Electronic Materials and Processing
Room 2003 - Session EM-TuM

Zinc Oxide

Moderator: S.M. Durbin, University of Canterbury, New Zealand

8:00am **EM-TuM1 Impact of Subsurface Defects in Metal-ZnO(000-1) Schottky Barrier Formation***, **H.L. Mosbacker**, M.J. Hetzer,* The Ohio State University*; Y.M. Strzhemechny,* Texas Christian University*; M. Gonzalez, S.A. Ringel,* The Ohio State University*; D.C. Look,* Wright State University*; G. Cantwell,* ZN Technology, Inc.*; L.J. Brillson,* The Ohio State University

ZnO has emerged as a leading candidate for next generation semiconductor electronics due to its superior optoelectronic, microelectronic, and nanoelectronic properties. Central to realizing ZnO device applications are their electrical contacts with metals, yet Schottky barrier studies over the past 4 decades have not taken a comprehensive approach to isolating effects due to surface contamination, lattice defects, impurity dopants, and interface chemical reactions. We have used low energy depth-resolved cathodoluminescence spectroscopy (DRCLS) at 10 K in an ultrahigh vacuum scanning electron microscope and macroscopic current-voltage (I-V) measurements to study Schottky barrier (SB) formation at metal interfaces to clean, ordered ZnO(000-1). We fabricated sets of 30 nm-thick, 0.4 mm diameter Au, Al, Ni, Pt, Pd, Mo, Ta and Ir diodes on the same single crystal surfaces from different vendors. Prior to metallization, DRCLS revealed orders-of-magnitude difference in native bulk defect densities for crystals grown by different techniques, and these defect densities varied substantially between the crystals' bulk and surface. For all crystals, surfaces treated with a remote oxygen (20% O2/80% He) plasma created clean, ordered surfaces and reduced defect emissions in the surface region. Micro-DRCLS taken through the metal diodes revealed defect transitions at 2.1,2.5, and 3.0 eV that change dramatically with process steps and metal. I-V measurements exhibited transitions from Ohmic to SBs and lower idealities for Pt, Au, Ir, and Pd with plasma treatment. Deep-level optical and transient spectroscopies correlated bulk and surface defects, showing deep levels at 2.54 eV and 0.53 eV, while DRCLS shows that these densities can increase by > 100x at the surface. Our results indicate that metals can induce defects at the ZnO surface and impact device performance. The magnitude of the metal's influence directly correlates to the defect densities at the surface and ZnO bulk.

8:20am **EM-TuM2 Surface and Optical Properties of Zn-face versus O-face ZnO***, S. Chevtchenko, J.C. Moore, U. Ozgur, X. Gu, **A.A. Baski**, H. Morkoc,* Virginia Commonwealth University

We have compared the surface and optical properties of Zn-face (0001) and O-face (0001bar) ZnO samples. The samples used in this study were diced from the same bulk crystal prepared by Cermet Inc.@footnote 1@ Each sample had a thickness of ~0.4 mm and carrier concentration of 4.5x10@sup 16@ cm@sup -3@ at room temperature, corresponding to a Fermi level 0.11 eV below the conduction band. For optical characterization, steady-state photoluminescence (PL) using a He-Cd laser was measured at 15 K and 300 K (RT). Low-temperature PL for both surfaces showed the expected main transitions (free exciton, donor bound exciton, donor acceptor pair), with the most intense donor bound exciton transition at 3.359 eV having a FWHM of 1.7 meV, indicating a high quality sample. We did not observe any significant difference in the low-temperature PL spectrum for samples with different polarity. However, at RT the O-face sample demonstrated nearly double the near-band-edge emission intensity as that seen for the Zn-face. Using scanning Kelvin probe microscopy, we have also measured surface contact potentials of 0.39 V (Zn-face) and 0.50 V (O-face), which correspond to an upward band bending of 0.20 eV (Zn-face) and 0.09 eV (O-face), assuming an electron affinity of 4.4 eV. This relatively small difference in band bending for the polar ZnO surfaces indicates that spontaneous polarization is not a dominant contributor. Rather, we attribute band bending to surface states associated with dangling bonds. Also, the lower band bending of the O-face surface is consistent with the higher band-edge emission observed for this surface in room temperature PL studies. Finally, conductive atomic force microscopy studies show enhanced reverse-bias current conduction for the O- versus Zn-face samples. This effect may be due to different interactions of the two surfaces with ambient, in particular with water and hydrogen. @FootnoteText@ @footnote 1@ B. Nemeth and J.E. Nause; http://www.cermetinc.com.

8:40am **EM-TuM3 Synthesis and Characterization of ZnO Thin Films***, **T.J. Coutts**, X. Li, T.M. Barnes, J.N. Duenow, C.L. Perkins, S.E. Asher, B.M. Keyes, T.A. Gessert, S. Zhang,* National Renewable Energy Laboratory **INVITED**

N-type ZnO has great promise as a transparent conducting oxide and possibly has the potential to replace indium tin oxide for some applications. The high cost of indium may make it vital to find a replacement for indium tin oxide. ZnO is commonly used as an n-type material but vigorous efforts have also been made in recent years to fabricate p-type thin films. As an n-type material, it already plays an important role in some thin-film solar cells and it may also have the potential to be valuable in flat-panel displays. P-ZnO may have a role to play in solid-state lighting, UV/blue LEDs and lasers, novel solar cell designs and the generation of hydrogen by the splitting of water using light. However, p-type thin films, with relatively high hole concentrations, have been difficult to fabricate, are irreproducible, have low hole mobilities, and tend to be unstable. Nevertheless, efforts continue because of the potential commercial importance. In this paper, we discuss our work on the development of n-ZnO films, fabricated by sputtering, using aluminum, hydrogen and other, less familiar, dopants. The need for high mobility, via higher quality films, remains vital and is being explored using alternative dopants, by alternative growth methods and by optimizing the growth conditions. In addition, we discuss our work on the fabrication of p-ZnO, for which we used both low-pressure metal organic chemical vapor deposition and plasma enhanced chemical vapor deposition. We used both nitric and nitrous oxides as dopants. The films were characterized using SIMS, FTIR, XPS and other techniques. We discuss progress and mechanisms of compensation that account for the relatively low hole concentrations observed. @FootnoteText@ This abstract is subject to government rights.

9:20am **EM-TuM5 Low Resistivity Aluminum-Doped Zinc Oxide Grown by Atmospheric Plasma Enhanced Chemical Vapor Deposition***, **M.D. Barankin**, E. Gonzalez II, A.M. Ladwig, R.F. Hicks,* University of California, Los Angeles

Zinc oxide is a promising material for the transparent conducting oxide in thin-film photovoltaic cells. Today there is a strong push towards low-cost photovoltaics that may be fabricated on flexible substrates in a roll-to-roll process. In this presentation we will demonstrate the low temperature growth of Al-doped ZnO using atmospheric pressure plasma deposition with diethyl zinc and carbon dioxide as the oxygen source. Films deposited at a substrate temperature of 225°C exhibited resistivities of 2â?¢10-3 @ohm@â?¢cm, with an average transparency to visible light of at least 90%. It was found that the resistivity decreased with increasing substrate temperature from 100 to 230°C and with decreasing diethyl zinc feed rate. Maximum growth rates were in the range of 50 - 100 nm/min. These results are in contrast to those obtained by thermal CVD of Al/ZnO using molecular oxygen and diethyl zinc. In this case a sheet resistance of 0.2 @ohm@â?¢cm was obtained for deposition at 225°C. The atmospheric pressure plasma deposition process is unique in its capability of generating transparent conductive zinc oxide at low temperature.

9:40am **EM-TuM6 Transparent Conducting Zinc Oxide Thin Films Doped with Aluminum, Molybdenum, and Vanadium***, **J.N. Duenow**,* Colorado School of Mines*; T.A. Gessert, T.M. Barnes, T.J. Coutts,* National Renewable Energy Laboratory

Transparent conducting oxide (TCO) thin films are an integral part of photovoltaic cells, flat-panel displays, and electrochromic windows. The most commonly used TCO, tin-doped indium oxide (ITO), offers excellent performance, but in recent years material costs have risen dramatically because of increased demand for limited indium resources. We are investigating alternative TCOs based on zinc oxide (ZnO). As is the case with many TCO materials, investigations by many groups have not provided clear guidance toward significant improvement of ZnO material quality. We have examined whether electron transport can be enhanced by incorporating dopants with multiple valence states into the ZnO matrix--specifically, whether molybdenum (Mo; valence +6, 5, 4, 3, 2) or vanadium (V; +5, 4, 3, 2) can surpass the performance of aluminum (Al; +3). We deposited these ZnO-based materials by radio frequency magnetron sputtering from fully oxidized targets. We evaluated electrical, optical, and structural properties of these films using Hall measurements, spectrophotometry, and X-ray diffraction, respectively. Baseline studies of undoped ZnO revealed surprisingly high mobility values of 48 cm@super 2@/Vs in films deposited with a hydrogen-to-argon partial pressure ratio of 0.3% at a substrate temperature of 200°C; corresponding carrier concentrations were ~3 x 10@super 19@ cm@super -3@. Similar baseline studies with Al-doped ZnO resulted in films with typical mobility values of

25 cm@super 2@/Vs and carrier concentrations of ~6 x 10@super 20@ cm@super -3@ when deposited in 100% argon at 200°C. Initial results for Mo-doped films deposited in a hydrogen partial pressure ambient show that Mo is an effective dopant of ZnO, suggesting that multi-valent dopants may have value in TCO materials beyond that considered previously. We also present studies of V doping. This abstract is subject to government rights.

10:40am **EM-TuM9 Study of Impurities and Dopants in CVD Grown ZnO:N***,* ***S.E. Asher****, T.M. Barnes, X. Li, C.L. Perkins, M.R. Young, T.J. Coutts,* NREL

ZnO is an attractive material for optoelectronics due to its wide bandgap and use as a transparent conductor in photovoltaic devices. Reported work shows the ability to dope this material both n- and p-type.@footnote 1@ Films grown by metalorganic chemical vapor deposition (MOCVD) and plasma enhanced chemical vapor deposition (PECVD) have demonstrated p-type conductivity when doped with nitrogen, however, hole concentrations and mobilities are low, and films spontaneously type-convert over time.@footnote 2,3@ Compensation and/or passivation of the nitrogen acceptors by impurities such as carbon and hydrogen are thought to contribute to the poor electrical properties. In this work we have used SIMS and XPS to study contaminant and nitrogen doping levels in ZnO and ZnO:N films grown by MOCVD, PECVD and reactive sputtering. The CVD material is found to contain high levels of carbon and hydrogen, while sputter deposited material is considerably cleaner. We find decreasing carbon and hydrogen as a function of growth temperature for undoped MOCVD grown material. However, we find significant differences in the carbon and hydrogen in both CVD processes when nitrogen is present. For N-doped MOCVD films we also find carbon content appears to be linked to the proportion of oxygen in the deposition ambient. A similar relationship is not observed for N-doped PECVD or sputter deposited material. XPS indicates the presence of carbon bound to nitrogen in the MOCVD material. The relationship between carbon and hydrogen impurities, and nitrogen doping will be discussed.@footnote 4@ @FootnoteText@ @footnote 1@S.J. Pearton, et.al., Prog. Mater. Sci., 50, 293 (2005). @footnote 2@X. Li, et.al., J. Vac. Sci. Tech., A.21, 1342 (2003). @footnote 3@T.M. Barnes, et.al., Appl. Phys. Lett., 86, 112112 (2005). @footnote 4@This work was performed with the support of US Department of Energy Contract No. DE-AC36-99GO10337. This abstract is subject to government rights.

11:00am **EM-TuM10 Carrier Dynamics of ZnO Thin Films - Degeneracy, Inhomogeneity and Multiple Carriers***,* ***W.C.T Lee****, C.H. Swartz,* University of Canterbury, New Zealand*; M. Cheung, A.N. Cartwright,* University at Buffalo*; S. Chandril, T.H. Myers,* West Virginia University*; S.M. Durbin,* University of Canterbury, New Zealand

Though mobility measured by conventional Hall effect systems has long been used as a figure of merit for the electronic quality of semiconductors, many factors such as multiple layers and inhomogeneity can affect the accuracy and validity of the technique. This is particularly true for ZnO thin films, where many studies report very low electron (and hole) mobility values. Thin films are complicated by degenerate interface layers arising from poor substrate wetting and/or low-temperature buffer layer. By varying the magnetic field strength and temperature in a Hall effect measurement system, it is possible to separate the different carriers. For example, where single-field Hall effect yields a mobility of less than 50 cm@super 2@/Vs for one molecular beam epitaxy (MBE) grown ZnO/sapphire sample, the variable field technique shows a low-mobility degenerate layer in parallel with a bulk layer having a mobility of 200 cm@super 2@/Vs, approaching the best reported bulk values. Another useful probe of electronic properties is time-resolved photoluminescence (TRPL), which yields carrier lifetime as a figure of merit. For samples with an electron concentration of 10@super 19@ cm@super -3@, a parabolic temperature dependence of carrier lifetime was observed, with a decrease in lifetime as the temperature increases from 14 K up to 150 K, followed by an increase for further increases in temperature. On the other hand, concentrations of 10@super 18@ cm@super -3@ yield lifetimes that increase monotonically as the temperature increases. Taken together, these two techniques offer a more detailed picture of the characteristics of the bulk film, which cannot be adequately evaluated by a simple single-field Hall effect measurement. This work is funded in parts by The MacDiarmid Institute for Advanced Materials and Nanotechnology, University of Canterbury and Tertiary Education Comission Doctoral Scholarship (W.C.T.L).

11:20am **EM-TuM11 On the Morphology and Conductivity Control of the Expanding Thermal Plasma-Deposited ZnO Films***,* ***I. Volintiru****, M. Creatore,* Eindhoven University of Technology, The Netherlands*; C.I.M.A. Spee,* TNO Science and Industry, The Netherlands*; M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands

The bulk of the extensive research on ZnO focuses on different applications, ranging from photovoltaics to organic light emitting diodes; the plasma and film processes during growth are not well studied and, therefore, not controllable. For specific applications, good control of the ZnO film electrical and optical properties, as well as the surface morphology, is required. In this work, undoped and Al-doped ZnO layers are deposited using an Ar-fed expanding thermal plasma in which oxygen, diethylzinc, and trimethylaluminum (for Al doping) are admixed downstream. Typical downstream ion energies in this remote plasma are <2 eV, therefore energetic ion bombardment should not affect the film growth. Conductive films (5*10@super-4@ @OHM@cm) with native roughness of ~45 nm for 1 µm thickness, suitable for solar cell applications, were already obtained in our process. The film conductivity, however, shows a strong inhomogeneous depth profile, which could affect the suitability of this material for applications requiring thinner (< 200 nm) films, i.e. diodes and thin film transistors. To make our process more versatile, the ZnO film growth was investigated by studying the overall effect of the substrate temperature, working pressure, and ion bombardment (as delivered by an external RF bias). We use in-situ spectroscopic ellipsometry to monitor the refractive index, thickness and roughness development during the film growth. Atomic force microscopy, Hall and X-ray diffraction measurements are used to determine the morphological, electronic and structural properties of the films. Preliminary results demonstrate that the working pressure and substrate temperature play an important role in controlling the surface roughness of the ZnO films: smooth films, i.e. 0.02% roughness, are obtained by decreasing the pressure from 1.6 to 0.4 mbar, whereas higher texture, i.e. 10% of the film thickness, is achieved by increasing the substrate temperature from 200 to 400°C.

11:40am **EM-TuM12 X-ray Excited Optical Luminescence Studies of ZnO Nanowires and ZnO/Mg@sub x@Zn@sub (1-x)@O Core-Shell Nanowires****,* ***R.A. Rosenberg****, G.K. Shenoy,* Argonne National Laboratory*; L.-C. Tien, D.P. Norton, S.J. Pearton,* University of Florida*; X.H. Sun, T.K. Sham,* University of Western Ontario, Canada

As nanostructures become more complex having additional tools to unravel their optical properties will become more valuable. Due to their inherent asymmetry, the orientation of a nanowire will strongly influence its optical absorption and emission properties. In this talk we show how core-level, x-ray-excited optical luminescence (XEOL) using tunable x-rays from a synchrotron light source can be used to understand luminescence anisotropy in a disordered array of ZnO nanostructures. Optical luminescence yields from ZnO nanostructures at the Zn L and O K edges for both the band edge (~380 nm) and defect (~510 nm) peaks will be presented. At the Zn L edge the yields of both peaks are proportional to the x-ray absorption spectrum (XAS) of the wire. However, at the O K edge, marked contrasts are observed between wire XAS and the luminescence yields. There is a distinct enhancement of the yield for the band edge luminescence following 1s to 2p@sub z@ excitation relative to 1s to 2p@sub x,y@ absorption. For the defect peak excitation dramatic differences are seen between the XEOL yield and XAS of the wire. We will discuss these results in terms of the polarization of the excited electronic states and the nature of the defect states involved in the luminescence. In addition we will present recent results of a XEOL study on nanowires with a wurtzite ZnO core surrounded by a sheath composed of cubic Mg@sub x@Zn@sub (1-x)@O. The ZnO band edge luminescence (~370 nm) is blue shifted relative to the unsheathed nanowire. We also detect a deep UV peak at ~270 nm. By determining the yields of these peaks following excitation of the O K, Zn L, and Mg K core levels we are able to determine both the atomic origin and symmetry of the sites responsible for these peaks. @FootnoteText@ *This work was performed at the Advanced Photon Source and was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. W-31-109-ENG-38.

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