Electronic Materials and Processing

Room: 612 - Session EM-ThM

Zinc Oxide

Moderator: R.M. Wallace, University of Texas at Dallas

8:00am **EM-ThM1 Bulk and Surface Impurities and Point Defects in ZnO**, ***D.C. Look***, Wright State University **INVITED**

ZnO is a popular material at present because of potential photonic and electronic applications, such as UV LEDs and transparent transistors. As with most semiconductors, the bulk optical and electrical properties are controlled by impurities and defects acting as donors, acceptors, traps, and recombination centers. However, ZnO is somewhat unusual in that the surface also has donors and acceptors that produce electrical activity and can affect Ohmic and Schottky contact formation, among other things. Bulk donors and acceptors can be quantified by temperature-dependent Hall-effect (T-Hall) measurements, and their identities can often be determined by correlation with low-temperature photoluminescence (PL) and SIMS measurements in conjunction with doping and electron-irradiation experiments. Surface donors and acceptors, however, are much more difficult to quantify, although in this work we show that fairly reliable concentrations of surface donors (but not acceptors) can be determined by means of a low-temperature Hall-effect measurement and a room-temperature electrochemical C-V (ECV) measurement. Information on the possible identities of these surface donors can be obtained with XPS, SIMS, and other surface-sensitive techniques. We present T-Hall, PL, and ECV data on bulk, commercially available, ZnO samples grown by the vapor-phase, melt, and hydrothermal methods. Accurate concentrations of bulk donors and acceptors are obtained in all cases; the donors are tentatively assigned to various combinations of H, Al, Ga, and a Zn-interstitial complex, and the acceptors, to Li and the Zn vacancy. Fairly accurate densities of surface donors are also obtained in each case, and it is speculated that they are due to H complexes since their concentrations can be significantly increased by forming-gas anneals. To our knowledge, this is one of the first quantifications of surface donors in any semiconductor material, and the methodology should have general applicability.

8:40am **EM-ThM3 Correlation of Native Point Defects to Thermal Stability of Schottky Barrier Formation at Metal-ZnO Interfaces**, ***H.L. Mosbacker***, *C. Zgrabik, S. El Hage,* The Ohio State University*, A. Swain,* Columbus School For Girls*, M. Kramer,* The Ohio State University*, G. Cantwell, J. Zhang, J.J. Song,* Zn Technology*, D.C. Look,* Wright State University*, L. Brillson*, The Ohio State University

ZnO is an important semiconductor system for spintronic, nanoelectronic and optoelectronic devices. Important to realization of these devices is control and thermal stability of the metal-ZnO interface. We investigated this interface on bulk single crystal substrates grown by different methods from 5 different vendors. Using a remote oxygen plasma to remove ZnO surface adsorbates, subsurface defects and hydrogen, we studied Al, Au, Ir, Ni, Mo, Pd, Pt, and Ta contacts. Depth-resolved cathodoluminescence spectroscopy (DRCLS) reveals the presence of 3 defects at energies of 2.1, 2.5 and 3.0 eV. These deep level states vary in concentration with vendor, with depth from the interface, and with metal contact. Current-voltage measurements show that material containing high concentrations of defects in the subsurface strongly affects reverse currents, idealities and barrier heights acquired from current-voltage measurements. After annealing these contacts at temperatures of 350ºC, 450 ºC, 550 ºC, and 650 ºC in an argon ambient, DRCLS spectra identify defect formation that correlates to the nature of the metal-ZnO interface. Metals that form oxides show increased deep-level emissions that have been attributed to oxygen vacancies, while metals that form eutectics with Zn reveal increased luminescence from defects associated with Zn vacancies. Ta contacts annealed at 550 ºC create blocking contacts to ZnO, and DRCLS in the interface region reveal the formation of a Ta oxide. Al contacts also form blocking contacts at temperatures that depend on the native point defect densities. DRCLS of the subsurface oxide interface reveal increases in a 2.5eV transition often associated with oxygen vacancies. Au contacts that are annealed above the eutectic temperature for Au-Zn exhibit an increase of the 2.1eV defect level that correlates to Zn vacancies. Elevated temperature results demonstrate that the thermal stability of Schottky barriers also correlates to the density of native point defects. These differences in native point defect densities have a significant impact on defect formation at both elevated and room temperatures. Samples with high native defect concentrations initially can increase reactions in the subsurface, thus creating more defects associated with the metal-ZnO surface chemistry. Overall we find that metal-ZnO chemical reactions introduce interface native defects.These and native bulk defects dominate Schottky barrier properties and thermal stability.

9:00am **EM-ThM4 Separation of Surface and Bulk Conduction in ZnO using Variable Magnetic Field Hall Effect Measurements***, C.H. Swartz, M.W. Allen,* ***S.M. Durbin****,* University of Canterbury, New Zealand*, T.H. Myers*, West Virginia University

One of the major advantages of ZnO over other wide bandgap semiconductors is the availability of bulk, single crystal growth of high quality material using a variety of techniques. Of these, hydrothermally grown ZnO is somewhat unique in that it is highly resistive with carrier concentrations typically 2 - 3 orders of magnitude lower than other bulk ZnO, due to compensation from unintentionally introduced Li and Na acceptor impurities. This high resistivity makes the measurement of its electrical properties particularly susceptible to complications such as persistent photoconductivity, increased temperature sensitivity and surface conduction effects. The surface conductivity of ZnO is known to depend strongly on the ambient atmosphere and can increase significantly under vacuum conditions. After being placed in a vacuum, the expiration of atmospheric effects on the surface can take many hours and, even when equilibrium is reached, the surface conductivity remains a significant, and often dominant, contributing factor to electrical measurements. Variable magnetic field Hall effect measurements can be used to separate surface or interface conducting layers from the bulk conductivity of a given sample. In this paper, we report on the results of temperature dependent, variable magnetic field Hall effect measurements on hydrothermally grown ZnO single crystal wafers from Tokyo Denpa Co. Ltd. (Japan). Measurements were carried out over a temperature range of 80 - 300 K and magnetic field strengths up to 12 T. Multiple carrier fitting was used to remove surface conduction effects and produce temperature dependent mobility and carrier concentration data for the bulk carriers only, which was then theoretically fitted. A significantly higher bulk carrier mobility and an order of magnitude lower ionised impurity concentration was found than is apparent from standard single field Hall effect measurements. These results also indicate that the use of single field, temperature dependent Hall effect measurements to determine donor concentration and activation energies may be problematic unless surface conduction effects are first isolated.

9:20am **EM-ThM5 Nuclear Reaction Analysis Investigation of H-doped ZnO Grown by Pulsed Laser Deposition**, ***Y.J. Li****, T.C. Kaspar, T.C. Droubay, S. Shutthanandan, S. Thevuthasan, P. Nachimuthu, S.A. Chambers*, Pacific Northwest National Laboratory

As a wide bandgap semiconductor with good light emission properties, ZnO has attracted much interest because of its potential as a multifunctional material. Recent developments in bulk crystal and epitaxial film growth, along with advances in characterization methods, have expanded our understanding of this material, and created possibilities for ZnO-based optoelectronic, spin electronic, and transparent electronic applications. However, progress has been impeded by a lack of understanding and control of dopants, impurities and defects in ZnO. Difficulties in p-type doping of ZnO result from high background donor compensation of acceptors. One of the suspected background shallow donors in ZnO is H, which has been suggested to be readily incorporated during growth.[1-2] Theoretical calculations have predicted that H can exhibit a substitutional (on the O site) multi-center bonding configuration (H_O).[3] However, there is thus far no experimental evidence for H_O in ZnO. The focus of this study is to use nuclear reaction analysis to determine the local structural environment of H in ZnO. ZnO films are being grown in ultra-high purity H_2 at 500°C by pulsed laser deposition. The $H(^{15}N,\alpha\gamma)^{12}C$ and $H(^{19}F,\alpha\gamma)^{16}O$ nuclear reactions are being used in channeling and random directions to determine the position of H in the lattice. Initial results indicate that growth of ZnO in 10 mTorr H_2 at 500°C results in a total H concentration of ~1 x 10^{20} cm^{-3}. High-resolution x-ray diffraction is being used to characterize out-of-plane and in-plane lattice parameters of the doped phase. The effects of growth conditions on crystallinity as well as H concentration and position in the lattice are being investigated, and will be described in this talk.

[1] C.G. Van de Walle, Phys. Rev. Lett. 85, 1012-1015 (2000).

[2] D.M. Hofmann, A. Hofstaetter, F. Leiter, H. Zhou, F. Henecker, B.K. Meyer, S.B. Orlinskii, J. Schmidt, and P.G. Baranov, Phy. Rev. Lett. 88, 5504 (2002).

[3] A.Janotti and C.G. Van der Walle, Nature Materials 6, 44 (2007).

9:40am **EM-ThM6 Effects of Hydrogen Ambient and Film Thickness on ZnO:Al Electrical Properties**, ***J.N. Duenow***, Colorado School of Mines, *T.A. Gessert*, National Renewable Energy Laboratory, *D.M. Wood*, Colorado School of Mines, *T.J. Coutts*, National Renewable Energy Laboratory

Transparent conducting oxide (TCO) thin films are a vital part of flat-panel displays, electrochromic windows, and photovoltaic cells. ZnO-based TCOs may allow cost advantages compared to indium-containing TCOs such as indium tin oxide (ITO) or indium zinc oxide (IZO). Undoped ZnO and ZnO:Al (0.1, 0.2, 0.5, 1, and 2 wt.% Al_2O_3) films were deposited by RF magnetron sputtering. Controlled incorporation of H_2 in the Ar sputtering ambient, for films grown at substrate temperatures up to 200°C, results in mobilities exceeding 50 $cm^2V^{-1}s^{-1}$ when using targets containing 0.1 and 0.2 wt.% Al_2O_3. Because high conductivity is achieved through high mobility at lower carrier concentration, these films demonstrate decreased infrared absorption compared to films containing the commonly used 2 wt.% Al_2O_3. ZnO:Al films grown in H_2 partial pressure (ZnO:Al:H) show no detectable changes in electrical properties during temperature-dependent Hall measurements conducted up to 170°C. Reduction in ZnO:Al mobility and carrier concentration with decreasing film thickness has been reported in the past, but mechanisms for these changes remain uncertain. Our studies show that ZnO:Al:H electrical properties are suboptimal if film thickness is less than ~300 nm. In attempts to improve the electrical properties of these thinner films, depositions were performed at room temperature with and without a 60-nm undoped ZnO nucleation layer. Results show that mobility values indeed benefit from this nucleation layer for film thicknesses less than 350 nm. However, films grown without the nucleation layer reached higher mobility values at thicknesses greater than 350 nm. This abstract is subject to government rights.

10:00am **EM-ThM7 Metallic Conductivity in Transparent Al:ZnO Films**, ***O. Bamiduro***, *A.K. Pradhan*, Norfolk State University

Recently, transparent conductive oxide electrode, such as Ga or Al-doped ZnO, has attracted much attention not only as a powerful candidate material generally used for $InSnO_2$ (ITO) transparent electrodes, but also has a potential to replace ITO due to low cost, non-toxicity, and high stability in H_2 plasma atmosphere with good electrical and optical properties. Here we report on the metal-like conductivity in highly crystalline transparent (>85% in the visible region) Al:ZnO films grown on sapphire and glass substrates by the pulsed-laser deposition technique. Crystalline quality, surface morphology were studied on both types of films. Temperature dependent resistivity measurements of the films grown on sapphire and glass show metal-like conductivity with electrical resistivity, ~0.17 mOhm-cm and ~0.39 mOhm-cm, respectively, at room-temperature followed by either residual conductivity or a metal-semiconductor transition at low temperature due to the localization effect caused by the defects.

10:20am **EM-ThM8 Mixed Anion ZnOTe Thin Films by Pulsed Laser Deposition**, ***W. Wang***, *W. Bowen*, *J. Phillips*, The University of Michigan Ann Arbor

deposition Zinc oxide and related wide-bandgap II-VI oxide alloys have received much interest for their potential application for optoelectronic and electronic devices. The primary challenges for this material remain the achievement of p-type material for junction devices, and alloy heterostructures to span the visible and ultraviolet spectral regions. The majority of recent research on ZnO and related alloys to address these challenges has focused on the doping of ZnO by group-V elements, and the investigation of mixed cation alloys CdZnO, MgZnO, and BeZnO. Very little attention has been given to mixed anion alloys related to ZnO. ZnTe is a II-VI compound semiconductor with a 2.29eV direct band gap, and typically exhibits p-type behavior. Furthermore, ZnTe has shown the ability for controllable p-type doping by nitrogen with hole concentrations of up to 1e20 cm-3. The ability to achieve p-type characteristics and the direct bandgap of ZnTe make mixed anion alloys based on ZnO and ZnTe attractive for optoelectronic devices including visible light emitters and solar cells. In this work, we report on mixed cation ZnOTe thin films deposited by pulsed laser deposition. Thin films were deposited on sapphire and GaAs substrates using a pulsed excimer laser, ZnTe target, and varying ambients oxygen, nitrogen, and high vacuum. Deposition under high vacuum resulted in crystalline ZnTe thin films with optical bandgap energy of approximately 2.3 eV based on transmission and reflectance measurements. Deposition under nitrogen ambient shows a significant red shift in optical bandgap energy, likely due to energy states introduced by nitrogen doping. Deposition of ZnTe under oxygen ambient results in a large blue shift in optical bandgap to more than 3.1 eV, with a strong dependence on oxygen partial pressure. The structural, electronic, and optical properties of these ZnOTe thin films will be presented.

10:40am **EM-ThM9 STM, LEED and ARXPS Study of MOCVD Grown a-plane ZnO and $Mg_xZn_{1-x}O$ (0 <= x <= 0.3) Thin Films**, ***O. Dulub***, *E.H. Morales*, *U. Diebold*, Tulane University, *G. Saraf*, *Y. Lu*, Rutgers University

ZnO and $Mg_xZn_{1-x}O$ (0 <= x <= 0.3) thin films with a-plane orientation were grown on r-plane (011bar2) sapphire substrates using metal-organic chemical vapor deposition (MOCVD). The surface morphology of ZnO films with various thickness (20 - 2000 nm) was characterized by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) in ultrahigh vacuum (UHV). LEED patterns show well-ordered (1x1) surfaces. STM images reveal uniform surfaces with small, rectangular terraces during the initial growth stage (20 nm-thick film). Films with thicknesses of 100 and 450 nm have a characteristic wave-like surface morphology with needle-shaped domains running along the crystallographic c-direction. Films with a thickness of 2000 nm exhibit more flat surfaces with 20-100 nm wide domains running perpendicular to the c-axis, indicating variation in the strain effect caused by mismatch between substrate and film. On these thickest films, areas with facets of a different surface termination were observed as well. Angle-resolved x-ray photoemission spectroscopy (ARXPS) analysis of $Mg_xZn_{1-x}O$ films show that Mg atoms substitute for Zn atoms in the lattice. LEED shows that the incorporation of Mg atoms into the lattice reduces the surface roughness.

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