

HL 45: ZnO II

Time: Thursday 14:00–17:30

Location: H17

HL 45.1 Thu 14:00 H17

Optical Investigation of Surface Defects in ZnO Nanostructures — ●JOHANNES FALLERT¹, ROBERT HAUSCHILD¹, HUIJUAN ZHOU¹, FELIX STELZL¹, MARKUS WISSINGER¹, MARIO HAUSER¹, DONG SIK KIM², MARGIT ZACHARIAS², CLAUS KLINGSHIRN¹, and HEINZ KALT¹ — ¹Universität Karlsruhe (TH), Karlsruhe, Germany — ²Max-Planck-Institute of Microstructure Physics, Halle,

The optical properties of different ZnO nanostructures are investigated. Thereby we focus on a photoluminescence (PL) emission band around 3.31 eV. Compared to bulk ZnO this band is observed to be strongly increased in ZnO nanoparticles. We assign the origin of this emission band to acceptors present at the particle surface since this emission band shows a clear dependence on the surface to volume ratio of the particles. Temperature dependent measurements reveal that this band plays a major role up to room temperature. Furthermore, time resolved and intensity dependent measurements have been carried out to confirm this designation and to understand the luminescence dynamics.

HL 45.2 Thu 14:15 H17

Electrical properties of compacted zinc oxide nanoparticles — ●SONJA HARTNER¹, HARTMUT WIGGERS², and AXEL LORKE¹ — ¹Experimental Physics, University of Duisburg-Essen, Lotharstr.1, 47057 Duisburg — ²Institute of Combustion and Gas Dynamics, University of Duisburg-Essen, Lotharstr.1, 47057 Duisburg

The present study investigates the electrical properties of mechanically compacted pellets of nanosized zinc oxide powders from gas phase synthesis by impedance spectroscopy (IS). The measurements were performed in air and in hydrogen atmosphere at temperatures ranging from 320K to 650K. As expected for semiconducting materials, the spectra measured in air show very poor conductivity under ambient conditions and an increase in conductivity with increasing temperature. Between 500 K and 650 K the activation energy was found to be 604 meV. The impedance spectra exhibit the typical structure known from ionic conductors with a low-frequency Warburg impedance. After annealing at temperatures of about 250 °C in hydrogen atmosphere, the absolute value of the conductivity increases up to four orders of magnitude. The electrical measurements show ohmic behavior over the complete temperature range and the activation energy has changed to -11 meV, meaning positive temperature coefficient conductivity as it is known from metals. The change in electrical behavior under air and hydrogen is reversible and is attributed to a change of the chemical composition. The current understanding is that by exposing zinc oxide to hydrogen gas, oxygen vacancies are formed, providing ZnO_{1-x} with free electrons which contribute to the overall conductivity.

HL 45.3 Thu 14:30 H17

Magnetoresistance in n-type conducting magnetic ZnO films — ●QINGYU XU, LARS HARTMANN, HEIDEMARIE SCHMIDT, HOLGER HOCHMUTH, MICHAEL LORENZ, and MARIUS GRUNDMANN — Universität Leipzig, Fakultät für Physik und Geowissenschaften, Institut für Experimentelle Physik II, Linnéstrasse 5, D-04103 Leipzig, Germany

The magnetoresistance (MR) of differently alloyed, n-type conducting ZnO films (Co, Mn, Ti, Cu, Nd) prepared by pulsed laser deposition (PLD) on a-plane sapphire substrates in oxygen atmosphere was probed in the temperature range from 5 K to 290 K with magnetic fields up to 6 T. At 5 K, large positive MR was observed in Co [1] and Mn doped ZnO films, while large negative MR was observed in Ti, Cu [2], and Nd doped ZnO films. The positive MR in doped ZnO was attributed to a giant spin splitting enhanced by s-d exchange interactions. This will affect considerably quantum corrections to the conductivity associated with the disorder modified electron-electron interactions [3]. The probed positive MR reveals that the s-d exchange interaction is strong in Co and Mn doped ZnO. Weak s-d exchange interaction has been observed in Ti, Cu, and Nd doped ZnO. Except for the Cu-doped ZnO, these results agree with magnetic circular dichroism results [4]. The positive and negative MR decreases drastically with increasing temperature, being nearly neglectable above 100 K. [1] Q. Xu, et al, Phys. Rev. B 73, 205342 (2006). [2] L. Hartmann, et al, J. Phys. D: Appl. Phys., in press. [3] T. Andrearczyk, et al, Phys. Rev. B 72, 121309(R) (2005). [4] K. Ando, et al, J. Appl. Phys. 89, 7284 (2001).

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Hydrogen induced charge state alteration of Mn trace impurities in ZnO — ●M. A. GLUBA, F. FRIEDRICH, and N. H. NICKEL — Hahn-Meitner-Institut Berlin, Abt. Silizium Photovoltaik (SE1), Kekuléstraße 5, 12489 Berlin, Germany

The source of the natural n-type doping of ZnO is still a subject of discussion. However, both theoretical [1] and experimental work [2] show that hydrogen plays a crucial role. To elucidate the paramagnetic behavior of H in ZnO low temperature X-band electron paramagnetic resonance (EPR) measurements were performed. For this purpose EPR spectra were taken from *pressurized-melt-grown* nominally undoped ZnO single crystals before and after hydrogenation.

As-grown ZnO exhibits a single EPR-line at $g=1.957$ arising from multiple centers, one of which was identified as a hydrogen shallow donor [2]. On the other hand, post-hydrogenated ZnO shows a distinctly different EPR spectrum. Besides the intensification of the hydrogen-related line additional fine and hyperfine split lines originating from ⁵⁵Mn appear. However, these features are not stable. While keeping the samples at room temperature for about four weeks the hydrogen line decays to its initial value. In the same period of time the manganese lines disappear completely. A likely mechanism for this correlation - the change of the Mn charge state due to hydrogen doping - will be discussed.

[1] C. G. Van de Walle, Phys. Rev. Lett. **85**, 1012 (2000)[2] D. M. Hofmann *et al.*, Phys. Rev. Lett. **88**, 045504 (2002)

HL 45.5 Thu 15:00 H17

Electronic Structure of Europium Impurities in ZnO — ●PRZEMYSŁAW IMIELSKI¹, WILLIAM BREWER¹, YURIY MANZHUR², KAY POTZGER³, and WOLF ZEITZ² — ¹Institut für Experimentalphysik, Freie Universität Berlin, D-14195 Berlin, Germany — ²Bereich Strukturforschung, Hahn-Meitner-Institut Berlin GmbH, D-14091 Berlin, Germany — ³Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf, P.O. Box 510119, 01314 Dresden, Germany

Utilizing perturbed angular correlation spectroscopy (PAC), the behaviour of isolated europium impurities in ZnO has been investigated. The radioactive probe rare earth atoms ¹⁴⁹Gd/¹⁴⁹Eu were produced and recoil implanted by nuclear reactions. After annealing at 500 degree Celsius, the first spectrum of a ¹⁴⁹Eu(11/2-) quadrupolar interaction has been measured. From spectra of the combined interaction, evidence for the realization of the Eu²⁺(7/2) ground state has been found.

HL 45.6 Thu 15:15 H17

Effects of annealing on the recombination dynamics of low-temperature grown ZnO nanorods — ●B. HILKER¹, C. BEKENY¹, T. VOSS¹, J. GUTOWSKI¹, R. HAUSCHILD², H. KALT², B. POSTELS³, ANDREY BAKIN³, and A. WAAG³ — ¹IFP, Universität Bremen, 28334 Bremen — ²Universität Karlsruhe, 76128 Karlsruhe — ³IHT, TU Braunschweig, 38023 Braunschweig

We present systematic temperature and excitation density dependent time-resolved photoluminescence (TRPL) measurements of as-grown and annealed ZnO nanorods fabricated by an aqueous chemical growth (ACG) technique at ~90°C. The as-grown nanorods show strong near-band-edge and rather weak deep-level emission indicating their already good optical quality. At 4K, we find a broad emission line at 3.36eV (line width 30meV) which we attribute to recombination from a donor band formed through the high donor concentration. After annealing in oxygen and nitrogen atmospheres at 600-800°C well-resolved and sharper excitonic transitions are observed. To understand the recombination dynamics in the nanorods we carried out TRPL measurements using a frequency-doubled femtosecond laser and a streak camera. The as-grown sample shows a very fast monoexponential decay time of ~10ps independent of temperature and excitation density. In contrast, the annealed samples exhibit a biexponential decay. Each a fast τ_1 and a slow τ_2 time constant have been determined for all annealed samples both of them significantly varying depending on the annealing atmosphere and temperature. This will be discussed on the basis of a phenomenological rate-equation model.

HL 45.7 Thu 15:30 H17

Acceptor doping of ZnO nanowires — •BINGQIANG CAO, MICHAEL LORENZ, ANDREAS RAHM, CHRISTIAN CZEKALLA, HOLGER VON WENCKSTERN, GABRIELE BENNDORF, JÖRG LENZNER, and MARIUS GRUNDMANN — Universität Leipzig, Institut für Experimentelle Physik II, Leipzig, Germany

We have grown phosphorous, lithium, and nitrogen doped ZnO nanowires both by carbothermal evaporation [1] and by high-pressure pulsed laser deposition [2] by mixing various amounts of P_2O_5 , $Zn_3(PO_4)_2$, Zn_3P_2 , Li_2O , Li_3N , and Li_2CO_3 into the ZnO source material. The diameter and length of the acceptor-doped and undoped ZnO wires was in the range from 100 nm to 3 μm and several micrometers, respectively. Cathodoluminescence spectra taken at 10 K on the acceptor doped wires show clearly resolved acceptor-related and donor-acceptor pair peaks, indicating the acceptor incorporation into the ZnO lattice. From these acceptor peak energies, thermal activation energies of the acceptor levels were determined. For comparison, temperature-dependent I-V measurements allow the determination of a (two-terminal) activation energy. Both the optical and electrical measurements will be discussed with dependence on the dopant element, its concentration, the wire geometry, and the growth route. The aim of the work is p-type conducting ZnO nanomaterial for nano p-n-junctions and light emitting devices.

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[1] M. Lorenz et. al. Ann. Phys. (Leipzig) 13 (2004) 39.

[2] M. Lorenz et. al. Appl. Phys. Lett. 86 (2005) 143113.

15 min. break

HL 45.8 Thu 16:00 H17

Homoepitaxial growth of ZnO thin film by pulsed laser deposition (PLD) — •MATTHIAS BRANDT, HOLGER VON WENCKSTERN, CHRISTIAN HANISCH, HOLGER HOCHMUTH, MICHAEL LORENZ, HEIDEMARIE SCHMIDT, and MARIUS GRUNDMANN — Universität Leipzig, Semiconductor Physics Group, Institut für Experimentelle Physik II, Leipzig, Germany

In this work ZnO thin films have been deposited homoepitaxially by PLD on ZnO single crystals grown by the hydrothermal method (purchased from CrysTec GmbH). These wafers have first been investigated by atomic force microscopy (AFM) and were found to show significant surface roughness in the as-received state. Therefore a thermal annealing method has been applied to the wafers prior to thin film growth, in order to improve the surface properties. An overview of the changes during annealing will be presented along with information on the optimal conditions for thermal annealing. Structural, morphological, optical and electrical properties of the thin films grown homoepitaxially on these optimized wafers will be discussed with respect to the growth conditions. Comparisons to properties of thin films grown heteroepitaxially on sapphire (Al_2O_3) and SCAM ($ScAlMgO_4$) will be provided.

HL 45.9 Thu 16:15 H17

Homo-MOVPE von ZnO auf optimierten kommerziellen ZnO-Substraten — •SÖREN HEINZE, ANDRE KRITSCHIL, JÜRGEN BLÄSING, ARMIN DADGAR, THOMAS HEMPEL, JÜRGEN CHRISTEN und ALOIS KROST — Otto-von-Guericke-Universität Magdeburg, Institut für Experimentelle Physik Otto-von-Guericke-Universität Magdeburg, Institut für Experimentelle Physik

Auf thermisch vorbehandelten ZnO-Substraten wurden mittels metallorganischer Gasphasenepitaxie dünne ZnO-Schichten abgeschieden. Die Qualität der Schichten ist stark abhängig vom Verhältnis des Sauerstoffprecursors (N_2O) zum Zinkprecursor (Dimethylzink) (VI/II-Verhältnis). Ein kleines VI/II-Verhältnis induziert eine raue Oberflächenmorphologie sowie dreidimensionale Pyramiden mit Abmaßen von einigen Mikrometern. Erhöht man das VI/II-Verhältnis, so verringern sich sowohl die Anzahl dieser dreidimensionalen Pyramiden als auch deren Größe. Bei hohen VI/II-Verhältnissen von ca. 25000 sind die Pyramiden komplett verschwunden und man erhält eine noch sehr raue abgeschiedene Schicht. Modifikationen an weiteren Wachstumsparametern wie der Temperatur und dem Reaktordruck verbessern die morphologischen Eigenschaften der Schicht deutlich. Bei höheren Temperaturen wachsen die einzelnen Domänen zusammen und die Schicht wird signifikant glatter. Durch eine Erhöhung des Reaktordrucks konnte das Wachstum bis hin zum Stufenwachstum verbessert werden. Insgesamt werden die Untersuchungsergebnisse der morphologischen, strukturellen, elektrischen und optischen Eigenschaften dieser homoepitaxial gewachsenen Schichten im Detail vorgestellt.

HL 45.10 Thu 16:30 H17

Homoepitaxially grown ZnO thin films — •STEFAN LAUTENSCHLÄGER¹, CHRISTIAN NEUMANN¹, JOACHIM SANN¹, NIKLAS VOLBERS¹, SWEN GRAUBNER¹, BRUNO MEYER¹, JÜRGEN BLÄSING², ALOIS KROST², FRANK BERTRAM², and JÜRGEN CHRISTEN² — ¹I. Physikalisches Institut, Justus-Liebig-Universität Gießen — ²Institut für Experimentelle Physik, Otto-von-Guericke Universität Magdeburg

We report on homoepitaxially ZnO thin films, grown on chemomechanically polished Crystec single crystals. To prepare the substrates for growth we employed a high temperature annealing step, which produced atomically flat surfaces and removed all of the surface and subsurface damage. We used Photoluminescence (PL), Cathodoluminescence (CL), Secondary Ion Mass Spectroscopy (SIMS), Hall measurements, high resolution X-Ray diffraction and Atomic Force Microscopy (AFM) to characterize the epilayers. Two dimensional epitaxial growth was achieved without an additional buffer layer. The substrate had a rocking halfwidth of 27" which can be compared with that of the film of 17". The films had superior band edge luminescence as compared with the substrate for which the green luminescence band is dominating. The impurity content in the substrates, especially Li is reduced by the high temperature annealing step and drops further to the detection limit in the thin films.

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Annealing Studies on N and As implanted Zinc Oxide — •NIKLAS VOLBERS¹, STEFAN LAUTENSCHLÄGER¹, JOACHIM SANN¹, KAY POTZGER², and BRUNO K. MEYER¹ — ¹I. Physikalisches Institut, Heinrich-Buff-Ring 16, Justus-Liebig-Universität Gießen, D-35392 Giessen, Germany — ²Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf, P.O. Box 51 01 19, 01314 Dresden, Germany

Both nitrogen and arsenic are considered possible acceptors in order to achieve p-type conductivity in ZnO. Ion implantation provides an accurate and reproducible method to incorporate these dopants into ZnO crystals.

In the presented work, high quality ZnO thin films were grown homoepitaxially on ZnO single crystals via a chemical vapour deposition process and were subsequently implanted with either ¹⁴N or ⁷⁵As ions, using implantation doses of 10¹⁶ atoms/cm². The films were annealed at temperatures of up to 1100°C. Dynamic SIMS measurements show the evolution of the implanted ions in the films and the corresponding motion of residual impurities. In addition, photoluminescence and hall effect measurements were performed to investigate the optical and electrical properties of the as-grown and the annealed samples.

HL 45.12 Thu 17:00 H17

Aqueous chemical growth and application of ZnO nanorods — •BIANCA POSTELS, ANNA KASPRZAK, AUGUSTINE CHE MOFOR, HERGO-HEINRICH WEHMANN, ANDREY BAKIN, and ANDREAS WAAG — Institute of Semiconductor Technology, Technical University Braunschweig, Hans-Sommer-Str. 66, 38106 Braunschweig, Germany

ZnO finds applications in many fields from sun tan lotion to optoelectronic applications. Especially the tendency of ZnO to form nanostructures opens the path to even more applications. A very promising fabrication process for ZnO nanostructures is the aqueous chemical growth (ACG), since it is a cost efficient and low temperature approach. Using this growth technique we generated wafer-scale ZnO nanorod arrays on Si, sapphire, ITO coated glass and even on flexible polymer substrates. ACG is found to be only weakly influenced by the substrate material and we are also able to control the dimensions of the ZnO nanorods. Another benefit of ACG is the ability to fabricate patterned arrays of ZnO nanorods by a selective growth process on structured metallised surfaces. Results of structural analysis with SEM and XRD are reported. Additionally, optical properties were investigated by PL measurements. First attempts on the preparation of dye sensitised solar cells (DSSCs) are also reported. Here, the traditional sintered TiO₂ nanoparticles are replaced by a densely packed and vertically aligned array of ACG ZnO nanorods. The size and morphology of the ZnO nanorods can be controlled. The influence of the length of the nanorods on the cell properties is investigated. A vapour phase transport technique was also used as alternative growth method.

HL 45.13 Thu 17:15 H17

Investigation of complex formation in pulsed-laser deposited Sb-doped ZnO thin-films — •FELICE FRIEDRICH and N. H. NICKEL — Hahn-Meitner-Institut Berlin, Abt. Silizium-Photovoltaik (SE1), Kekuléstraße 5, 12489 Berlin, Germany

Antimony (Sb) as group V element is a doping candidate for p-type ZnO. However, because of its large atomic size theory predicts that formation of a defect complex is more favorable. Growth temperature might play a critical role in this process. In this study the influence of Sb concentration and deposition temperature on the structural and vibrational properties of Sb-doped ZnO thin-films was investigated.

The samples were grown by pulsed laser deposition (PLD) on MgO substrates. Ceramic targets were produced from ZnO and Sb₂O₃ powder (0-2 at.% Sb). A XeCl excimer laser operating at a fluence of 1.5 J/cm⁻² was used for the deposition process. The deposition temperature was varied between 450-800°C. The samples were character-

ized by scanning electron microscopy (SEM), energy dispersive X-ray scattering (EDX) and Raman backscattering spectroscopy.

Firstly, it is observed that a higher Sb concentration leads to a reduced film thickness. Raman measurements show that this is accompanied by a deterioration of the ZnO crystallinity. Secondly, a surprising change of the Raman spectra was observed at a temperature of 600°C. Below this temperature additional Raman modes are observed at 530, 575 and 700 cm⁻¹. Above 600°C the mode at 530 cm⁻¹ is strongly suppressed. These results will be discussed in terms of the temperature-dependent formation of Zn-Sb-O complexes.