



Strasbourg (France)

E-MRS 2005 Spring Meeting
May 31 – June 3, 2005

SYMPOSIUM G

ZnO and related materials

Symposium Organizers :

Jürgen Christen, University Magdeburg, Germany

Bernard Gil, University Montpellier, France

Axel Hoffmann, Technical University Berlin, Germany

David C. Look, Wright State University, Dayton, USA

Takafumi Yao, Tohoku University, Sendai, Japan

Papers to be published in Superlattices and Microstructures

E-MRS 2005 Spring Meeting

SYMPOSIUM G

Tuesday, May 31, 2005
Mardi 31 mai 2005

Morning
Matin

Session I : Optical properties

Session chair : J. Christen

- G-I.01** 8:30 -Invited- ZnO – REDISCOVERED ONCE AGAIN
C. Klingshirn, H. Kalt, H. Priller, M. Decker, J. Brückner, J. Zeller, R. Hauschild, Institut für Angewandte Physik der Universität, D-76128 Karlsruhe, Germany
- G-I.02** 9:00
RESONANT COUPLING OF BOUND EXCITONS WITH LO PHONONS IN ZnO
S.J. Xu, S.L. Shi and S.-J. Xiong, Department of Physics and HKU-CAS Joint Laboratory on New Materials, The University of Hong Kong, Pokfulam Road, Hong Kong, China
Electron (exciton)-phonon coupling has been an essential issue in solid states. In this presentation, we report on the resonant coupling of bound excitons with LO phonons in high quality ZnO single crystal. Such resonant coupling due to comparable value of the total binding energy of excitons bound at shallow impurities with the characteristic energy of LO phonons leads to not only observation of up to 4 order LO phonon Stokes lines but also appearance of anti-Stokes lines in low-temperature photoluminescence spectra of ZnO. Furthermore, the anti-Stokes lines and corresponding Stokes lines are found to be not mirror symmetric with respect to the zero-phonon line. We also observed a surprising Fano line shape for the first-order LO Stokes line. As the temperature increases, the Fano line shape of the first-order Stokes line gradually disappears. These new findings indicate that the microscopic mechanisms of exciton-phonon interactions under resonant conditions are needed to reexamine.
- G-I.03** 9:15
IMPACT OF EXCESS EXCITATION ENERGY ON THE RECOMBINATION LIFETIMES OF BOUND EXCITONS IN ZnO EPILAYERS
F. Bertram, S. Giemisch, J. Christen A. Dadgar and A. Krost, Institute of Experimental Physics, Otto-von-Guericke-University Magdeburg, Germany
We investigate the excess energy dependence of the relaxation and recombination kinetics of the excitonic system in MOVPE grown ZnO under resonant and tuned off-resonant laser excitation using spectrally tuned ps-photoluminescence (PL). The cw-PL spectrum is dominated by the impurity bound exciton I8 ($E = 3.3586$ eV, $\text{FWHM} < 3$ meV). The free exciton XA (3.374 eV), the bound excitons I0, I1, I2, I3, I6 (3.3597 eV), and I9, as well as the LO phonon replica from I8 are clearly visible. No spectral shift is observed in the spectral-time-resolved measurements. The spectrally integrated decay as well as the decay of all individual excitonic lines is strictly mono-exponential yielding decay times of 114 ps, 303 ps, and 290 ps for XA, I8, and I9, respectively at 3.8 K. The decay times of I8 and I9 explicitly depend on the laser excitation photon energy. A distinct resonance, i.e. a drop of lifetime, is found for an excess energy of 5meV ($E(\text{laser}) - E(\text{I8}), E(\text{I9}) = 5$ meV), indicating the resonance of an efficient scattering of the holes into the B valence band. In addition, we show temperature-dependent lifetimes of the excitonic lines I8 and I9. At higher temperatures the lifetimes rises and an additional much slower decay-channel appears.
- G-I.04** 9:30
TIME RESOLVED PHOTOLUMINESCENCE OF ZnO / (Zn,Mg)O QUANTUM WELLS. INTERNAL ELECTRIC FIELD EFFECTS
T. Bretagnon, P. Valvin, P. Lefebvre, B. Gil, Groupe d'Etude des Semiconducteurs, CNRS, Université Montpellier II, Case Courrier 074, 34095 Montpellier Cedex 5, France and C. Morhain, Centre de Recherche sur l'Hétéro-Epitaxie et ses Applications, CNRS, Rue Bernard Grégory, 06560 Valbonne, France
We have investigated a series of samples embedding ZnO/(Zn,Mg)O quantum wells of sizes varying between 1.5 and 9 nm, in wurtzite phase, by using temperature dependent, time-resolved photoluminescence. The samples were grown by molecular beam epitaxy on ZnO templates, themselves deposited on sapphire substrates. The presence of large internal electric fields in these quantum wells manifests itself not only through the energies of the optical recombinations, but also through the size dependence of the recombination times. Generally, for laser excitation above the barrier band-gap energy, characteristic decay times as large as several hundreds of nanoseconds are observed, with a strongly nonexponential decay shape. These results are analysed by taking account of the screening of internal fields by photo-injected electron-hole pairs, when appropriate.

G-I.05 9:45

CATHODOLUMINESCENCE CHARACTERIZATION OF HYDROTHERMAL ZNO CRYSTALS

J. Mass, M. Avella, J. Jiménez, Física de la Materia Condensada, ETSII, 47011 Valladolid, Spain; M. Callahan, E. Grant, K. Rakes, D. Bliss, Air Force Research Laboratory, Hanscom AFB, MA, USA; Buguo Wang, Solid State Scientific Corp., Nashua NH, USA

Low dislocation density large ZnO single crystals can be grown by the hydrothermal method; however, the impurity incorporation is far to be controlled. This is a key issue because the impurities influence the carrier lifetime and the light emission mechanisms. The analysis of the luminescence is essential to understand the incorporation of the impurities and the role of the native defects to improve the growth conditions. Cathodoluminescence (CL) is a powerful tool to study the luminescence of wide band gap semiconductors. It allows mapping the distribution of the spectral parameters of the luminescence bands, enabling better understanding about the distribution of impurities and the role of the non radiative recombination centers. The incorporation of impurities and native defects is dependent on the growth sectors. We present herein a CL study of different growth sectors of (1000) ZnO wafers. The CL spectrum of each sector is studied as a function of the temperature and the e-beam excitation conditions. Special emphasis is paid to the green orange luminescence. Spectral images show perceptible differences between the growth sectors.

G-I.06 10:00 -Invited-

OPTICAL PROPERTIES OF ZnO-BASED QUANTUM STRUCTURES

Takayuki Makino, Photodynamics Research Center, The Institute of Physical and Chemical Research (RIKEN), Aramaki aza Aoba 519-1399, Sendai 9800845, Japan

The optical properties of ZnO multiple quantum wells (MQWs), which have potential application of short-wavelength semiconductor laser utilizing a high-density excitonic effect, were investigated. Recently ZnO MQWs have been grown by laser molecular-beam epitaxy (laser-MBE) on lattice-matched ScAlMgO₄ substrates. We discuss mainly the experimental aspect. Systematic temperature-dependent studies of optical absorption and photoluminescence were used to evaluate the well-width dependence and the composition dependence of the major excitonic properties. Based on these data, the localization of excitons, the influence of exciton-phonon interaction, and quantum-confined Stark effects are discussed. The optical spectra of dense excitonic systems are shown to be determined mainly by the interaction process between excitons and biexcitons. The high-density excitonic effects play a role for the observation of room-temperature stimulated emission. Stimulated emission of excitons was observed at temperatures well above room temperature, whose mechanism is discussed. The binding energies of exciton and biexciton are enhanced from the bulk values, as a result of quantum-confinement effects.

10:30

BREAK

Session II : Growth 1

Session chair : **B.K. Meyer**

G-II.01 11:00 -Invited-

CURRENT STATUS OF ZnO MOVPE GROWTH

A. Dadgar, Otto-von-Guericke Universität Magdeburg, FNW-IEP, Postfach 4120, 39106 Magdeburg, Germany

G-II.02 11:30

GROWTH OF UNDOPED ZNO THIN FILMS ON R-SAPPHIRE SUBSTRATES USING PULSED LASER DEPOSITION

A. Meaney, J.-R. Duclere, E. McGlynn, J.-P. Mosnier, R. O'Haire, M.O. Henry, School of Physical Sciences, NCPST, Dublin City University, Glasnevin, Dublin 9, Ireland

Pure ZnO thin films were grown by Pulsed Laser Deposition (PLD) on R-sapphire substrates at ~ 560 °C, followed by an annealing step of 30 minutes at the same temperature, under half an atmosphere of O₂. X-ray diffraction data show that the films are epitaxially grown and (11-20) oriented, indicating that the c-axis lies in the substrate plane. For these growth conditions, the low temperature photoluminescence of the samples is of higher quality than is found for c-Al₂O₃ substrates, with only one donor bound exciton line (due to Al contamination from the substrate) being observed, with a linewidth of 1.5meV. However, from X-ray data, rocking-curve (Dq) values are found in the same range for the two cases. We attribute the superior optical quality for R-sapphire substrates to the fact that the columnar growth of ZnO, oriented along the c-axis, will increase the density of grain boundaries in the case of c-Al₂O₃ substrates, while having the c-axis lying in the plane reduces their density. Our results show that PLD, in combination with suitable substrates, provides a flexible and powerful technique for the growth of high purity epitaxial ZnO films.

G-II.03 11:45

HIGH-QUALITY ZnO LAYERS GROWN BY MBE ON SAPPHIRE

A. El-Shaer, A. Che Mofor, A. Bakin, M. Kreye, A. Waag Institute of Semiconductor Technology, Technical University Braunschweig, Germany

Recently we reported on the novel approach to zinc oxide Molecular Beam Epitaxy (MBE) growth employing H₂O₂ as an oxidant. In this paper we present further improvements on the MBE ZnO layer growth technology. ZnO layers were grown on sapphire in a modified Varian Gen II MBE system using H₂O₂ as an oxidant. Layers with thickness from 100 nm to 600 nm were obtained. The surface morphology of the samples was studied by atomic force microscopy (AFM), optical microscopy with Nomarski contrast and scanning electron microscopy (SEM).

Surface roughness (rms) measured by Atomic Force Microscopy for the best layers is about 0.2 nm. X-Ray Diffractometry measurements of the obtained ZnO layers show excellent quality of the single crystalline ZnO heteroepitaxially grown on sapphire. The FWHM of the XRD (0002) rocking curve is as low as 55 arcsec. The influence of growth parameters on structural properties as well as on surface morphology of the zinc oxide layers on sapphire is investigated and discussed.

G-II.04 12:00

MOCVD OF PURE AND Ga-DOPED EPITAXIAL ZnO

A.R. Kaul, O.Yu. Gorbenco, A.N. Botev, V.S. Kalitka, Department of Chemistry, Lomonosov Moscow State University, 119992, Moscow, Russia

ZnO films find the growing application in the microelectronics, optoelectronics, laser and semiconductor technologies. Doping with the trivalent cations is intended to improve the electrical conductivity of ZnO. Here we report the expansion of the Ga₂O₃ solubility range in ZnO films on single crystal substrates due to the epitaxial stabilization contribution. The epitaxial relations were characterized for ZnO and a broad spectrum of the substrates including C- and R-Al₂O₃, (111) ZrO₂(Y₂O₃), (111) SrTiO₃, (111) Nd₃Ga₅O₁₂, (111) MgO, (111) MgAl₂O₄. Preliminary the deposition kinetics was measured in the range 300-800°C using Zn(acac)₂ and Ga(acac)₃, where acac= acetylacetonate-anion. The maximum deposition rate corresponds to the range 500-550°C. The particular feature of the deposition process is switching to the whiskers growth with the increase of the deposition rate.

The films on (111) ZrO₂(Y₂O₃), (111) SrTiO₃, are characterized by the higher epitaxial quality than films on sapphire traditionally used for the ZnO epitaxy. This results in the higher solubility of Ga₂O₃; in ZnO films on (111) ZrO₂(Y₂O₃) (up to 2 mol. %) as compared to the films on R- Al₂O₃ (1 mol. %) because of the epitaxial stabilization. Intensity of the UV photoluminescence (PL) correlates with the epitaxial quality of ZnO films. Ga-doping resulted in the quenching of green PL band because of Ga³⁺ occupancy of the octahedral interstitials in ZnO structure (in agreement with the variation of ZnO(Ga₂O₃) film lattice parameters).

G-II.05 12:15

METAL ORGANIC CHEMICAL VAPOR DEPOSITION OF ZnO

Ming Pan(a), William Fenwick(a), Todd Steiner(a), Ali Asghar(a), Ian Ferguson(a,b), Rengarajan Varatharajan(c), Jeff Nause(c), Paul Fabiano(d) and Nada El-Zein(e), (a)School of ECE, Georgia Institute of Technology, Atlanta GA 30332, USA, (b)School of MSE, Georgia Institute of Technology, Atlanta GA 30332, USA, (c)Cermet Inc, 1019 Collier Rd, Atlanta GA 30318, USA, (d)VEECO, 394 Elizabeth Ave, Somerset NJ 08873, USA, (e)Akzo Nobel LLC, 1525 W. Van Buren St, Chicago IL 60607, USA

ZnO thin films were grown on sapphire substrates using a customized rotating disk, vertical injection MOCVD tool as part of a comprehensive study of the factors affecting ZnO growth by MOCVD. The understanding gained here will be useful in future work involving p-type doping of ZnO. X-ray diffraction (XRD), photoluminescence (PL), and Hall effect were used to characterize the films. Effects of growth pressure, temperature, VI/II ratio, and disk spin speed on film growth and quality were studied. Growth pressure was varied from 5 to 200 Torr and temperature was varied from 500 to 700DegC. VI/II ratios from 200 to 600 were investigated, and disk spin speed was varied from 500 to 1500 rpm. Of the process parameters studied so far, disk spin speed was found to be the most dominating. Also, dry etching of ZnO material was conducted in a low pressure reactor to investigate the sensitivity of ZnO to hydrogen at different temperatures.

G-II.06 12:30

INFLUENCE OF PULSED LASER DEPOSITION (PLD) PARAMETERS ON THE H₂ SENSING PROPERTIES OF ZINC OXIDE THIN FILMS

N. Brilis(a), D. Tsamakis(a) and M. Kompitsas(b), (a)School of Electrical Engineering and Computer Science, National Technical University of Athens, Iroon Polytechniou 9 Zografou, 15773 Athens, Greece, (b)Theoretical and Phys./Chem. Institute, National Hellenic Research Foundation, Vas. Konstantinou Ave. 48, 116 35 Athens, Greece

ZnO thin films have been widely used, among other applications, as basic elements in gas sensing devices. Gas sensing is based on the reversible change of the electrical conductivity of thin films, when placed in gas-to-trace ambience. The deposition method and the growth parameters of thin films are determinative of the sensing properties under exposure in specific gases. Doped thin films and even mixed oxide films^{1,2} have often proven as better candidates for gas detection. The film growth process used mostly thus far (rf sputtering, PLD, CVD etc), are either time-consuming for target preparation or do not allow doping at all.

ZnO thin films were produced by a novel 2-target, 2-pulsed laser deposition technique. Starting by two pure metallic targets, the method allows the on-line control of the film doping by only changing the laser parameters. A number of deposition parameters including the dopants (Al, Au, Pd, In), the pressure of the ambient (O₂) reactive gas, the deposition temperature as well as the substrate type (Si, SiO₂, glass), have been changed. The influence of the deposition parameters on the electrical transport properties of ZnO thin films has been investigated using electrical resistivity and R_{Hall} measurements. The sensing properties of the films were tested under H₂ flow in air ambience at working temperatures between 150 - 210 °C. ZnO films, deposited at 300 °C on SiO₂ substrates in ambient O₂ of 0.2 mbars, have exhibited a relative response ($\Delta R/R_0$) higher than 97% and a response time of about 3 minutes at working temperatures 180 °C.

[1]Z. Zhon et al, J. Europ. Cer. Soc. vol. 24, p. 139-146, 2004.

[2]K. Zakrzewska, Thin Solid Films, vol. 391, p. 229-238, 2001.

G-II.07 12:45

REACTIVITY OF ZnO: IMPACT OF POLARITY AND NANOSTRUCTURE

Maria Losurdo, Maria M. Giangregorio, Pio Capezzuto, Giovanni Bruno, Institute of Inorganic Methodologies and of Plasmas, IMIP-CNR and INSTM UdR Bari, via Orabona, 4, 70126 Bari, Italy, Graziella Malandrino, Manuela Blandino, Ignazio L. Fragalà, Dipartimento di Scienze Chimiche, Università di Catania, and INSTM, UdR Catania, Viale A. Doria 6, 95125 Catania, Italy

ZnO is of high technological interest for optics and optoelectronics due to its wide band gap of 3.4 eV, a strong excitonic feature and lasing properties at room temperature suitable for ultraviolet laser applications. Applications of ZnO-based systems are also known in catalysis and for gas-sensor applications. Furthermore, it is also a suitable substrate for the heteroepitaxial growth of III-nitride (GaN, AlN) by MOCVD and MBE. For all the above applications, it is of great interest to study the ZnO behaviour in a reactive environment of hydrogen, nitrogen and oxygen.

This contribution presents a study of the ZnO modifications upon interaction with atomic hydrogen, nitrogen and oxygen produced by remote plasmas of H₂, N₂ and O₂, respectively. Data on material properties are correlated with the kinetics of the interaction monitored in real time using spectroscopic ellipsometry. Being the crystal structure of ZnO wurtzite with two inequivalent sequences of atomic planes along the c-axis, with the (0001) being the Zn-polar face and the (000-1) O-polar face, we investigated both single-crystals and epitaxial films with different microstructures deposited by MOCVD. It is shown that reactivity and ZnO modifications depend on polarity, being the Zn-polar surface more reactive toward atomic hydrogen and nitrogen than the O-polar ZnO surface, and on the microstructure, i.e., grain size, density. The impact of the nanostructure on the kinetics of the gas-surface reaction is fingerprinted by ellipsometry, which yields information on the surface coverage, in-diffusion and reactivity of hydrogen and nitrogen on the various ZnO nanostructure. A correlation between polarity, nanostructure of ZnO and its reactivity to hydrogen, nitrogen and oxygen is presented and discussed.

13:00

LUNCH

Session III : Nano Structures 1
Session chair : T. Makino

G-III.01 14:00

NEW NANOCRYSTALLINE COLORED OXYNITRIDES THIN FILMS FROM ZnO NANOCOLLOIDS

L. Spanhel, F. Grasset, Laboratoire "Verres et Céramiques" UMR UR1-CNRS 6512, Institut de Chimie Rennes, Université de Rennes 1, Campus de Beaulieu, CS74205, 35042 Rennes Cedex, France, S. Ababou-Girard, PALMS, UMR UR1-CNRS 6627, Université de Rennes 1, Campus Beaulieu, 35042 Rennes Cedex, France, D. Su, A. Klein, Department of Inorganic Chemistry, Fritz-Haber-Institut der MPG, Faradyweg 4-6, 14195 Berlin, Germany
This contribution highlights our efforts to elaborate new semiconductor nanostructures for solar technologies by colloidal sol-gel route. Of particular interest to us at present are the colored powder and layers of zinc-titanium oxynitrides nanomaterials. In order to get colored oxynitrides, one can perform an ammonia induced replacement of oxygen by nitrogen. We firstly prepare alcoholic high concentrated ZnO nanocolloids containing hexagonal Wurtzite particles with sizes around 5 nm. To the fresh sols, we add titanium precursors which readily reacts with the ZnO nanocrystals. Wet films prepared from these Ti⁴⁺-functionalized ZnO sols via dip coating of glass slides are then pre-sintered at 400°C in air and annealed under ammonia gas at temperatures between 550°C and 800°C. Above the dissociation temperature of ammonia, the spectra are progressively red-shifted with increasing nitriding temperature. Our new low cost colloidal sol-gel route to nanosized colored "ZnTiON" powders and porous layers on glass will be presented in detail. A structural XRD-, XPS- analysis of our "ZnTiON" nano-structures will be discussed.

G-III.02 14:15

PHOTOLUMINESCENCE AND EPR OF ZnO-LATEX COMPOSITES CRYSTALLIZED FROM AQUEOUS MEDIUM

R. Muñoz-Espí(a,b), G. Jeschke(a), I. Lieberwirth(a), C.M. Gómez(b), G. Wegner(a), (a)Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany, (b)Institute of Materials Science, Univ. of Valencia, PO Box 22085, 46071 Valencia, Spain
Micro- and submicro-sized ZnO crystals were synthesized from aqueous medium in presence of surface-functionalized latex particles, giving ZnO-polymer hybrid materials. The influence of the polymeric additives on the morphology and the optical properties of the products were studied with respect to a pure ZnO reference sample, crystallized in absence of any polymer. Typical photoluminescence (PL) spectra of the samples, at room temperature under excitation at 310 nm, showed a UV emission peak at 3.2 eV and a broad green-yellow band centered at 2.2 eV. The intensity of this second band is strongly quenched when the quantity of latex additive increases. Temperature-dependent spectra were also registered, showing that by cooling down, the intensity of both emission peaks increases and, parallelly, the visible band shifts to the red, while the UV band shifts to the blue. Electron paramagnetic resonance (EPR) spectra, measured in order to understand the visible emission, showed for all the samples a $g=1.96$ signal, presumably attributable to oxygen vacancies, but its intensity does not correlate with the intensity of the PL visible band. Consequently, the green-yellow emission of our samples does not appear to originate from the transition between a singly charged oxygen vacancy and a photoexcited hole, as assumed by many authors. Finally, from the width of the EPR signal, relaxation times were estimated, being significantly different for hybrid samples and reference.

G-III.03 14:30

SUBSTRATE INDEPENDENT HYDROTHERMAL GROWTH OF ZnO NANOWIRE

A. Sugunan, Department of Microelectronics, Asian Institute of Technology, Thailand, C. Warm Singh, National Electronics and Computer Technology Center, Thailand, M. Boman Angstrom laboratory, Department of Material Chemistry, Uppsala University, Sweden and J. Dutta, Department of Microelectronics, Asian Institute of Technology, Thailand

Synthesis and characterization of nanostructured materials have been major areas of research in recent years. Since the room temperature lasing properties of highly aligned arrays of ZnO nanowires were reported, their synthesis has received great attention. These ZnO nanowires have promising applications in a wide range of fields including sensors, electronic and optoelectronic devices. The commercial potential for conventional synthetic techniques like metal-organic chemical vapor deposition, and vapor-liquid-solid epitaxy are constrained by the need for an insulating and/or expensive substrate necessary to obtain the proper growth orientation of the nanowires, and also the complexities and cost of the high temperature and vacuum systems. Recently reported wet chemical synthesis of ZnO nanowires involving a hydrothermal growth process at much lower temperatures alleviates these concerns.

We have synthesized highly uniform nanowires of ZnO with average diameter of 30 nm on glass substrates, which can be repeated on various types of substrates including Si[100] and ITO. Typically, the hydrothermal growth was carried out at 65 C for 6-12 hours. Based on a recent report, we have optimized the process to achieve a higher uniformity in the diameters of the grown nanowires, which is an essential requirement for their application in most optoelectronic devices such as field emitters for field emission display devices. Contrary to the previous report, the synthesized nanowires showed no signs of lateral growth upon prolonging the growth period. The relative ease in obtaining aligned nanowires of ZnO and the availability of a simple synthetic high yield production technique will make them a promising alternative for carbon nanotube based field emitters.

G-III.04 14:45

THE EPITAXIAL GROWTH OF ZNO FILM ON ZNO NANORODS

Soon-Hong Park(a), Sun-Hyo Kim(a), Sang-Wook Han(b), (a)Department of Material Science and Engineering, Pohang University of Science and Technology, Pohang 790-784, Korea, (b)Division of Science Education, Chonbuk National University, Jeonju 561-756, Korea

Well-aligned ZnO nanorods with diameter of ~80 nm were fabricated on sapphire [0001] substrates and consecutively covered with ZnO film by using a catalyst-free metal-organic vapor-phase epitaxy method. The structural and electric properties of the ZnO film/nanorods were characterized with x-ray diffraction (XRD), field-emission tunneling electron microscopy (TEM), field-emission scanning microscopy (SEM), atomic force microscopy (AFM) and photoluminescence (PL) measurements. The XRD measurements showed only {001} plane diffractions from the ZnO film/nanorods with no extra structural distortion, suggesting the ZnO film grown epitaxially on the ZnO nanorods. The TEM measurements showed that both ZnO film and nanorods were well-crystallized and that no structural disorder/distortion existed at the boundary of the film, in the film and in the nanorods, confirming the film epitaxially grown on the nanorods horizontally as well as vertically. The rms surface roughness of the film was estimated to be about 3.8 nm by the AFM measurements. The PL measurements of the ZnO film/nanorods at 10 K showed that the main bound state was split into two branches of 3.356 and 3.362 eV. The PL signals were dominantly contributed by the ZnO film at the top. The structures of the epitaxial ZnO film on the ZnO nanorods could be used in many practical applications.

G-III.05 15:00

EPITAXIAL GROWTH, OPTICAL, AND ELECTRICAL PROPERTIES OF ZNO NANOWIRE ARRAYS

H. J. Fan(a), W. Lee(a), B. Fuhrmann(b), A. Dadgar(c), F. Bertram(c), K. Nielsch(a), A. Krost(c), J. Christen(c), M. Zacharias(a) (a) Max Planck Institute of Microstructure Physics, Halle, Germany, (b) The Interdisciplinary Center of Materials Science, Martin-Luther-Universität Halle, Germany (c) Institute of Experimental Physics, Otto-von-Guericke-University Magdeburg, Germany

We report the successful fabrication of large-scale periodical arrays of ZnO nanowires by combining substrate nanopatterning and catalyst-directed epitaxial growth. First, ordered arrays of catalytic Au nanoparticles were obtained by thermal deposition through two types of shadow masks, viz., metal nanohole membranes and microsphere monolayers. Subsequent vapor-phase growth resulted in vertical-aligned and hexagonal-arranged ZnO nanowires on GaN/Si substrates. The single-crystallinity of the nanowires and epitaxial growth was verified by transmission electron microscopy investigations. A spatial luminescence mapping of the nanowire arrays was obtained by using scanning cathodoluminescence spectroscopy. The I-V property of individual ZnO nanowire, as well as the carrier transport through the n-ZnO/p-GaN heterojunctions was studied using a SEM-based nanomanipulator system.

G-III.06 15:15

PHOTOPHYSICAL PROCESSES IN HYBRID BULK HETEROJUNCTIONS OF ZnO NANOPARTICLES AND CONJUGATED POLYMERS

Pieter A.C. Quist(a), Waldo J.E. Beek(b), Martijn M. Wienk(b), René A.J. Janssen(b), Tom J. Savenije(a) and Laurens D.A. Siebbeles(a), (a)Opto-Electronic Materials Section, DelftChemTech, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands, (b)Molecular Materials and Nanosystems, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

The work of P.A.C. Quist forms part of the research program of the Dutch Polymer Institute. Recently, efficient hybrid solar cells based on spin-coated blends of ZnO nanoparticles and a conjugated polymer, were reported. In this work the photophysical processes in blends of ZnO nanoparticles with MDMO-PPV or P3HT were studied by means of microwave photoconductivity measurements. The blend films were excited with 3 ns laser pulses of varying intensity and wavelength (420-700 nm). Photo-excitation of the polymer was found to yield a photoconductivity, which is attributed to mobile electrons in ZnO produced by interfacial exciton dissociation. The photo action and attenuation spectra were found to exhibit a different wavelength dependence, in particular for P3HT. This is attributed to disturbed aggregation of polymer chains in direct vicinity of the ZnO nanoparticles. Increasing the weight fraction of ZnO from 0.33 to 0.83 leads to increased photoconductivity, due to the smaller distance excitons need to diffuse to reach a ZnO nanoparticle. Exposure of the samples to UV light leads to a tenfold increase of the photoconductivity lifetime. This is attributed to the filling of electron traps. The photoconductivity in annealed blends prepared from a ZnO-precursor was found to be comparable to that of the blends with ZnO nanoparticles after UV exposure.

G-III.07 15:30

COMPARISON OF TWO-STEP AND SINGLE-STEP GROWTH OF ZnO NANOWIRES USING THE VLS METHOD

Justyna Grabowska, Karuna Kar Nanda, Enda McGlynn, Martin O. Henry, Jean-Paul Mosnier, School of Physical Sciences / NCPST, Dublin City University, Glasnevin, Dublin 9, Ireland

The conventional vapour-liquid-solid (VLS) growth mechanism for ZnO nanorods involves a single step growth process at temperatures in the region of 900C. We compare this single step process with a two step procedure developed in our laboratory involving gold catalysed growth on a-plane sapphire where the growth is initiated by heating to a temperature of 760C, the sample is subsequently cooled to 350C and heated to 1125C, and held at this temperature for ~ 60 minutes. Both methods allow growth of vertically well-aligned nanowires, and our data show that the nanostructures grown by the two step process show excellent optical and structural properties compared to the material grown by the one step method. We have compared the effects of varying the gold layer thickness on the nanostructure morphology, and observe that a mixed nanowall/nanowire structure is observed in both methods. The structures have been studied using photoluminescence, x-ray diffraction and high resolution SEM. Control of the gold layer thickness and the temperatures in the two step process allows us to control this morphology and the relative nanowall / nanowire dominance. Our results indicate that the nanostructures grown have very good optical properties and may be suitable for efficient photonic devices, and that the two step process offers excellent control over the morphology of these nanostructures.

G-III.08 15:45

SELF-ASSEMBLED GROWTH ZNO NANOSTRUCTURES FOR FUTURE ELECTRICAL AND OPTOELECTRONIC APPLICATION

G.W. Ho(a), A.S.W Wong(b), S.N. Cha(c), D.J. Kang(a), M.E.Welland(a), (a)Nanoscience Centre, University of Cambridge, 11 J.J. Thomson Ave, Cambridge CB3 0FF, U.K., (b)Department of Materials Science and Metallurgy, University of Cambridge, New Museum Site, Pembroke Street, Cambridge CB2 3QZ, U.K., (c)Department of Engineering, University of Cambridge, Trumpington Street, Cambridge CB2 1PZ, U.K.

Control of size and dimensionality of nanostructure to tune its properties has already been shown, however to date no reports have demonstrated the ability to control both the dimensionality of the nanostructures and the assembly of the nanostructures into a highly ordered system. Here we report a vapor based approach to control the morphology in addition to the ability of self-assembling ZnO nanostructures into a metamorphosis of architectures. By observing the fundamental crystallographic design rules for the control of self-assembled integrated structures, we can now organize multi-dimensional building blocks into a hierarchical heterostructure arrays. Coaxing these ZnO nanostructures into self-assembling is an avenue that we are exploring since the traditional fabrication methods are limited in resolution. Unlike the artificially ordered system, such as the existing integrated circuits technology, self-assembled processes allow the creation of complex device architectures which depends solely on the intrinsic ability to organize itself into ordered system. Thus this method provides a promising route to integrate multi-dimension nanostructures into the future generation of complex nanodevices which would otherwise be very difficult to fabricate directly. Both electrical and optical properties can be derived from the as-grown ZnO nanostructures whereby the potential of fabricating transistor device can be realized with its well-defined linear I-V characteristics as well as feasibility of fabricating optoelectronic devices can be shown with the significant UV light emission.

16:00

BREAK

Session IV : Nano structures 2
Session chair : C. Klingshirn

G-IV.1 16:30 -Invited-

ELECTRICAL PROPERTIES OF ZnO THIN FILMS AND OPTICAL PROPERTIES OF ZnO-BASED NANOSTRUCTURES

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17:00-19:00

POSTER SESSION 1

POSTER SESSION 1
Tuesday, May 31, 2005
17:00 – 19:00

- G/PI.01** ZnO Nanorods GROWN FROM NITROGEN-DOPED ZnO FILM ON (111) Si SUBSTRATE BY THERMAL ANNEALING IN N₂ AMBIENT
Y.F. Mei, G.G. Siu, Ricky K.Y. Fu, and Paul K. Chu, Dept. of Physics & Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China, C.W. Lai, H.C. Ong, Department of Physics, The Chinese University of Hong Kong, Shatin, Hong Kong, China
Polycrystalline ZnO films were produced on (111) silicon substrate and doped with nitrogen using plasma immersion ion implantation. Using an annealing treatment in N₂ ambient, ZnO nanorods were grown on the surface of the N-doped ZnO films. The diameter of the ZnO nanorods varies from 50 to 100 nm whereas their length is about several hundred nanometers. In our cathodoluminescence (CL) studies, the ZnO nanorods exhibit different intensities and wavelengths in both the ultraviolet (UV) and visible bands compared to nitrogen-doped ZnO films. The growth mechanism and the change of CL are discussed in details.
- G/PI.02** CONTROL OF PROPERTIES AND STRUCTURE OF ZINC OXIDE THIN FILMS BY A WIDE VARIATION OF OXYGEN PRESSURE DURING REACTIVE MAGNETRON DEPOSITION AND BY POSTDEPOSITION ANNEALING
M. Vinnichenko(a,c), L. Poperenko(a), T. Lebyedyeva(b), P. Shpylovyi(b), N. Shevchenko(c), A. Rogozin(c), V. Sudovtsova(a), A. Kolitsch(c), (a)Kyiv National Taras Shevchenko University, 01033 Kyiv, Ukraine, (b)Glushkov Institute of Cybernetics, National Academy of Sciences of Ukraine, 03680 Kyiv, Ukraine, (c)Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf, 01314 Dresden, Germany
Due to recent progress in crystal growth and unique optical and electrical properties ZnO becomes a prospective material for use in optoelectronic devices. ZnO thin films have been prepared at unheated glass substrates by reactive DC magnetron sputtering. The oxygen fraction in Ar + O₂ gas mixture was varied from 0 to approximately 83%. The films have been characterized by spectroscopic ellipsometry (SE), atomic force microscopy (AFM) and X-ray diffraction (XRD). The dielectric function of ZnO layers was parameterized using Drude-Lorentz oscillator. As shown by SE, the dielectric functions of the films prepared at low oxygen fraction are characteristic for cermet materials (mixture of oxide and metal particles). XRD confirms the presence of both ZnO and metallic Zn phases in these films. The layers produced at high oxygen fractions (above 60%) are insulating and their dielectric functions can be reasonably described by Lorentz oscillator alone. Importantly, that the latter films are polycrystalline with pronounced (002) type texture even at a thickness of only 50 nm. The XRD results point to a high mechanical stress in these films that can be related to the bombardment by negative oxygen ions during the film growth.
ZnO films prepared at medium oxygen fraction of 48% were annealed in vacuum at about 340 °C for 1.5 hour with in situ control of optical properties by SE and resistivity by two point probe measurement. The influence of the structural ordering during annealing on the refractive index is higher than the free electron density variation. An enhancement of the film resistivity at the final annealing stage (last 40 min) with concomitant decrease of the free electron concentration could be an indication of the acceptor-like defect formation.
- G/PI.03** ZnO TETRAPOD FORMATION IN Zn - O SYSTEM
A.Kh. Abduev, A.K. Akhmedov, A.Sh. Asvarov Institute of physics, DSC of RAS, Yaragscogo str., 94 Makhachkala, Dagestan 367003, Russia
It is known, that nonequilibrium conditions of a scattering and a cooling of gas plasma leads to interactions of plasma components and the formation of clusters.
Our previous studies have shown that the interaction of zinc vapor and oxygen in a gas phase result in the step-by-step formation of clusters, fractal clusters and nanoparticles according to the Witten-Sander mechanism. Also it has been shown, that formation of whiskers at surplus of Zn vapour in gas phase proceeds on vapour-liquid-solid (VLS) mechanism. We believe that the liquid-forming agent was ZnO_{1-x} surface phase with low melting-point. In order to model the processes of cluster formation in a gas phase at a surplus of zinc vapour we carried out the effusion of zinc vapour in the oxygen atmosphere. There is the nucleation and the growth of ZnO tetrapods in a gas phase. The nucleus of such tetrapods cannot be a close-packed crystallite. Our speculating is that the nucleus of such aggregate should have tetragonal structure that leads to the further growth of four hexagonal whiskers. Hence, we suggest the following model of Zn₁₂O nucleus-cluster. The nucleus-cluster has the shape of the truncated tetrahedron with 12 atoms of zinc and one atom of oxygen in the center. Such nucleus-cluster is a loosely coupled system formed by an atom of oxygen and 12 equidistant atoms of zinc. At scattering of zinc vapor at increased partial pressure of oxygen, the nucleation and the growth of ZnO whiskers on four facets of the Zn₁₂O cluster occurs.
- G/PI.04** GROWTH MECHANISMS FOR ZnO NANORODS FORMED BY PULSED LASER DEPOSITION
Ye Sun, Gareth M. Fuge and M.N.R. Ashfold, School of Chemistry, University of Bristol, Bristol BS8 1TS, U.K.
Arrays of well-aligned ZnO nanorods have been grown on Si substrates at 600°C using a catalyst-free pulsed laser deposition (PLD) method, with and without pre-deposition of a thin ZnO layer at a lower substrate temperature. Deposited products were analyzed and characterized by scanning and transmission electron microscopy (SEM and TEM), electron dispersive X-ray analysis, X-ray diffraction and photoluminescence (PL) measurements. EM revealed that rods grown directly on Si exhibit needle-like morphologies, with diameters, d, typically in the range 20-60 nm, lengths ~200-800 nm and, in most cases, a capping particle of similar cross-section at the tip. HRTEM images show that these nanoparticles are ZnO also, suggesting that these derive from post-growth crystallisation of oxygen rich molten zinc droplets that cap the nanorods during growth. PLD of ZnO onto Si substrates that have been pre-coated with a thin ZnO film deposited at 300°C yields denser, more uniform arrays of longer (~1-1.2 µm), thinner (d ~6-20 nm) nanorods, without any obvious capping particle. This suggests that a ZnO buffer layer can play a useful role in providing a high density of nucleation sites for subsequent growth of smaller diameter nanorods. The respective product arrays are most readily understood in terms of vapor-liquid-solid (V-L-S) and vapor-solid (V-S) growth models, respectively. Comparative studies of the room temperature PL from the respective samples reveal much higher UV emission intensity from nanorod arrays grown on the ZnO pre-coated Si substrates.

- G/PI.05** STRUCTURE AND FERROMAGNETISM OF Mn ION IMPLANTED ZnO THIN FILMS ON SAPPHIRE
 G. Brauer, W. Anwand, and W. Skorupa, Institut für Ionenstrahlphysik und Materialforschung, Forschungszentrum Rossendorf, Postfach 510119, 01314 Dresden, Germany, and H. Schmidt, M. Diaconu, M. Lorenz, and M. Grundmann, Institut für Experimentelle Physik II, Fakultät für Physik und Geowissenschaften, Universität Leipzig, Linnestr. 5, 04103 Leipzig, Germany
 Nominally undoped ZnO films of about one micron thickness were grown by pulsed laser deposition on c-plane sapphire. A mean crystallite size of about 260 nm was estimated by atomic force microscopy. Doping was then achieved by implantation of 250 keV Mn⁺ ions at 300 °C with three different fluences 1E16, 3E16, and 6E16 cm⁻². The depth distribution of open volume damage, being always connected with ion implantation, was estimated by slow positron implantation spectroscopy (SPIS). Ferromagnetism (magnetic domains) could be detected by magnetic force microscopy (MFM) only at the film implanted with the lowest fluence.
 A subsequent thermal annealing of the films was performed at 500 °C and 750 °C for 30 min in air. Evolution of the open volume damage, its depth distribution, and the magnetic behavior was again investigated by SPIS and MFM, respectively. No indication of magnetic domains was found in any of the three films after the first annealing step, whereas after the second annealing step the two samples having the higher fluence showed magnetic domains.
- G/PI.06** SYNTHESIS OF ZnO NANOPARTICLES FROM POLYMER PRECURSOR CONTAINING CARBOXYL GROUP
 Guangqiang Lu, Ingo Lieberwirth, Gerhard Wegner, Max Planck Institute for Polymer Research, Ackermannweg 10, 55128, Mainz, Germany
 Zinc oxide is an important material used in a wide range of applications such as pigments, rubber additives, varistors, chemical sensors and luminescent devices due to its special chemical and microstructural properties. Various methods have been developed to produce high-quality zinc oxide with a small sized particle, narrow size distribution as well as a homogeneous morphology. The method of using polymer precursor offers a versatile way to prepare metal oxides. In this study, we report a simple procedure that achieves production of nanosized zinc oxide (about 40 nm in diameter) particles using polymers containing chelating (carboxyl) groups as precursors. The zinc poly(meth)acrylate complex was determined to have a hexacoordinated structure from UV, IR and Raman spectra. The setting-up of proper annealing conditions was accomplished with the aid of thermogravimetric analysis (TGA) data. The obtained zinc oxide was confirmed by X-ray diffraction and its morphological and optical properties were investigated as well.
- G/PI.07** CONTROL OF MORPHOLOGY OF ZnO NANORODS GROWN BY CHEMICAL VAPOR DEPOSITION WITH LASER ABLATION OF ZnO
 Takashi Hirate, Takashi Kimpara and Tomomasa Satoh, Kanagawa University, Japan
 We fabricated flat-topped ZnO nanorods oriented vertically to Si(111) substrate. The fabrication method is a low pressure thermal CVD combined with laser ablation of a sintered ZnO pellet. Metal Zn vapor and O₂ gas are used as precursors to synthesize ZnO and N₂ is used as carrier gas. The ZnO pellet is placed near a substrate in a deposition chamber and ablated by a pulsed Nd:YAG laser beam (10 shots/sec, 0.12 J/shot) during ZnO growth. We investigated the effects of O₂ flow rate on morphology of ZnO nanostructures in detail. The growth conditions are as follows. O₂ flow rate is 0.5 to 12 SCCM. The growth temperature is 530 C. The growth pressure is 67 Pa. The growth time is 15 min.
 When the O₂ flow rate is 0.5 SCCM, non-uniform ZnO whiskers with diameter of a few nanometers to several tens nanometers are grown in random direction. The averaged length is about 2.5 μm. When the O₂ flow rate is in a range from 1.0 SCCM to 1.4 SCCM, however, flat-topped ZnO nanorods with about 40 nm diameter and 2.5 μm length are grown vertically. In this region of O₂ flow rate, morphology of ZnO nanorods is not so dependent on the O₂ flow rate. When the O₂ flow rate is larger than 1.4 SCCM, a growth rate in lateral (a-axis) direction of ZnO nanorod becomes higher with increasing O₂ flow rate and that in axial (c-axis) direction becomes slower. When the O₂ flow rate is 3 SCCM, the dispersions of diameter and length of ZnO nanorods become larger and the averaged length is 0.65μm. When the O₂ flow rate is 12 SCCM, almost continuous ZnO layer is grown. We consider that the ratio of growth rate in c-axis direction to that in a-axis is very sensitive to O₂ flow rate. When the O₂ flow rate is small, the ratio is very large and decreases with increasing O₂ flow rate.
- G/PI.08** NON-EQUILIBRIUM DEFECTS FORMED IN ZNO AND (Zn,Mg)O FILMS STUDIED BY SOLID STATE DIFFUSION
 Naoki Ohashi(a), Haruki Ryoken(a,b), Isao Sakaguchi(a), Shunichi Hishita(a) and Hajime Haneda(a,b), (a)National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044 Japan, (b)Department of Applied Science for Electronics & Materials, Kyushu University, 6-1 Kasuga Koen, Kasuga, Fukuoka 816-8580, Japan
 We investigated defect structures in ZnO and (Zn,Mg)O films to reveal nature of non-equilibrium defects formed in ZnO and (Zn,Mg)O thin films. In order to characterize defects in ZnO thin films, we applied solid state diffusion study for detection and semi-quantitative analyses of defect concentration. The diffusion coefficients of the films were evaluated by means of tracer diffusion method using secondary ion mass spectrometer. As a result, presence of compensated meta-stable defects was detected. For example, diffusion coefficient of both oxygen and cation in (Zn,Mg)O film with high Mg concentration was much higher than those of undoped ZnO films, while electron concentration in those films were nearly the same in spite of different Mg concentration. Since the diffusion coefficient is proportional to the concentration of defects, the result means that (Zn,Mg)O alloy film contains compensated defects. The compensated defects in (Zn,Mg)O were assigned to meta-stable defects, which were introduced when the Mg concentration of the film exceeded the solubility limit defined under equilibrium conditions.
- G/PI.09** PIEZOELECTRIC CHARACTERISTICS OF ZnO FILMS GROWN BY PULSED LASER DEPOSITION FOR FILMS BULK ACOUSTIC
 Gun Hee Kim, Hong Seong Kang, Sung Hoon Lim and Sang Yeol Lee, Department of Electrical and Electronic Engineering, Yonsei University, 134, Shinchon-dong, Seodaemoon-ku, 120-749, Seoul, Korea
 The piezoelectric properties of ZnO films are reported depending on different deposition conditions. The ZnO films have been deposited on Au films evaporated on p-type (100) silicon substrate by pulsed laser deposition (PLD) technique using a Nd:YAG laser. We have investigated surface morphology, orientation toward the c-axis, resistivity, and electromechanical coupling coefficient of ZnO films for films bulk acoustic resonator. These results show the possibility of FBAR devices using by PLD.

G/PI.10**ZnO NANOSTRUCTURES FORMED BY OFF-AXIS PULSED LASER DEPOSITION**

Jong Hoon Kim, Hong Seong Kang, Kyung Ah Jeon, and Sang Yeol Lee, Department of Electrical and Electronic Engineering, Yonsei University, 134 Shinchondong, Seodaemunku, Seoul, 120-749, Korea

ZnO nanostructures were formed on a Si substrate by using an off-axis pulsed laser deposition (PLD) system in which a substrate plane was tilted to the plume propagation direction. Atomic force microscopy (AFM) showed the island structures of 20~40 nm in width and the average height of 3 nm. An X-ray diffraction (XRD) patterns exhibited only the ZnO (002) peak and this indicated that the island structures observed in AFM images were well crystallized. Expansion of optical bandgap from 3.26 to 3.35 or 3.47 eV was observed at room temperature and from 3.37 to 3.46 or 3.57 at 13 K by photoluminescence (PL), which results from the quantum confinement effect of the ZnO nanostructures.

G/PI.11**PROPERTIES OF ZnO FILMS GROWN BY CLOSE SPACED VAPOUR TRANSPORT (CSVT) ON SAPPHIRE SUBSTRATE**

J.F. Rommeluère, M. Barbe, F. Jomard, A. Tromson-Carli, Y. Marfaing and P. Galtier, Laboratoire de Physique des Solides et de Cristallogénèse, CNRS, 1 Place Aristide Briand, 92195 Meudon Cedex, France and J. Mimila-Arroyo, Cinvestav-IPN, Mexico D.F., Mexico

We present first a study of the growth of ZnO films deposited by CSVT on C and R sapphire substrates. H₂ and N₂ were used as transport agent. The deposition on R oriented sapphire substrates give rise to a-(11-20) oriented ZnO films. Under optimised conditions, flat surfaces can be achieved and rocking curves with full half width below 500 arsec can be achieved.

Then we report on the electrical activity of ZnO films grown on sapphire substrate. The n type conductivity of the epitaxially deposited films has been studied for thicknesses ranging from 0.1 to 60µm. The carrier concentration, measured by Hall effect, is found to decrease linearly with the film thickness. This result is explained by the dominant contribution of an interface layer to the measured conductivity in relation with Al diffusion from the substrate as demonstrated by Secondary Ion Mass Spectrometry (SIMS). We show that this strong interface conductivity can be compensated on thin films using thermal annealing under oxygen atmosphere at 850°C. Under these conditions, n-carrier concentration in the 10¹⁴cm⁻³ range can be achieved. Furthermore, the effect of this annealing under oxygen is found to be completely reversible after a further thermal annealing under argon atmosphere at the same temperature. The creation of complexes formed by an Al donor and a Zn vacancie (p-type) whose creation is favoured by oxygen annealing is proposed to explain our results. The low level of carriers achieved after oxygen annealing suggests that the compensation phenomenon observed with Al can is also effective for other n-dopants. We conclude that any attempt to achieve and measure p-type doping on ZnO thin films is conditioned by the use of an alternative substrate to sapphire.

G/PI.12**OBTAINING OF P-TYPE ZNO SAMPLES IMPLANTED BY P+ IONS**

L.T. Trapaidze, T.V. Butkhuzi, T.G. Khulordava, M.M. Sharvashidze, E.E. Kekelidze, L.G. Aptsiauri, D.N. Peikrisvili, G.G. Natsvlshvili, Dept. of Physics, Tbilisi State University, 3 Chavchavadze Avenue, 0128 Tbilisi, Georgia

In order to obtain conductivity type inversion in wide band gap II-VI compounds, the low temperature ion implantation by group V elements could be used. In II-VI binary compounds group V elements, such as phosphorus and nitrogen act as amphoteric. The ion implantation of ZnO crystals by P⁺ ions was carried out. P⁺ ions were implanted in ZnO n-type samples (n⁺10²-10³ Wcm) at E=150 keV energy and at the dose of implantation D=10¹⁴ to 10¹⁶ cm⁻². The range of current density was j=0.3 to 3 mA/cm². Then implanted ZnO samples were treated by Radical Beam Quasi Epitaxy (RBQE) method in oxygen radicals [1]. Mentioned quasiepitaxial method differs from the known gaseous-phase epitaxial method in that, to form new layers, one component (the non-metal) comes from the gaseous phase and the other (the metal) comes from the crystal volume. ZnO quasiepitaxial layers have obtained by RBQE on the previously implanted by P⁺ ions surfaces of ZnO monocrystals.

In the atmosphere of oxygen singlet radicals the treatment of implanted ZnO basic crystals are possible in the temperature range of 300 to 1100 K. Thermal duration was 45 min to 2 hours. Concentration of oxygen singlet radicals was 10¹⁴-5*10¹⁵cm⁻³. Electrical and optical properties of new ZnO layers as well as ZnO basic monocrystals implanted by P⁺ ions have been studied. We have obtained p-type ZnO (n⁺10⁻¹⁰³ Wcm) quasiepitaxial layers at T=300-450°C temperatures. Such treatment temperatures are connected with phosphorus amphoteric nature. In photoluminescence spectra of p-type ZnO samples the centers responsible for emission bands are identified.

[1] Butkhuzi T.V., Georgobiani A.N., Khulordava T.G., Tsekvava B.E., Jashiashvili D.L., "Exciton Photoluminescence of Hexagonal ZnO", Phys. Rev. B Vol. 58, #16, p.10692, 1998

G/PI.13**EFFECTS OF LASER ABLATION IN FABRICATION OF ZNO NANORODS BY CHEMICAL VAPOR DEPOSITION**

Hiroshi Miyashita, Tomomasa Satoh and Takashi Hirate, Kanagawa University, Japan

We studied on a role of laser ablation in fabrication of ZnO nanorods by chemical vapor deposition (CVD) combined with laser ablation of Mn. Metal Zn vapor and O₂ gas are used as precursors to synthesize ZnO and N₂ is used as carrier gas. The Mn pellet is placed near a Si(111) substrate in a deposition chamber and ablated by a pulsed Nd:YAG laser beam (10 shots/sec, 0.04 J/shot) for a certain period during ZnO growth. In this study, both the laser ablation and CVD were initiated at the same time, but the laser ablation was terminated before the completion of CVD for 15 min. The growth conditions are as follows. The growth temperature is 550 °C. The growth pressure is 27 Pa. O₂ flow rate is 1.5 SCCM.

When no laser ablation was performed, a mixture of ZnO whiskers, nanosheets and nanocombs randomly oriented was sparsely grown with averaged layer thickness of 2 µm. When laser ablation was performed for only 3 sec, however, flat-topped ZnO nanorods with about 90 nm diameter were grown. But the growth directions of nanorods are randomly distributed with the layer thickness of 2.7 µm. When the laser ablation period was 5 sec, the growth direction of nanorods was approximately vertical to the substrate and the length was about 4 µm. When the laser ablation period was 15 sec the growth direction was improved. For longer laser ablation period, the growth direction was well aligned, and the length decreased slightly and the size increased with increasing laser ablation period. We consider that a laser ablated species take any role as nucleus for growth of nanorods at its very initial stage and to orient the growth direction to the vertical direction at the next stage. Then it takes a role to control the growth rates of a- and c-axis of nanorods.

- G/PI.14** ELECTRONIC PROPERTIES OF ZNO SURFACES IN DEPENDENCE ON THE DEPOSITION PARAMETERS
 Frank Säuberlich(a), Christoph Körber(a), Juan Angel Sans(b), Andreas Klein(1), (a)Surface Science Division, Institute of Materials Science, Darmstadt University of Technology, Petersenstr. 23, 64287 Darmstadt, Germany, (b)Institut de Ciència dels Materials, Departament de Física Aplicada, Universitat de València, Ed. Investigació, 46100 Burjassot, Spain
 Surfaces of the transparent conducting oxide (TCO) zinc oxide (ZnO) are investigated with X-ray photoelectron spectroscopy (XPS) and UV photoelectron spectroscopy (UPS) to observe the electronic and chemical properties of the prepared thin zinc oxide films. These films are deposited by magnetron sputtering in an ultra high vacuum analysis and preparation system (DAISY-MAT) which allows in-situ XPS and UPS analysis. We have varied sputtering pressure, oxygen partial pressure, sample temperature, sample-target distance and plasma power densities with DC or RF excitation. Intrinsic ZnO (i-ZnO) and aluminium-doped ZnO (ZnO:Al, 2 wt-%) targets were used. Those parameters, which mainly affect the deposition rate of the thin film do not have a major impact on the electronic properties. The surface Fermi level is mainly affected by the oxygen partial pressure.
- G/PI.15** BRILLOUIN LIGHT SCATTERING CHARACTERIZATION OF THE ACOUSTIC WAVES VELOCITY IN ZNO/SI3N4/SI(100) SYSTEM
 E. Céspedes, R. J. Jiménez-Riobó, M. Vila and C. Prieto. Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas. Cantoblanco, 28049 Madrid, Spain
 Thin film semiconductor piezoelectric materials, as ZnO, are potential candidates to be used in surface acoustic wave (SAW) radio-frequency devices. These materials show some advantages over those usually employed in SAW technology, namely, the integration with signal amplifiers and therefore size and consumption reduction. Due to the importance of the SAW propagation velocity on these devices, it is essential to have a method to determine its value and its possible variation inside the film plane. We study the behaviour of the surface acoustic waves by Brillouin Light Scattering Spectroscopy in order to determine the influence of a high elastic constants substrate (or buffer-layer) on the SAW phase velocity in ZnO thin films. Buffer-layers of Si3N4 have been deposited on Si(100) by reactive magnetron sputtering in order to prepare a layer with high SAW velocity. ZnO thin films of different thickness have been deposited on top of the Si3N4/Si(100) system using the same deposition technique. Results are discussed in terms of theoretical studies, which predict an increase of the acoustic waves phase velocity when a hard buffer-layer is present.
- G/PI.16** ZnO SINGLE CRYSTALS AND EPITAXIAL THIN FILMS STUDIED BY SECOND HARMONIC GENERATION AND PHOTOLUMINESCENCE
 G. Buinitskaya, L. Kulyuk, V.Mirovitskiy, E. Rusu, Institute of Applied Physics, Academy str. 5, Kishinev, MD-2028, Moldova; E. Mishina, N. Sherstyuk, Moscow State Institute of Radioengineering, Electronics and Automation, prosp. Vernadskogo 78, Moscow 117454, Russia
 Zinc oxide provides very efficient harmonic generation and excitonic luminescence in UV range. Additionally harmonic generation can be used as the measure of crystallinity. Here we report the results of a comparative study of ZnO single crystals and epitaxial thin films on a sapphire substrate by second harmonic generation (SHG) and photoluminescence (PL). Bulk crystals were grown by a gas transport reaction technique, the film of 100nm was fabricated by a modified chemical vapor deposition method. The film as confirmed by AFM consists of 20-30nm grains. SHG studies show that in the film the values of nonlinear susceptibility tensor equal to the ones of the single crystal, the symmetry analysis of SHG characteristics reveals the textured structure with nanocrystallines misaligned from the exact (110) orientation by 1.5 degrees. PL studies reveal strong excitonic radiation in the crystal in the range of 3.2 - 3.4eV. In the film excitonic luminescence is sufficiently suppressed in comparison of defects (impurities) PL signal. The reason for a strong defect-induced PL may be due to contribution from the inter-grain interfaces, the relative are of which is quite high in nanograin material. SHG and PL techniques are complementary in these studies probing mostly bulk and interface properties respectively.
- G/PI.17** k.P ENERGY-BAND PROPERTIES OF ZnO/Zn1-xMgxO QUANTUM WELL HETEROSTRUCTURES
 K. Zitouni and A. Kadri, Laboratoire d'Etude des Matériaux Optoélectronique & Polymères (L.E.M.O.P.), Department of Physics, University of Oran (Es-Senia), Oran 31100, Algeria, P. Lefebvre and B. Gil, Groupe d'Etudes des Semiconducteurs (G.E.S.) UMR-CNRS N°5650, Université de Montpellier II, 34095 Montpellier Cedex 5, France
 The ZnO/MgO system is attractive in various electronic and optoelectronic applications [1]. In order to determine various ZnO/MgO based devices parameters and performances, it is necessary to study first its band parameters, and mainly, those related to the valence band.
 In this work, we use a Luttinger-type effective mass 6x6 Rashba-Sheka-Pikus [2] model to describe the valence band of Würtzite ZnO/Zn1-xMgxO Quantum Well Heterostructures (QWH) with x<0.40. By using the k.P parameters given by Lambrecht et al.[3], we first compute the valence band energy dispersions of bulk ZnO, and we find good agreement with both of their k.P and ASA-LMPTO results. Then we compute the valence subband dispersions and confinement energies in ZnO/Zn1-xMgxO QWH at various x<0.40, and well widths. Good agreement is found with the pump-probe PL results of Chia et al. [4]. The peak energies of linear absorption for various QWH are closely fitted by using the band parameters of ref. [3] and a conduction band/valence band offset ratio=9/1 as given in ref.4.
 [1] Th.Grubler et al., Appl. Phys. Letters 84(26), 5359 (2004)
 [2] E.I.Rashba et al., Fiz.Tverd.Tela 1,407 (1959), Fiz.Tverd.Tela (special vol.), 162 (1959)
 [3] W.R.L. Lambrecht et al. Phys. Rev.B65, 75207, (2002)
 [4] C.H Chia et al., Appl. Phys. Letters 82 (12), 1848 (2003)

- G/PI.18** **MICROSCOPIC PHOTOLUMINESCENCE SPECTRA OF ZnO NANOCRYSTALS IN SiO₂ FILMS**
 A. Yamamoto, Y. Satake, Y. Taguchi, Graduate School of Materials Science, Nara Institute of Science and Technology, Takayama 8916-5, Ikoma, Nara 630-0192, Japan and Y. Kanemitsu, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan
 There are few reports on optical properties of ZnO nanocrystals at low temperatures, though the researches on ZnO nanostructures have been carried out extensively. In order to study excitonic properties of ZnO nanocrystals, it is essentially important to measure their optical properties at low temperatures. We dispersed ZnO nanocrystals into glass films and measured absorption and photoluminescence (PL) spectra at low temperatures. Three PL peaks were observed at ~3.37 (B1), ~3.33 (B2), and ~3.27 (B3) eV. The B1 line is due to the neutral donor bound exciton, while the origin of the B2 and B3 lines are controversial up to now. When the nanocrystal density in the film decreases, B2 and B3 lines disappear and only B1 line remains. This result suggests that B2 and B3 lines are not the intrinsic PL from the individually separated nanocrystals. We measured microscopic PL spectra and found that the PL intensity ratios of the three PL peaks strongly depend on the sample position. Furthermore, new PL peak due to the free exciton emerges at some positions of the microscopic PL spectra. This new PL peak was not resolved in macroscopic PL spectra, and was able to be observed only in microscopic PL spectra. We also measured time-resolved PL spectra, and the origin of the B2 and B3 lines is discussed.
- G/PI.19** **EVALUATION OF THE FINE STRUCTURES OF ISOLATED ZNO NANOROD SINGLE-QUANTUM-WELL STRUCTURES USING NEAR-FIELD SPECTROSCOPY**
 T. Yatsui(a), M. Ohtsu(a,b), J. Yoo(c), S.J. An(c), and G.-C. Yi(c), (a)JST, Tokyo, 194-0004 Japan, (b)Univ. of Tokyo, Tokyo 113-8656, Japan, (c)National CRI Center for Semiconductor Nanorods and POSTECH, Gyeongbuk 790-784, Korea
 ZnO nanocrystallites are promising material for realizing nanometer-scale photonic devices, i.e., nanophotonic devices, at room temperature, owing to their large exciton binding energy and large oscillator strength. Furthermore, the recent demonstration of semiconductor nanorod quantum-well structure enables us to fabricate nanometer-scale electronic and photonic devices on single nanorods. Recently, ZnO/ZnMgO nanorod single-quantum-well structures (SQWs) were fabricated and the quantum confinement effect of the SQWs was successfully observed. To confirm the promising optical properties of individual ZnO/ZnMgO SQWs for realizing nanometer-scale photonic devices, we performed low-temperature near-field spectroscopy of isolated ZnO nanorod SQWs.
 First, the high quality of our crystalline sample was confirmed using the absorption spectra of isolated ZnO SQWs and the small Stokes shift. Furthermore, we performed polarization spectroscopy of isolated ZnO SQWs, and observed valence-band anisotropy of ZnO SQWs in photoluminescence spectra directly for the first time. Since the exciton in a quantum structure is an ideal two-level system with long coherence times, our results provide criteria for designing nanophotonic devices.
- G/PI.20** **INCORPORATION OF DOPANTS INTO THE LATTICE OF ZNO NANOPARTICLES TO CONTROL PHOTOACTIVITY**
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 Nanoparticulate oxides such as ZnO and TiO₂ are increasingly being used as pigments and UV absorbers in personal care products such as sunscreens, coatings and paints, predominantly because their absorbance efficiency increases with decreasing particle size. However, TiO₂ and ZnO can also function as photocatalysts. One approach to quenching photoactivity is alteration of the band gap by the inclusion of metal ion dopants into the lattice. To this end we prepared a series of doped and undoped ZnO nanopowders and tested their photoactivity on exposure to UV via a chemical method based on the photobleaching behaviour of the stable radical, 1,1-diphenyl-2-picrylhydrazyl (DPPH). For undoped ZnO, it was observed that the photoactivity significantly increased with decreasing crystallite size (>100 nm to 20 nm). For doped ZnO, it was seen that depending on the type and level of the dopant, the photoactivity could be reduced by an order of magnitude. In order to try to understand the effect of the dopants and their location in the nanoparticle lattice, a new variant of the method of atom location by channelling-enhanced microanalysis (ALCHEMI) was used to distinguish between sub 1 atom % dopants exclusively accommodated on cation sublattice sites or as a foreign phase on the surface.
- G/PI.21** **STRUCTURAL, OPTICAL, AND ELECTRICAL PROPERTIES OF HETEROSTRUCTURED n-ZnO/p-GaN THIN FILMS**
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 Although ZnO has several advantages over GaN, the devices using ZnO have not been accomplished due to the lack of reproducibilities for forming the p-type ZnO thin films. In order to overcome this problem, recently, ZnO/GaN heterostructures have been demonstrated because ZnO and GaN have similar characteristics in physical properties. However, the interpretations on physical properties of ZnO/GaN heterostructures are not fully understood. Therefore, we have investigated the growth of n-ZnO/p-GaN heterostructures and their physical properties. The p-GaN layers were grown on Al₂O₃ (0001) by MOCVD, and then the unintentionally-doped n-ZnO thin films were grown at 600 °C; on p-GaN layers by r.f. magnetron sputtering. From the result of x-ray diffraction measurements, the separated peaks of ZnO (0002) and GaN (0002) were observed for 2θ = 26.6° and 28.4°; scans. These results indicate that the heterostructured n-ZnO/p-GaN thin films have sharp interface without distortions. The heterostructured films showed the peaks at 376, 385, and 415 nm for the measurements of cathodoluminescence at 77K. The peaks at 385 nm and 376 nm are attributed to near-band-edge emission of ZnO and near-band-edge emission of GaN, respectively. The peak at 415 nm is originated from acceptor-related emission of GaN. From the measurements of current-voltage relationships for n-ZnO/p-GaN heterojunction diodes, the rectifying behavior was clearly observed. Using analysis of diode characteristics, the turn-on voltage and the breakdown voltage are determined to be 2.13 V and -14.5 V, respectively. In addition, the n-ZnO/p-GaN heterojunction diode showed clearly the improved current confinement, which can lead to higher recombination and improved device efficiency.

- G/PI.22** EPITAXIAL GROWTH OF ZnO THIN FILMS BY MOCVD
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 High quality ZnO crystal films on sapphire(0001)or substrates were grown by metal organic chemical(MOCVD) method. The crystal structures were measured by high resolution X-ray diffraction (HRXRD). XRD θ-rocking curve for (0002) reflection peak showed a full width at half maximum (FWHM) value as narrow as 0.25 \circ . Furthermore, XRD φscan measurements were performed, with the sample rotated on c-axis of ZnO by monitoring the asymmetric reflection of . The reflections of 6-fold symmetric patterns were clearly observed indicating that the ZnO films were epitaxially grown. Based on the experience of growing high quality ZnO crystal films, p-type N-doping in ZnO was attempted with N atom activated by a RF source using MOCVD technology, and the obtained ZnO films crystallized well and showed p-type conduction with good electrical properties.
- G/PI.23** ATOMIC LAYER GROWTH OF ZnO THIN FILMS ON VARIOUS SUBSTRATES
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 In order to investigate the influence of the substrate on the atomic layer growth of ZnO thin films, various substrates such as glass, c-plane sapphire and ZnO substrates were used. Diethylzinc (DEZ) and H₂O were used as Zn and O precursors, respectively, and these precursors were alternately introduced into the growth chamber. It was found that the atomic layer growth was achieved at the substrate temperatures ranging from 175 to 250 ℃. The surface roughness of ZnO thin films grown on sapphire and ZnO substrates were improved compared with those on glass substrates. Both the (0 0 0 2) and (1 0 -1 1) orientations were observed at low substrate temperatures, while only the (0 0 0 2) orientation was observed at high substrate temperatures. The critical substrate temperature at which (0 0 0 2) orientation became dominant was decreased by using sapphire and ZnO substrates instead of glass substrates. ZnO thin films grown on sapphire substrates showed higher resistivity than those on glass substrates at the substrate temperatures ranging from 125 to 300°C, and the resistivity of ZnO thin film grown at 200°C on sapphire substrate was more than 100 Ωcm. The results of Raman spectroscopy and photoluminescence (PL) measurements will be presented at the symposium.
- G/PI.24** IMPROVED ELECTRICAL PROPERTIES OF ZnO:Al TRANSPARENT CONDUCTING OXIDE FILMS USING A SUBSTRATE BIAS
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 ZnO is an n-type II-VI semiconductor with a wide band gap of approximately 3.3eV at room temperature. Group III donor elements, such as Al, B, and Ga, were added to improve electrical properties of ZnO film. Aluminium doped zinc oxide (ZnO:Al) films were deposited on glass substrate by DC magnetron sputtering from a ZnO target mixed with a various wt% Al₂O₃. The lowest resistivity of 8.54X10⁻⁴ Ωcm as well as over 90% of optical transmission of the ZnO:Al film was obtained with 2 wt% Al₂O₃ doped ZnO target for the following processing conditions: substrate temperature of 400°C; discharge power of 40W; Ar pressure of 1 mtorr. The optical transmission is comparable to an ITO film. However the electrical resistivity of 8.54X10⁻⁴Ωcm is much higher. In order to reduce the electrical resistivity, positive and negative biases (-60V~+40V) were applied to the substrate. The substrate biases can attract ions and electrons to bombard the growing films. These bombardments provide additional energy to the growing ZnO:Al film on the substrate, resulting in significant variation in film structure and electrical properties. We report the effects of substrate bias on the structure, deposition rate, electrical properties, and optical transmission of ZnO:Al thin films. Films deposited with either positive or negative bias have strong (002) preferred orientation. Electrical resistivity of the film decreases significantly as either the positive or negative bias increases. However, as the positive and the negative bias increases over 30 V and -40 V, the resistivity decreases. The film with electrical resistivity as low as 4.3X10⁻⁴ Ωcm and optical transmittance of 91.5% were obtained with a substrate bias of +30 V.
- G/PI.25** ZINC OXIDE NANODOTS ON SILICON
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 Self assembled ZnO nanodots are grown by electron beam evaporation of Zn on thermally oxidized silicon substrates and subsequent annealing in oxygen. Characterization by TEM and EELS shows that the quantum dots are indeed zinc oxide single crystals grown with their c-axis perpendicular to the substrate; their distribution and size depends on the deposition parameters of zinc onto the substrates.
- G/PI.26** EFFECTS OF N DOPING ON MAGNETIC PROPERTIES OF (Zn,Mn)O THIN FILMS DEPOSITED BY RF MAGNETRON SPUTTERING
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 Ferromagnetic p-type (Zn,Mn)O has been predicted to have a Curie temperature higher than room temperature. Recently, nitrogen has been reported as a promising p-type dopant for ZnO as well as mitigating ferromagnetism if co-doped with Mn. In this vein, we investigated the effect of N-doping on the magnetic properties of (Zn,Mn)O thin films. N-doped (Zn,Mn)O thin films were prepared by RF magnetron sputtering with different N-doping levels using c-plane sapphire substrates. A 2 mm-thick GaN thin film grown by a metalorganic chemical vapor deposition system was employed as a buffer layer to grow high quality N-doped (Zn,Mn)O thin films. Superconducting quantum interference device (SQUID) magnetometer measurements revealed an obvious room temperature magnetic hysteresis of N-doped (Zn,Mn)O with a coercive field of ~ 80 Oe. The effects of N-doping on the Mn incorporation, structural, optical, and magnetic properties of (Zn,Mn)O thin films through analyses by high resolution X-ray diffraction, optical absorption, SQUID, and transmission electron microscopy measurements, will be discussed. The possible origins of the observed ferromagnetic room temperature hysteresis of N-doped (Zn,Mn)O thin films will be also discussed.

- G/PI.27** INFLUENCE OF GAS AMBIENT ON THE GROWTH AND ACTIVATION OF PHOSPHORUS DOPED P-TYPE ZnO
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 Phosphorus (P)-doped p-type ZnO thin films have been grown on a c-plane sapphire substrate using an undoped ZnO as a buffer layer under the different Ar/O₂ sputtering gas ratios by radio frequency (RF) magnetron sputtering. It was found that properties of P-doped ZnO thin films significantly depend on the Ar/O₂ sputtering gas ratios. As the O₂ partial pressure increases, the morphology of P-doped ZnO was changed from columnar structure to dense flat thin film structure. P-doped ZnO thin films grown under the Ar/O₂ gas ratio of 1:3 showed p-type characteristics after RTA activation process. In the activation process, the hole concentration of p-type ZnO under O₂ rich condition showed low hole concentration (2.01×10^{17} at 850 °C) compared to those annealed under N₂ (8.33×10^{18} at 850 °C) and/or Ar (6.49×10^{18} at 850 °C) rich condition. The role of oxygen gas on the growth of P-doped ZnO and the thermal activation process will be further discussed in this work.
- G/PI.28** TYPE CONVERSION OF ZnO THIN LAYERS GROWN BY PULSED LASER DEPOSITION
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 ZnO has attractive characteristic features, such as a large band gap of 3.37 eV, low power threshold for optical pumping at room temperature, and highly efficient UV emission resulting from a large exciton binding energy of 60 meV at room temperature. Thus, ZnO is of potential importance for its application for light emitting diodes (LEDs), laser diodes (LDs) and ultra-violet (UV) photodetectors. To realize such devices, the growth of high-quality p-type ZnO is essential. Fabrication of ZnO-based optoelectronic devices, however, is still extremely difficult to achieve, because of self-compensation effect and more importantly difficulty in obtaining high quality p-type materials.
 We have investigated on the growth of undoped p-type ZnO films on Si(111) substrates by pulsed laser deposition. Hall effect measurements show that the undoped ZnO films change from n-type to p-type material at oxygen pressures of 3×10^{-4} and 5.6×10^{-3} Torr. Ti/Au contacts produce ohmic behaviour to n-type ZnO, but leaky Schottky behaviour to p-type ZnO. Photoluminescence results measured at 50 K indicate that oxygen and zinc vacancies could play an important role in producing the particular type of the conductivity of the undoped ZnO films.
- G/PI.29** PREPARATION OF ZnO/ RARE EARTH HYDROXIDE COMPOSITE THIN FILMS BY AN ELECTROCHEMICAL METHOD
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 It is well-known that high quality zinc oxide can be prepared by electrodeposition. The method is based on the fine tailoring of the electrode surface pH and direct oxide precipitation as a film. This behaviour can be simply predicted by calculating the solubility curves of the different oxide and hydroxide compounds involved. We have calculated the solubility plot of ZnO, Eu(OH)₃, Er(OH)₃ and Er₂O₃, at 70 °C (the classical experimental deposition temperature of ZnO) by using recent reliable thermochemical data and with the help of the HSC Chemistry 5.1 software. We have defined different concentration regions in the diagrams in which the coprecipitation of zinc and rare earth element could be predicted. The co-precipitation process has been subsequently checked experimentally. By adjusting the ion balance between Zn²⁺ and RE³⁺ in the deposition bath we have demonstrated that the RE film content could be tuned over a large concentration range. In the case of Er(III), increasing its concentration in solution at fixed Zn(II) lead to more dispersed ZnO crystallite on the substrate surface whereas a thin passivating layer is formed, Zn and Er rich. On gold surface, we have shown that pure compound with Er₂O₃ stoichiometry can be grown in the absence of Zn(II). In the case of Eu(III) in similar deposition conditions, a singular composite structure was observed : hexagonal ZnO crystallites in the submicrometer range were dispersed in a matrix made of amorphous Eu(OH)₃. The fraction of amorphous europium hydroxide increases with Eu³⁺ content in the deposition bath. Experiments are in progress to characterize the luminescence properties of these different films
- G/PI.30** IMPROVEMENT OF CRYSTALLINITY OF ZnO THIN FILM AND FREQUENCY CHARACTERISTICS OF FILM BULK ACOUSTIC WAVE RESONATOR BY DIFFERENT BUFFER LAYER THICKNESSES
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 In order to improve the crystallinity of ZnO thin film, we investigated Pt buffer layer between ZnO and Al film due to showing good resonant frequency characteristics by these improvement in the film bulk acoustic wave resonator (FBAR) and the buffer layer thicknesses were varied from 5 to 50 nm. To confirm the interface of ZnO/Pt/Al thin film by changing the thicknesses, field emission scanning electron microscopy (FE-SEM) was employed. Also we utilized full width half maximum (FWHM) to verify the good crystallinity using x-ray diffraction (XRD), atomic force microscopy (AFM) for checking the microstructure and surface roughness of Pt and ZnO thin film, respectively. In addition, we finally manufactured the membrane resonator, calculated the effective electromechanical coupling coefficient ($k_{t\text{eff}}$) using network analyzer and confirmed the resonant frequency properties of single resonator with ZnO thin film which has good crystalline as a function of Pt buffer layer thicknesses.

- G/PI.31** NOVEL COMPOSITES OF POLYMER/OXIDES/CARBON-BLACK AS ROOM TEMPERATURE GAS SENSORS
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Novel composites of polymer/oxides/carbon-black were prepared to act as gas sensing materials by chemical reaction between two or more oxides at high temperature. X-ray diffraction was used to determine the final composition of the materials. This paper investigates the use of thick film gas sensors based on ZnO and TiO₂ to detect propanol and toluene at room temperature. ZnO and TiO₂ were mixed in various proportions and wet-ball milled in alcohol for 24h, dried at 120°C, then pressed at 2 tons, fired at 1250°C at a rate of 5°C/min in the air for 5h, followed by cooling at a rate of 3°C/min. The solid lump was mechanically broken up and ground down to a powder using a Gy-RO Mill. The polymer pastes were prepared from these powders, mixed with carbon and suitable binder. It was noted that the binder material and the percentage of carbon used affected the films sensitivity to gases. Thick films were screen-printed on glass substrates with interdigitated silver electrodes. These gas sensors were used to detect propanol and toluene at concentration range 0-5000ppm. The sensitivities of the films were determined as $R = (R_{gas} - R_{air}/R_{air}) * 100$ and increased with the increase in gas concentration (ppm). The effect of 10000 ppm of different gases such as methanol, ethanol, THF, chloroform and Acetone on the films was studied.
- G/PI.32** BULK Zn_{1-x}CoxO:Na MAGNETIC SEMI-CONDUCTORS SYNTHESIZED BY CO-PRECIPITATION PROCESS
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Na doped Zn_{1-x}CoxO polycrystalline powders were synthesized by co-precipitation method. The precursor was prepared by mixing 0.4 mol/L aqueous solutions of zinc and cobalt acetates with 0.4 mol/L aqueous solution of oxalic acid. The quantity of sodium was 1% and x was varied from 0 to 0.1. X-ray diffraction, optical measurements, transmission electron microscopy observations and energy dispersive X-ray spectroscopy analysis have revealed that divalent cobalt ions Co⁺² were successfully substituted for Zn⁺² ions in ZnO matrix up to 10% without modifying the wurtzite structure. The UV-visible transmittance spectra show an increase of the absorption band intensity associated to tetrahedral Co⁺² and a red shift of the band edge with increasing x. Preliminary magnetic measurements indicate that despite the presence of Na⁺ induced free charge carriers the samples show a paramagnetic behaviour. The effect of annealing treatments in various atmospheres on the magnetism will be investigated.
- G/PI.33** SEA-URCHIN LIKE ZnO NANOSTRUCTURES ON Si BY OXIDATION OF Zn METAL POWDERS
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Sea-urchin like ZnO nanostructures were grown on Si (100) substrates by oxidation of metallic Zn powders at 873 K. The ZnO nanostructures consist of straight nanowires of ZnO with the blunt faceted ends with sudden reduction in diameter projecting out, having the diameter of 30-60 nm and the length of 2-4 micron meters. TEM analysis and SAED patterns showed that the as-grown nanostructures are highly crystalline nature and preferably grown along the [0001] direction which is consistent with XRD analysis. Room temperature photoluminescence (PL) measurements showed a reduced near band-edge emission in the UV region at 380 nm while a strong deep level emission was observed in the visible region at 500-530 nm. A model for vapor-solid (VS) growth mechanism of ZnO nanowires was presented. Most importantly, these ZnO nanowires have been produced by a simple, easy, and low cost method without the use of any catalyst.
- G/PI.34** CHARACTERISATION OF PRECIPITATION SYNTHESIZED ZnO NANOSTRUCTURES
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Zinc oxide (ZnO) nanostructures were synthesized by precipitation from alcoholic solution containing dissolved zinc and hydroxide ions. The effects of using differing experimental conditions, such as temperature, solvent and reactant ratios were explored using X-ray diffraction, scanning electron microscopy (SEM) and cathodoluminescence (CL) spectroscopy.
A weak near band-edge emission at around 390 nm due to free exciton recombination was observed in addition to a strong, broad visible emission, attributed to defects and impurities in the ZnO structure. These measurements were performed at both 83 K and 300 K over a range of excitation power (E₀I_b) densities to measure the saturation behaviour of each observed CL peak. Rare earth and transition metal salts were added proportionally to the reaction mixture to obtain doped ZnO nanostructures with a range of dopant concentrations. These products were also characterised using the methods mentioned above. CL spectroscopy, following heat treatments in air, O₂, N₂, H₂/N₂ and Ar at 700°C, was used to assess the effect of post processing on the excitonic and impurity/defect luminescence of the doped and undoped ZnO.
- G/PI.35** STUDY OF ELECTRICAL, STRUCTURAL AND LUMINESCENT PROPERTIES OF ZINC OXIDE THIN FILMS
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Electrical, structural and photoluminescent properties of zinc oxide thin films grown by reactive magnetron sputtering method and the dependence of thin film parameters on preparation conditions have been investigated. The photoluminescence of undoped ZnO films at room temperature was revealed. Volt-ampere characteristics of p-n-heterojunctions formed by reactive magnetron deposition of ZnO films on silicon substrates were measured. The optimal regimes of deposition and annealing for obtaining of minimum resistivity, intensive photoluminescence, n-ZnO - n(p)-Si heterostructures and crystallinity of ZnO films investigated by X-ray diffraction measurements were determined.
Reversible changes of resistance, free carrier Hall concentration, crystallites dimensions and X-ray diffraction peaks intensity depending on conditions of annealing were observed.

G/PI.36**ZnO NANOSTRUCTURES GROWN BY THE PULSED LASER DEPOSITION TECHNIQUE**

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In the last few years, ZnO has been at the forefront of materials research due to its attractive physical properties for applications in ultraviolet optoelectronic devices, gas sensors or biomedical science, for example. Considerable research has also been devoted to the integration of these unique material properties into quantum-confined structures.

Using a solid-vapour phase thermal sublimation technique, Wang [1] has produced ZnO nanowires, nanohelices/nanosprings, nanocombs, nanorings, nanobelts and nanocages, thus showing that ZnO is one of the most versatile materials for nanostructure fabrication. ZnO Nanorods have also been successfully fabricated using the Pulsed Laser Deposition (PLD) technique [2]. PLD presents distinctive advantages for the growth of complex nanostructured devices such as the controlled incorporation of dopants or the in-situ growth of nanorods on epitaxial sub-layers, for example. Here, we report the fabrication of self-assembled ZnO nanorods and nanoislands and show how these are preferentially obtained depending on the growth conditions and the nature of the substrate used. The various nanostructures are observed using Scanning Electron Microscopy and Atomic Force Microscopy. The corresponding photoluminescence data, measured at room or low temperatures, are also presented and testify to the high optical quality of these nanostructures.

[1] Z. L. Wang, *J. Phys. Condens. Matter.*, 16 (2004) 829

[2] Mitsuhsa Kawakami et al, *Jpn. J. Appl. Phys* 42 (2003) L33-L35

G/PI.37**INVESTIGATION OF ANNEALING-TREATMENT ON THE OPTICAL AND ELECTRICAL PROPERTIES OF SOL-GEL-DERIVED ZINC OXIDE THIN FILMS**

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Highly preferential c-axis orientation ZnO thin films on Si(100) and quartz substrates have been achieved by sol-gel method. Structural investigation including surface morphology and microstructure was carried out by XRD, SEM and AFM measurements. Also, optical properties were determined by photoluminescence, ellipsometry and UV-VIS spectrum analyses. XRD results indicated that an extremely sharp (002) peak will dominate under optimum annealing-treatment condition. Moreover, thin film quality and the morphology were improved by annealing treatment. The SEM images show that the grains sizes increased with increasing annealing temperature up to 750 °C, where the particle size was about 50 nm. Photoluminescence spectra revealed two main peaks centered at about 380 nm and 520 nm, corresponding to the band-edge and defect-related emission. The variation in relative emission intensities are related to the annealing temperature. In addition, optical transmittance spectra demonstrated that these films, with thickness of 180 nm, are very transparent (~90%) in the range of 380-800 nm wavelength, and optical band-gap was determined accordingly. The dependence of the electrical resistivity on the annealing-treatment condition was discussed in detail as well.

G/PI.38**CHARACTERIZATION OF THE HETEROJUNCTION ZnO(n)/ Si (p) FILMS GROWN BY MAGNETRON SPUTTERING**

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ZnO is a wide band gap semi-conductor that has attracted tremendous interest for its potential applications in optoelectronic, solar cell, gas detection...

In this work, ZnO films were deposited by RF magnetron sputtering on single p-Si substrates to form n-ZnO/ p-Si heterojunctions. Various substrate temperatures of 25, 100, 200, 300 and 400°C were used. The electrical junction properties were characterized by current-voltage (I-V) and capacitance-voltage (C-V) methods. Calculations of barrier height elevation from classical $1/C^2$ -V characterizations and from I-V characterizations indicate merely the same value of 0.7 eV. Moreover, the optical spectra showed that the reflectance of the ZnO films grown with different substrate temperatures is smaller than that of bare silicon substrates on the UV and visible region. The smallest reflectance was found for films grown at 400°C indicating a possible application of these films as anti-reflection coatings on silicon substrates. The aim of this paper is the use of polycrystalline n-ZnO films as practical anti-reflection coatings for Si-based optoelectronic devices.

G/PI.39**ZINC OXIDE FILM GROWTH ON ZIRCONIUM BORIDE**

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ZnO is now receiving much attention due to its potential use in electronic and optoelectronic devices. Many research works have been reported for achieving high-quality ZnO thin films. Various substrates such as c-Al₂O₃, a-Al₂O₃, AlN/Al₂O₃, GaN/Al₂O₃, etc. have been used for growing the epitaxial ZnO thin films. Here we will present the ZnO film growth on a new substrate, ZrB₂(0001). Zirconium boride has a hexagonal structure (P6/mmm) with a=0.3165 nm and c=0.353 nm. The lattice mismatch between ZnO and ZrB₂ is about 2.6%.

The ZnO film was grown by MBE method. RHEED was used to evaluate the film growth mode. A few monolayers of Zn were firstly deposited on a clean ZrB₂(0001) at room temperature. The grown Zn layer was incommensurate to the substrate. Molecular oxygen of 5E-6 Torr was then introduced to the MBE chamber. Zn metal layer was slowly oxidized at room temperature to form an epitaxial ZnO. The film structure was examined by RHEED, LEED, AFM and XPS.

G/PI.40**ATOMIC ABSORPTION PHOTOMETRY OF ZnO**

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The concentration level of native defects (i.e. interstitial zinc) was the topic of controversial defect models of ZnO during many years. Atomic absorption photometry (AAP) is a proper method for determination of deviation from the stoichiometric composition of the crystal. To determine the excess zinc, the atomic absorption photometry of zinc vapour is used in the conditions of solid-vapour equilibrium. The ZnO samples tested were prepared by heat treatment of ZnO different samples at temperature 900C and at fixed Zn pressures from 0,1 to 0,9 of saturated Zn vapour pressure at given treatment temperature. The time to achieve the vapour-crystal equilibrium in ZnO:Zn crystal was less than one hour. Optical absorbance, proportional to the concentration of zinc atoms in the vapour phase, was registered photoelectrically on Zn resonance line. Excess Zn in polycrystalline, ceramic and monocrystalline ZnO from different sources was determined. The dominating role of contaminating impurities in ZnO appeared in our experiments. The experimental results were used for preliminary high temperature defect equilibrium calculations for ZnO. The concentration of excess Zn calculated on basis of our experiments did not exceed 10^{19} cm^{-3} in our Frenkel native defect models for all ZnO objects under investigation.

G/PI.41**WET-ETCHING CHARACTERISTICS OF ZnO USING ACID SOLUTIONS**

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Characteristics of wet-etching of ZnO thin films were investigated using a hydrochloric and a sulfuric acid solution as etchants. The etch rate of ZnO films which were grown by magnetron sputtering method and molecular beam epitaxy are relatively high and measured to be 1.4 $\mu\text{m}/\text{min}$ and 1.8 $\mu\text{m}/\text{min}$, using 2 % hydrochloric acid solutions and 1 % sulfuric acid solutions, respectively. The etch rate was linearly increased as the acid concentration increase, indicating that the etch process is reaction-rate limited process.

The etched surface, observed by scanning electron microscopy, showed high density of cones and the sidewall profile of masked area were similar to those of cones on the surface. We believe that the nipple, observed on the top of the cones as well as sidewall of masked area, may play a critical role in the formation of cones by chemical wet etching. A detailed analysis of the time-evolution of the surface morphology will be described as a function of acid concentration and a method to enhance the roughness of etched surface will be also discussed.

G/PI.42**EFFECT OF ALUMINIUM DOPING ON ZINC OXIDE, AZO, THIN FILMS GROWN BY SPRAY PYROLYSIS**

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Thin films of ZnO doped with aluminium (AZO) are obtained by chemical spray pyrolysis in air atmosphere. Crystal structure, chemical composition, electrical and optical properties were investigated by XRD, XPS, resistivity, photoluminescence, optical transmission, and Raman spectroscopy. All films are polycrystalline with a hexagonal wurtzite-type structure. The undoped ZnO film had preferred (002) orientation but samples with Al doping concentration higher than 2% present lower crystal quality. The chemical composition corresponds to ZnO and not other products can be detected. All films exhibit a transmittance above 80-90% along the visible range up to 750nm and a sharp absorption onset at about 375 nm corresponding to the fundamental absorption edge (3.31 eV). Undoped ZnO films show two emission peaks: one in the UV (369 nm) due to bound excitons, and other in the green region (500 nm), mainly attributed to different intrinsic defects such as zinc vacancy (VZn) and oxide antisites OZn forming deep levels in the band gap. Doped films present different PL spectra, they show a small blue band around 410 nm and a broad red emission peak centered at 700 nm whose intensity increases with the Al doping concentration and its intensity and width changes with the Al concentration in ZnO films. The minimum resistivity of all films was found for the 1% Al doping. Finally, the main difference in the Raman spectra between the undoped ZnO and AZO is the increase of the A1(LO) mode with increasing Al doping. The observation of this mode in the doped samples, with the higher electron concentration, may be due either to defect-assisted Raman scattering (DARS) or to electric-field-induced (EFI) Raman scattering.

G/PI.43**MICROSCOPIC DISTRIBUTION OF BOUND EXCITONS IN SELF-ORGANIZED ZnO PYRAMIDS**

F. Bertram, S. Giensch and J. Christen, Institute of Experimental Physics, Otto-von-Guericke-University Magdeburg, Germany; A.-H. Elshaer, A. Bakin and A. Waag, Department of Semiconductor Technology, Braunschweig Technical University, Germany

Self-organized ZnO pyramids were grown by MBE on sapphire substrates on top of a ZnO (0001) buffer layer. The hexagonal pyramids have 1 μm diameter and are terminated by cascaded inclining side walls resulting in a distinct narrowing towards the top. The lateral distribution is homogeneous and random (density of about $2.4 \times 10^7 \text{ cm}^{-2}$). However, the pyramids are preferentially oriented having their side facets well aligned with respect to each other. The luminescence is characterized by using cathodoluminescence microscopy. The spatially averaged spectrum is dominated by the impurity bound exciton I8. The free exciton XA and the bound excitons I2 / I3, as well as a sharp line at $E = 3.31 \text{ eV}$ are visible in the near band gap region. The luminescence from the plain buffer layer is weak and spectrally unstructured. In contrast, the pyramids exhibit a very intense emission consisting of several individual sharp excitonic lines. A strong increase of I2 / I3 can be found in the vicinity of the pyramids. Starting at the base of the pyramids I8 emerges, monotonously increases, and becomes dominant at the tip of the pyramid where I2 / I3 has almost disappeared.

SYNTHETIC AND PHOTOLUMINESCENCE STUDIES ON RE DOPED ZnO NANOSTRUCTURES

M. Peres, A. Neves, J. Soares, T. Monteiro, Department of Physics, University of Aveiro, 3810-193 Aveiro, Portugal; Angela Sofia Pereira, Ana Catarina Esteves, Tito Trindade, Department of Chemistry, University of Aveiro, CICECO, 3810-193 Aveiro, Portugal

ZnO has a wide range of industrial applications, including UV-protection films and chemical sensors. In the past decade, various methods have been employed to produce ZnO, including vapour decomposition, precipitation, and thermal decomposition. Commercial exploitation of ZnO nanoparticles is currently limited by the high synthesis costs and large-scale production of high quality materials. Nevertheless, it is well conceived that preparation of ZnO via solution chemical routes provides a promising option for the production of high quality ZnO nanoparticles.

Recently, doped ZnO colloids have been studied because of their size-dependent electronic and optical properties, which offer possibilities for the fabrication of devices: one particular application focuses the use of semiconductor particles as optical markers for cell labelling due to their luminescent properties. In this work, ZnO and Eu (Tb) doped ZnO colloids were synthesized. Several experimental parameters such as the concentration of Eu (Tb), were varied in order to investigate their effect on the structural, morphological and optical properties of the semiconductor. The photoluminescence properties of the starting colloids and the resulting nanocomposites were investigated.

Session V : Defects and impurities
Session chair : B. Gil

- G-V.1** 14:00 -Invited- EPR AND OPTICAL CHARACTERIZATION IN ZnO CRYSTALS
L. Halliburton, Physics Department, West Virginia University, P.O. Box 6315, Morgantown WV 26506, USA
- G-V.2** 14:30 OXYGEN-INTERSTITIAL DEFECTS IN ZINC OXIDE
Paul Erhart, Karsten Albe, Andreas Klein, TU Darmstadt, Institute for Materials Science, Germany
A detailed understanding of the defect physics of zinc oxide is essential for optimizing the electronic and optical properties. In the past first-principles studies have dealt with intrinsic point defects but the role of oxygen interstitials were investigated in depth. In this contribution we present a detailed study of various possible oxygen interstitial configurations based on density-functional theory calculations within the local density approximation. Depending on the charge state the most stable geometry varies: (1) for negative charge states a configuration is assumed which is characterized by a preference for zinc-oxygen bonds; (2) in contrast for neutral and positive charge states the lowest formation energy is obtained for a structure in which two oxygen atoms share one site ("dumbbell"). The two oxygen atoms form a strong covalent bond giving rise to the particular stability of this defect. In this configuration positive surplus charges can be well compensated which is reflected by the fact that the formation energy stays almost constant as the charge state changes from 0 to 2+ whence the dumbbell-defect effectively acts as a donor. Our calculations predict the dumbbell-interstitial defect to be the dominant hole-killer defect under oxygen-rich conditions and for Fermi levels in the lower half of the bandgap. In this context our results are of importance for the interpretation of numerous recent attempts to synthesize p-type conducting zinc oxide.
- G-V.3** 14:45 THE EFFECT OF TIME REVERSAL SYMMETRY ON THE VIBRATIONAL MODES IN ZnO/Al₂O₃ AND OTHER RELATED COMPOUNDS: GaN, CdS, BeO, ZnS, CdSe
H.W. Kunert(a) and J. Barnas(b), (a)Department of Physics, University of Pretoria, 0001 Pretoria, South Africa, (b)Department of Physics, Adam Mickiewicz University, ul.Umultowska 85, 61-614 Poznan, Poland
Vibrational states of a crystal are classified according to irreducible representations (irrps) of the corresponding factor group Gk/T. The wave vector k runs over the entire first Brillouin zone (BZ). When the irrps involved are complex, time reversal symmetry has to be taken into account. In the absence of spin, symmetry with respect to time reversal results in an additional degeneracy. This happens if an irreducible representation is not equivalent to the corresponding complex conjugate one, or if it is equivalent but cannot be reduced to a real form. Consequently, before constructing dynamical matrices for the frequencies of phonons one should first investigate irrps involved. The most comprehensive source of irrps of the 230 space groups, generated by a suitable computer programme, are the Tables of Kronecker Products [1]. Applying Herring criterion for space groups and using the Tables we have tested the irrps of the factor group of ZnO (C_{6v}4/T) and related compounds, as well as of the sapphire (D_{3d}6/T). Several irrps of the high-symmetry points (A, L, H - see the first BZ) and lines (, U, S,...) in ZnO (and also in Al₂O₃) cannot be reduced to a real form. Therefore, extra degeneracy due to the time reversal symmetry occurs at these points and lines. The experimental phonon dispersion curves of ZnO have been studied by Thomas et al [2] and Hewat [3]. In both cases the group-theoretical assignment of the modes measured by neutron scattering has not been considered. Using our results, we have assigned the vibrational modes present on their spectra according to the corresponding irrps, removing this way some discrepancies between the two authors. An interesting thing is that the experimental data indeed confirm the time reversal degeneracy at the point A and line ((Figs.1 in both papers). Similarly, appropriate group theoretical assignment for sapphire removed some errors in the calculations of phonon dispersion curves [4].
[1] A.P. Cracknell, B.L. Davies, S.C. Miller, F.W. Love, Kronecker Product Tables (IFI/Plenum, New York, Washington, London, 1979), vols.1-4.
[2] K. Thoma, B. Dorner, G. Duesing, W. Wegener, Solid State Communication.15, 1111 (1974).
[3] A.W. Hewat, Solid State Communication 8, 187 (1970).
[4] R. Heid, D. Strauch, K.P. Bohnen, Phys. Rev. 61, 8625 (2000).

- G-V.4** 15:00 INVESTIGATION OF THE ELECTRICAL ACTIVITY OF DISLOCATIONS IN ZNO-EPILAYERS BY TRANSMISSION ELECTRON HOLOGRAPHY
E. Müller, P. Kruse and D. Gerthsen, Laboratorium für Elektronenmikroskopie, Universität Karlsruhe, 76128 Karlsruhe, Germany, R. Kling Abteilung Halbleiterphysik, Universität Ulm, 89069 Ulm, Germany, A. Waag, Institut für Halbleitertechnologie, Universität Braunschweig, 38106 Braunschweig, Germany
It has been frequently demonstrated in the past that dislocations or point defects in the vicinity of dislocations can be electrically active. Due to the high density of dislocations in epitaxial ZnO layers we have investigated the possible electrical activity associated with dislocations in this material. Electron holography was used to study the interaction of the incident electrons with the electrostatic potential of a charged dislocation with high spatial resolution. To eliminate the influence of dynamical electron diffraction, the sample was tilted out of the zone axis. Using a cross-section sample, the dislocations do not intersect the sample surface which eliminates the contribution of phase shifts due to preparation-induced local thickness variations. The phase and amplitude of the image wave were extracted numerically from the sideband of the digitized hologram. The relative phase shift of the transmitted beam of the image wave with respect to the reference wave traveling through the vacuum yields the electrostatic potential of the local charge. Comparing this potential with the theoretically expected distribution, a line charge of approximately $2 e/nm$ was found.
- G-V.5** 15:15 DEFECTS IN ELECTRON IRRADIATED ZnO SINGLE CRYSTALS
M.H. Fenollosa, L.C. Damonte and B. Marí, Dpt. Física Aplicada, Universitat Politècnica de València, Camí de Vera s/n, 46022-València, Spain
ZnO is being the object of intense studies owing to its attractive applications on UV optoelectronic. Intrinsic and induced point defects in ZnO lead to the generation of bounded states with important effects on the material properties. A complete knowledge of point defect structure is needed to understand its optical behaviour. We have used two experimental techniques highly sensitive to defects: positron annihilation lifetime spectroscopy (PALS) well adapted for open volume defects studies and photoluminescence (PL) which directly probes the optical activity of the centres. ZnO single crystals commercially provided were exposed to different 10 MeV electrons fluences giving rise to irradiation doses between 60 and 240 Gy. After irradiation, samples were annealed in air atmosphere from 100 to 600°C in order to follow the evolution of irradiation defects and their effect on the emission properties. Positron lifetimes and intensities measured by PALS as a function of radiation doses show that the generated defects act as effective positron traps. The PL spectra for all the analyzed samples consist of a near-band-edge (NBE) emission centred at 369 nm and a broad deep-level (DL) emission around 550 nm. The main observation is that the most intense PL emission is found for the higher electron dose used, i.e. 240 Gy. This effect is similar to that observed after processes leading to an improvement of the crystal quality but it should be interpreted as an annihilation of the non radiative recombination centres which strongly enhances the radiative recombination mechanisms. The trends observed by both experimental techniques were discussed in terms of the possible origin, nature and state of charge of the radiation induced defects involved.
- G-V.6** 15:30 -Invited- ACCEPTORS IN ZnO
B.K. Meyer, I. Physics Institute, Justus Liebig University Giessen, Heinrich Buff Ring 16, 35392 Giessen, Germany
In order to realize controlled p-type doping in ZnO the role of extrinsic and intrinsic donors relevant for compensation have to be clarified. The extrinsic n-type dopants Al, Ga and In are commonly found in bulk ZnO crystals and in thin films but also hydrogen as a shallow donor appears in relevant concentrations. The optical properties of the donors can be studied by low temperature photoluminescence (PL), the neutral donor bound excitons dominate in the PL spectrum. Two electron satellite transitions (TES) of the donor bound excitons allow to determine the donor binding energies ranging from 46 to 73 meV. We report on the optical properties of the shallow acceptors in ZnO incorporated by diffusion, by ion implantation and by in-situ doping in epitaxial films. Nitrogen doping gives rise to a pronounced donor-acceptor pair band located around 3.21 eV, the nitrogen acceptor level is appr. 160 meV above valence band. Lithium and Sodium doping induces apart from the deep centres (Li and Na on Zn sites) also shallow levels (binding energies around 300 meV) which might originate from Li(Na) complexes. Of particular interest is ZnO:P where at elevated temperatures in PL a free (bound) to bound (free) transition appears located at 3.30 eV. With the incorporation of P the band edge luminescence changes from neutral to ionized donor bound exciton recombination.

16:00 **BREAK**

Session VI : Growth 2

Session chair : A. Dagmar

G-VI.1 16:30 -Invited-

ISSUES IN ZnO HOMOEPITAXY

M.W. Cho(a), H. Suzuki(a) T. Minegishi(a), T. Yao(a,b), K. Maeda(c) and I. Nikura(c), (a)Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan, (b)Center for Interdisciplinary Research, Tohoku University, Aramaki, Aoba-ku, Sendai, 980-8578, Japan, (c)Tokyo Denpa Company Ltd., 430 Hakoishi Tamamura-machi, Sawa-gun, Gunma 370-1113, Japan

Zinc Oxide (ZnO) is a very attractive material for optical applications, such as blue to ultraviolet, light emitting diodes (LEDs) and laser diodes (LDs), and a high exciton binding energy of 60 meV, which provides efficient excitonic emissions at room temperature. At present time, sapphire is the most extensively used substrate for ZnO growth. However, hetero-epitaxial films have a high dislocation density due to large lattice mismatch and different thermal expansion coefficient, which lead to a high residual carrier concentration in hetero-epitaxial films. ZnO device applications have suffered from one major disadvantage. High residual carrier concentration makes the fabrication of p-type ZnO difficult. To fabricate current injection p-n junction devices, the realization of p-type conductivity is indispensable. Although recent reports show that p-type ZnO has can be homoepitaxially grown using Zn-polar ZnO substrate, it is difficult to obtain stable p-type ZnO [1]. Since Zn-polar ZnO films have rough surface, pre-treatments of substrate prior to grown are very critical in achieving a flat surface. In this study, we evaluate the properties and surface damage of the mechanically polished ZnO substrates, which were grown by hydrothermal technique (supplied by Tokyo Denpa Company Ltd.). In order to suppress a polishing damage and improve the initial surface morphology, we suggest the optimized pre-treatment process to homoepitaxially grow ZnO film on epi-ready ZnO substrate. Also, we grow ZnO homoepitaxial films using plasma-assisted molecular beam epitaxy (PA-MBE), and characterize in terms of surface morphology, structural quality and optical properties.

[1] Look D C, Reynolds D C, Litton C W, Jones R L, Eason D B and Cantwell G 2002 Appl: Phys. Lett. 81 1830

G-VI.2 17:00

CARRIER CONCENTRATION AND SHALLOW ELECTRON STATES IN IN-DOPED HYDROTHERMALLY GROWN ZnO

Ulrike Grossner, Jens S. Christensen, Andrej Yu. Kuznetsov, and Bengt Gunnar Svensson, Department of Physics / SMN, University of Oslo, PO Box 1048 Blindern, 0316 Oslo, Norway

Single crystal ZnO has been hydrothermally grown with additional In_2O_3 in the solution. Schottky barrier contacts have been deposited by electron beam evaporation of Pd onto the (000-1)-face. Capacitance-voltage measurements have been performed to reveal the carrier concentration as a function of the In_2O_3 content in the solution, and Secondary Ion Mass Spectrometry was used to measure the In content in the samples. For an In_2O_3 content of 0.01% in the solution, the average free electron concentration was increased to $5 \times 10^{18} \text{ cm}^{-3}$ compared to the value of $4 \times 10^{17} \text{ cm}^{-3}$ for non-doped material. An increase of the In_2O_3 content to 0.02% in the solution leads to a measured carrier concentration of approximately $1 \times 10^{19} \text{ cm}^{-3}$ in the sample. From thermal admittance spectroscopy measurements two prominent electronic levels have been found. However, in contrast to the non-doped material the freeze-out of the shallow doping in the In-doped samples takes place at lower temperatures (below 80 K). In addition, in the Arrhenius plot a split of the shallow level is indicated. This effect is more pronounced in the samples with higher In content, and the change in shallow electron states is, therefore, attributed to the intentional doping with In.

G-VI.3 17:15

Withdraw

G-VI.4 17:30

THE EFFECT OF DISLOCATIONS, HYDROGENATION AND ANNEALING ON THE ELECTRICAL PROPERTIES OF ZnO AND Au/ZnO CONTACTS

M.A. Lahmer and K. Guergouri, Laboratoire de physique-chimie des semiconducteurs, Département de Physique, Université Mentouri, Constantine 25000, Algérie

Zinc Oxide has been receiving much attention in recent years due to its many technological applications including gas sensor, phosphors, varistors, surface acoustic wave devices, piezoelectric transducers and as a window material for display and solar cells. Recent progress in single crystal growth has also opened up prospects for optoelectronics applications, as a substrate for growth of GaN or as a light emitting material in its own right. In this work, we study the effect of dislocations, hydrogenation and annealing on the electrical properties of ZnO and Gold contact to ZnO. Our ZnO single crystals were prepared in LPCS-Meudon laboratory (C.N.R.S. France) by the chemical vapor transport method using carbon (C) and methane (CH₄) as the transport agents. Dislocations in sample were introduced by Vickers microhardness. The hydrogenation of sample was realized by exposition to hydrogen plasma in a plasma reactor operating at 13.56 MHz frequency and temperature of 260°C for 2 hours. We report on fabrication and electrical characterization of Au/ZnO contacts with new behavior, these contacts present a constant capacitance values and an hysteresis in the I(V) characteristics with a 0.5 μA current under zero bias. The origin of this behavior is not defined. Au layer deposited on dislocated ZnO show the same behavior of as grown ZnO. However, an decrease in the barrier height and capacitance values was observed. Au contact to hydrogenated ZnO behave as ohmic contact which confirm the dopant-donor behavior of hydrogen atoms in ZnO. In the other part Au contact on dislocated and hydrogenated crystal show the same behavior but an increase in the resistivity of ZnO and specific contact resistivity was observed which means that dislocations passivation by hydrogen atoms was produced in the material. Annealing treatment under air conditions produce an increase in the resistivity of material, while RTA treatment in the same conditions decrease the resistivity of ZnO, which means that a possible acceptor complexes dissociation was produced in ZnO during rapid thermal annealing.

G-VI.5 17:45

THE EFFECTS OF OXYGEN PARTIAL PRESSURE ON LATTICE DYNAMICS AND MICROSTRUCTURES FOR GA-DOPED ZNO THIN FILMS PREPARED BY REACTIVE PLASMA DEPOSITION METHOD

T. Yamamoto(a), T. Mitsunaga(b), M. Osada(c), K. Ikeda(a), S. Kishimoto(a), K. Awai(a), T. Sakemi(d) and S. Shirakata(e), (a)Materials Design Center, Research Institute, Kochi University of Technology, 185 Miyanokuchi, Tosayamada-cho, Kouchi 782-8502, Japan, (b)Application Laboratory, Rigaku Corporation, 3-9-12 Matsubara-cho, Akishima-shi, Tokyo 196-8666, Japan, (c)Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan, (d)Research & Development Center, Sumitomo Heavy Industries, Ltd., 5-2 Soubiraki-cho, Niihama, Ehime 792-8588, Japan, (e)Faculty of Engineering, Ehime University, 3 Bunkyo-cho, Matsuyama, Ehime 790-8577, Japan

The dependence of the lattice parameters and grain size of Ga-doped ZnO (GZO) films on O₂-partial pressure were investigated so as to study what determines the electrical properties of GZO films. GZO films have been prepared by reactive plasma deposition method. A series of GZO thin films were deposited on glass substrates with varied O₂-partial pressure (0.2 - 3 × 10⁻⁴ Torr): O₂ gas flow rate was varied from 0 to 20.0 sccm. The resistivity as low as 2.8 × 10⁻⁴ Ω·cm with a carrier concentration of 8 × 10²⁰ cm⁻³ and Hall mobility of 25-27 cm²/Vs were obtained from the film deposited at O₂ gas flow rates below 10 sccm. Under excess O₂ gas flow rate, carrier concentrations substantially decrease. X-ray diffraction (XRD) analysis was performed to determine lattice parameters of wurtzite-type GZO films. For comparison, we calculated lattice parameters using first-principle calculations. XRD line broadening analysis, using the Williamson-Hall method, was also carried out to estimate the grain size. In a range of O₂ gas flow rate from 0 to 10 sccm, we find large c-axis parameters and little changes in a-axis parameters compared with those of undoped ZnO, together with an increase in the grain size. This means that Ga donors substitute Zn atoms in the GZO films, from the theoretical calculations. Excess O₂ gas flow rates decrease c-axis parameter. This indicates a decrease in the number of Ga at Zn sites. These findings explain electrical properties of GZO films very well.

G-VI.6 18:00

CL STUDIES OF TRANSITION METAL DOPED ZnO PRODUCED BY RF MAGNETRON SPUTTERING

M.R. Phillips, University of Technology, Sydney, PO Box 123, Broadway, NSW 2007, Australia and M. Wagner, E. Malguth and A. Hoffmann, Technische Universität Berlin, PN6-1, Hardenbergstr. 26, 10623 Berlin, Germany

ZnO films were deposited on Si (100) and glass substrates by RF magnetron sputtering with a high purity ZnO target using different O₂/Ar partial pressure ratios. Transition metals (TM) were incorporated (< 10 wt%) during growth using a second magnetron using high purity TM targets. The CL and optical properties of these films were investigated as a function of substrate temperature, O₂/Ar ratio, working pressure (1 - 10 mTorr) and post-deposition thermal annealing in N₂ at 500°C for 1 hour. The position of the optical absorption edge red shifted with increasing O₂ partial pressure. Heat treatment enlarged the film's grain size from 20 to 50 nm and significantly increased the intensity of the near band edge CL but had virtually no effect on the defect CL or the CL due to the TM dopants. The quality ZnO films improved with increasing O₂ partial pressure initially, however, at higher pressure it was found to degrade due to the lower landing energy of the Zn and O atoms. The relative intensity of the green, orange and red defect CL bands exhibited a complex dependence on growth conditions. Relationships between the CL in ZnO, TMs and structural point defects will be discussed.

G-VI.7 18:15

HIGH QUALITY NANOSTRUCTURED ZnO FILMS BY METAL-ORGANIC CHEMICAL VAPOR DEPOSITION

Graziella Malandrino, Manuela Blandino, Ignazio L. Fragalà Dipartimento di Scienze Chimiche, Università di Catania, and INSTM, UdR Catania, Viale A. Doria 6, 95125 Catania, Italy

ZnO is a wide band gap ($E_g = 3.37$ eV) semiconductor material. Recently ZnO has attracted much interest due to high photocatalytic activity, to excellent chemical and mechanical stability and to its potential applications in optoelectronic devices, such as short-wavelength lasers and light-emitting diodes (LEDs). Most of the research has been focused on the growth of ZnO thin films. Many groups have reported on optically transparent ZnO thin films deposited by techniques such as sputtering, spray pyrolysis, sol-gel, electron-deposition and metal organic chemical vapour deposition (MOCVD). Among them, MOCVD possesses the advantage of growing high-quality films due to its versatility in controlling various thermodynamic interactions.

This work reports the fabrication of high quality ZnO films by MOCVD on quartz and Si (100) using the $Zn(TTA)_2tmed$ (HTTA=2-thenoyltrifluoroacetone, $tmed=N,N,N',N'$ -tetramethylethylenediamina) precursor. The surface morphology and the structural and optical properties of ZnO films have been evaluated. It has been found that ZnO films are highly transparent, have the same wide band-gap of the single crystal and their morphology depends on the substrate deposition temperature. In addition, nanorod arrays have been fabricated under particular conditions selected after optimization of several processing parameters such as substrate temperature, oxygen partial pressure and precursor vaporization temperature.

19:00

AWARD CEREMONY

The symposium organizers and the candidates to the graduate student award are requested to attend.

CONFERENCE RECEPTION

Session VII : Doping
Session chair : T. Yao

- G-VII.1** 8:30 -Invited- p-TYPE ZnO AND LED APPLICATIONS
S. Park, Department of Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju 500-712, Republic of Korea
- G-VII.2** 9:00 THE CHARACTERIZATION OF PHOSPHORUS DOPED ZnO MULTI-LAYER THIN FILMS TO CONTROL CARRIER CONCENTRATION
Sung Hoon Lim, Jae Won Kim, Hong Seong Kang, Hyun Woo Chang and Sang Yeol Lee, Department of Electrical and Electronic Engineering, Yonsei University, 134, Shinchon-dong, Seodaemun-ku, 120-749, Seoul, Korea
Phosphorus doped ZnO multilayer (ZnO:P) thin films were deposited according to various oxygen partial pressures on (0001) sapphire substrates by pulsed laser deposition (PLD). The phosphorus doped ZnO multilayer was composed of phosphorus doped ZnO layer and two pure ZnO layers on a sapphire substrate. The ZnO/ZnO:P/ZnO multilayer thin films were post-annealed at various annealing temperatures and times. Upper ZnO layer plays an important role to encapsulate phosphorus atom in ZnO:P layer activated by post-annealing process. The ZnO multi-structure decreases the carrier concentration. We have investigated the structural, electrical and optical properties of the ZnO thin films by X-ray diffraction (XRD), Hall measurements and photoluminescence (PL).
- G-VII.3** 9:15 DOPING ENGINEERING OF P-TYPE ZnO
Y. Marfaing and A. Lusson, LPSC-CNRS, 92195 Meudon cedex, France
The formation energies of defects in ZnO obtained from recently published first-principles calculations [1] are used to simulate the incorporation and compensation of group-V impurities. A detailed analysis is carried out for the specific case of nitrogen-doped ZnO as a function of doping temperature, O/Zn stoichiometric ratio, dopant activity. This study shows that p-type doping of ZnO:N in thermodynamic equilibrium conditions is rather limited and involves a delicate balance between the achievement of high dopant solubility (on Zn-rich side) and low compensation by donor defects (on O-rich side). Efficient doping appears possible in various alternative ways : simultaneous incorporation of hydrogen as an interim compensating donor to be subsequently eliminated ; use of a high activity dopant in external phase (atomic N, NO) while preventing the formation of [N₂](O-site) compensating donors ; planar doping for separate optimisation of nitrogen incorporation and defect-free crystal ; N clusters around a group III donor [2]. The other group V impurities (P, As) introduce deep acceptor levels when substituted for O, but could form a single acceptor complex in antisite position, like [As(Zn)-2V(Zn)], with both low formation and ionisation energies [3]. Throughout these simulations comparison will be made with reported experimental data.
[1] Kohan et al, Phys. Rev. B 61 (2000) 15019. Zhang et al, Phys. Rev. B 63 (2001) 075205. Lee et al, Phys. Rev. B 64 (2001) 085120. Oba et al, J. Appl. Phys. 90 (2001) 824.
[2] Wang and Zunger, Phys. Rev. Lett. 90 (2003) 256401.
[3] Limpijumnon et al, Phys. Rev. Lett. 92 (2004) 155504.
- G-VII.4** 9:30 NOVEL PREPARATION OF P-TYPE ZnO FILM USING P2O5 AS DOPING SOURCE
Liping Zhu, Zhizhen Ye, Fugang Chen, Weizhong Xu, Binghui Zhao, State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, People's Republic of China
It is well known that it is necessary to obtain p- and n- type ZnO films to develop devices based on ZnO. However it difficult to prepare p- type ZnO thin films with low resistivity because of its native donor defects such as zinc interstitials (Zni) and oxygen vacancies (VO). In our previous study, p-type conduction was realized in zinc oxide ZnO thin films by doping nitrogen using different doping methods, such as N-doping in NH₃-O₂ atmosphere, solid-source chemical vapour deposition, co-doping of Al-N using reactive magnetron sputtering, metalorganic chemical vapor deposition (MOCVD) using NO as the dopant source. Recently, a special technique was prompted to prepare p- type ZnO thin films by MOCVD using P₂O₅ as dopant source. The obtained p- type ZnO thin films crystallized well and showed better electrical properties than the ones obtained in our previous studies, especially the mobility of the sample was as high as 7.0 m²V⁻¹s⁻¹. Furthermore, the obtained phosphorus doped p-type ZnO films showed excellent stability and reproducibility. It can be expected that ZnO p-n homo-junctions with good I-V characterizations can be fabricated next step using the p- and n- type ZnO films obtained by MOCVD.

G-VII.5 9:45

DOPING OF PULSED LASER DEPOSITED ZnO THIN FILMS

M. Novotny, J.-R. Duclere, A. Meaney, R. O'Haire, E. McGlynn, M.O. Henry, J.-P. Mosnier, School of Physical Science, NCPST, Dublin City University, Glasnevin 9, Dublin, Ireland

ZnO is a very attractive material for use in ultraviolet optoelectronic devices due to remarkable properties, such as a direct wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature. However, the most significant impediment to the widespread exploitation of ZnO-related materials is linked to the difficulty in carrier doping. Whereas n-type doping is relatively easy to realize, it is rather difficult to achieve some good and reproducible p-type conductivity in ZnO samples. One of the favoured routes to try to produce p-type doped ZnO material is by substitution of an oxygen atom by one atom of the Group V elements (N, P...). Another route will be the substitution of Zn atoms by alkali metals such as Li. Here, we report on three different ways of doping the PLD grown ZnO thin films. First, a pre-doped ZnO:P2O5 target was used in order to incorporate some phosphorus in the films. Then, ZnO:Li thin films were fabricated by taking advantage of the Li diffusion that occurs at high temperature, during ZnO growth on c-LiNbO3 substrates. The effects of post-annealing treatments were studied. To finish, an ECR plasma source, operating in ion and atomic configurations, was also used in order to incorporate N in the samples. The impact of such parameters like ions energy, microwave power, N2 flow and ambient oxygen pressure on the doping efficiency was studied. For each way, photoluminescence spectra and Hall measurements are discussed.

G-VII.6 10:00

SUBSTITUTIONAL INCORPORATION OF IMPLANTED Fe IN ZnO

U. Wahl, E. Rita, J.G. Correia, E. Alves, Instituto Tecnológico e Nuclear, EN10, 2686-953 Sacavém, Portugal, J.C. Soares, Centro de Física Nuclear da Universidade de Lisboa, 1649-003 Lisboa, Portugal, The ISOLDE collaboration, CERN-PH, 1211 Geneva 23, Switzerland
Iron-doped ZnO is currently one of the systems for which ferromagnetism has been reported above room-temperature [1] and hence a candidate for possible spintronic devices [2].

We report here on the combined characterization of Fe-implanted ZnO by means of emission channeling and Rutherford Backscattering (RBS) ion beam channeling. Single-crystalline ZnO was implanted at room temperature with 56Fe at 60 keV up to a dose of 1×10^{15} cm⁻², and subsequently with 2×10^{14} cm⁻² of radioactive 59Fe impurities. The lattice location of the radioactive 59Fe was then studied using the electron emission channeling technique, i.e. by means of detecting the angular emission patterns of its beta particles. We found that already in the as-implanted state around 100% of 59Fe occupied substitutional Zn sites with small rms displacements around 0.07-0.12 Å, which is quite surprising given the total implanted dose. Prior to any annealing ~0.8% of Zn atoms should thus be substituted by Fe atoms in the peak of the implantation profile. Vacuum annealing up to 900°C had little influence on the substitutional Fe fraction and merely decreased its rms displacement to values around 0.06-0.09 Å. The sample was subsequently investigated by RBS which confirmed good crystalline quality of the ZnO lattice. Our measurements thus give evidence that it is possible to perfectly incorporate relatively high concentrations of implanted Fe on ideal substitutional Zn sites by means of ion implantation. Measurements of the magnetic moment of the sample by means of SQUID are currently under way.

[1] S.J. Han et al, Appl. Phys. Lett. 81 (2002) 4212.

[2] S.J. Pearton et al, J. Vac. Sci. Technol. B 22 (2004) 932.

G-VII.7 10:15

EFFECTS OF DONOR IMPURITY BANDS ON HALL-EFFECT ANALYSIS IN ZnO

David C. Look, Wright State University and Air Force Research Laboratory, USA

Temperature-dependent Hall-effect (TDH) measurements are an important technique for determining donor and acceptor concentrations and energies in semiconductors. In n-type ZnO, grown from the vapor phase, it is typical to find two relatively shallow donors, D1 and D2, of approximate energies $E_{D1} = 30 - 40$ meV, and $E_{D2} = 60 - 70$ meV, respectively. When annealed at 700 deg C or higher, it is found that n vs. T exhibits a sharp minimum at about 70 K, and then increases and becomes constant below that temperature, i.e., behaving as a degenerate semiconductor. The mobility also attains a constant value at low temperatures. This anomalous behavior can be completely explained by including two impurity bands, formed from the D1 and D2 donors, in the analysis. The carrier concentrations in the bands, n_1 and n_2 , are easily determined from the respective Fermi functions, dependent only on the usual fitting parameters, ND_1 , ND_2 , ED_1 , ED_2 , and NA . The mobilities, associated with tunneling between donors, are simply taken from their constant low-temperature values: $\mu_1 = 600$ cm²/V-s and $\mu_2 = 50$ cm²/V-s. Thus, the inclusion of the two impurity bands in the overall analysis adds no new fitting parameters. It is likely that D1 is interstitial H, which is known to leave the sample at annealing temperatures above 600 deg C. Thus, ND_1 is decreasing, but at the same time NA is increasing, partly because of the breakup of neutral donor-acceptor pairs involving H, such as H-N. As long as $ND_1 > NA$, D1 will dominate the electrical properties; however, when ND_1 falls below NA , at higher annealing temperatures, then the deeper donor D2 becomes dominant. In short, the observed anomalous effects in n vs. T and μ vs. T arise from the interplay of electrons flowing within three different bands.

10:30

BREAK

Session VIII : Magnetic properties 1

Session chair : S. Pearton

- G-VIII.01** 11:00 -Invited- THEORY OF MAGNETIC ZnO: CHARGE AND SPIN CONTROL FOR THE SEMICONDUCTOR SPINTRONICS
H. Katayama-Yoshida(a,b), T. Fukushima(a,b) and K. Sato(b), Department of Condensed Matter Physics(a) & Department of Computational Nanomaterials Design(b), The Institute of Scientific and Industrial research (ISIR), Osaka University, Osaka 567-0047, Japan
We review our recent results on the materials design of the transparent and half-metallic ferromagnetism in 3d-transition-metal(3d-TM)-doped ZnO, ZnS, ZnSe and ZnTe based on ab initio calculation by KKR-CPA-LSDA. It is shown that V-, Cr-, Fe-, Co- and Ni-doped ZnO are ferromagnetism, on the other hand, Mn-doped ZnO is spin-glass. Hole-doping stabilize the ferromagnetism in Mn-doped ZnO, however, electron-doping does ferromagnetism in Fe-, Co- and Ni-doped ZnO.
The stabilization mechanism on ferromagnetism is due to the Zener's double-exchange mechanism. The magnetism is determined by ferromagnetic Zener's double-exchange interaction and the anti-ferromagnetic or ferromagnetic super-exchange interactions. We discuss the carrier-concentration and 3d-TM concentration dependences of Curie temperature (T_c) by the mean field approximation (MFA) and Monte Carlo (MC) calculation based on the ab initio calculation of the magnetic interactions. We predict the ferromagnetism in C-doped ZnO without magnetic-impurity doping. References:
(1) K. Sato and H. Katayama-Yoshida, Jpn. J. Appl. Phys. 39, (2000), L555.
(2) K. Sato and H. Katayama-Yoshida, Jpn. J. Appl. Phys.40 (2001) L334 .
(3) K. Sato, and H. Katayama-Yoshida, Jpn. J. Appl. Phys. 40 (2001) L485.
(4) K. Sato and H. Katayama-Yoshida, Jpn. J. Appl. Phys. 40 (2001) L651.
(5) K.Sato and H. Katayama-Yoshida, Semicond. Sci. Technol. 17 (2002) 367.
(6) T. Fukushima, K. Sato, H. Katayama-Yoshida, and P. H. Dederichs, Jpn. J. Appl. Phys. 43 (2004) L1416.
- G-VIII.02** 11:30 EPR STUDY ON MAGNETIC Zn_{1-x}Mn_xO
Mariana Diaconu, Heidemarie Schmidt, Andreas Pöpl, Rolf Böttcher, Joachim Hoentsch, Andreas Rahm, Holger Hochmuth, Michael Lorenz and Marius Grundmann, Institut für Experimentelle Physik II, Fakultät für Physik und Geowissenschaften, Universität Leipzig, Linnéstrasse 3-5, 04103 Leipzig, Germany
Diluted magnetic semiconductors (DMS), systems formed by substituting cations of the host semiconductor material with transition-metal ions, are developed for further use in spintronics. A good combination as DMS is Zn_{1-x}Mn_xO due to the ZnO wide band gap (3.37eV) and to the matching ionic radii of Mn²⁺ and Zn²⁺. Using electron paramagnetic resonance (EPR) we determined the valence of Mn ions in Zn_{1-x}Mn_xO thin films to be 2+. This is required for explaining the origin of room-temperature ferromagnetism observed in Zn_{1-x}Mn_xO films.
We studied films grown on c-plane sapphire substrates by pulsed laser deposition with the Mn content ranging from x=0.001 to x=0.091 and a single crystal with x=0.035 for comparison. We observed the hyperfine and fine-structure lines of Mn²⁺ for x=0.001, while for higher Mn contents the fine-structure lines were broadened by dipole-dipole interactions and onto these lines a very broad single line, due to Mn ions in higher local concentrations, was superposed. We modeled the experimental spectra and separated the broad single-line from the hyperfine and fine-structure lines. The obtained hyperfine and fine-structure parameters have values characteristic for Mn²⁺ in Zn²⁺ lattice sites. We found that the D fine-structure parameter depends on the lattice distortion and Mn content. For example |D| amounts to 675 MHz for a single crystal with x=0.035 and to 757 MHz for a film on c-plane sapphire with x=0.001.
- G-VIII.03** 11:45 GROWTH AND CHARACTERIZATION OF ZnMnO THIN FILMS
A.I. Savchuk, V.I. Fediv, S.A. Savchuk, Department of Physics of Semiconductors and Nanostructures, Chernivtsi National University, 2 Kotsubinsky Str., 58012 Chernivtsi, Ukraine, A. Perrone, University of Lecce, Physics Department and INFN, Via per Arnesano, 73100 Lecce, Italy
Initially interest to oxide-based semimagnetic semiconductors was stimulated by the theoretical work [1], in which exhibition of room-temperature ferromagnetism in Mn-doped ZnO was predicted. Obviously this opens promising opportunities of applications in spintronics. However, situation with obtaining of experimental evidence for ferromagnetism in ZnO doped with transition metals is still unclear. We report here on growth, magnetic, optical and magneto-optical characterization of Zn_{1-x}Mn_xO thin films. To obtain thin films we used rf magnetron sputtering and pulsed laser ablation techniques. For the latter method growth conditions were differ by using deposition in vacuum and in oxygen atmosphere. Magneto-optical experiments (magnetoabsorption and Faraday rotation spectra) were carried out at temperature range of (4.2-300) K in magnetic fields up to 5 T. The observed features in magneto-optical properties of Zn_{1-x}Mn_xO thin films can be explained in framework of exhibition of paramagnetic state which is typical for III-xMn_xVI semimagnetic semiconductors. On the other hand, the revealed ferromagnetic behavior for several samples perhaps is associated with special conditions during growth process of Zn_{1-x}Mn_xO thin films.
The research is supported by grant No.M/128-2004 from Ministry of Education and Science of Ukraine.
[1] T.Dietl, H.Ohno, F.Matsukura, J.Cibert, D.Ferrand, Science,287,1019 (2000).

G-VIII.04 12:00**RAMAN SCATTERING STUDY OF ZnO:Ti AND ZnO:Mn BULK CRYSTALS**

W. Gebicki(a), K. Osuch(a), C. Jastrzebski(a), M. Godlewski(b), Z. Golacki(b), (a)Faculty of Physics, Warsaw University of Technology, ul. Koszykowa 75, 00-661 Warsaw, Poland, (b)Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland

We report Raman scattering spectra of two systems- ZnO:Ti and ZnO:Mn. Raman scattering spectra of both systems have been measured vs. temperature, excitation wavelength and vs. composition (doping level).

The major results are as follows: a) ZnO:Ti system: 1. New strong and temperature dependent peak has been found as a satellite of E2 (high) phonon peak. The peak is visible only in low temperature, approximately below 80K. The temperature dependence suggests electronic nature of the excitation. 2. The LO modes are nearly completely washed out from the spectra. We interpret a weak peak at 550 cm⁻¹ as resulting from local vibrations of Ti related complex. 3. A broad band at approximately 470 cm⁻¹ coincides with the peak of phonon density of states known in literature (disorder activated short wavelength phonon modes). b) ZnO:Mn system 1. A broad well structured band has been observed in the LO phonon spectral region (500cm⁻¹ - 600cm⁻¹). At least three well resolved peaks can be distinguished in the band. The frequency of the 574 cm⁻¹ peak coincides with the frequency of the A1(LO) lattice mode, the two other peaks are probably Mn related. Strong resonance enhancement of the Raman peaks is observed. 2. A broad band centered at 470 cm⁻¹, quite different than the ZnO:Ti peak is observed. An attempt has been made to correlate the above-mentioned experimental results, specially the nature of the electronic transition observed in ZnO:Ti, with recent results of M. Venkatesan et al on ferromagnetism in ZnO doped with transition metal elements. For example, we relate electronic transitions observed in ZnO:Ti Raman spectra to shallow donor levels hybridized with localized 3d states, responsible for ferromagnetism in the system.

G-VIII.05 12:15**EXCHANGE POLARISATION COUPLING IN WURTZITE-PEROVSKITE INTERFACES: ELECTRICAL AND OPTICAL PROPERTIES OF Pt/ZnO/BaTiO₃/Pt AND Pt/ZnO/BaTiO₃/ZnO/Pt HETEROSTRUCTURES**

M. Schubert, N. Ashkenov, E. Twardowski, H. v. Wenckstern, H. Hochmuth, M. Lorenz, G. Wagner, M. Grundmann, Fakultät für Physik und Geowissenschaften, Institut für Experimentelle Physik II, Universität Leipzig, Linnestrasse 5, 04103 Leipzig, Germany

Because of many interesting properties ZnO (wurtzite structure) and BaTiO₃ (perovskite structure) are promising candidates for next generation micro- and optoelectronic devices. Of interest here is the electric polarization in both materials. Whereas the spontaneous wurtzite-type polarisation is inherently tied to one distinct lattice direction, the spontaneous perovskite-type polarization can be reversed and switched by external electric fields within the perovskite lattice. Coupling between the fixed ionic wurtzite interface charges and the switchable ferroelectric interface charges should give rise to ferroelectric polarization exchange phenomena. Switching of ferroelectric domains in ZnO-BaTiO₃-ZnO heterostructures may allow for controllable free-charge-carrier accumulations at heterointerfaces, band-to-band transition characteristics as well as for electro-optical properties. Structural, electrical and electro-optical properties of Pt/ZnO/BaTiO₃/Pt and Pt/ZnO/BaTiO₃/ZnO/Pt heterostructures, grown by pulsed laser deposition on (001)Si are reported. Structural properties are investigated by XRD, TEM and Raman-Scattering techniques. Temperature-dependent electric polarisation, current-voltage and capacitance-voltage studies reveal the interplay between spontaneous wurtzite and switchable ferroelectric polarization. Electro-optical investigations performed by means of Spectroscopic Ellipsometry show very interesting hysteresis behaviour of electro-optical properties, which may be used for optical transparent memory storage.

G-VIII.06 12:30**LOCAL STRUCTURE AND MAGNETISM IN EPITAXIAL ZnCoO FILMS**

K. Rode(a), M-A. Arrio(b), E. Fonda(c), P. Bencok(d), A. Anane(a), F. Petroff(a), V. Cros(a), J-P. Contoux(a), A. Fert(a) and N.B. Brookes(d), (a)Unité Mixte de Physique CNRS/Thales, Domaine de Corbeville, 91404 Orsay Cedex, France and Université Paris-Sud, 91405 Orsay Cedex, France, (b)Laboratoire de Mineralogie-Cristallographie de Paris, UMR CNRS 7590 - Universités Paris 6 et Paris 7 - IPGP, Case 115, Campus Boucicaud, 140 rue Lourmel, 75015 Paris, France, (c)Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin - BP 48, 91192 Gif-sur-Yvette Cedex, France, (d)European Synchrotron Radiation Facility, BP 220, 38043 Grenoble, France

We have grown Zn_{1-x}Co_xO (x=0.05 - 0.30) thin films by pulsed laser deposition (PLD) on sapphire (0001) substrates. The films have been characterized by standard laboratory techniques such as RHEED, X-ray diffraction, AFM/TEM microscopy and SQUID magnetometry. The films show (0001) directional growth and good planarity. The films are ferromagnetic with a Curie temperature well above our measuring range (400K) for 25% Co substitution. Al co-doped samples are conductive and we found evidence for tunnel magnetoresistance (TMR) effects in patterned ZnCoO/Al/Co magnetic tunnel junctions (I = insulator). We focus here on the local structural and magnetic properties investigated by X-ray Absorption (XAS) spectroscopies. The analysis of the XANES and EXAFS at the Co and Zn K edges confirms the preserved ZnO wurtzite crystal structure together with the ionic state of Co. The circularly polarized XAS at the Co L_{2,3} edges gives information on the magnetic ground state, and by means of a multiplet calculations we are able to give an estimate of the crystal field parameters. The experimental data is in good agreement with the calculated spectra of Co²⁺ in a Td crystal field. In particular, the fine structures at the Co L₃ edge unambiguously rules out Co clusters as being the origin of the observed magnetism. Moreover, the Co ground state in ZnCoO is found to be ferromagnetic at low temperature (10K). The spin and orbital magnetic moments, as estimated using the sum-rules, are close to the calculated values.

Session IX : Devices
Session chair : D. Look

G-IX.01 14:00 -Invited-

ZnO DETECTORS AND OTHER DEVICES

Yicheng Lu, Department of Electrical and Computer Engineering, Rutgers University, 94 Brett Road, Piscataway NJ 08854-8058, USA

There has been increasing interest in high quality ZnO films. ZnO has a direct energy bandgap ($E_g \approx 3.3$ eV at room temperature). Furthermore, ZnO can be alloyed with CdO and MgO to form the ternaries $Cd_xZn_{1-x}O$ and $Mg_xZn_{1-x}O$, extending the direct energy band from 2.8eV to 4.0eV. Through proper doping, ZnO can be made transparent and conductive, semiconducting, piezoelectric, or ferromagnetic. It is possible to use ZnO based multilayer structures to design and construct new integrated devices, such as tunable RF devices and multifunctional sensors.

We have grown high quality epitaxial ZnO and $Mg_xZn_{1-x}O$ films on r-plane sapphire substrates by MOCVD. The ZnO based multilayer structures have been used to demonstrate various new devices, including high speed MSM photoconductive type ultraviolet (UV) detector, ZnO Schottky diode photodetector, high frequency and low loss surface acoustic wave (SAW) filters, and integrated bulk acoustic wave (BAW) resonators. A monolithically integrated SAW UV photodetector consists of a semiconductor ZnO layer as a photoconductor and piezoelectric ZnO layer as the SAW device. Such photodetector has output signal in a frequency domain, leading to the wireless and low power sensing technology. MOCVD has been used to deposit single crystal ZnO nanotips on piezoelectric substrates, which are used to make a novel biosensor with enhanced DNA immobilization.

The work has been sponsored by NSF grants ECS-0088549, CCR-0103096, and ECS-0224166.

G-IX.02 14:30

OXIDE ENGINEERING OF ZnO THIN FILM TRANSISTORS

P.F. Carcia, R.S. McLean, and M.H. Reilly, DuPont Research and Development, Experimental Station, Wilmington DE 19880, USA

Macroelectronics on plastic substrates is attractive because of lighter weight, greater robustness, and the potential for lower cost manufacture. However, the low working temperature (< 120 C) of common plastics precludes most silicon based electronics. And while the requirement for low temperature processing would seem to favor recently studied organic semiconductors, their mobility, typically less than 1 $cm^2/V\cdot s$, is insufficient for important future applications such as high frequency identification tags and active-matrix transistor arrays to drive organic light emitting displays (OLEDs). In this work we show that field-effect mobility in n-type ZnO can be engineered from 0.1 $cm^2/V\cdot s$ up to 50 $cm^2/V\cdot s$ by controlling oxygen stoichiometry, i.e. the concentration of oxygen vacancies, in thin film ZnO. The best overall device properties were obtained when ZnO films had a high resistivity (> 100 $\Omega\cdot cm$), above the metal to insulator transition. Films we sputtered on unheated substrates were polycrystalline, and device properties for films grown on high quality dielectric surfaces (e.g., thermally grown SiO_2) could be accounted for by a grain boundary model for trapping of charge carriers in the ZnO layer. Device performance on lower quality dielectric surfaces, made by physical or chemical vapor deposition, was more complex and depended on details of the dielectric synthesis. Finally we will also discuss issues of device stability with a non-stoichiometric ZnO semiconductor.

G-IX.03 14:45

EFFECTS OF ELECTRICAL BIAS STRESS ON ZnO THIN FILM TRANSISTORS

R. Navamathavan, Eun-Jeong Yang, Jae-Hong Lim, Dae-Kue Hwang, Jin-Yong Oh, Jin-Ho Yang and Seong-Ju Park, Nanophotonic Semiconductors Laboratory, Department of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), 1 Oryong Dong, Buk-Ku, Gwangju 500-712, South Korea

ZnO based thin film transistors (TFTs) have been fabricated by radio frequency (rf) magnetron sputtering at a temperature of 300 $^\circ C$. The stability of ZnO TFTs was investigated under different electrical bias stress conditions. The TFT structure used in this study was a bottom gate type. This consists of SiN_x as a gate insulator and indium tin oxide (ITO) as a gate, which was deposited onto a glass substrate. The TFTs had a field effect mobility of 3.683 $cm^2/V\cdot s$, a drain current on to off ratio of greater than 10^6 , the off current of less than 10^{-10} A, and a threshold voltage of 2.4 V. It was found that the ZnO TFT was stable up to certain electrical stress condition ($V_G = -10$ and 10 V at $V_{DS} = 5, 10$ V) for the duration 200 s. As the bias stress and the duration of stressing time were increased the interface layer was broken and led to major physical degradation of the device. It is demonstrated that the quality of dielectric layer (SiN_x) is critical for the ZnO TFT device performance and the device degradation, threshold voltage instabilities are mainly attributed to the interface states and the quality of the dielectric layer.

G-IX.04 15:00**HIGH EFFICIENCY n-ZnO/p-SiC HETEROSTRUCTURE PHOTODIODES GROWN BY PLASMA-ASSISTED MOLECULAR-BEAM EPITAXY**

Ya. I. Alivov, Ü. Özgür, S. Dogan, D. Johnstone, V. Avrutin, N. Onojima, C. Liu, J. Xie, Q. Fan and H. Morkoç, Virginia Commonwealth University, Department of Electrical Engineering, Richmond VA 23284, USA

The direct band gap semiconductor ZnO ($E_g \sim 3.3$ eV, $T = 300$ K) is attractive for optoelectronics applications due to advantages over GaN such as the availability of ZnO bulk single crystals and a large exciton binding energy (~ 60 meV). Fabrication of ZnO based p-n heterojunctions has received considerable attention lately and various p-type materials have been used as the p-layer. Among these materials 6H-SiC is a good candidate since it has the same crystal structure (wurtzite) and relatively good lattice matching to ZnO with lattice mismatch of only $\sim 4\%$, and p-6H-SiC substrates are commercially available. In this work, n-ZnO/p-6H-SiC heterojunction diodes were fabricated after growing n-ZnO films on commercial p-6H-SiC substrates by plasma-assisted molecular-beam epitaxy (MBE). Mesa diode structures with a diameter of 250 μm were fabricated using 300/1000 \AA thick Au/Al and Au/Ni metal layers for ohmic contacts to n-ZnO layer and p-SiC, respectively. From I-V measurements a very good rectifying diode-like behavior with a leakage current less than 10^{-7} A, a forward current of $\sim 10^{-3}$ A at 8 V bias, and a breakdown voltage of ~ 20 -23 V were observed. Spectral photoresponse of the diodes was measured with illumination from the ZnO side and zero bias photoresponsivity as high as ~ 0.06 A/W was observed at 3.280 eV. With increasing reverse bias the photoresponse increased linearly reaching 0.18 A/W at -10 V. These results show that the n-ZnO/p-SiC type photodiodes are promising candidates for ultraviolet photodetectors.

G-IX.05 15:15**ZnO/SrTiO₃ TRANSPARENT FIELD EFFECT TRANSISTORS**

E. Bellingeri, D. Marré, L. Pellegrino, G. Canu, I. Pallecchi and A.S. Siri, INFN-Lamia, Corso Perrone 24, 16152 Genova, Italy, Dipartimento di Fisica, Università di Genova, Via Dodecaneso 33, 16146 Genova, Italy

Thin ZnO films (thickness from 20 to 1000 nm) were deposited by pulsed laser ablation on strontium titanate substrates. The growth is carried on in different oxygen pressures (from 10^{-5} to 10^{-1} mbar), at substrate temperatures varying from 550 to 800 °C, using a stoichiometric ZnO target.

By monitoring the growth with an in situ Reflection High-Energy Electron Diffraction (RHEED) system and by ex situ x-ray analysis, we found out that zinc oxide grows epitaxially on the 110 surface of SrTiO₃ with high crystalline quality. All the samples were also characterized by spectroscopic ellipsometry and atomic force microscopy finding a roughness which decreases with the substrate temperature and optical properties similar to those of single crystals. Electrical properties were studied by measuring the resistivity and the Hall effect as a function of the temperature and of the magnetic field. Mobility values up to 60 cm²/Vs at room temperature and 300 cm²/Vs below 50 K were obtained. By exploiting the semiconducting properties of ZnO thin films and the dielectric properties of the SrTiO₃ substrate (dielectric constant up to 10000 at low temperature), we realized field effect transistors transparent at visible wavelength. Such ZnO/SrTiO₃ field effect transistors have been fabricated both using a traditional stacked structure and a side gate planar geometry. In both cases, an on/off ratio of 106 at gate electric field as low as 1 kV/cm has been obtained.

G-IX.06 15:30**NITROGEN-DOPED ZnO THIN FILM: COMPENSATION/PASSIVATION BY IMPURITIES**

T.J. Coutts(a), X. Li, S. Limpijumnong(b), B. Keyes(a), S. Asher(a), C.L. Perkins(a), H. Moutinho(a), S.B. Zhang(a), Su-Huai Wei(a), (a)National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden CO 80401, USA, (b)School of Physics, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima, Thailand

p-type transparent conducting oxides may have potential advantages in fabricating novel solar cell structures (inverted CdTe devices, improved contacts to both p-type absorbers and organic semiconductors), in addition to being of interest for ultraviolet light emitters. Recently, reports on p-type ZnO have brought this potential closer to reality. However, there are still many problems to be overcome before p-ZnO, with opto-electronic properties adequate for device fabrication, can be made. In this article, we report on our work at NREL, in which we attempt to fabricate p-type ZnO by nitrogen doping. ZnO films demonstrating p-type behavior have been deposited on both glass and sapphire substrates using metalorganic chemical vapor deposition. Diethyl zinc and nitric oxide are used as the growth and doping precursors. However, p-type films were achieved in a narrow deposition window even though very high levels of nitrogen incorporation (~ 1 -3 at. %) have been observed for a wide range of deposition conditions. In addition, relatively low carrier concentrations compared with the nitrogen concentration were observed. Various characterization methods and first principles theoretical calculation have been utilized to analyze the problem. Possible causes for the low carrier concentration and restricted deposition window will be discussed.

G-IX.07 15:45

IN-SITU MASS SPECTROMETRY OF VAPOUR PHASE DURING Au-CATALYSED SELF-ASSEMBLY OF ZnO NANORODS

P. Prete, Istituto per la Microelettronica e i Microsistemi (IMM) del CNR, Sez. di Lecce, Via Arnesano, 73100 Lecce, Italy, A. Quarta and N. Lovergine, Dipartimento di Ingegneria dell'Innovazione, Università di Lecce, Via Arnesano, 73100 Lecce, Italy

Semiconductor nanocrystals, such as nanowires and nanorods, have gathered considerable interests due to both fundamental physics and potential applications in nanoscale electronics and photonics.

ZnO nanorods can be grown by metal-catalyst assisted Vapour-Liquid-Solid (VLS) self-assembly based on the high temperature carbothermal reduction of ZnO powders. Despite its straightforward application, the method is far from being understood. While Zn, CO, CO₂ and O₂ are obviously expected to form in the reactor, their kinetics under growth conditions is not known. In this work the vapour composition during VLS growth of ZnO was monitored by in-situ mass spectrometry to identify fundamental chemical reactions driving the VLS self-assembly mechanism. The growth of ZnO nanorods was realised by preparing ZnO-graphite mixtures with different molar ratios, and the carbothermal reduction performed at ~910 °C under N₂ flow; the growth of ZnO nanorods was carried between 750 °C and 800 °C on (100)Si using Au nanoislands as catalyst. Wurtzite-phase ZnO nanorods, with the c-axis perpendicular to the Si substrate, ranged between 40 nm and 100 nm in diameter and up to a few microns in length. We study the formation of CO, CO₂ and O₂ in the reactor during the carbothermal reduction of ZnO as function of ZnO:C molar ratios and time, and show that the carbothermal reduction occurs within the first 5-10 min since the process starts, after which the ZnO dissociative sublimation sets in. Comparison of the ZnO growth as function of time, allows to determine the effect of vapour transients and ZnO-C ageing on the VLS growth. The consequences on the growth chemistry at the Au-catalyst surface during VLS self-assembly will be discussed.

16:00

BREAK

Session X : Piezo-effects

Session chair : Y. Lu

G-X.01 16:30 -Invited-

EXPERIMENTAL OBSERVATION OF PIEZOELECTRIC FIELDS IN ZnO-ZnMgO QUANTUM WELLS

C. Morhain, CNRS, Valbonne-Sophia-Antipolis, France

17:00-19:00

POSTER SESSION 2

POSTER SESSION 2
Thursday, June 2, 2005
17:00 – 19:00

- G/PII.01** INVESTIGATION ON THE VARIATION OF GREEN, YELLOW, AND ORANGE EMISSION PROPERTIES OF ZnO THIN FILM
Hong Seong Kang, Jae Won Kim, Sung Hoon Lim, Hyun Woo Chang and Sang Yeol Leea, Department of Electrical and Electronic Engineering, Yonsei University, 134 Shinchon-dong, Seodaemun-ku, 120-749 Seoul, Korea
ZnO thin films were fabricated by pulsed laser deposition. ZnO thin films showed the various photoluminescence bands centered around ultraviolet (380nm), green (490~530 nm), yellow (570~590 nm), and orange region (610~640 nm) depending on fabrication conditions or impurity doping such as Si and P. Pure ZnO thin film showed ultraviolet emission and green emission and the intensity of that was controlled by annealing process. Si doped ZnO exhibits the ultraviolet and yellow emission. Orange emission was controlled by P diffusion into ZnO. ZnO-Si-ZnO multi-layer structure and InP substrate were used for Si doping and P doping in ZnO. Si doping and P doping was confirmed by Rutherford back scattering (RBS) and Secondary ion mass spectrometry (SIMS). The mechanism of visible emission of ZnO was investigated.
- G/PII.02** OPTICAL AND STRUCTURAL ANALYSIS OF UNDOPED AND RE DOPED BY ION IMPLANTATION BULK ZnO SAMPLES
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ZnO with its high energy band gap, 3.37 eV at room temperature, has been in the last year's one of the more studied materials. The main driving force of the research performed in this oxide semiconductor is directly related with the ability and potentialities of ZnO for optoelectronic and spintronic applications.
In the domain of optoelectronics, short wavelength light emitting devices are amongst the most important devices compound semiconductors. Their many applications include the read/write devices in optical data storage. The possibility of p-type doping relaunches the ZnO in this area. Spin electronics can be considered using ZnMeO compound semiconductor, Me being a transition metal. However, many issues related to material synthesis, defects/impurities originated in the different used growing processes are still under development and need more investigations. In this work the optical and structural characterization of bulk ZnO RE doped by ion implantation using photoluminescence and RBS is presented. Namely, the site location of Tm and Er in the ZnO lattice as well as its optical activation will be analysed in detail. The Tm and Er emission was observed at ~ 1.54 eV and ~ 0.8 eV respectively.
- G/PII.03** EFFECTS OF RAPID THERMAL ANNEALING ON NATIVE DEFECT-RELATED EMISSIONS OF ZnO THIN FILMS
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The effect of rapid thermal annealing on emission properties related to native point defects of ZnO thin films has been investigated. The ZnO thin films were grown on Al₂O₃ (0001) substrates by metal organic chemical vapor deposition method, and the rapid thermal annealing treatments were performed at 600 ~ 900 °C for 60 s in N₂ ambient. The temperature-dependant photoluminescence spectra for as-grown ZnO thin films showed three resolved peaks at 3.36 eV, 3.32 eV, and 3.16 eV. The peaks at 3.36 eV, 3.32 eV, and 3.16 eV originates from the neutral donor bound exciton, the acceptor bound exciton, and the donor-acceptor pair, respectively. The activation energy of the neutral donor bound exciton and the acceptor bound exciton is 16.11 meV and 13.56 meV, respectively. These values are in good agreement with the values in literatures. After annealing at 600 °C, the acceptor-related emission was increased strongly. However, the ratio of acceptor-related emission to donor-related emission is significantly decreased with increasing the annealing temperature. After annealing at 900 °C, the dominant luminescence is changed into emission from the neutral donor bound exciton. It is considered that these results are strongly related to the thermodynamic behavior of acceptor-related defects and donor-related defects. The correlation of defects with emission properties for the annealed ZnO thin films was confirmed through measurements of carrier behaviors, and it was observed that the similar behavior of native defects appears in Hall effect measurements and persistent photoconductivity measurements.
- G/PII.04** BAND ALIGNMENTS AND VALENCE BAND MAXIMUM ENERGIES OF ZnO AND(ZnMg)O
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The absolute energetic position of the band edge states of semiconductors can be strongly shifted by the contribution of shallow d-states of the metal. This has been particularly discussed for II-VI compounds, particularly suggesting a strong contribution of d-states to the valence bands of ZnO. The absolute energy position of the band edges determines the band alignment to other materials. We have systematically studied the band alignment of ZnO and (ZnMg)O with the II-VI semiconductor CdS with photoelectron spectroscopy. The experiments were carried out in order to determine whether the valence band maximum or the conduction band minimum is primarily affected by the increased Mg content. Thin films of ZnO and (ZnMg)O were prepared by magnetron sputtering from ceramic targets with 0% and 15% Mg content, respectively. CdS was evaporated from a compound source. All thin film deposition and surface analysis using photoemission were carried out in an integrated surface analysis system without breaking vacuum. Our results suggest that the major change is in the conduction band.

G/PII.05 EFFECT OF HYDROGEN PEROXIDE TREATMENT ON THE CHARACTERISTICS OF Pt SCHOTTKY CONTACT ON N-TYPE ZnO

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To realize ZnO based high-performance optical and electronic devices, high-quality ohmic and Schottky contacts are essential. High-quality Schottky contacts are also needed for the investigation of defect nature in ZnO using capacitance-based defects characterization techniques such as capacitance-voltage measurement, deep-level transient spectroscopy and admittance spectroscopy.

We report on the formation of good Pt Schottky contacts on the Zn-terminated n-type ZnO (0001) surfaces ($\sim 2 \times 10^{17} \text{ cm}^{-3}$) using surface treatments with a hydrogen peroxide solution. The Pt contacts on organic solvent-cleaned ZnO (0001) shows leaky behaviour with a high leakage current of $\sim -0.05 \text{ A}$ under -5 V reverse bias voltage, whereas the hydrogen peroxide-treated contacts show Schottky behaviour with very low leakage current of $\sim -6.5 \times 10^{-8} \text{ A}$ under -5 V reverse bias voltage. Schottky barrier heights estimated from current-voltage and capacitance-voltage characteristics are 0.89 and 0.93 eV, respectively. The surface treatment effect could be explained in terms of the removal of deep level defects. The PL results showed that the surface treatment is very effective in reducing deep-level defects, such as Zn interstitials and oxygen vacancies, which are known to serve as donors. The removal of such deep level defects may occur through the reactions with oxygen radicals supplied from the dissociation of hydrogen peroxide, e.g., filling vacancies or forming ZnO. Thus, the net carrier concentration of the surface-treated ZnO surface region would be reduced, consequently leading to the formation of good Schottky contacts.

G/PII.06 ELECTRICAL AND OPTICAL PROPERTIES OF LARGE AREA Ga-DOPED ZnO THIN FILMS PREPARED BY REACTIVE PLASMA DEPOSITION

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Optical (transmittance, reflectance and photoluminescence:PL) and Hall effect measurements have been carried out on large polycrystalline Ga-doped ZnO (GZO) films prepared by reactive plasma deposition (RPD). The GZO films of 180 nm thick were deposited at 200 degrees on the large glass substrate (1m wide) using two plasma guns with a traveling substrate technique. Film properties were studied with relation to the oxygen flow rate (OFR: 0~20 sccm). Films of the lowest resistivity ($2.8\text{E-}4 \text{ ohm.cm}$) was obtained for OFR of 5 sccm. Increase in OFR leads to increase in resistivity (from $2.8\text{E-}4$ to $1.8\text{E-}3 \text{ ohm.cm}$) and the decrease in carrier concentration (from $1\text{E}21$ to $2.2\text{E}20 \text{ cm}^{-3}$). The mobility tends to be maximum ($26 \text{ cm}^2/\text{Vs}$) for OFR of 10 sccm. Transmittance was more than 90% in visible. Carrier concentration dependence of infrared (1100-2400nm) transmittance and reflectance was also studied. PL exhibited a broad near-band-edge emission (peak at 3.33~3.42 eV and FWHM of 400~600 meV), in which the above bandgap emission is due to the recombination of electrons in the degenerated conduction band with holes due to the non-k-conserving band-to-band transition. The PL line shape and PL intensity reflected carrier concentration and non-radiative defect centers, respectively. By comparing these properties with those in small GZO films (10 cm square), the successful scale up in area has been performed with no degradation of the physical film properties.

G/PII.07 As-DOPED P-TYPE ZnO STUDIED BY POSITRON ANNIHILATION SPECTROSCOPY

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An evaporation/sputtering process has been recently applied to produce As-doped p-type ZnO with an As concentration of about $5 \times 10^{19} \text{ cm}^{-3}$, resulting in a hole concentration of $4 \times 10^{18} \text{ cm}^{-3}$ [1]. A recent theoretical study [2] proposes that the As-doped material is p-type due to the substitution of the As atoms onto the Zn sublattice, where the As impurities (triple donors) would attract two Zn vacancies (double acceptors) forming a defect complex $V_{\text{Zn}}\text{-As}_{\text{Zn}}\text{-}V_{\text{Zn}}$, a single acceptor. To test the model, we have performed positron annihilation experiments on a 500 nm thick As-doped ZnO sample produced by the evaporation/sputtering process. The coincidence measurements of the Doppler broadening with two Ge detectors show the presence Zn vacancy related defect clusters, based on comparison to previous experimental results [3] and preliminary theoretical calculations. The measured data does not change as a function of temperature, indicating saturation trapping of positrons into these defects. Thus, the concentration of these defects can be estimated to be more than $1 \times 10^{19} \text{ cm}^{-3}$, which is in good agreement with the acceptor concentration of about $1 \times 10^{20} \text{ cm}^{-3}$ obtained in Hall measurements [1].

[1] D.C. Look et al., APL 85, 5269 (2004). [2] S. Limpijumngong et al., PRL 92, 155504 (2004). [3] F. Tuomisto et al., PRL 91, 205502 (2003).

G/PII.08**LATTICE SITES OF IMPLANTED Cu AND Ag IN ZnO**

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The group Ib impurities Cu and Ag on substitutional Zn sites have been considered as possible candidates for p-type doping of ZnO [1]. However, in both cases only deep acceptor levels (0.17 eV for Cu [2] and 0.23 eV for Ag [3]) below the conduction band have been reported and it is questionable whether these impurities are actually incorporated on substitutional Zn sites.

In order to explore possible lattice sites of Cu and Ag we have implanted the radioactive impurities ⁶⁷Cu and ¹¹¹Ag at low doses (0.4-2x10¹³ cm⁻² at 60 keV) into ZnO single crystals. The emission channeling effects of beta particles from the decay were studied by means of position-sensitive electron detectors, giving direct evidence that in the as-implanted state large fractions of Cu and Ag atoms (60-70% for Cu and 30% for Ag) occupy almost ideal substitutional Zn sites with root mean square (rms) displacements of 0.16-0.17 Å. However, following vacuum annealing at 600°C and above both Cu and Ag were found to be located increasingly on sites that are characterized by large rms displacements (0.3-0.5 Å) from Zn sites. We conclude that in high-temperature treated ZnO Cu and Ag are most likely not simply replacing Zn atoms but are incorporated in complexes with other crystal defects or as clusters.

[1] S.J. Pearton et al, J. Vac. Sci. Technol. B 22 (2004) 932.

[2] Y. Kanai, Jpn. J. Appl. Phys. I 30 (1991) 703.

[3] Y. Kanai, Jpn. J. Appl. Phys. I 30 (1991) 2021.

G/PII.09**SYNTHESIS AND GROWTH MECHANISM OF ZnO MICRO SPHERES AND CAGES BY THERMAL EVAPORATION METHOD**

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High density of micro-sized ZnO hollow spheres and cages have been prepared on two different substrates, Si(100) and steel alloy, by a very simple thermal evaporation method using metallic Zinc and oxygen at 300-600°C. The possible growth mechanism indicates that the formation of these cages and hollow spheres consists of aggregation of Zn droplets, oxidation on the sheath, and sublimation/evaporation of the Zn from the interiors of these spheres. The average size of the deposited materials ranges from 1-5 μm. The chemical compositions, observed by EDS spectra, of the inner and outer surfaces of the deposited spheres and cages indicate that the ratios of the Zn and oxygen on the both surface was almost same. Transmission electron microscope and X-ray diffraction analysis showed the wurtzite hexagonal structure of the synthesized materials which are highly crystalline and grown along the [0001] direction. The room temperature photoluminescence spectra in both the cases showed a broad band in the visible region with suppressed and short indicating that these structures having the more structural defects.

G/PII.10**MEASUREMENT OF THE MEAN INNER POTENTIAL OF ZNO NANORODS BY TRANSMISSION ELECTRON HOLOGRAPHY**

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The mean inner potential of ZnO was measured by means of electron holography in a transmission electron microscope. Accurate measurements of the mean inner potential by transmission electron holography are often hampered by imprecise knowledge of the sample thickness. To overcome this problem, ZnO nanorods with a well-defined geometry and diameter were used in our study. Likewise artifacts due to typical specimen preparation procedures could be avoided. Holograms were taken under kinematical diffraction conditions using high-resolution transmission electron microscopy images for magnification calibration. The phase and amplitude of the image wave were extracted numerically from the sideband of the digitized hologram. The phase shift of the transmitted beam of the image wave with respect to the reference wave traveling through the vacuum yields the mean inner potential which was determined to be (15.9 ± 1.4) V for ZnO. This experimental value is in good agreement with the calculated value of 15.8 V using ab initio density functional theory computations and 16.1 V from Doyle Turner electron scattering factors computed for isolated atoms.

G/PII.11**OPTICAL AND MORPHOLOGICAL FEATURES OF BULK AND HOMOEPITAXIAL ZnO**

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While zinc oxide (ZnO) has been known and utilized since long time, the interest in this material as a semiconductor has been renewed during the recent years thanks to the advancement in bulk and epitaxial growth technology. Despite the progress made in growing ZnO with several contemporary techniques, the material still needs to be mastered in order to achieve reproducibly a desired quality and to understand important properties. We have studied hydrothermally grown ZnO single crystals and homoepitaxial layers deposited on such substrates by MOCVD. The epi-layers grown on the (000-1) O terminated surface exhibit dense morphology up to a thickness of ~400 nm. Hillocks characteristic of growth on well-oriented substrates are observed by AFM along with specific tail-like defects on the layer surface extending to 100 μm along the [1-100] direction. The morphology and surface defects will be discussed in details. Optical properties of both bulk crystals and epi-layers were assessed by low temperature PL and CL measurements. Luminescence from all samples extends from the band edge to the green spectral range with features characteristic of excitonic, donor-acceptor pair and deep level emission. The excitonic peaks from the epilayer are narrower and more intense. Some shift of characteristic peaks was observed in differently doped samples, as well as depending on the spot position. EPR measurements indicate presence of V, Mn and other transition metals. The influence of annealing on defects in substrates is studied

- G/PII.12** CHARACTERIZATION OF ZNO THIN FILMS FOR SURFACE ACOUSTIC WAVE APPLICATIONS
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 Zinc oxide (ZnO) is a versatile material for many applications due to its structural, electrical and optical properties. Piezoelectric polycrystalline thin films of ZnO have emerged as excellent candidates for surface acoustic waves (SAW) devices because of their desirable c-axis preferential growth, their high coupling coefficient and their technological compatibility with conventional silicon process.
 In this paper, we investigate various deposition conditions (pressure, argon-oxygen ratio, substrate temperature and RF power) on the properties of ZnO thin films grown by reactive magnetron sputtering technique. The crystallinity and crystal orientation of the films are analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The film quality was also studied in term of acoustic wave propagation by developing different SAW devices. Interdigital transducers (IDTs) were fabricated on ZnO/substrate by classical photolithography process. Two types of substrate have been tested silicon and quartz. In order to get the best performances for our sensor applications different ZnO thickness layers and different wavelengths have been developed. In the ZnO/Si structure, the ZnO layer is employed as piezoelectric film and also as sensitive film for gas sensor application whereas for ZnO/quartz structure, the ZnO film is used to enhance the device performances (i.e. increase electromechanical coupling factor and to achieve a zero temperature coefficient of frequency) and also as sensitive layer.
- G/PII.13** PHOTOLUMINESCENCE PROPERTIES OF CO²⁺ DOPED ZNO NANOCRYSTALS
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 Semiconductors can be made ferromagnetic by partially replacing non-magnetic elements with magnetic transition ions. Recently, room temperature ferromagnetism was reported for ZnO doped with transition metals such as Co and Ni. The origin of ferromagnetism in ZnO remains as yet unclear. In this study, photoluminescence of Co²⁺ doped ZnO nanocrystals in the strong confinement regime, is used to study the electronic properties of Co²⁺ in a ZnO host. This enables us to monitor delocalization of the Co²⁺ levels by means of the quantum confinement effect. The Co²⁺ doped ZnO quantum dots were prepared using a colloidal synthesis. Room temperature emission measurements showed an additional emission (1,8 eV), next to the ZnO exciton recombination and yellow trap emission (2.2 eV). The additional emission is due to transitions between cobalt d-d levels. Its energetic position and structure do not show any size or Co²⁺-concentration dependence. Measurements at 4.2 K demonstrate that the Co²⁺ emission has a lifetime of 80 ns and consists of a series of narrow peaks, separated by the ZnO E₂ phonon energy. These results indicate that the Co²⁺ states in the ZnO host are very localized, questioning interpretations of ferromagnetism in ZnO in terms of the formation of a cobalt spin-split d-band.
- G/PII.14** INTRINSIC FERROMAGNETISM IN SPUTTERED (Zn,Co)O(0001) THIN FILMS
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 Room temperature ferromagnetism has been recently observed in Co doped ZnO and this system has therefore potential application for spin injection into semiconductors. We have elaborated (Zn,Co)O/Al₂O₃(0001) thin films by reactive DC magnetron sputtering in order to understand the origin of their outstanding magnetic properties. Quasi-epitaxial films have been grown at 600°C that present room temperature ferromagnetism, a magnetic moment around 0.5mB at 10K and strong out of plane magnetic anisotropy for Co concentration of 25%. Channeling Rutherford backscattering along c axis and out of plane Bragg direction show that most Co atoms are located in substitutional crystallographic sites. This conclusion is further supported by the observation of Co²⁺ optical transitions and we rule out the possible presence of Co metal clusters as the origin of ferromagnetism. X-MCD experiments have been performed at Co L II,III edges. The Co magnetic moment deduced from the application X-MCD sum rules is in good agreement with SQUID magnetometry, but the strong orbital moment (ml/ms ~ 0.6-0.8) rules out a Co S=3/2 ground state. Finally we show that post deposition He irradiation or annealing can lead to improvement of both structural and magnetic properties.
- G/PII.15** STRUCTURAL AND OPTICAL MICRO-CHARACTERIZATION OF ZnO GROWTH ON PATTERNED SUBSTRATE
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 Growth on a pre-patterned substrate was used to improve the quality of heteroepitaxial grown ZnO. The layer was grown by RF plasma-assisted molecular beam epitaxy (RF-PAMBE) on (0001) sapphire directly patterned with stripes of a 100 nm thick SiO₂ mask. The width of the stripe masks and the windows is 7 μm and 3 μm, respectively. This structure is subsequently overgrown with a 1 μm thick ZnO layer. Electron backscattered diffraction (EBSD) indicated that growth was directed epitaxially by the sapphire, although a number of misoriented grains were detected.
 We present the microscopic analysis of such grown ZnO layers by means of scanning cathodoluminescence microscopy (CL). The spatially integrated spectrum of the sample shows a red shift of 3.7 meV with respect to the fully relaxed position of excitons in ZnO. The regions between the mask, the coherently grown regions, are dominated by a sharp I5 emission. In contrast, the local spectra of the overgrown areas show a new luminescence channel at a spectral position just about the I3a line.

- G/PII.16** IMPACT OF ELECTRON BEAM IRRADIATION ON THE OPTICAL PROPERTIES OF ZnO
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 We present a detailed analysis the effect of electron beam irradiation on the optical properties of ZnO. The CVD grown sample was doped with NH₃. The spatially averaged cathodoluminescence (CL) spectrum recorded from the sample surface is dominated by the impurity bound exciton I8 (E = 3.356 eV, FWHM = 8.5 meV). In addition, the bound excitons I0/I1 (3.370 eV) and I2/I3 (3.365 eV) as well as a bound exciton line (Ix) at 3.348 eV (between I10 and I11) are visible. All lines are 3.5 meV red shifted with respect to their fully relaxed position. For our study a certain sample region (30 μm x 20 μm) was exposed to electron beam irradiation of high excitation density at 5K. The temporal evolution of the spatially integrated spectrum was in situ recorded every 5 ms. A strong impact on the luminescence spectra is found. At the start of the irradiation, the spectrum is dominated by I2/I3. The I8 and the Ix line are also visible, but with much lower intensity. With longer lasting electron beam irradiation the intensity of I8 increase and that of I2/I3 decrease. The dominance of I2/I3 vanishes within the first seconds. In contrast, the intensity of Ix remains constant.
- G/PII.17** PREPARATION AND PROPERTIES OF LUMINESCENT ZNO NANOPARTICLES IN THE MESOPOROUS SILICA MATRICES
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 In the present work we investigate the formation of luminescent zinc oxide nanoparticles in one-dimensional solid state nanoreactors formed by the porous systems of mesoporous silica with different pore diameters. The formation of ZnO nanoparticles in mesoporous silica matrices was achieved by intercalation technique based on the introduction of a hydrophobic Zn compound, Zn acetylacetonate, into the hydrophobic part of silica-surfactant composite, followed by thermal modification at different temperatures. The alternative route used for the preparation of nanocomposites ZnO/SiO₂ is so-called direct synthesis, which involves an intercalation of hydrophobic Zn²⁺ compound into liquid crystal surfactant micelle at initial stage of the synthesis. Nanocomposites were characterized by N₂ physisorption, SAXS, chemical analysis, TEM, XRD, EDX, UV-vis and photoluminescent (PL) spectroscopy. The UV-vis spectra of the as-prepared samples show a significant blue shift of an absorption band edge comparing with bulk ZnO, which demonstrates an increasing band gap of ZnO due to the quantum size effect. The PL spectra of the as-synthesized samples under excitation with 337 nm light show an intensive UV emission band of ZnO with a maximum at 370 nm, while emission in the visible range of spectra almost disappeared. The intensity ratio I_{UV}/I_{visible} for the as-synthesized nanocomposites is up to 200 (at 77 K).
- G/PII.18** X-RAY STUDIES ON THE OPTICAL AND STRUCTURAL PROPERTIES OF ZnO NANOSTRUCTURED FILMS
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 ZnO is a promising material for short-wavelength light emitting devices and for a wide range of technological applications due to its wide band-gap and peculiar optical, electrical and piezoelectrical properties. We have prepared pure and doped ZnO thin films using different techniques: DC magnetron sputtering, atmospheric pressure chemical vapor deposition (APCVD) and hydrolyzes of zinc acetate in methanol. In this way, we have obtained nanostructured samples with different thickness and different optical properties. The characterisation of the films has been performed by luminescence spectroscopy and x-ray diffraction measurements at room temperature. ZnO polycrystalline powder samples have been used as reference. We have focused our attention on the APCVD samples which, according to XRD measurements, reveal an highly (002) oriented crystalline structure and exhibit a very intense green band emission. We have carried out Zn K-edge x-ray absorption near-edge fine structures studies (XANES) using synchrotron radiation at BM08 of ESRF (France) by detecting x-ray excited optical luminescence (XEOL) and x-ray fluorescence (FLY). The aim of these studies is to characterize the local structure of the different luminescent nanostructures.
- G/PII.19** PEMOCVD OF ZNO THIN FILMS, DOPED BY GALLIUM AND THEIR MAIN PROPERTIES
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 Gallium (Ga) is a shallow donor in ZnO and it is used to introduce stable conductive behaviour in order to produce transparent ZnO conducting films. In this work, thin films of ZnO, doped by Ga were deposited by plasma enhanced metalorganic chemical vapor deposition (PEMOCVD). Highly conducting and transparent ZnO:Ga thin films were obtained on various substrates: sapphire (0001), Si/SiO₂, Glass. The electrical and optical properties of the films deposited at various substrate temperatures were investigated. All deposited films have demonstrated an optical transmittance about 85-90 % in the range of the visible light (400 -800 nm) and low resistivity (as compared with ITO). The advantages and perspectives of the PEMOCVD technology in case of using low temperature polymer substrates for flexible electronics are revealed.

- G/PII.20** PREPARATION AND CHARACTERIZATION OF Ga-DOPED ZnO THIN FILMS BY PULSED LASER DEPOSITION
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 In this communication we report on the preparation and characterization of Gallium doped ZnO. Contrary to what happens when doping with Al, it has been shown that Ga-doping increases the photoluminescence efficiency of ZnO [1]. In spite of this, Ga remains as one of the less studied donor impurities in ZnO. Gallium doped ZnO thin films were prepared by pulsed laser deposition on different substrates (c-plane sapphire, natural mica and ScAlMgO₄) at 400°C and studied by optical absorption, photoluminescence, transport measurements and atomic force microscopy.
 As deposited samples have very high conductivity and present a broad absorption edge, blue-shifted with respect to the one of intrinsic ZnO due to Moss-Burnstein effect. Annealing in air at temperatures up to 800°C improves the optical properties by compensating the oxygen deficiency. The exciton structure is observed even in samples with relatively large Ga contents. These annealing processes reduce the thin film conductivity, but the Ga donor is shown to remain electrically active. The photoluminescence spectra of Ga-doped ZnO exhibits a donor-acceptor-pair band centered at about 3.32 eV at 15 K and with a FWHM of about 100 meV. The intensity of the DAP increases with the Ga content and while the maximum shifts to lower photon energies.
 [1] T. Makino, Y. Segawa, S. Yashida, T. Tsukazaki and M. Kawasaki, Appl. Phys Lett. 85, 759 (2004)
- G/PII.21** COMPOSITIONAL ANALYSIS AND HIGH RESOLUTION IMAGING OF GRAIN BOUNDARIES IN Pr-DOPED ZnO CERAMICS
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 Metal oxide varistors are multijunction materials whose highly nonlinear current-voltage characteristics derive from the electrical activity of their grain boundary regions. To obtain high degree of nonlinearity in polycrystalline ZnO it has been found to be necessary to add a minimum of two types of cation dopants in sufficient concentrations (~0.5 - 1.0 mol%) and to follow sintering with an oxidative anneal at ~600° C. The common dopants include transition metals, such as Co and Mn which have ionic radii similar to that of Zn and therefore have high solubilities and low grain boundary segregation coefficients, an dopants with large ionic radii, such as Bi and Pr, which segregate at grain boundaries and usually form intergranular phases.
 In the present investigation an electron microscopy investigation has been conducted in ZnO:Pr:Co varistor structures prepared by a new in-diffusion method. It has been shown that some boundaries host intergranular precipitates of a Pr_xO_y-based phase. All observations lead to the conclusion that grain boundaries exhibit Pr segregation, while Co is homogeneously distributed in the ZnO matrix. No continuous intermediate layer is present at the ZnO/ZnO boundary nor at the Pr₂O₃/ZnO interfaces. This is consistent with a barrier model solely on a space charge depletion region (s).
- G/PII.22** EFFECT OF THERMAL ANNEALING ON THE OPTICAL PROPERTIES OF ZINC OXIDE THIN FILMS GROWN BY PLD
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 ZnO thin films of about 120 nm thick were deposited by Pulsed Laser Deposition (PLD) on different substrates (fluorite, sapphire and mica) at 400°C. The optical properties of these ZnO films were studied by means of photoluminescence (PL) and optical absorption (OA) as a function of the annealing atmosphere and temperature.
 Good crystalline quality is observed for all the substrates used which is evidenced by the characteristics (intensity and width) of the well known UV photoluminescence peak related to the bound exciton in ZnO as well as the two phonon-satellites observed. The subsequent thermal annealing gives rise to different PL spectra depending on the temperature and atmosphere used. The main aspect of the annealed samples is the apparition of a broad PL emission band centred at about 500 nm. The evolution and the ratio between the intensity of the two PL signals strongly depend on the atmosphere used (oxidizing or reducing). In general the green emission band decreases with temperature in reducing atmosphere and increases when annealing in reducing atmosphere. The fundamental absorption edge was also obtained by 'in situ' measurements at different temperatures during the annealing procedure. The wide and blue shifted absorption edge of the as-grown degenerated thin films progressively becomes more intrinsic and exhibits exciton peaks as the film acquires the stoichiometric oxygen proportion.
- G/PII.23** OPTICAL AND ELECTRICAL PROPERTIES OF ZnMnO LAYERS GROWN BY PEROXIDE MOLECULAR BEAM EPITAXY
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 In recent years, Mn-doped wide-gap semiconductors such as ZnO and GaN have attracted considerable attention. The interest in these materials was triggered by theoretical predictions of ferromagnetism with Curie temperatures above 300 K. However, the experimental results are still controversial. The electronic properties of Zn(Mn)O are of interest regardless, because the effect of Mn incorporation on the band gap allows one to increase the functionality of structures by combining magnetoelectronics and band gap engineering. In this work we investigate the optical and electronic properties of Zn(Mn)O layers grown by peroxide MBE and discuss a possible correlation with their magnetic behavior.
 The Zn(Mn)O layers containing up to 50% of Mn were characterized by HRXRD, PL, and optical absorption. Depth profiles for Mn were studied using SIMS and Auger, and the measured Mn concentrations agree with those estimated from the flux measurements. A blue shift of the band edge revealed from optical absorption measurements points to the incorporation of at least a part of Mn atoms on lattice sites. A linear increase in the Zn(Mn)O band gap and an enhancement of the broad below band gap absorption associated with Mn ions were observed with increasing Mn composition. Surprisingly, no shift in near band edge emission was detected in the PL data. Additionally, as indicated by Hall effect measurements, the layers were highly resistive suggesting strong electrical compensation of the Zn(Mn)O films by Mn incorporation.

G/PII.24**CONDUCTION BAND PARAMETERS OF ZnO**

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We calculated the ordinary and extraordinary imaginary part of the dielectric function (DF) close to and above the absorption edge of ZnO. Discrete exciton, band-to-band, and exciton enhanced interband optical transitions were included. The valence band structure was calculated using an A-set of parameters reported by Lambrecht et al., Phys. Rev. B 65, 075207 (2002). Comparison to experimental data for the DF of ZnO at room temperature yielded a value of 0.26 (0.23) for the relative transverse (longitudinal) effective mass of electrons at the bottom of the conduction band. The momentum matrix element was found to be 10.5 eV and 11.4 eV for the polarisation of light perpendicular and parallel to the optic axis, respectively. We observe that the conduction band is nonparabolic, with the nonparabolicity being close to the one predicted by a two-level (Kane) model indicating that effects of remote bands are not large in ZnO. Further, the reliability of the results will be discussed in view of accuracy of experimental data and parameters involved into the calculation.

G/PII.25**PHONON AND PLASMON PROPERTIES IN (N,Li,P,Sb,Ga,Al)-DOPED ZnO AND (Mg,Cd,Mn,Ni,Co,Fe,Cu)ZnO ALLOY THIN FILMS**

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Pathways to band gap tailoring, n- and p-type conductivity, ferroelectricity and ferromagnetism in ZnO semiconductors are provided by doping and alloying with different elements, and visions for potential applications in electronic, optoelectronic or spintronic nanostructure architectures are at hand. Raman scattering resembles a tool of excellence to study optical phonon modes in doped or alloyed thin films, with the potential to identify dopant or alloy material incorporation in ZnO-based thin films and, eventually, ZnO based nanostructures.[1,3] Infrared spectroscopic ellipsometry (IRSE) allows for the determination of phonon mode parameters, and free charge carrier parameters, such as density, anisotropic mobility, and eventually the effective mass parameters.[2] We report on a detailed study of phonon and plasmon properties in (N,Li,P,Sb,Ga,Al)-doped ZnO and (Mg,Cd,Mn,Ni,Co,Fe,Cu)ZnO alloy thin films grown by pulsed laser deposition on sapphire substrates.[3] We present results on dopant and alloying induced resonance modes and effects on carrier mobility and effective mass parameters. Experimental phonon modes are compared with MREI model and local mode calculation schemes. Mode assignment can be done for particular dopant elements suggesting use of Raman scattering for their identification.

[1] A. Kaschner et. al, APL80, 1909 (2002).

[2] A. Kasic et. al, pss(c) 0, 1750 (2003).

[3] C. Bundesmann et. al, APL81, 2376 (2002); APL83, 1974 (2003); APL85, 905 (2004).

G/PII.26**DEPENDENCE OF ELECTRICAL PROPERTIES OF UNDOPED ZnO THIN FILMS PREPARED BY ELECTRON BEAM DEPOSITION WITH RF PLASMA ON FILM THICKNESS**

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Polycrystalline undoped ZnO films prepared by electron beam deposition with rf plasma deposited on glass substrates with a size of 4 inch were studied. In this work, substrate temperature was kept to be 473 kelvin. Film thickness was varied: 25, 50, 100, 200 and 300 nm. Critical film thickness which determines electrical properties, resistivity, carrier density, and carrier mobility obtained from Hall effects measurement, was found to be 100 nm: Below a film thickness of 100 nm, Hall mobility increases with increasing film thickness; Beyond 100 nm, carrier density and Hall mobility was almost constant against film thickness. Electrical properties of ZnO films prepared with O₂ flow rate (OFR) ranging from 0 to 50 sccm were investigated. Below OFR of 30 sccm, for ZnO films with film thickness of 50, 100, 200 and 300 nm, dependence of resistivity, on the order of 10⁻² ohm-cm, of the films on OFR was found to be little. Beyond OFR of 30 sccm, resistivity of those films described above substantially increased with increasing OFR. On the other hand, for ZnO with a film thickness of 25 nm, there increases resistivity on the order of ranging from 10⁻² to 10⁺⁶ ohm-cm with increasing OFR. On the basis of analysis of data of film thickness, maximum of film growth rate and minimum of resistivity of ZnO films was obtained at OFR of 30 sccm for all ZnO films except for that with a film thickness of 25 nm.

G/PII.27**THE IMPROVEMENT OF GaN LED USING ZnO BASED TRANSPARENT CONDUCTING OXIDE**

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The overall performance of GaN LEDs is strongly affected by the resistances and light transmission efficiencies of p-ohmic contact materials. Among transparent conducting oxides, ZnO is a good conducting oxide which has a high transparency in the visible spectral region, a high electrical conductivity, and a large work function which can be controlled by doping. In this study, we investigated the indium oxide doped ZnO (IZO) ohmic scheme as a transparent and low resistance contact layer on p-GaN. The IZO based contact yielded a very low specific contact resistance of 3.6×10⁻⁵ Ω•cm² when annealed at 500 °C for 1 min in a nitrogen ambient, and the transparency was above 80 % at wavelengths of 450 nm. In addition, we fabricated an InGaN/GaN MQW LED with a dimension of 300×300 μm²; using transparent IZO based ohmic contact as a current spreading layer for p-GaN in order to study the optical output power. GaN LED with the transparent IZO based ohmic contact showed that the forward voltage is lowered by 0.15 V under a nominal forward current of 20 mA compared to GaN LED with Ni/Au ohmic contact. The light output power of LED with IZO based contact was increased by 38.9 % at 20 mA due to the improvement of ohmic contact and light transmission efficiency.

G/PII.28**MICROWAVE SYNTHESIS OF ZnO MICROTUBE**

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ZnO is a kind of wideband semiconducting materials, microwave is a rapid synthesis method in materials synthesis, also can improve the properties of materials. ZnO microtube is prepared in 2450MHz microwave synthesis system which was made domestically, characterized in XRD, SEM and Raman shift in this paper. It shows that the ZnO microtube is single crystal microtube with perfect blue light emitting property, microwave is satisfied method to synthesis advanced materials such as ZnO single crystal materials.

G/PII.29**RAMAN SPECTROSCOPY ON ZnO CRYSTALS GROWN BY VAPOUR TRANSPORT**

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ZnO crystals were grown by transport in vapour phase, under zinc-rich conditions. Some of these crystals were annealed at temperatures in the range 900-1200 °C in vacuum, as well as oxygen and zinc atmospheres. In order to understand the influence of the growth conditions and annealing processes on the structural properties we have performed a characterisation using Raman spectroscopy. All active Raman modes of ZnO and some second order phonons, which disappear at low temperature (25 K), have been observed. Besides, the evolution of E2l and E2h modes as a function of the annealing atmosphere has been analyzed. A significant reduction of the FWHM, for both modes, has been observed in all annealed samples. Thus, we can conclude that the used annealing temperatures, higher than 900°C, improve the structural quality of ZnO crystals. However, some differences can be observed between the samples whose were annealed at different atmospheres. We have attributed the differences to intrinsic point defects. The analysis of these differences, taking into account the strong dependence of E2l and E2h modes with zinc and oxygen mass fluctuations respectively [1], have allowed us to gain a further insight on the chemical nature of the intrinsic point defects of ZnO crystals.

[1] J. Serrano, F.J. Majón, A.H. Romero, F. Widulle, R. Lauck, M. Cardona, Phys. Rev. Lett. 90 (2003) 055510.

G/PII.30**REACTIVITY OF THE Fe/ZnO(000-1) INTERFACE**

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Numerous publications have shown the potential of zinc oxide in the field of catalysis, sensors and optoelectronic devices.

In connection with the development of new magnetic storage devices, our investigation is aimed for the properties of the Fe/ZnO(000-1) interface regarding the temperature dependence of both reactivity and diffusion processes at the contact area.

Using photoelectron and Auger electron spectroscopy as well as LEED experiments the sequential deposition of iron at UHV conditions on a ZnO(000-1) single crystal at room temperature was monitored to investigate simultaneously the oxidation state and the crystallinity of the thin films. We found a dominating layer by layer growth mode as well as an oxidation of approximately 50% of the first monolayer of iron mostly to FeO. Beside the sixfold symmetry LEED pattern of the Zn(000-1) substrate before deposition no indication of a superstructure or crystallinity of the films could be detected. To investigate the thermal stability of the interface the crystal was heated up stepwise to 600° C. During this procedure the deposited iron film was not only oxidised completely to Fe₂O₃ but showed a sharpening of a sixfold symmetry LEED pattern. Most likely during thermal treatment oxidised iron forms islands on ZnO (000-1) uncovering simultaneously the substrate.

By means of sputtering with Ar⁺-Ions at room temperature Fe₂O₃ could be completely reduced to FeO and oxidised again through thermal treatment at 600°C.

G/PII.31**ELECTRICAL CHARACTERISTICS OF PT-RU ALLOY SCHOTTKY CONTACT ON ZNO FABRICATED BY A COMBINATORIAL METHOD**

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ZnO has been attracting attention for use in light emitting and light detecting devices in the UV wavelength region. For these applications, high quality and thermally reliable Schottky contacts are inevitable. In this paper we have demonstrated hetero structures consisted of composition spread metal-alloys on ZnO and quick screening for their electrical properties with combinatorial alloy synthetic technique to fabricate the Schottky UV region photodiode. New binary alloy with high Schottky barrier heights and thermally reliable contacts is developed using the combinatorial ion beam assisted deposition system. Pt-Ru alloy composition spreads were deposited as the Schottky metal alloys on a patterned ZnO single crystal. Pt is a candidate for high work function value metal and Ru is a candidate for thermally stable metal with lower work function. It was obtained that the compositional fraction of the Schottky binary alloys changed continuously, and the Schottky barrier heights measured by current-voltage measurements increased with increasing Pt content. Their electric properties will be discussed in detail in the presentation.

G/PII.32 INFLUENCE OF TIME, LIGHT AND TEMPERATURE ON THE ELECTRICAL PROPERTIES OF ZINC OXIDE TFTS

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Transparent active devices are assumed to be the next big step in optoelectronics. The possibility of producing these devices in large scale depends greatly on the reliability of the transparent transistors.

In this work we present a study about the influence of some of the most important external factors on the electrical properties of transparent TFTs, using zinc oxide produced at room temperature as the semiconductor material. Electrical characterization performed one year after the production of the devices showed a decrease in the on/off ratio of about one order of magnitude (from ~105 to ~104), mainly due to the increase of the off-current, and also a very small decrease in the saturation mobility and threshold voltage (by a factor of only about 0.9 in both parameters). Exposure to ambient light doesn't appear to have a noticeable effect on the electrical properties, resulting only in a slight increase of the off-current. This is an important point concerning the application of these devices into active matrix displays. In order to evaluate the thermal resistance of the TFTs, they were tested with temperatures ranging from 20 to 75 °C. At the higher temperatures we noticed that the off-current increased almost two times, while the other electrical properties remained essentially the same. After cooling, the off-current returned to its initial values, meaning that the process is totally reversible.

G/PII.33 STRUCTURAL, ELECTRICAL AND OPTICAL PROPERTIES OF THE THIN ZNO FILMS PREPARED BY CHEMICAL PRECIPITATION

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This paper presents a chemical method for production of thin ZnO films through chemical precipitation technique. The method consists in obtaining thin ZnO film (300-500 nm) by thermal decomposition of zinc hydroxide formed as a consequence of precipitating from alkaline solution of zinc acetate, in presence of ethylenediamine on a solid support (glass, i.e.). Utilization of this method implies investment economies, simplicity as work technique and the final production of some good quality thin ZnO films. The surface morphology and crystallinity of the obtained ZnO films are characterized by scanning electron microscopy (SEM) and x-ray diffractometry (XRD). Optical transmission through the films is measured spectrophotometrically in the wavelength range 300-1000 nm. The optical energy gap is estimated by extrapolating the square of the absorption coefficient versus the wavelength energy. The electrical conductivity is measured by the van der Pauw method. The SEM micrographs of the ZnO samples reveal existence of regular-shaped crystals, i.e. hexagonal-shaped crystals. The XRD patterns for the pure ZnO samples points out only the reflection maximum characteristic to ZnO and indicates that the crystallites of ZnO films are preferentially oriented along the c-axis, [002] direction of the hexagonal crystal structure. The ZnO thin films are transparent (90 % optical transmittance) in the near UV, VIS and near IR ranges. These films have a band gap of 3.20-3.25 eV. The electrical conductivity of ZnO films increases with film thickness. Measurements of the activation energy show that ZnO films have one donor level around 50 meV under the conduction band and another at 150 meV below the conduction band.

G/PII.34 CONTROLLABLE GROWTH OF 1D ZnO NANO-STRUCTURES

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Considerable research efforts were focused recently on one-dimensional (1D) nanomaterials due to their potential for fundamental studies and applications as building blocks for nanodevices. Zinc oxide (ZnO) is recognized as a promising material for short-wavelength photonic device applications because of its superior optical properties of a wide direct band gap of 3.4 eV and a large exciton binding energy of 60 meV. A lot of methods were used to prepare quasi-1D ZnO nanostructures such as nanowires, nanobelts, nanoneedles and nanotubes etc. But it is difficulty to controllably grow 1D ZnO nanostructures. In this work, aligned ZnO nanotubes and nanowires have been grown on Si substrates by a catalyst-free MOCVD method. The morphology and structure were characterized by scanning electron microscopy (SEM), x-ray diffraction (XRD) and transmission electron microscopy. Figure 1 shows the SEM images of the ZnO nanotubes and nanowires grown on Si substrate. The outer diameters of the nanotubes are in the range of 50~100 nm with an average value of 80 nm (Fig. 1a). Figure 1 also shows the nanowires with different diameters of 6-200 nm, which have been controlled by the growth conditions. XRD and TEM show that these 1D ZnO nanostructures are with wurtzite crystal structure. Room-temperature photoluminescence (PL) measurements indicate that the nanostructures have high optical properties.

G/PII.35 WEAK FERROMAGNETISM IN TEXTURED Zn_{1-x}(TM)_xO THIN FILMS

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Room-temperature ferromagnetic Zn_{1-x}(TM)_xO semiconductor thin films have been grown by pulsed laser deposition (PLD) on sapphire substrates and the effect of the substitution of Zn²⁺ ions by the transition metal ions (Mn²⁺ or Ti²⁺) has been investigated.

The magnetic properties of the Zn_{1-x}(TM)_xO films have been investigated by a superconducting quantum interference device (SQUID). For electrically nearly isolating Zn_{1-x}(TM)_xO films with specific structural properties we observed a weak ferromagnetism for temperatures up to 400 K [1], while other films were paramagnetic or super-paramagnetic. As already observed by magnetic force microscopy (MFM) in other soft ferromagnets like irradiated graphite [2], also the ferromagnetic Zn_{1-x}(TM)_xO films revealed a stripe-like domain formation. Here we study the possibility to prove the intrinsic nature of the observed ferromagnetism by correlating the results of SQUID and spatially resolved MFM measurements.

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[2] P. Esquinazi, D. Spemann, R. Höhne, A. Setzer, K.-H. Han, and T. Butz, Phys. Rev. Lett. 91 (2003) 227201.

G/PII.36**ALIGNED ZNO NANORODS GROWN ON ZnO THIN FILMS AND METALLIC CLUSTERS**

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One dimensional semiconductor materials such as GaN, ZnO,... nanowires have attracted much interest because of various remarkable physical and chemical properties distinctive from conventional bulk or thin film ones. Actually many groups work on ZnO nanostructures as nanorods, nanobelts, nanowires. The large surface area of these nanostructures makes them attractive for gas and chemical sensing. Moreover, due to the radial quantum confinement, ZnO nanowires possess high density of states at the band edge. So the ZnO nanowire based nanodevice, which can realize UV lasing action at room temperature with low lasing threshold is quite potentially feasible. Finally the ability to control their nucleation sites makes them candidates for micro-lasers or memory arrays.

We present a simple physical vapor-phase transport technique of single crystalline ZnO nanostructures synthesis. These nanostructures are supported by different kinds of substrates: Si, metallic clusters/Si, ZnO/Si and metallic clusters/ZnO/Si. ZnO thin film deposited on Si substrate can be used as a buffer layer and metal can be deposited in order to form nanosized particles. Depending on the metal used we show that different kinds of nanostructures can be obtained (nanorods, nanobelts...). Moreover the density and size can be tuned by the size of the metallic clusters and in some cases vertical aligned perpendicularly to the substrate ZnO nanorods was successfully obtained. A boundary assistant nucleation mechanism followed by a vapor-solid (VS) process was proposed to explain the nanorod growth and some photoluminescence measurements will be presented.

G/PII.37**REAL TIME GROWTH STUDIES ON THE EXPANDING THERMAL PLASMA DEPOSITED ZnO FILMS BY MEANS OF IN SITU SPECTROSCOPIC ELLIPSOMETRY**

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One of the most studied transparent conductive oxides in the last decade has been zinc oxide. Due to its remarkable properties (i.e., wide bandgap, large exciton binding energy, piezoelectric character), zinc oxide is considered a versatile material in applications such as UV light emitters, solar cells, surface acoustic wave devices and polyLEDs. The use of plasma technology has the advantage of compatibility with thermally sensitive substrates, i.e. polymers, for applications in the field of plastic electronics. Good material with reproducible electro-optical and structural properties has already been obtained by many groups. However, film growth studies by means of in situ and real time techniques have rarely been reported.

In this work, an argon-fed expanding thermal plasma in which diethylzinc and oxygen are admixed downstream has been used for undoped zinc oxide deposition. Chemical analysis and morphological/structural characterization have shown that the films are sub-stoichiometric and natively textured (surface roughness), crystalline ((002) oriented). Moreover, electrical measurements have provided low resistivity and high mobility values of 5×10^{-3} Wcm and 50 cm/Vs, respectively. In situ real time spectroscopic ellipsometry has been used to investigate the film growth i.e. its optical properties. Particular attention has been paid to the evolution of the surface roughness, an important property in solar cells applications where a rough front electrode is needed for light trapping.

G/PII.38**ACCEPTOR RELATED LUMINESCENCE IN ZnO**

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G/PII.39**OPTICAL PROPERTIES OF ZnO NANORODS AND NANOWIRES. INFLUENCE OF (Zn,Mg)O ENCAPSULATION**

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We report continuous-wave and time-resolved optical spectroscopy of ZnO nanorods of varying diameters and nanowires grown by MOVPE, under varying thermodynamical conditions. We discuss the influence of these conditions and of encapsulation of some nanorods by (Zn,Mg)O on the efficiencies and dynamics of the different spectral components. Generally, photoluminescence spectra are dominated by a strong excitonic contribution related to a series defect-bound excitons and to their two-electron satellites. The relative intensities of the various contributions and of the lower-lying donor-acceptor band appear to be strongly dependent of the grown conditions and of the diameter of the nano-structures.

- G/PII.40** MICROSTRUCTURE AND CATHODOLUMINESCENT PROPERTIES OF THERMALLY SPRAYED ERBIUM-DOPED ZIN OXIDE FILMS
 J.L. Bubendorff(b), A. El Hichou(a), J. Ebothe(a), (a)Université de Reims, UFR Sciences, Laboratoire de Microscopies & d'Etude de Nanostructures, E.A. n° 3977, 21 rue Clément Ader, 51685 Reims cedex 02, France, (b)Université de Haute Alsace, Laboratoire de Physique & de Spectroscopie Electronique, UPRESA-CNRS 7014, 4 rue des Frères Lumières, 68093 Mulhouse cedex 02, France
 Erbium-doped ZnO specimens of 0.50 µm thickness prepared by thermal spray technique from an initial 0.05 M ZnCl₂ aqueous solution are here investigated. It is shown that the presence of erbium species in zinc oxide matrix affects both, the microstructure and the luminescent properties of this material. The samples are prepared under optimal conditions achieved at substrate temperature $T_s = 723$ K and flow rate $f = 5$ ml/min. The Er-content in samples is ranged between 1 and 10 at%.
 It is observed that undoped ZnO exhibits hexagonal compact structure depicting a single x-ray peak related to [002] growth direction, normal to the substrate plane. The insertion of Er goes together with the appearance of two supplementary peaks corresponding to (100) and (101) planes whose intensities increase with the dopant content. The luminescent study only concerns the near ultra violet and visible region. The spectral results show that the intensity of the band edge emission at $\lambda = 382$ nm is free of erbium content, which contrasts with the behaviour observed for the blue and blue-green emissions peaking at $\lambda = 455$ and 528 nm, respectively. It is revealed that the integrated intensity of the blue-green emission attains a maximal value for Er-content close to 3 at%. It is also shown that this intensity is proportional to both, the Er-content and the electron beam energy of luminescent experiment.
- G/PII.41** PIEZOELECTRIC PROPERTIES OF PULSED LASER DEPOSITED ZnO THIN FILMS
 M. Benetti(a), D. Cannatà(a), F. Di Pietrantonio(a), E. Verona(a), P. Verardi(a), N. Scarisoreanu(b), G. Dinescu(b), A. Moldovan(b), D.G. Matei(b), M. Dinescu(b), (a)CNR-Istituto di Acustica, Via del Fosso del Cavaliere 100, 00133 Rome, Italy, (b)National Institute for Laser, Plasma and Radiation Physics, PO Box MG-16 Magurele, 077125 Bucharest, Romania
 Zinc oxide thin films were obtained on Pt coated silicon, r-cut Sapphire and MgO substrates by laser ablation of a Zn target in oxygen reactive atmosphere, the oxygen being supplied either by a standard gas inlet valve or from a radio frequency (RF) oxygen plasma. The influence of the deposition parameters as laser wavelength (266 nm, 355 nm, 1064 nm), laser fluence (1.5-20 J/cm²), oxygen pressure (1-60 Pa) and of RF plasma beam addition on the morphological properties of zinc oxide films was particularly investigated. Before piezoelectric measurements the obtained films, with thicknesses in the range of 50 nm - 4 microns have been characterized by Atomic Force Microscopy (AFM), X-ray diffraction (XRD), Transmission Electron Microscopy (TEM). The acoustic properties of the ZnO layers have been tested by implementing a surface acoustic waves (SAW) delay line. Frequency domain and time domain measurements have been performed using a Network Analyzer (HP8753A). Before the realization of the device, theoretical calculations of SAW propagation along the multilayered structures have been performed using the PC Acoustic Wave Software, from McGill University (Canada), considering the substrate as semi-infinite. The obtained results have been correlated with theoretical simulations.
- G/PII.42** INFLUENCE OF SYNTHESIS CONDITIONS ON THE MORPHOLOGY AND GRAIN SIZE OF ZINC OXIDE NANOPARTICLES
 Tomasz Strachowski(a), Edward Reszke(b), Ewa Grzanka(a), Adam Presz(a), Witold Lojkowski(a), Larisa Grigorjeva(c), Donats Millers(c), (a)Institute of High Pressure Physics PAS, Sokolowska 29/37, 01-142 Warsaw, Poland, (b)Ertec Poland, Rogowska 146/5, 54-440 Wrocław, Poland, (c)Institute of Solid State Physics, University of Latvia, 8 Kengaraga, Riga 1063, Latvia
 Zinc oxide nanopowders has been successfully prepared by hydrothermal process. The nanoparticles of zinc oxide with different morphologies and grain size have obtained by controlling different parameters of the precipitation process: kind of precursors used (urea, KOH, ammonia), solution concentration, pH, pressure, temperature and synthesis time. The effects of synthesis conditions and chemical additives on the particulate properties such as the particle morphology, grain size and luminescence properties are discussed. Grain size and morphology was monitored by XRD, SEM, TEM and BET analysis.
- G/PII.43** OPTOELECTRONIC PROPERTIES OF SnO₂/TiO₂ JUNCTIONS
 M. Kunst, T. Moehl, F. Wunsch and H. Tributsch, Bereich Solarenergetik, Hahn Meitner Institut, Berlin, Germany
 In several newly developed solar cells, as for example the injection solar cell, an optically transparent contact is required. Based on the experiences with thin film solar cells conductive oxides as highly doped ZnO and SnO are used. In the injection solar cell colloidal TiO₂ is deposited on F doped SnO₂ (FTO) or In doped SnO₂ (ITO) covered substrates. The theoretical description of the functioning of this solar cell considers the FTO (ITO) film as a metal serving as an ideal sink for electrons at the photo-active side of the device. This neglects the properties of these materials as (degenerate) semiconductors.
 Contactless and non invasive measurements of the transient photoconductance in the microwave frequency range (TRMC measurements) offer a versatile tool for the characterization of semiconductors and semiconductor junctions. In the present work the electronic properties of TiO₂/FTO junctions are investigated by TRMC measurements induced by UV (355nm) laser pulses.
 -Illumination of FTO films by 355 nm laser pulses (10ns FWHM) yields an appreciable photoconductance monitored by TRMC measurements in spite of the low sensitivity of the TRMC technique for highly conductive samples. This signal is proportional to the excitation density. These observations point to the semiconductor character of the FTO-films.
 -If colloidal TiO₂ films on FTO covered glass substrates are illuminated through the glass substrate, whereas the detecting microwaves are incident on the other (TiO₂) side the initial signal is identical to those in bare FTO films. Consequently this signal is due to excess charge carriers (probably electrons) generated and mobile within the FTO film. However, in the TiO₂/FTO/glass sample a slowly (compared to the optical generation of excess charge carriers finished in about 10ns) rising additional component is observed after 10ns. This is due to injection of electrons generated in TiO₂ (where they do not contribute to the TRMC signal due to the low mobility) into the FTO part of the sample. Details of the injection process are studied.
 This indicates that in the theoretical description of the injection solar cell the semiconductor character of the FTO-coated substrate must be taken into account and band bending at the TiO₂/FTO interface must be considered.

G/PII.44**MAGNETIC PROPERTY INVESTIGATIONS ON ZnMnO**

A. Che Mofor, A. El-Shaer, A. Bakin, H.-H. Wehmann, A. Waag, Institute of Semiconductor Technology, Technical University Braunschweig, Braunschweig, Germany, H. Ahlers, U. Siegner, S. Sievers, M. Albrecht, Physikalisch-Technische Bundesanstalt (PTB), Braunschweig, Germany, W. Schoch, N. Izyumskaya, V. Avrutin, Department of Semiconductor Physics, University Ulm, Ulm, Germany J. Stoimenos Physics Department, Aristotele University Thessaloniki, Greece

Diluted magnetic semiconductors are expected to play an important role in interdisciplinary material science, especially in magneto- and spin-electronics. Thus, doping conventional compound semiconductors with transition metals to obtain ferromagnetic semiconductors has gained enormous attention in recent years. Theory reveals that Mn-doped ZnO could be ferromagnetic with Curie temperature well above 300 K. In this contribution, we report on our findings concerning magnetic property measurements on $Zn_xMn_{1-x}O$ layers grown on sapphire.

$Zn_xMn_{1-x}O$ (x from 0.02 to 0.30) layers were grown on (0001)-sapphire using a MgO buffer and on (11-20) sapphire using a low-temperature ZnO buffer by Molecular Beam Epitaxy using H_2O_2 as oxidant. Prior to epitaxy, the back side of sapphire substrates was coated with Ti to improve heat transfer from heater to growth surface. The crystal quality of the layers was analysed using HRXRD and TEM. Magnetic property investigations were carried out using a Quantum Design SQUID magnetometer and Magnetic Force Microscopy (MFM). The samples were magnetised in-plane and the temperature dependence of magnetisation was investigated for temperatures ranging from 4.5 K to 300 K. A hysteresis with remnant magnetisation on the order of 0.8 emu/cm³ and coercive field strength of 120 Oe was observed only for some samples, which would eventually point to a ferromagnetic behaviour. However, further investigations on other samples and also on Ti-coated substrates without layer and simply chemically cleaned sapphire, coupled with MFM and TEM results lead us to the conclusion that our ZnMnO layers show paramagnetic rather than ferromagnetic behaviour. The critical influence of the substrate on magnetisation measurements will be discussed.

G/PII.45**A COMPARATIVE STUDY OF Mn-DOPED ZnO LAYERS DEPOSITED BY MBE AND RF MAGNETRON SPUTTERING**

M. Abouzaid and P. Ruterana, SIFCOM UMR 6176 CNRS-ENSICAEN, 6 Boulevard du Marechal Juin, 14050 Caen Cedex, France, C. Liu, F. Yun, B. Xiao, S.-J. Cho, Y.-T. Moon and H. Morkoç Department of Electrical Engineering, Virginia Commonwealth University, Richmond VA 23284, USA

Doping of ZnO thin films has been mostly carried out by pulsed-laser deposition (PLD), molecular-beam epitaxy (MBE), and sputtering deposition. Among these deposition techniques, radio frequency (RF) sputtering is a simple and popular method for preparing high quality ZnO thin film. In this work, we carry out structural analysis of ferromagnetic Mn-doped ZnO thin films deposited by radio frequency magnetron sputtering, using transmission electron pceded either by MBE or rf sputtering at around 600°C followed a higher temperature anneal. The ZnO layer is either deposited directly on sapphire or on top of a GaN template. In case of rf sputtering, the doping is usually started after the deposition of about a 300 nm pure ZnO layer on top of the sapphire substrate. When the Mn composition is low (< 5%) the rf sputtered layers exhibit a columnar growth on top of sapphire. The domains are rotated from one another even up to 90° angles, putting [10-10] and [11-20] directions face to face in adjacent domains. The structural relationships between such domains is investigate. At high Mn concentration this columnar structure is disrupted and this analysis revealed Mn-rich cubic and hexagonal precipitates in the wurtzite ZnO films.

Session XI : Processing
Session chair : L. Halliburton

G-XI.01 8:30

ANNEALING STUDY OF ION IMPLANTED AND AS-GROWN ZnO

Thomas Moe Børseth(a), Jens S.Christensen(a), Kestutis Maknys(a),Anders Hallén(b),Bengt.G.Svensson(a) and Andrej Yu.Kuznetsov(a),(a)Centre for Materials Science and Nanotechnology,Department of Physics, University of Oslo,Oslo, 0316 Norway,(b)Department of Microelectronics and IT, Royal Institute of Technology, Stockholm, Sweden

In this work we have studied annealing behaviour of hydrothermally as-grown ZnO samples as well as damage recovery, diffusion and electrical activation in Al,As,In and Sb implanted ZnO samples using Rutherford backscattering spectrometry in the channeling mode (RBS/c),secondary ion mass spectrometry (SIMS), scanning spreading resistance microscopy (SSRM) and scanning capacitance microscopy (SCM). For example, As⁺ ions were implanted with an energy of 300 keV using doses in the range of 1E14-2E15 As⁺/cm². The samples were then annealed at 600C, 800C and 1000C both in vacuum and different atmospheres, e.g., air or pure oxygen. After each annealing step the samples were characterized with SSRM/SCM and SIMS.The thermal treatments above did not induce any significant impurity redistribution as measured by SIMS, while electrical compensation is observed by SSRM/SCM yielding less n-doping than in the as-grown samples. However, RBS/c measurements reveal only limited residual damage produced in the as-implanted samples and a study of impurity locations in the ZnO lattice versus annealing temperature is in progress.

G-XI.02 8:45

DAMAGE FORMATION AND ANNEALING AT LOW TEMPERATURES IN ION IMPLANTED ZnO

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Nitrogen, argon and erbium ions were implanted into ZnO at 15 K with fluences between 1×10^{11} and 7×10^{16} at/cm² and energies of 80, 200 and 380 keV, respectively. The Rutherford Backscattering technique in the channelling mode was used to study the formation of implantation damage in the Zn-sublattice as well as annealing processes at temperatures between 15 K and room temperature.

Several stages in the damage built-up were observed for all ions, comparable to similar measurements in GaN. For low ion fluences a linear increase of damage with the fluence is observed, due to the formation of point defects. When the damage regions produced by single ions start to overlap, vacancies and interstitials can recombine, resulting in a plateau-like slow increase of the damage level. For higher fluences more stable defect complexes form, and the damage level increases steeply before reaching another plateau. Annealing measurements between 15 K and room temperature confirm the assignment of the different stages of damage formation. For a sample implanted with low dose, before the first plateau in the damage curve, a significant reduction of lattice damage was observed starting at temperatures between 90 and 130 K. Samples with damage levels beyond the first plateau do not reveal any damage recovery up to room temperature, confirming the formation of more stable defect complexes. From the linear increase of the damage for low implantation fluences, a displacement energy of 59 eV could be estimated for Zn atoms.

G-XI.03 9:00

EVOLUTION OF HIGH-DOSE IMPLANTED HYDROGEN IN ZnO

E.V. Monakhov, J. Christensen, K. Maknys, B.G. Svensson and A.Yu. Kuznetsov, Department of Physics/SMN, University of Oslo, PO Box 1048 Blindern, 0316 Oslo, Norway

We have investigated evolution of implanted H in single crystalline ZnO in the temperature range from room temperature (RT) to 600oC. H was implanted at RT with an energy of 100 keV and a dose of 2×10^{17} cm⁻². Secondary Ion Mass Spectrometry (SIMS) was used for the study of H distribution. The effect of the implanted H on electrical properties of ZnO as a function of depth was investigated by Scanning Spreading Resistance Microscopy (SSRM) and Scanning Capacitance Microscopy (SCM). After the implantation, the SIMS measurements reveal a H profile with a peak concentration of $\sim 10^{22}$ cm⁻³ at a depth of 0.7 μ m. An increased carrier concentration is observed by SSRM and SCM in the as-implanted sample in the H implanted region. After heat treatment for 2 h at 200oC, no change in either H or carrier concentration profiles is detected. Annealing for 2 h at 400oC leads to a decrease in the peak H concentration down to 2×10^{21} cm⁻³. However, no diffusion-like broadening of the H profile is revealed. Heat treatment at 600oC results in a further decrease of the H concentration to 2×10^{20} cm⁻³ and, similarly to the 400oC annealing, no broadening of the H profile is observed. However, an evolution in the carrier concentration profile is detected after the 600oC heat treatment: a region with a decreased carrier concentration appears beyond the H implanted region at a depth of 1-1.5 μ m.

G-XI.04 9:15

TEMPERATURE-DEPENDENT CAPACITANCE STUDIES OF PALLADIUM/ZINC OXIDE SCHOTTKY DIODES

C. Weichsel, O. Pagni, E. van Wyk, and A.W.R. Leitch Department of Physics, Nelson Mandela Metropolitan University, P.O. Box 77000, Port Elizabeth, South Africa
Palladium (Pd) Schottky contacts were prepared on ZnO films that were deposited by MOCVD on GaAs substrates. We characterize the Schottky contacts by means of current-voltage measurements, show their sensitivity to hydrogen gas and demonstrate the advantage of using Pd as a gate metal and highly conductive GaAs as a substrate. The capacitance of the Schottky diodes was studied at temperatures between 293 K and 373 K and different bias voltages. Our measurements reveal that the capacitance of the Schottky diode not only depends on the temperature itself but also on the rate at which the temperature of the sample changes. We discuss diffusion, the pyroelectricity of ZnO and the temperature-dependent hydrogen sensitivity of the Pd/ZnO system as possible explanations for this behaviour.

G-XI.05 9:30

ANALYSIS OF A CONDUCTING CHANNEL AT THE NATIVE ZINC OXIDE SURFACE

Oliver Schmidt(a), Arnd Geis(a), Peter Kiesel(a), Noble Johnson(a), Andrey Bakin(b), Andreas Waag(b) and Gottfried Doehler(c), (a)Palo Alto Research Center, 3333 Coyote Hill Rd., Palo Alto CA 94304, USA, (b)University of Braunschweig, Institute for Semiconductor Technology, Hans-Sommer Str. 66, 38106 Braunschweig, Germany, (c)University of Erlangen, Institute for Technical Physics I, Erwin Rommel-Str. 1, 91058 Erlangen, Germany
The measured electrical properties of high-resistivity zinc oxide (ZnO) bulk and epi-samples are strongly influenced by the sample ambient. Temperature dependent Hall-effect measurements were performed on Li- and Cu-doped bulk crystals in both air and vacuum. Repeating the measurements under a given test ambient produced stable results. Changing the ambient systematically changed the measured results. We explain this behavior in terms of a surface conducting channel that exists in vacuum but is destroyed upon exposure to air. We propose that the surface conducting layer is eliminated in air due to changes of the surface condition (e.g., molecular adsorption from the gas phase and/or surface reconstruction mechanisms). For a more detailed analysis we have characterized the nature of the conducting channel with capacitance measurements.

G-XI.06 9:45

ELECTRICAL CHARACTERIZATION OF GROWTH- AND ETCH-INDUCED DEFECTS IN BULK-GROWN ZnO

F.D. Auret, J.M. Nel, M. Hayes and L. Wu, Physics Department, University of Pretoria, Pretoria 0002, South Africa

We have investigated and compared the defects present in bulk ZnO grown by two methods, namely seeded chemical vapour transport (SCVT) and melt-grown (MG), by conventional deep level transient spectroscopy (DLTS) and high-resolution (Laplace) DLTS, using Au and Ru Schottky barrier diodes on the ZnO. The results show that the major electron trap in SCVT ZnO is the shallow donor, E1, at EC - 0.12 eV. The other prominent defect in this material is the E3 with a level at EC - 0.29 eV, speculated to be the oxygen vacancy, VO. On the other hand, in the MG ZnO the major electron trap is the E3, in a concentration of about 2-4 times that of E1. These observations suggest that the E1 may be hydrogen related because of the higher concentration of hydrogen present in the SCVT process than in the MG process. In (0001) SCVT grown ZnO etched in HCl we found that the oxygen (000-1) face showed visible roughness after etching for 15 seconds in HCl:H₂O (1:1). This roughness is accompanied by the presence of a new electron trap, E2, not observed before, at EC - 0.20 eV. At the same time we found that the shallow donor at EC - 0.12 eV was no longer present in the etched ZnO. This suggests that the etching process has either passivated the E1 level and introduced a new level, E2, or transformed the E1 level into the new E2 level.

G-XI.07 10:00

STRUCTURAL AND OPTICAL PROPERTIES OF QUALITY ZnO FILMS ON Si BY ATOMIC LAYER DEPOSITION AT LOW TEMPERATURES

Suk Lee, Yong-Whan Im, Sang-Hoon Kim, and Yoon-Bong Hahn, School of Chemical Engineering and Technology, Nanomaterials Processing Research Center, Chonbuk National University, Chonju 561-756, Korea

Quality ZnO films were grown on Si substrates at low temperatures by a two-step growth technique using atomic layer deposition. The two-step growth process is: first, the growth of buffer layer at 175°C; and second, the growth of main layer at 270°C. Structural and optical properties of the ZnO films deposited on ZnO-buffer/Si(111) were investigated as a function of buffer layer thickness. To optimize the growth process, the effects of pretreatment of Si wafer and postannealing were also investigated in terms of crystallinity and photoluminescence property of the ZnO films. It was found that the pretreatment of the substrate is not necessary and the optical property is degraded with annealing at 400-600°C. The films showed a strong UV emission at 380 nm and a weak green emission at 520-570 nm. The ZnO films deposited on a 33-nm-buffer layer showed overall the best surface morphology, structural, and optical properties.

G-XI.08 10:15

RAMAN SCATTERING IN ZnO NANOPARTICLES

C. Pinquier, F. Demangeot, A. Zwick, V. Paillard, J. Frandon, Laboratoire de Physique des Solides, IRSAMC, Université Paul Sabatier, 31062 Toulouse Cedex 4, France, C. Pages, M.L. Kahn, A. Maisonnat and B. Chaudret, Laboratoire de Chimie de Coordination, 205 route de Narbonne, 31077 Toulouse Cedex 04, France

Zinc oxide is a wide bandgap semiconductor displaying interesting luminescent properties. For example, ZnO nanowires have been recently proved to be a potential laser source in the ultraviolet range. In this contribution we present a Raman study of various crystalline ZnO nanoparticles of controlled size, grown by organo-metallic synthesis. Their shape is either that of a disk (with a typical thickness of 1 nm) or that of a rod (with a typical diameter of 2 nm). The micro-Raman measurements have been performed under various ultraviolet excitations (in the 3.41eV - 4.51 eV range), in order to get a resonant enhancement of the signal from the nanoparticles. The present study gives a Raman signature of such objects. In addition, the small differences evidenced in the Raman spectra, with respect to the shape and size of the nanoparticles, are also discussed.

10:30

BREAK

Session XII : Magnetic properties 2

Session chair : **A. Hoffmann**

G-XII.01 11:00 -Invited-

FERROMAGNETISM IN ZnO

S. Pearton, University of Florida, Gainesville FL, USA

G-XII.02 11:30

MAGNETIC AND OPTICAL PROPERTIES OF SINGLE CRYSTALS OF TRANSITION METAL DOPED ZNO

M.H. Kane(a,b), W.E. Fenwick(a), M. Strassburg(a), B. Nemeth(c), R. Varatharajan3, C.R. Vestal(d), Z. John Zhang(d), J. Nause(c), C.J. Summers(b) and I.T. Ferguson(a,b), (a)Georgia Institute of Technology, School of Electrical and Computer Engineering, Atlanta GA 30332-0245, USA, (b)Georgia Institute of Technology, School of Materials Science and Engineering, Atlanta GA 30332-0250, USA, (c)Cermet, Inc., Atlanta GA 30318, USA, (d)Georgia Institute of Technology, School of Chemistry and Biochemistry, Atlanta GA 30332-0400, USA

Considerable effort has been devoted to the study of transition metal doped zinc oxide following various theoretical predictions of room temperature ferromagnetism in these materials. Reports of ferromagnetic behavior in ZnMnO and ZnCoO indicate non-optimal growth or post processing techniques are required for ferromagnetism. Near equilibrium growth techniques may be suitable for the production of dilute transition metal doped ZnO because the transition metal solubility in ZnO can be relatively high. This work reports on the optical and magnetic properties of single crystals of Co-, Mn-, and Fe- doped ZnO grown by a modified melt-growth technique. X-ray diffraction reveals that the as grown crystals are pure single crystals with no second phases. Mn doping up to 5% results in an increase in c-axis lattice parameter (5.207 Å to 5.211 Å), and in X-ray linewidths (78 arcsec to 252 arcsec) at doping levels of 5% Mn. Optical transmission shows distinct absorption spectra related to the color of the ZnTMO sample resulting from interatomic transitions within the divalent transition metal ion in a tetrahedral crystal field. Magnetization measurements reveal a paramagnetic behavior at all temperatures for both Mn- and Co-doped ZnO. A faint hysteresis (<0.01 uB/Co atom) is observed in a single sample of 1%-doped ZnO, but is attributed to trace amounts of second phase clusters. due to a large irreversibility in the zero field cooled and field cooled temperature dependent magnetization. The dominant exchange mechanism in the Mn-doped ZnO crystals is found to be antiferromagnetic superexchange with $J_1 = -17.9/K$. The influence of annealing and codoping in the framework of relevant current theories of ferromagnetism will also be discussed.

G-XII.03 11:45

FABRICATION OF VERTICALLY WELL-ALIGNED FERROMAGNETIC (Zn,Mn)O NANORODS

J.M. Baik and J.-L. Lee, Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea

Diluted magnetic semiconductors (DMSs) have attracted much attention due to their physical properties and spintronic device applications, such as spin light-emitting diode and spin field effect transistor. Many DMSs including (Ga,Mn)N, (Ti,Mn)O₂, and (Zn,Mn)O have been fabricated for device applications. However, little is known about ferromagnetic properties of nanometer-sized materials. Ferromagnetic nanorods have considerable potential as high intensity data storage devices and nano-sensors due to nanosize and anisotropic magnetic response. In this work, we have fabricated vertically well-aligned ferromagnetic (Zn,Mn)O nanorods. Microstructural and optical properties of nanorods were investigated. The nanorods were grown on 30Å-Au-coated sapphires by the reaction of pure Zn and MnCl₂ powders in a horizontal CVD chamber at temperature of 700 oC. The nanorods exhibited diameters ranged from 80 to 150 nm. Only ZnO (00•l) and Au peaks were observed in XRD measurements, meaning that nanorods were grown with a c-axis orientation. No secondary phases were observed in HRTEM images. Hysteresis loops showed clear ferromagnetic behaviors. When magnetic fields were applied vertically to the sample plane, the coercive field increased by the factor of 35 %. In Raman spectra, E₂ longitudinal optical modes were observed and shifted toward the higher energy side by Mn incorporation. The effects of N₂O plasma treatment to the nanorods also were investigated.

G-XII.04 12:00

OPTICS AND MAGNETO-OPTICS IN (Zn,Co)O THIN FILMS

E. Beaurepaire, G. Schmerber, J.-P. Likhoman, A. Dinia, M. Gallart, O. Crégut, P. Gillot, B. Honerlague, IPCMS (CNRS-UMR 7504), 23 rue du Loess, BP 43, 67034 Strasbourg Cedex2, France, and K. Rode, A. Anane, J.-P. Contour, UMP CNRS-Thalès, Domaine de Corbeville, 91404 Orsay, France

We have measured optical and magneto-optical properties of (Zn,Co)O thin films deposited by laser ablation or reactive DC sputtering on sapphire substrates. In both cases, epitaxial growth along wurtzite (0001) direction is observed, and room temperature ferromagnetism for cobalt concentration around 25%. Optical transmission measurements show the Co²⁺ transition around 2eV, and the presence of optical transitions below ZnO band gap ($E_g(\text{ZnO}) \sim 3.3\text{eV}$). Pump-probe differential transmission experiments allow the measurement of the relaxation time for photo-created electron population. This relaxation time varies from few ten picoseconds to few picoseconds when cobalt concentration varies from 1 to 25%. A spectrally resolved magneto-optical characterization (1.5-3.5eV) has been undertaken in order to compare such films with metallic materials for magneto-optical recording and also in order to bring some information about the electronic structure of this system. Faraday signals have a quasi-resonant behavior for photon energy around ZnO band gap, whereas the spectral signature is weak at photon energy around intra-ionic Co²⁺ transitions.

G-XII.05 12:15 -Invited-

POLARITON LASERS IN WIDEGAP SEMICONDUCTORS

A. Kavokin, University Clermont-II, France

12:45

LUNCH