity of the assigned optical transitions still remains. In the visible and infrared ranges of the FFO spectrum, spin- and parity-forbidden transitions between the levels of 3d ions in the internal crystal field are apparent [5].

In order to confirm the transitions assigned to both normal ZFO spinel and inverse FFO spinel and to investigate the intermediate structure, composite thin films, $Zn_xFe_{3−x}O_4$ with $x$ varying from $(0−1)$, were grown on $(100)$ MgO substrate in Argon atmosphere at $500$ °C by pulsed laser deposition (PLD). In the MDF, transitions involving cations, as indicated in (Fig. 1.20), were assigned. Below $4.5$ eV, the transitions were found to be either inter-valence or inter-sublattice charge transfer transitions between 3d bands of $Fe^{2+}$ and $Fe^{3+}$ tetrahedrally and octahedrally coordinated cations. Above this energy, the transitions are mostly between $O_{2p}$ and 4s orbitals of $Fe^{2+}, Fe^{3+}$ and $Zn^{2+}$.
Figure 1.21: (Top) Magnetization as a function of applied magnetic field measured at 5 K. (Bottom) Saturation and twice of remanence magnetization as well as the amplitude of transition involving tetrahedral Fe$^{3+}$ cations obtained from the model dielectric function versus growth temperature.

cations. Depending on the Fe$^{2+}$ concentration and equivalently the oscillator strength of the transitions located at 0.8 eV and 2.0 eV, a change from disordered normal to disordered inverse spinel is visible between $x = 0.5$ and 0.2. Magnetic response shows expected behaviour at the extremes, but little difference for films with intermediate Zn$^{2+}$ concentrations. Further methods such as magneto-optical Kerr effect as well as X-ray photoelectron spectroscopy were employed for obtaining further information on the thin film composition.

ZFO thin films, of 40 nm, were deposited by PLD on (100) SrTiO$_3$ (STO) substrate at temperatures ranging from 400–600 °C and at highest O$_2$ pressure in order to avoid oxygen vacancies as well as to have the lowest concentration of Fe$^{2+}$ [6]. While little difference in the MDF as well as the magnetic response was seen for thin films grown

Figure 1.22: (Left) Magnetic response as a function of applied magnetic field for a ZFO thin film annealed in Argon atmosphere at temperatures indicated. (Right) Model dielectric function, ($\varepsilon_2$), obtained by SE for the same thin film.
at 500 °C and 600 °C, the film grown at lowest temperature, 400 °C, showed the greatest amount of disorder. The increase in amplitude of the transition involving tetrahedral Fe$^{3+}$ with decrease in deposition temperature correlates directly to the increasing ferromagnetic response measured at 5 K, as depicted in (Fig. 1.21) [4]. Mechanism behind this effect is likely due to the dominating magnetic coupling between the octahedral and tetrahedral lattice sites for the thin film grown at lowest temperature.

A further study has been conducted in order to investigate the influence of annealing temperature as well as environment on the structural and magnetic properties. ZFO thin film, grown at 300 °C on STO by PLD exhibited similar properties as described above. While annealing the film in Argon atmosphere resulted in the increase of the low energy peak, Fig. 1.22 (right), thus the increase in Fe$^{2+}$ concentration, annealing the film in Oxygen atmosphere showed little change in the MDF up to the growth temperature of 300 °C. For both of the thin films, a clear change in the MDF as well as the magnetization response is visible between temperatures of 300 °C and 400 °C, suggesting a transition in the crystal structure from disordered to ordered normal spinel.


1.15 Temperature dependence of the dielectric tensor of monoclinic Ga$_2$O$_3$

C. Sturm, V. Zviagin, R. Schmidt-Grund, M. Grundmann

The large band gap energy of about 4.8 eV [1] makes Ga$_2$O$_3$ interesting as transparent conductive oxide (TCO), since even in the presence of defects or impurities, e.g. caused by doping, a high transmissivity can be obtained in the visible and even in the UV-A/B spectral range. At ambient conditions Ga$_2$O$_3$ crystalizes in a monoclinic crystal structure. In this case the dielectric function (DF) is a tensor with four complex quantities. Recently these quantities were determined by generalized spectroscopic ellipsometry for the infrared [2, 3] up to the UV spectral range [1, 2] at room temperature.

For the determination of the temperature dependence of the dielectric function of Ga$_2$O$_3$ we investigated two bulk single crystals in the temperature range $T = 10−300$ K by generalized spectroscopic ellipsometry. For the lineshape analysis of the experimentally determined Mueller matrix spectra we described the dielectric tensor of Ga$_2$O$_3$ by a model dielectric function taking into account oriented excitonic dipole transitions [2]. The contribution of each excitonic transition to the dielectric function (DF) was described by a model function developed by Tanguy [4]. A detailed description of the model and the used model functions is given in Ref. [2].
In doing so, we found that the change of the DF as a function of temperature is mainly determined by the red shift of the exciton transition energies with increasing temperature (Fig. 1.23a). A strong enhancement or narrowing of the transition peaks is not observable. This indicates that the oscillator strength as well as the broadening are almost independent of the temperature. Since the exciton transition energy is connected to the band gap by the exciton binding energy, the observed temperature dependence can be described by a Bose-Einstein-Model introduced by Viña et al. [5] (Fig. 1.23b). The electron-phonon coupling strength and averaged energy of the phonons which are involved in the electron-phonon coupling was determined to be about 1 meV K$^{-1}$ and 56 meV, respectively. This energy agrees very well with the bary center of the phonon density of states calculated by density functional theory [6]. The deduced broadening as a function of temperature is shown in Fig. 1.23c. The increase in broadening with increasing temperature can be attributed to a dephasing caused by the interaction with LO-phonons with an average energy of about 21 meV. Interestingly, the determined zero temperature broadening of the excitonic transition increases with increasing transition energy. The reason for this behaviour is not fully understood up to now.

1.16 Exceptional points in dispersive and absorbing structures - biaxial Ga$_2$O$_3$ and anisotropic microcavities

S. Richter, C. Sturm, T. Michalsky, B. Rosenow*, M. Grundmann, R. Schmidt-Grund

*Universität Leipzig, Institute for Theoretical Physics, Brüderstr. 16, 04103 Leipzig, Germany

Optically biaxial (orthorhombic, monoclinic or triclinic) systems reveal two classic optic axes in the transparent spectral range, i.e. there exist two distinct directions for which the light propagation is independent of the light polarization. However, as W. Voigt noted already in 1902 [1], the two classic optic axes split into four singular optic axes in the absorptive spectral range which he named “Windungsachsen”. Along a singular axis, only left- or right-circularly polarized light is allowed to propagate, which is the so-called Voigt wave.

Biaxiality can be observed in different systems such as anisotropic bulk crystals or anisotropic layered structures. In any case, the singular axes can be mathematically described as so called exceptional points (EP) [2–4]. EPs are characterized by a one-dimensional eigenspace of the propagation operator. For a complex symmetric matrix like the dielectric tensor this yields directly eigenstates describing a circular light polarization. Generally, the requirement for such a matrix operator is its non-Hermiticity. This again requires non-vanishing imaginary parts of the matrix entries and (for real diagonal elements) non-vanishing complex off-diagonal elements. Both result from biaxility along with absorption or dissipation.
1.16.1 Singular optic axes in bulk crystals

In the absorption regime, the change of the polarization for a propagation along a certain direction is given on the one hand by the phase change, caused by the real part of the dielectric tensor, and on the other hand by the polarization dependent attenuation, caused by the imaginary part. For optically biaxial materials, the orientation of the dielectric axes of the real and imaginary part and the ratio of the major axes of the corresponding ellipsoid do not coincide with each other. The interplay between both effects leads to the formation of the singular optic axes. Interestingly, in contrast to the transparency regime, the crystal symmetry of biaxial materials can be distinguished by the properties of the singular optic axes, which also reflects the different symmetry of the dielectric tensor for these crystal systems. For instance, for orthorhombic crystals, the orientation of the dielectric axis for the real and imaginary parts of the dielectric tensor coincide with each other. However, the ratio of the major axes of the corresponding ellipsoids differ from each other. Thus four singular optic axes are formed on the surface of a cone and the corresponding Voigt waves propagate with the same velocity \[5\]). In contrast to that, for a triclinic material all major axes differ in orientation and ratio between the real and imaginary part, so that the symmetry in the orientation of the singular optic axes is lifted and all four Voigt waves propagate with a different velocity.

For the energy dependence of the orientation of the singular optic axes for orthorhombic and monoclinic crystals, we provided analytical expression which can be found in Ref. \([5]\) and proved that only 4 singular optic axes in maximum can exist. As a model material, the orientation of these axes in monoclinic Ga\(_2\)O\(_3\) was investigated in detail. The dielectric function of this material was determined by generalized spectroscopic ellipsometry \([6, 7]\). The calculated orientation of the singular optic axes is shown in Fig. 1.24. It was found that in the energy range \(E \approx 7.23 \text{–} 7.33\text{eV}\) all four singular optic axes are oriented almost parallel to the [010]-direction so that the crystal in this regime behaves almost like an optically uniaxial material. Another interesting situation was found for energies \(E \approx 8.14\text{eV}\) and \(E \approx 8.37\text{eV}\). At these energies, two singular optic axes coincide with each other, forming a conventional “absorbing” optic axis which coexists with two singular optic axes. At this energy the material can be considered triaxial.

1.16.2 Anisotropic planar microcavities

Orthorhombic or monoclinic symmetries can be implemented in stratified structures, if layers of optically uniaxial materials are used. One such example is a planar microcavity with uniaxial cavity layer embedded between distributed Bragg reflectors (DBR). Such a microcavity reveals photonic modes (“cavity modes”) which can reveal EPs in the momentum space even if only transparent media are used \([8]\). The above described imaginary contribution to the propagation operator is then provided by photonic loss, i.e. mode broadening. A complex mode energy requires a non-Hermitian transmission Jones matrix.

Planar microcavities are in principle well studied but, if the optic axis of a uniaxial cavity layer is arbitrarily oriented, often used separation of the mode computation into transversal electric (TE) and magnetic (TM) polarization is no longer valid. Instead, modes become generally elliptically polarized and do not even need to be orthogonal.
Figure 1.25: Characteristics of the cavity photon modes of a λ/2 microcavity, depending on the in-plane wavevector \( \vec{k}_{||} \). 5 DBR layer pairs with central wavelength (at normal incidence) 496 nm are assumed while the cavity thickness is 130 nm with \( n_{||} = 2.26 \) and \( n_{\perp} = 2.20 \). (a-f): Mode polarization as Stokes vector, for the energetically higher ((a-c)) and lower ((d-f)) mode. (g,h): Difference of the real (\( E \)) and imaginary (\( \gamma = \text{HWHM} \)) parts of the complex mode energy. (i): Position of EPs with varying number of DBR layer pairs as indicated by the colorbar.

As model system we assumed a λ/2 microcavity consisting of a uniaxial cavity layer with optic axis aligned in the cavity plane. An example is shown in Fig. 1.25. As for cylindrically symmetric microcavities, the λ/2 mode is split into two modes. The modes can degenerate in (real) energy or broadening at certain in-plane wavevectors \( \vec{k}_{||} \) (Fig. 1.25 (g),(h)). At four finite values of \( \vec{k}_{||} \), EPs occur, characterized by either left or right circularly polarized light (Fig. 1.25 (c),(f)). In particular, they occur pairwise, and a pair of EPs establishes a vortex center for the linear polarization. Such characteristics are similar to the singular optic axes. In order to observe EPs, a slight detuning between the DBRs’ central wavelength and the optical cavity thickness is necessary to observe EPs. Otherwise, they move out of the vacuum light cone. Furthermore, dissipation, which is controlled by the number of DBR layer pairs, determines the exact position of
the EPs in momentum space, as Fig. 1.25 (i) depicts.

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1.17 Lasing processes in Microcavities

R. Schmidt-Grund, M. Wille, T. Michalsky, S. Lange, E. Krüger, L. Trefflich, C. Sturm,
S. Richter, O. Herrfurth, S. Blaurock*, V. Gottschalch*, V. Zviagin, M. Kneiß, G. Benndorf,
H. Krautscheid*, M. Grundmann

*Institut für Anorganische Chemie, Universität Leipzig, Johannisallee 29, 04310 Leipzig,
Germany

Like in the past years, also in 2016, we intensively investigated ZnO-based microcavities
(MC), but also extended our investigations to the recently upcoming material CuI,
which is very promising for opto-electronic applications due to its very high exciton
oscillator strength [1]. MC physics is in focus of current research because it still provides
new and fascinating fundamental physical effects like quantum-optical properties in the
strong light-matter coupling regime or even topological non-trivial states [2]. Further,
MCs are of considerable interest for applications in quantum-information technology
or optoelectronic devices like laser structures.

We continued our research on nano- and microwire based structures yielding versa-
tile optical mode properties enabling different regimes of light-matter interaction.
Particularly, we investigated lasing due to emission from electron-hole-plasma and
exciton-scattering states as gain in ZnO and CuI nano- and microstructures and could
explain different lasing mode energies, observed for different structures by spatially dif-
f erent absorption properties caused by the excitation geometry (cf. Sects. 1.17.1-1.17.3).
Further we succeeded in the observation of the propagation of coherent whispering
gallery mode polariton states in a microwire of more than 10 µm in diameter at room
temperature by ps-resolved real- and momentum-space imaging spectroscopy and
could prove by interferometry their spatial coherence over distances of at least 20 µm
(Sect.1.17.3).

In order to conclusively deduce if the excited state in MCs are thermal, coherent,
single-photon sources, or entangled, the photon statistics or rather the second-order
temporal correlation function of the emitted light has to be measured. In 2016, we thus
started to build up a Hanbury-Brown & Twiss (HBT) setup and obtained first results from ZnO single crystals and microwires in regimes of thermal and coherent (lasing) emission (Sect. 1.17.4).

1.17.1 Lasing in cuprous iodide microwires

The synthesis of cuprous iodide (CuI) micro- and nanostructures is almost unexplored in contrast to other compound semiconductors such as zinc oxide (ZnO), cadmium sulfide (CdS), gallium nitride (GaN) and gallium arsenide (GaAs). However, CuI is a promising material for future optoelectronic devices due to its intrinsic p-type conductivity, its high oscillator strength of the exciton resonance expressed by its large longitudinal-transversal splitting, and its rich variety of intense optical recombination channels including pronounced phonon replica in the near ultraviolet (NUV) range.

Here, we demonstrate lasing emission of single CuI microwires under optical excitation. We succeeded with the synthesis of high quality CuI microwires. These microwires grow self-organized in zincblende $\gamma$-CuI phase and exhibit a balanced stoichiometry of Cu : I = 1 : 1. Figure 1.26(a) shows an SEM image of an exemplary microwire with a length of $l = 49 \mu$m and a diameter of $d = 4.0 \mu$m. Conspicuously, the microwire surface is smooth and free of any structural defects. Having a closer look, a rounded triangular shape of the microwire cross section was found, which indicates that the (111) direction of zincblende CuI is the preferred growth direction.
Excitation density dependent µ-PL spectra of this microwire at a temperature of \( T = 10 \) K are shown in Fig. 1.26(b). In the low excitation density regime (black line) the emission of acceptor bound excitons (A\(^0\)X) and further defect bound excitons (DBX) as well as their LO-phonon replica, and an additional emission band in the energy range of 3.029 – 3.035 eV can be observed. This probably originates from inelastic exciton-exciton scattering (P-band), where the radiatively decaying exciton emits a photon and scatters another exciton into a higher excited state [3]. Tanaka et al. already demonstrated P-band-correlated optical gain of \( \sim 400 \) cm\(^{-1}\) by stripe length technique and the accompanied stimulated emission in CuI thin films [4]. With increasing excitation density, the initially strongest emission bands saturate and at an excitation density of around 5.3 mJ/cm\(^2\), narrow modes appear in the spectral vicinity of the P-band emission. With further increasing excitation density, additional modes appear at lower energies and cover a spectral range from 3.015 – 3.035 eV for the highest density of 15.9 mJ/cm\(^2\) (blue line in Fig. 1.26(b)). Figure 1.26(c) depicts the emitted integrated PL intensity from the microwire as a function of excitation density. The double-logarithmic plot depicts a distinct S-shape course which represents the threshold behavior of the underlying laser transition. Below the laser threshold of around \( E_{\text{Th}} = 5 \) mJ/cm\(^2\), the emission intensity increases linearly with the excitation density. In the threshold regime, the slope becomes strongly nonlinear (\( I \sim x^4 \)) and declines back to a linear slope in the lasing regime. This observation clearly demonstrates lasing in our microwires.

1.17.2 Absorptive lasing mode suppression in ZnO nano- and microcavities

In literature, lasing modes in ZnO micro- and nanostructures were observed to emerge in different spectral ranges without a conclusive explanation for the observed mode energies. In this study (details can be found in ref. [5]), we conclusively explain the different lasing mode energies. In order to do this, we studied the influence of the excitation conditions in correlation with the size and geometry of the active medium on the laser mode energy. Therefore, we compare the lasing mode energies of different single micro- and nanostructures, as they are depicted in Fig 1.27(a), and discuss the results in terms of the spatial gain region, which results from the spatial inhomogeneity of the excitation spot and the limited penetration depth of the exciting laser light.

Figure 1.27(b) shows the room temperature emission spectra of the three investigated nano- and microstructures for different excitation energy densities. All three structures exhibit lasing emission under high excitation which expresses through sharp lines in the emission spectra and through a nonlinear increase of emission intensity in the threshold regime. The lasing thresholds are similar and vary from \( \sim 180 \) µJ/cm\(^2\) for the investigated microwire to \( \sim 190 \) µJ/cm\(^2\) for the nanowire and to \( \sim 270 \) µJ/cm\(^2\) for the tetrapod-like nanoparticle. However, the lasing mode energies are different for the different structures. The lasing mode energy of the microwire is around 3.18 eV. It turns out that smaller structures like nanowires exhibit lasing modes at higher energies, here in an energy range from 3.19 – 3.23 eV. Tetrapod-like particles show even higher emission energies in a range of 3.30 – 3.35 eV.

Furthermore, it was found, that the emission energy of single nanowires is slightly tuneable by changing the spot size of the excitation laser. Figure 1.27(c) depicts the lasing emission spectra of a \( \sim 4.2 \) µm long nanowire (see inset) slightly below and above the
Figure 1.27: (a) Scanning electron microscope images (SEM) of a ZnO nanowire \((L = 7.9 \, \mu\text{m}, d = 165-190 \, \text{nm})\), microwire \((d = 3.5 \, \mu\text{m})\) and a tetrapod-like nano particle (leg length of \(\sim 800 \, \text{nm}\) and leg diameter of \(\sim 450 \, \text{nm}\)). The white bars have a length of 1 \(\mu\text{m}\). (b) Room temperature PL spectra for three different structure types and three excitation powers reveal lower lasing mode energies for larger structure dimensions. The structures were excited with a frequency doubled Ti:Sa laser \((\lambda_{\text{ex}} = 355 \, \text{nm}, t_{\text{pulse}} = 2 \, \text{ps})\). (c) Lasing emission spectra of a ZnO nanowire (see inset: \(L = 4.2 \, \mu\text{m}, d = 245 \, \text{nm}\)), shown for two excitation spot diameters of \(1.8 \, \mu\text{m}\) (red) and \(2.9 \, \mu\text{m}\) (black). The excitation with a larger spot size leads to a mode enhancement on the high energy side of the spectrum.

The different lasing mode energies of the respective micro- and nanostructures can be well explained by considering the spectral gain profile of the semiconductor material under high excitation and the spatial distribution of electronically inverted regions in the respective structures. The complex refractive index for carrier concentrations of \(1 \times 10^{15} \, \text{cm}^{-3}\) and \(5 \times 10^{19} \, \text{cm}^{-3}\), which represent the cases of excitation far below and slightly above the Mott density, respectively, is depicted in Fig. 1.28(a). The excitonic resonance/absorption, visible as a pronounced peak for low carrier concentration, vanishes at high carrier concentrations, accompanied by the formation of optical gain for energies between 3.1 \, eV and 3.35 \, eV. To obtain further insight into the carrier density dependent complex refractive index and its temporal dynamics after a high power excitation pulse, the reader is referred to reference [6]. The spectral gain range is shown magnified in Fig. 1.28(c). Each of the differently highlighted areas represents a variety of experimentally observed lasing energies for the respective microwires, nanowires/nanobelts and nanoparticles/tetrapods. Obviously, particles of smaller size exhibit lasing modes with higher energies compared to several \(\mu\text{m}\)-long nanowires and \(\mu\text{m}\)-thick microwires.
Figure 1.28: (a) Calculated carrier density dependent complex refractive index for $1 \times 10^{15}$ cm$^{-3}$ (solid line) and $5 \times 10^{19}$ cm$^{-3}$ (dashed line). (b) Sketch of the spatial gain regions in different nano- and microstructures (microwire, nanowire, nanoparticle) under excitation with a gaussian laser profile. Red color indicates high carrier densities and thus high gain whereas white color indicates regions without any excited carriers. (c) Sketch of differently hatched energy ranges in the enlarged gain spectra for a carrier density of $5 \times 10^{19}$ cm$^{-3}$, for which lasing was observed for different nano- and microstructures in literature.

This behavior can be explained by considering the spatial absorption profile of the excitation laser light in the respective structures, see Fig. 1.28(b). Depending on the structure size, a certain structure volume remains weakly or even non-excited after excitation (backside of microwires, endfacet near regions of nanowires). This leads to mode absorption outside of the spatial gain region. For hexagonal microwires with diameters of several microns, the effect is most pronounced due to the small gain region close to the front facet. In the case of lasing nanoparticles, the carrier concentration is spatially homogeneous. Hence, gain distribution correlated absorption effects are negligible and lasing modes are observable in the center and on the high energy side of the gain profile. Nanowires behave in an intermediate fashion due to the weaker excitation in the end facet near region. By changing the spot size, the length of absorbing end facet region was varied. As a consequence, we observed lasing modes on the high energy side of the emission spectra in the case of homogeneous carrier density distribution, i.e. larger spot size. For a smaller spot size, high energy lasing modes are suppressed outside of the transparency region.

1.17.3 Spatial and temporal evolution of coherent polariton modes in ZnO microwire cavities

We investigated the spatial and temporal behaviour of coherent whispering gallery modes (WGMs) in ZnO microwires after excitation with a fs-laser pulse at room tem-
Figure 1.29: a) Excitation density dependent spectra at room temperature for \( k_\parallel = 0 \), normalized to the applied pump energy density. With increasing excitation density, the WGMs with mode numbers \( N = 50, 51, 52 \) exhibit a super-linear increase in intensity while the underlying PL signal slightly shifts to lower energies. b) The log-log plot of PL intensity vs. excitation energy density exhibits a distinct S-shape behavior. The dashed red line corresponds to the adapted multimode laser model \[8\] with a threshold density of 27 \( \text{mJ/cm}^2 \).

Figure 1.30: a) WGM broadening (HWHM; black symbols) and blue-shift (blue symbols) for the three dominating WGMs \( (N = 50, 51, 52) \) from Fig. 1.29 a) in dependence on the excitation energy density. The lines are a guide to the eye. b) Calculated refractive indices (blue) and extinction coefficients (black) for carrier densities far below (straight lines) and above (dashed lines) the Mott density. The dotted line indicates zero extinction. After \[6, 9\].
perature. The estimation of the carrier density ($n_{th} \approx 5 \times 10^{20} \text{cm}^2$) at the threshold excitation power density of $I_{th} = 27 \text{ mJ/cm}^2$ reveals that the gain process responsible for the build up of the coherent states is connected to the (stimulated) recombination in an electron-hole plasma [7]. Excitation energy density dependent photoluminescence (PL) spectra and a corresponding fit with a multi-mode laser model [8] are shown in Fig. 1.29.

Regarding the WGMs which exhibit a nonlinear increase in intensity, the increasing excitation energy density leads to a blue shift of these modes and to a minimum linewidth at the nonlinear threshold, as shown in Fig. 1.30 a). The blue shift $\Delta E$ can be explained with the change in the carrier density dependent refractive index $\Delta n$. As the WGM resonance energies are indirectly proportional to the refractive index of the cavity material, for small changes of the refractive index the blue shift can be expressed as

$$\Delta E \approx -E_0 \frac{\Delta n}{n_0 + \Delta n}. \quad (1.1)$$

The subscript 0 indicates the low carrier density limit for the corresponding quantities. In Fig. 1.30 b) the modeled complex DF [6, 9] is plotted for carrier densities below and beyond the Mott carrier density. It can be seen that in the high carrier density limit the refractive index is reduced in the spectral range of interest (energetically below the exciton groundstate resonances at 3.3 eV). This is a direct consequence of the screening of the excitonic oscillator strength and leads to the aforementioned blue shift. A quantitative comparison between theory and experiment is hardly possible as only a small part of the closed light path in the cavity is pumped (see Fig. 1.35 a)) and the carrier diffusion length, determining the carrier density, remains an unknown parameter so far.

But, if we assume that the modeled change in DF gives reasonable values, it is possible to estimate the carrier diffusion length $L_d$ via the measured blue shift. Therefore we have to replace $\Delta n$ in equation (1.1) with $\Delta n L_d / L_{tot}$. The quantity $L_{tot}$ is the resonator length which is known from modeling the WGM energies for the investigated sample ($L_{tot} = 9.0 \mu m$). The three lasing modes ($N = 50, 51, 52$) and their corresponding blue shifts give three different values for $L_d$ namely (0.1, 0.2, 0.3) $\mu m$. This might be an indication that the modeled DF differs from the real one as similar values for $L_d$ are expected. Additionally, the blue shift is obtained from time integrated measurements after fs-excitation introducing further uncertainties [6].

Regarding the WGM linewidth, their reduction in the vicinity of the threshold is typical for the onset of lasing as in this situation, the material gain (negative $\kappa$, see Fig. 1.30 b)) compensates all resonator losses, which predominantly determine the WGM linewidth [10]. The increase in linewidth beyond threshold is mostly determined by the pulsed excitation conditions in combination with the time integrated measurement scheme applied here. Therefore, after each single excitation pulse, the carrier density changes in time, resulting in different blue shifts over which is integrated, affecting the measured (time integrated) linewidth [6].

The energetically resolved real and $k$-space distribution of the WGM PL emission below and above threshold are shown in Fig. 1.31. Above threshold, the emission stems from distinct points of the dispersion relation $E_{WGM}(k_\parallel)$ ($k_\parallel$ is the in-plane wavevector) of the WGMs in the low density limit. These points indicate the intersections of the blue
shifted WGM ground state energies with their corresponding dispersion relation. In the frame of exciton-polariton Bose-Einstein condensation this was explained [11] with the conversion of potential energy (due to repulsive polariton-polariton interaction, given by $\Delta E$) in kinetic energy ($(\hbar k)^2/(2m_{\text{eff}})$) of the quasiparticles. Second, in the photonic crystal approach, the optical potential for photons (as quasiparticles) is defined by $1/\varepsilon$ ($\varepsilon$ is the actual value of the dielectric function), thus photons are accelerated to regions with higher $\varepsilon$. Third, this effect can also be explained under ray-optical consideration [12], where the locally varying refractive index leads to a change of the $k_\parallel$-component of the wavevector as light rays tend to bend into the direction of higher refractive index (cf. inset in Fig. 1.31d)). The maximum achievable in-plane wavevector component $k_{\parallel\text{max}}$ for a mode generated at $k_\parallel = 0$ in dependence on the refractive index change $\Delta n$ is given
by:

$$k_{\parallel\text{max}} \simeq \frac{2\pi}{\lambda_0} \sqrt{2n_0|\Delta n|} \approx \frac{2\pi}{\lambda_0} \sqrt{2n_0^2} \frac{\Delta E}{\Delta E + E_0},$$

with $\lambda_0$ being the vacuum wavelength of the corresponding mode. Independent of the picture which is chosen (interacting particles with effective mass $m_{\text{eff}}$ or light rays in a polarizable medium where the $\chi^3$ susceptibility (carrier dependent refractive index) is taken into account), the spatially narrow excitation leads to an acceleration of the coherent states away from the excitation center. This is directly reflected in the real space emission pattern, as shown in Fig. 1.31, where below threshold, the contribution of low $k_{\parallel}$ states results in effectively lower spatial expansion compared to the lasing case. There, the high $k_{\parallel}$ states dominate the emission resulting in an effectively larger spatial expansion.

In order to resolve the spatial expansion of the coherent WGMs in time, we combined the micro imaging setup with a streak camera. For technical reasons the spatiotemporal resolution of the high $k_{\parallel}$ states, depicted in Fig. 1.31 b), could not be achieved. Thus, we used a larger excitation spot in order to generate coherent states distributed around $k_{\parallel} = 0$, as shown in Fig. 1.32, with a HWHM of 0.8 $\mu$m$^{-1}$. The reconstructed spectrally resolved real space images for different time steps are shown in Fig. 1.33, revealing the spatial expansion of the lasing modes with increasing time after excitation with a fs-laser pulse. Investigating a single mode (see Fig. 1.34), a velocity $v_{\text{meas}} \approx 1.5 \mu$m/ps could be measured which corresponds to wavenumber of $k_{\parallel,\text{meas}} \approx 0.4 \mu$m$^{-1}$. This value is smaller than expected from the HWHM in the $k$-space distribution and may be a result of the fact that WGMs accelerate in the spatially varying potential, whose size is given by the carrier diffusion length here. Due to trigger jitter of the streak camera system, this acceleration process appears to be hidden.

In order to investigate the spatial coherence properties of the WGM states a Michelson interferometer was put in the collimated beam behind the microscope objective.

Figure 1.32: $k$-space mode distribution in dependence on the excitation spot size beyond the nonlinear threshold. A small (submicron) excitation spot (red) size results in the appearance of the coherent modes from the dispersion of the unperturbed WGMs at $k_{\parallel} > 0$, whereas a large (micron) exciton spot (black) ($\approx 1.5 \mu$m FWHM) results in coherent states distributed around $k_{\parallel} = 0$. Here, the large excitation spot leads to a $k_{\parallel}$-distribution with a HWHM of 0.8 $\mu$m$^{-1}$.
Figure 1.33: Spectrally resolved spatiotemporal evolution of coherent WGMs after fs-excitation with a large (micron) excitation spot. The time steps are given in the corresponding image. The absolute value of the time scale does not represent the time difference to the excitation laser pulse.

Figure 1.34: Spatiotemporal expansion of a single coherent WGM ($E = 3.188$ eV, compare Fig. 1.33) after fs-excitation with a large (micron) excitation spot. The measured velocity is $v_{\text{meas}} \approx 1.5$ $\mu$m/ps, corresponding to an average wavenumber of $k_{\parallel,\text{meas}} \approx 0.4$ $\mu$m$^{-1}$. The log-spectra are normalized to their corresponding maximum and shifted with a constant offset, corresponding to a spatial separation of 0.5 $\mu$m.
### Figure 1.35: Spatial coherence

- **a)** Pump laser beam reflection from the wire surface.
- **b)** Interferogram of the PL signal from the wire surface below threshold.
- **c)** Interferogram of the PL signal from the wire surface beyond threshold.
- **d)** Normalized intensity of the interferogram depicted in c).

One arm of the interferometer was equipped with a retro-reflector, which acts as an inverter for the image of the sample surface. In Fig. 1.35 the results are shown. In order to determine the excitation spot size in our experiments, the spatially resolved reflection of the excitation laser light was imaged on the CCD using only one arm of the interferometer. The result is depicted in Fig. 1.35 a), from which an oval excitation spot size can be determined. The two diameters of the excitation spot (FWHM) are 0.70 µm along the wire axis and 0.38 µm perpendicular to the wire axis, respectively, resulting in an excited area of approximately 0.28 µm². Below threshold (see interferogram in Fig. 1.35 b)), the spontaneous PL emission can be observed from the wire surface and edges with a spatial extension of about 4 µm (FWHM), exceeding the excited area. The interferogram shows no fringes as the emission is dominated by spontaneous excitonic recombination which is spectrally broad (FWHM ≈ 100 meV) at room temperature. The situation changes if the excitation energy density is beyond threshold (see Fig. 1.35 c)), where the wire emission is dominated by WGMs coupling out of the wire edges. Here, clear interference fringes appear. In Fig. 1.35 d) the normalized intensity $I_{\text{norm}}(\vec{x})$ calculated after equation:

$$I_{\text{norm}}(\vec{x}) = \frac{I_{\text{interf}}(\vec{x}) - I_1(\vec{x}) - I_2(-\vec{x})}{2 \sqrt{I_1(\vec{x})I_2(-\vec{x})}} = g^I(\vec{x}, -\vec{x}) \cos (k_{\text{interf}} \vec{x} + \phi)$$

is plotted, where $I_1$, $I_2$ and $I_{\text{interf}}$ describe the intensity patterns of the single arms and their combined image, respectively. The quantities $k_{\text{interf}}$ and $\phi$ describe the setup-defined interference wavevector and phase. The amplitude of the interference fringes of the normalized intensity gives the first order spatial coherence function $g^I(\vec{x}, -\vec{x})$ and
it is obvious that the coherence is highest at the wire edges away from the excitation center (see also Fig. 1.36). This can be attributed to the fact that at the excitation center, a non-vanishing population of uncoherent states is present, lowering the coherence. Contrarily, away from the excitation center, only the emission from the highly coherent propagating WGM states is detectable. The reason for $g^1$ being always noticeably below 1 can be found mainly in the fact that during the measurements vibrations of the sample were unavoidable introducing intensity fluctuations in emission on the one hand and a smearing of the interference fringes on the other. Furthermore, the single (interferometer-) arm measurements had to be performed separately which together with the intensity fluctuations result in an uncertainty in the normalized intensity which, of course, affects the spatial coherence $g^1$.

In summary we have shown how to generate and manipulate propagating coherent WGM states at room temperature and investigated their spatial coherence properties.

1.17.4 Buildup of a photon correlation measurement setup and first results for the thermal and lasing regime in ZnO

In order to unambiguously prove if light is emitted by coherent or thermal states investigation of the second order temporal correlation function $g^{(2)}(\tau)$ is indispensable. This is true at least for the case of sufficiently narrow spectral bandwidth of thermal light, as it is the case for emission out of whispering gallery modes in the low-excitation density regime in our high-quality microwire cavities. For characterization of the statistics of light emitted from such structures and assignment of the regime around the lasing threshold to be amplified spontaneous emission or photon/polariton lasing, we built up an intensity interferometer according to Hanbury-Brown & Twiss (HBT). Photoluminescence of the sample is spectrally filtered by a monochromator, split by a 50:50 beam splitter, and focussed onto single photon avalanche photodiodes (SAPDs). The electrical pulses of the detectors are transferred to a single photon counting module.
Figure 1.37: (a) Experimental results of \( g^{(2)}(\tau) \) obtained from a \( \text{cw} \)-HeNe laser (black line) and from a pseudothermal light source simulated by scattering the HeNe emission on a rotating diffuser disc for different rotation frequencies and thus for different correlation time \( \tau_c \) (colored lines). (b) Measured photon statistic of the HeNe laser (red bars) calculated with different time windows (indicated in the right corners) and therefore varying mean photon numbers \( \langle n \rangle \). Black lines indicate a least-squares fit with a poisson distribution.

(SPCM) where they act as start/stop signals for a time-correlated single photon counting (TCSPC) unit.

We tested the functionality of the setup by measuring \( g^{(2)}(\tau) \) for a \( \text{cw} \)-HeNe laser and a quasi-thermal lightsource using only one of the detectors as shown in Fig. 1.37(a). Due to the dead time of the detection electronics, only subsequent events with a time difference of at least 100 ns can be observed. The laser emission shows the theoretically predicted behavior of \( g^{(2)}(\tau) \approx 1 \). The small peak at 150 ns is due to afterpulsing of the SAPD. The corresponding photon statistic is Poisson-like, as can be seen in Fig. 1.37(b). A pseudothermal light source was used to simulate the correlation properties of natural thermal light, but with adjustable coherence time \( \tau_c \). Here, the HeNe emission is scattered by a rotating diffuser disc, thus inducing temporal decoherence, where the coherence time \( \tau_c \) can be adjusted by the rotation frequency. We found a dependence \( g^{(2)}(\tau) \propto a + b \cdot \exp^{-c(\tau_c/\tau)^2} \) with \( a, b, c, \tau_c > 0 \), which is typical for thermal behavior. \( g^{(2)}(\tau) \) does not reach 1 for \( \tau \to \infty \) due to the inhomogeneous roughness distribution of the diffuser disc.

The photon statistics (photon coincidence rates) of the emission from a ZnO bulk single crystal as well as microwire excited with a pulsed Ti:Sa laser below and above the nonlinear threshold power density is shown in Fig. 1.38. The emission from the Ti:Sa laser shows, as expected, \( g^{(2)}(\tau) \approx 1 \) (Fig. 1.38(a)). The emission from the ZnO bulk single crystal at low excitation power (Fig. 1.38(b)) shows, with respect to the laser, a broadened temporal behaviour due to the decay of free excitons with a time constant of about 100 ps. Evaluation of \( g^{(2)} \) at \( \tau = 0 \) provides a value of 1.01, indicating a coher-
Figure 1.38: Photon coincidence counts obtained from (a) pulsed Ti:Sa laser, (b) PL of a ZnO single crystal, PL of a ZnO microwire below (c) and above (d) lasing threshold with the corresponding spectrum (e). The numbers above the peaks indicate the value of $g^{(2)}$ for the time delay at the maximum of the peak.

ent state. However, one would expect the semiconductor to be in a thermal state. A possible explanation can be found in the ratio of the temporal resolution of the setup to the correlation time of the emitted photons which gives approximately 10%. Thereby the correlation time is given by the exciton linewidth according to the Wiener-Khinchin theorem, which is determined at room temperature by the strongly inhomogeneous decay properties of the excitons. This corresponds to an averaging of the measured signal over uncorrelated decay channels over the entire inhomogeneous exciton lifetime. We found the same behaviour for the ZnO microwire at excitation power below threshold (Fig. 1.38(c)). Above threshold (Fig. 1.38(d)), we found $g^{(2)}(\tau = 0) = 1.328$. This is counter-intuitive, as one would expect values larger than 1 below threshold and equal to 1 above threshold. One possible explanation might be that the wire is in a transition regime between spontaneous and stimulated emission, where amplified spontaneous emission can be expected to contribute. Here, non-linear emission intensity increase takes place, but the material is mainly still in the thermal regime, but with strongly decreased effective exciton lifetime due to increased exciton-exciton scattering [6]. This effect reduces the inhomogeneous character of the excitonic decay by preferring one decay channel, thus increasing the correlation time to be similar to the current resolution of the setup, such that correlation effects are visible.

In the next step we will increase the time resolution of the setup by perfecting the two-detector correlation setup.

1.18 Development of a femtosecond time-resolved spectroscopic ellipsometry setup


*ELI beamlines, Za Radnicí 835, Dolní Břežany, Czech Republic

Time-resolved spectroscopic ellipsometry (SE) was recently reported to provide a time-resolution below picoseconds [1]. However, electronic dynamics occur on an even shorter time scale. Further, the UV spectral range could not be accessed up to now. This spectral range is of special interest for wide-gap semiconductor materials such as ZnO, which are promising for the application in optoelectronic devices. In particular, it is still a topic of current research to explore the dielectric functions of semiconductors at short time scales after intense optical excitation and to understand the physical processes underlying the transient optical properties.

A successful way to obtain the desired time-resolution is provided by pump-probe techniques. Thereby, the temporal resolution is determined by the pump and probe pulse width. As a result of first experiments at Universität Leipzig [2], a pump-probe femtosecond time-resolved SE setup was established in cooperation with the group of Jakob Andreasson (RP4, ELI Beamlines, Czech Republic). An amplified Ti:Sa laser (35 fs, 6 mJ, 1 kHz) was employed. Its third harmonic was used as pump and a small part of the laser power was used to create a continuum white light probe beam using a CaF$_2$ crystal, which allows to probe a spectral range from NIR to 3.6 eV with a single shot. Different polarization states were measured in polarizer-sample-compensator-analyzer (PSCA) configuration for certain compensator positions with an estimated time resolution of 200 fs. The signal-to-noise ratio could be greatly improved by the application of a two-chopper technique coupled to the CCD detector, which allows to measure quasi real-time correction spectra for fluctuations of both pump and probe pulse.

The pseudo dielectric function of a c-plane ZnO single crystal, calculated from
pump-probe SE measurements, is shown in Fig. 1.39 for several relative delays between pump and probe pulse. The highest induced charge carrier density amounts to $8 \times 10^{-18}$ cm$^{-3}$. One can clearly see that at early times the exciton resonance peak around 3.3 eV is suppressed, which can be explained by the screening of excitons due to the high charge carrier density, induced by the pump pulse. The spectral minimum of the imaginary part of the pseudo dielectric function ($\langle \epsilon_2 \rangle$) being present in the 1–15 ps range hints to the occurrence of optical gain. For longer times, the decreasing charge carrier density allows re-appearance of the excitonic peak. In the next step, modelling of such data will yield the dielectric function of semiconductors as a function of charge carrier density and more insight into relaxation and scattering processes will be obtained.


1.19 Polarization patterns of the sky

M. Scholz, S. Richter, T. Michalsky, L. Trefflich, R. Schmidt-Grund

*Gymnasium Engelsdorf, Arthur-Winkler-Str. 6, 04319 Leipzig, Germany

Sunlight which is scattered from molecules in the atmosphere becomes linearly polarized. This is a consequence of Rayleigh scattering based on excited molecular dipoles. The orientation of the linear polarization observed on earth should hence be described by concentric circles around the sun. The degree of polarization is expected to be maximum for a viewing angle of 90° with respect to the sun, leaving light unpolarized...
which arrives directly from the sun or anti-sun direction. However, multiple Rayleigh scattering processes result in linearly polarized light with polarization orientation exactly perpendicular to that of single Rayleigh scattering. The (incoherent) superposition of the light of both scattering processes yields the appearance of unpolarized points at the sky, which differ from the sun and anti-sun directions [1]. In particular, there are four points aligned on a great circle covering sun, anti-sun and zenith positions [2]. The Babinet and Brewster points are situated above and below the sun, respectively. The Arago and second Brewster points are situated above and below the anti-sun position, respectively. Hence, they cannot be observed at the same time. The exact positions depend on the sun’s elevation, wavelength and albedo. The unpolarized points are vortex centers for the linear polarization orientation.

During a two-weeks internship in September, the polarization of the sky was investigated using a commercial digital camera with fisheye objective, equipped with rotatable linear-polarization filter. Light intensity values were re-calculated from the red, green and blue color channel values of the images and the polarization was evaluated from sets of images. The expected polarization patterns, including the Babinet and Arago points, could be observed during the day and around sunset, respectively. The degree of polarization was found to be highly dependent on the wavelength. Brewster points could not be observed because they occur too near to the horizon and are hence prone to atmospheric distortions. Distortions in the polarization pattern are also caused by clouds. Even clouds which are hardly visibly by eye can be clearly detected in polarization images. Additionally, right- and left circular polarization filters have been used to investigate the circular degree of the sky polarization. Circular polarization is expected to arise from Mie scattering processes, mainly caused by aerosols. Relevant circular polarization patterns could only be found during twilight, probably caused by
atmospheric haze. Finally, also polarization of the moon-lit sky was detected, which is similar to that of the sun-lit sky, as illustrated in Fig. 1.40.


### 1.20 Funding

*Leipzig School of Natural Sciences - Building with Molecules and Nano-objects (Build-MoNa)*

Prof. Dr. M. Grundmann  
DFG GS 185/2

**Polarisationsteilung in Laser-MBE Wurtzit-Perowskit-Heterostrukturen**  
Prof. Dr. M. Lorenz  
SFB 762/3, TP A2 within SFB 762 *Funktionalität Oxidischer Grenzflächen*

**Optische Untersuchungen zu magneto-elektro-optischen Wechselwirkungen in ihrer Dynamik in oxidischen Heterostrukturen**  
Dr. Rüdiger Schmidt-Grund  
SFB 762/3, TP B03 within SFB 762 *Funktionalität Oxidischer Grenzflächen*

**Lateraler Transport in oxidischen Feldwechflucht-Strukturen**  
Dr. H. von Wenckstern, Prof. Dr. M. Grundmann  
SFB 762/3, TP B04 within SFB 762 *Funktionalität Oxidischer Grenzflächen*

**Spinabhängigtes Tunneln in oxidischen Heterostrukturen**  
Prof. Dr. M. Grundmann, Prof. Dr. I. Mertig (Martin-Luther-Universität Halle-Wittenberg)  
SFB 762/3, TP B06 within SFB 762 *Funktionalität Oxidischer Grenzflächen*

**Extrem verzerrte Nano- und Mikrodrähte**  
Prof. Dr. M. Grundmann  
DFG GR 1011/23-1

**Quantum Gases and Liquids in Semiconductor Rods conformally coated with Bragg Mirrors**  
Dr. R. Schmidt-Grund, Prof. Dr. M. Grundmann  
DFG SCHM 2710/2-1, SCHM 2710/2-2, TP P1 within FOR 1616 *Dynamics and Interactions of Semiconductor Nanowires for Optoelectronics*

**Whispering Gallery Moden: Einfluss der Resonatorform auf Lasing-Eigenschaften**  
Prof. Dr. M. Grundmann  
DFG GR 1011/26-1

**Amorphe Spinelle als p-Typ Halbleiter**  
Prof. Dr. M. Grundmann  
DFG GR 1011/27-1
REPORT OF THE SEMICONDUCTOR PHYSICS GROUP

Cupferiodid: Epitaxie, Dioden und Ferromagnetismus
Prof. Dr. M. Grundmann
DFG GR 1011/28-1

Dioden auf der Basis von MBE und MoVPE oxid-Dünnfilmen
Prof. Dr. M. Grundmann
DFG GR 1011/30-2

Flexible analoge und digitale Grundschaltungen in amorphen Metallocidoxiden
Prof. Dr. M. Grundmann
DFG GR 1011/31-1, within SPP High Frequency Flexible Bendable Electronics for Wireless Communication Systems (FFLexCom)

Graduiertenschule: Wolken, Aerosole und Strahlung am Beispiel des Mineralstaubes
Prof. Dr. M. Grundmann, Prof. Dr. A. Macke (Leibniz-Institut für Troposphärenforschung e. V.)
SAW-2012-IfT-4

Transparente MESFET für digitale Anwendungen
Prof. Dr. M. Grundmann, Dr. H. Frenzel
BMBF 03V0509

SolarSens: Herstellung von wellenlängenselektiven DUV-Photoelektroden,
Dr. H. von Wenckstern
BMBF 01DR15008

High-resolution fingerprint sensing with piezoelectric nanowire matrices: PiezoMat
Prof. Dr. M. Grundmann
European Union, Seventh Framework Programme 611019

LOMID - Large cost-effective OLED microdisplays and their applications
Prof. Dr. M. Grundmann, Dr. H. von Wenckstern
European Union, Horizon 2020 644101

1.21 Organizational Duties

M. Grundmann
• Prodekan Forschung der Fakultät für Physik und Geowissenschaften
• Direktor des Instituts für Experimentelle Physik II
• Stellvertretender Sprecher der Graduiertenschule ”Leipzig School of Natural Sciences - Building with Molecules and Nano-objects” (BuildMoNa), http://www.buildmona.de
• Stellvertretender Sprecher des Sonderforschungsbereiches ”Funktionalität Oxidischer Grenzflächen” (SFB762), http://www.physik.uni-halle.de/sfb762
• Stellvertretender Sprecher der Forschergruppe FOR 1616, http://www.for1616.uni-jena.de
• Sprecher der Fächerübergreifenden Arbeitsgemeinschaft Halbleiterforschung Leipzig (FAHL), http://www.uni-leipzig.de/~fahl
• Mitglied des wissenschaftlichen Beirats des Leibniz-Instituts für Oberflächenmodifizierung e. V., Leipzig (IOM)
• Member Editorial Board: Physica Status Solidi (a), (b), RRL
• Member International Advising Board: Advanced Electronic Materials
• Project Reviewer: Deutsche Forschungsgemeinschaft (DFG), Alexander von Humboldt-Stiftung (AvH), Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung (FNSNF), Fonds zur Förderung der Wissenschaften (FWF), EU, Österreichische Forschungsförderungsgesellschaft mbH (FFG), Agence Nationale de la Recherche (ANR, France)

M. Lorenz
• Editorial Board Member Journal of Physics D: Applied Physics (IOP, Bristol, U.K.)
• Project referee: Deutsche Forschungsgemeinschaft (DFG), Czech Science Foundation, Technology Foundation STW (The Netherlands)

H. von Wenckstern
• Project Reviewer: U.S. Department of Energy – Office of Science, National Research Fondation RSA

R. Schmidt-Grund
• Vice Chair of the German Association on Ellipsometry (Arbeitskreis Ellipsometrie – Paul Drude e.V.)
• Project Reviewer: Deutsche Forschungsgemeinschaft (DFG), US Department of Energy – Office of Science

H. Frenzel
1.22 External Cooperations

Academic

- Leibniz-Institut für Oberflächenmodifizierung e. V., Leipzig, Germany
  Prof. Dr. B. Rauschenbach, Prof. Dr. S. Mayr, Dr. J. Gerlach, Dr. C. Bundesmann, Dr. A. Lotnyk
- Universität Leipzig, Fakultät für Chemie und Mineralogie, Germany
  Prof. Dr. H. Krautscheid, Prof. Dr. R. Denecke
- Universität Halle-Wittenberg, Germany
  Prof. Dr. I. Mertig, Prof. Dr. W. Widdra, Prof. Dr. S. G. Ebbinghaus, Prof. Dr. W. Hergert
- Max-Planck-Institut für Mikrostrukturphysik, Halle/Saale, Germany
  Dr. O. Breitenstein, Dr. A. Ernst, Dr. P. Werner, Prof. Dr. D. Hesse
- Forschungszentrum Dresden-Rossendorf, Germany
  Prof. Dr. M. Helm, Dr. K. Potzger
- Technische Universität Berlin, Germany
  Prof. Dr. D. Bimberg, Prof. Dr. A. Hoffmann
- Universität Magdeburg, Germany
  Dr. J. Bläsing, Prof. Dr. J. Christen
- Universität Jena, Germany
  Prof. Dr. C. Ronning
- University of Pretoria, South Africa
  Prof. F. D. Auret
- University of Canterbury, Christchurch, New Zealand
  Prof. Dr. M. Allen
- Centre de Recherche sur l’ Hétéro-Epitaxie et ses Applications (CNRS-CRHEA), Valbonne, France
  Dr. J. Zúñiga-Pérez, Dr. Guy Feuillet
- Western Michigan University, USA
  Prof. Dr. S. M. Durbin
- Katholieke Universiteit Leuven, Belgium
  Dr. V. Lazenka, Prof. Dr. K. Temst

Industry

- Freiberger Compound Materials GmbH, Freiberg, Germany
  Dr. G. Leibiger
1.23 Publications

Journals


M. Grundmann, J. Zúñiga-Pérez: Pseudomorphic ZnO-based heterostructures: from polar through all semipolar to nonpolar orientations, phys. stat. sol. (b) 253(2), 351-360 (2016)


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A. Mavlonov, S. Richter, H von Wenckstern, R. Schmidt-Grund, M. Lorenz, M. Grundmann: Temperature dependent self-compensation in Al and Ga-doped Mg0.05Zn0.95O thin films grown by pulsed laser deposition, J. Appl. Phys. 120, 205703 (6 pages) (2016)


C. Yang, M. Kneiß, M. Lorenz, M. Grundmann: Room-temperature Synthesized Copper Iodide Thin Film as Degenerate p-Type Transparent Conducting Material with a Boosted Figure of Merit, PNAS 113(46), 12929-12933 (2016)


Books


Patents


Talks


M. Grundmann: *Bipolar Oxide Diodes: Role of the Interface for Type-I, -II and -III Heterostructures*, 43rd Conference on the Physics and Chemistry of Surfaces and Interfaces (PCSI-43), Palm Springs, CA, USA, January (invited)


M. Grundmann: *Semiconducting oxide thin films: Novel rectifying contacts for electronic and photonic applications*, 18th International Conference on Solid Films and Surfaces (ICSFS 18), Chemnitz, August 2016 (invited)


C. Kranert C. Sturm, R. Schmidt-Grund, M. Grundmann: *Raman Tensor Formalism for Anisotropic Crystals*, DPG spring meeting, Regensburg, Germany, March 2016


P. Schlupp, H. von Wenckstern, M. Grundmann: *Schottky barrier diodes on amorhpous zinc tin oxide*, DPG spring meeting, Regensburg, Germany, March 2016


P. Schlupp, H. von Wenckstern, M. Grundmann: *Flexible elektronische Bauelemente auf Basis transparenter Oxide*, 6. EFDS Workshop "Transparente leitfähige Materialien (TCO/TCM)", Erfurt, Germany, November 2016 (invited)

R. Schmidt-Grund: *Lasing and Quantum Gases in ZnO Nanostructures*, CIMTEC 2016, Perugia, Italy, June 2016 (invited)

R. Schmidt-Grund: *Emerging materials - magnetic spinels and biaxial Ga2O3*, 1st ELIps User Workshop, Dolní Brezany & Brno, Czech Republic, October 2016 (invited)

A. Shkurmanov, C. Sturm, H. Hochmuth, M. Grundmann: *CMOS-compatible PLD-growth of ultrathin ZnO nanowires*, DPG spring meeting, Regensburg, Germany, March 2016


C. Sturm, C. Kranert, J. Furthmüller, F. Bechstedt, R. Schmidt-Grund, M. Grundmann: Dielectric function of optically anisotropic materials and its application to monoclinic beta-Ga$_2$O$_3$, 7th International Conference on Spectroscopic Ellipsometry (ICSE-7), Berlin, Germany, June 2016

C. Sturm, A. Shkurmanov, J. Volk, I Lukács, N.Q. Khánh, M. Grundmann: On chip integration of piezoelectric Nanowires, Eurosensors XXX, Budapest, Hungary, September 2016 (Talk at the PiezoMat Open Session)

H. von W彭克施滕: Semiconducting oxides - From material design to basic devices, Orlando, USA, January 2016 (invited)

H. von W彭克施滕: Defects in wide bandgap semiconducting oxides - Bulk material, epitaxial thin films and microresonators, EMRS spring meeting Lille, Symposium BB: "Defect-induced effects in nanomaterials", Lille, France, May 2016 (invited)

H. von W彭克施滕: Semiconducting oxides - From material design to basic devices, Aalto University School of Science, Antimatter and Nuclear Engineering Group, Espoo, Finland, May 2016 (invited)

H. von W彭克施滕: Deep-UV photo detectors based on group-III sesquioxides, German-Japanese Gallium Oxide Technology Meeting 2016, Berlin, Germany, September 2016 (invited)

M. Wille, C. Sturm, T. Michalsky, R. Röder, C. Ronning, R. Schmidt-Grund, M. Grundmann: Carrier density driven lasing dynamics in ZnO nanowires, DPG spring meeting, Regensburg, Germany, March 2016


Posters

K. Dorywalski, M. Piasecki, B. Andriyevsky, R. Schmidt-Grund, M. Grundmann, N. Lemee, T. Krzyzynski: Optical properties of epitaxial Na$_x$Bi$_{1-x}$TiO$_3$ lead-free piezoelectric thin films: ellipsometric and theoretical studies, Poster at the 7th International Conference on Spectroscopic Ellipsometry (ICSE-7), Berlin, Germany, June 2016

C. Kranert, C. Sturm, R. Schmidt-Grund, M. Grundmann: *Determination of the Raman Tensor of Optically Anisotropic Crystals*, 7th International Conference on Spectroscopic Ellipsometry (ICSE-7), Berlin, Germany, June 2016


A. Shkurmanov, C. Sturm, H. Hochmuth, G. Feuilett, F. Tendille, P. De Mierry, M. Grundmann: *Growth of tilted ZnO nanowires by PLD on pre-structured sapphire substrates*, DPG spring meeting, Regensburg, Germany, March 2016


C. Sturm, R. Schmidt-Grund, M. Grundmann: *Singular Optical Axes in Biaxial Crystals*, 7th International Conference on Spectroscopic Ellipsometry (ICSE-7), Berlin, Germany, June 2016 (Best-Poster Award)


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1.24 Graduations

Doctorate

- Michael Bonholzer
  *Magnetic Tunnel Junctions based on spinel Zn_xFe_{3-x}O_4*
  October 2016

- Abdurashid Mavolonov
  *Doping Efficiency and Limits in Wurtzite (Mg,Zn)O Alloys*
  November 2016

- Stefan Müller
  *Schottky-Kontakte auf Zinkoxid- und β-Galliumoxid-Dünnschichten: Barrierenformation, elektrische Eigenschaften und Temperaturstabilität*
  February 2016

- Zhipeng Zhang
  *Ultraviolet Photodiodes Based on (Mg,Zn)O and (Ga,In)_2O_3 Thin Films*
  October 2016

Master

- Max Knieß
  *Transporteigenschaften und optische Charakterisierung von CuI-Kristallen und -Dünnschichten*
  April 2016

- Michael Scheibe
  *Defekte in (Mg, Zn, O) Dünnschichten: Einfluss der Pufferschicht und des Substratschnitts*
  January 2016

Bachelor

- Tobias Abel
  *Deposition and characterization of Zn-doped CuI Thin Films*
  March 2016

- Selina Helmbold
  *Schottky-Kontakte auf Zinkoxinitrid basierend auf Silber-Platin-Mischungen*
  September 2016

- Florian Jung
  *Growth and characterisation of MgO/TiN superlattices*
  October 2016
• Evgeny Krüger  
  *Lasingprozesse in ZnO-Mikrodrähten bei Raumtemperatur*  
  January 2016

• Oliver Lahr  
  *Strukturelle und elektrische Charakterisierung epitaktischer SnO₂ Dünnfilme*  
  July 2016

• Julian Pohl  
  *Herstellung und elektrische Charakterisierung von Galliumoxid-Transistoren*  
  September 2016

• Benjamin Wehr  
  *Untersuchung des Wachstumsverhaltens von Kupfer-Gallium-Oxiden auf c-orientiertem Zinkoxid*  
  July 2016

### 1.25 Guests

• M.S. Ramachandra Rao  
  Indian Institute of Technology (IIT) Madras, India  
  June 2016

• Martin Allen  
  University Christchurch, New Zealand  
  December 2016
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Transparent Conductive Oxides – Fundamentals and Applications
18-22 September 2017

Transparent materials are used for ohmic applications such as transparent contacts in displays and solar cells or electro-magnetic shielding. Also semiconducting transparent oxides for diodes and transistors have gained tremendous interest due to applications in transparent and flexible active electronics.

The TCO2017 meeting will focus on:
- theory of oxide electronic materials
- growth of bulk semiconducting oxides
- epitaxial oxide heterostructures
- metal-like n-type TCOs
- novel oxide semiconductors
- point defects in oxides
- oxide devices and applications

140 years ago Karl W. Bädeker, grandson of the founder of the Baedeker tour guides, was born in Leipzig. He reported 110 years ago in 1907 at Universität Leipzig the first transparent, conductive thin films, namely from cadmium oxide (n-type) and copper iodide (p-type). He also achieved the first doping of semiconductors via the variation of the iodine concentration in Cul.

Invited speakers
Oliver Bierwagen, PDI, Berlin
Armin Dadgar, OvG-Univ. Magdeburg
Peter Deák, Universität Bremen
Judith Driscoll, Cambridge University
Klaus Ellmer, HZB, Berlin
Geoffroy Hautier, Univ. Cath. de Louvain
Kevin D. Leedy, WP-AFB, Dayton, OH
Chris McConville, RMIT Univ., Melbourne
Marjorie Olmstead, U Washington, Seattle
Takahisa Omata, Tohoku University
Chris Sturm, Universität Leipzig
Joel B. Varley, Lawrence Livermore
Garcia Villora, NIMS, Tsukuba
Lasse Vines, University of Oslo
Jesús Zúñiga-Pérez, CRHEA, Valbonne

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Holger von Wenckstern, Univ. Leipzig

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Venue: Lecture Hall for Theoretical Physics, Linnéstraße 5, Leipzig