Electronic Materials and Processing
Room: 210 - Session EM-TuM

ZnO Materials and Devices
Moderator: J. Phillips, University of Michigan

8:00am **EM-TuM1 Synchrotron-based X-ray Spectroscopy of Transparent Conducting Oxides: ZnO and CdO**, ***L.F.J. Piper***, *A. DeMasi, K.E. Smith,* Boston University, *A.R.H. Preston, B.J. Ruck,* Victoria University of Wellington, NZL, *A. Schleife, F. Fuchs, F. Bechstedt*, Friedrich-Schiller-Universität, Germany

Solids that combine electrical conductivity and optical transparency are essential for today's flat-panel display and solar cell technologies. Post-transition-metal oxides (such as In2O3, ZnO and CdO), with their large band gaps (typically > 3 eV) and ability to sustain high concentrations of electrons with high mobility satisfy this condition. We present recent results from synchrotron-based resonant x-ray emission spectroscopy (RXES) of the O K-edge of ZnO [A. H. R. Preston et al., to be published (2008)] and CdO.[Piper et al., Phys. Rev. B 77, 125204 (2008)]. Bulk sensitive, "photon-in, photon-out" RXES - consisting of both x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES) - is an alternative to conventional photoemission spectroscopy for examining the valence and conduction band structure of wide band gap semiconductors, such as ZnO. Direct comparisons between RXES spectra and quasiparticle band structure calculations within the GW approximation reveal excellent agreement for both ZnO and CdO.

8:20am **EM-TuM2 Ultrahigh Vacuum Studies of Silane-Functionalized Nanocrystalline and Single Crystal Zinc Oxide**, *J. Singh, J. Im,* ***J.E. Whitten***, University of Massachusetts Lowell, *J.W. Soares, D.M. Steeves*, U.S. Army Natick Soldier Center

Zinc oxide has a unique bimodal photoluminescence spectrum consisting of UV and visible emission peaks, with the latter believed to originate from surface dependent processes. Possibilities exist to tailor the optical properties of ZnO by appropriate surface functionalization. Adsorption of a variety of silanes on nanocrystalline and single crystal zinc oxide surfaces has been investigated toward the goal of modifying the valence electronic structure and photoluminescence spectrum. Adsorbates include various fluorinated, electron-withdrawing silanes and 3-mercaptopropyltrimethoxysilane (MPS). In the case of nanocrystalline ZnO, adsorption has been carried out from solution, and XPS and FTIR confirm successful covalent attachment to the surface. Comparative studies have also been carried out in which sputter-cleaned ZnO(0001) has been dosed in ultrahigh vacuum (UHV) with model silane molecules. MPS has a high enough vapor pressure to be dosed in UHV, and angle-resolved XPS demonstrates adsorption with the sulfur at the vacuum interface, with minimal polymerization of the MPS monolayer. The effect of coadsorbed water has also been investigated by simultaneously exposing clean ZnO(0001) to water and silane vapors. Ultraviolet photoelectron spectroscopy (UPS) has been used to measure the valence electronic spectra and differences between nanocrystalline and ZnO(0001), and the effect of nanoscale dimensions on the ionization energy of the HOMO valence band (mainly due to nonbonding O 2p orbitals) has been studied. The effects of silane adsorption on the UPS spectra has also been investigated, and attempts have been made to correlate these with changes in photoluminescence.

8:40am **EM-TuM3 Factors Influencing the Formation of Schottky Contacts to Zinc Oxide**, *M.W. Allen,* ***S.M. Durbin***, University of Canterbury, New Zealand

Historically, most attempts to fabricate Schottky contacts to ZnO have resulted in devices with relatively high ideality factors, and barrier heights in the 0.6 – 0.8 eV range regardless of the Schottky metal used.[1] For ZnO applications, such as UV photodiodes, power diodes, and field effect transistors, homogeneous Schottky contacts with low ideality factors, high barrier heights and low reverse leakage currents are required. Recently, significant progress has been made towards understanding the conditions necessary for the reproducible fabrication of high quality Schottky contacts. In particular, studies into the effects of oxidation treatments, such as remote oxygen plasmas, hydrogen peroxide, and ozone, have established the link between improved Schottky contact performance and a reduction in surface hydroxide concentration,[2] while the importance of reducing intrinsic point defects plus additional defects introduced by the metallization process has been established.[3] We have fabricated 'almost ideal' Schottky contacts, with ideality factors approaching the image force limit, on hydrothermally grown bulk ZnO using a number of different Schottky metals. In this paper, we examine the key factors contributing to the success of these contacts. In particular, the polar and non-polar surfaces of bulk ZnO are naturally terminated by a hydroxide layer. Mechanisms for the removal of this accumulation layer are discussed, including the use of a reactive oxygen ambient in the fabrication of silver rich, silver oxide Schottky contacts which produce the highest reported Schottky barriers (1.00 - 1.20 eV) to ZnO. We will also provide evidence for the dominating influence of oxygen vacancies in Schottky contact formation via a relationship between the barrier heights of Ge, Ni, Ir, Pd, Pt Schottky contacts (on the same hydrothermal ZnO material) and the free energy of formation of their metal oxides.

[1] K Ip. et al., J. Crys. Growth 287, 149 (2006).
[2] B. J. Coppa et al., J. Appl. Phys. 97, 103517 (2005).
[3] L. J. Brillson et al., Appl. Phys. Lett. 90, 102116 (2007).

9:00am **EM-TuM4 Metal Contacts to Zn- and O- Polar Bulk ZnO Grown by Vapor-Phase Process**, ***Y. Dong***, *L.J. Brillson,* The Ohio State University, *Z.Q. Fang, D.C. Look,* Wright State University, *D.R. Doutt, M.J. Hetzer, H.L. Mosbacker*, The Ohio State University

Fabricating high quality ZnO contacts remains a challenge and there is little known about the comparison between two ZnO surface polarities (O or Zn-surface) on (i) surface morphologies, (ii) surface defect concentrations and energy levels, (iii) surface reactivities with various metal contacts, and (iv) the Schottky barrier heights and their metal correlations. We used depth-resolved cathodoluminescence spectroscopy (DRCLS), current-voltage and capacitance-voltage measurements, atomic force microscopy (AFM) and deep level transient spectroscopy (DLTS) to probe the possible different behavior of metal contacts to (0001) Zn- and (000-1) O- polar surfaces of high-quality vapor-phase grown ZnO. ZnO (0001) surfaces exhibited higher quality with smaller surface roughness, higher near band edge (NBE) emission and lower surface and near-surface defect emission. Remote O_2/He plasma (ROP) can effectively decrease the 2.5 eV near-surface DRCLS defect emission by removing surface adsorbates and subsurface native defects. Au and Pd diodes in-situ deposited by e-beam evaporation on the ROP treated surfaces can form Schottky barrier diodes (SBDs), while forming good Ohmic contacts on as-received surfaces. The transport properties of the SBDs are not only dependent on metal but also very sensitive to the surface polarities. Generally, gold diodes exhibit better rectifying properties than Pd, while Pd SBDs on the Zn-face have the largest reverse current. This was correlated to the surface morphologies, the DRCLS defect emissions, the CV carrier profiles and the surface and bulk traps revealed by DLTS. The effective donor concentrations for Pd and Au SBDs on the Zn-face were decreased by a factor of ~1.5 than on the O-face in the near surface region, which was accompanied by the higher 2.5eV defect/NBE emission ratio in DRCLS and an additional trap in DLTS for the O-face. The large leakage current for Pd SBDs is due to the sharp increase of carrier concentration at the upper interface region (< 80 nm) and tunneling, especially for Pd SBDs on the Zn face. In addition, for Pd/ZnO(0001) diodes, DLTS identified a new surface trap possibly related to hydrogen at ~0.50 eV below the conduction band and localized within the outer 80-100 nm. Our findings demonstrate the importance of polar effects on forming surface and near-surface defects that control the transport properties.

9:20am **EM-TuM5 Surface and Interface Electronic Properties of Bulk and Epitaxial ZnO**, ***C.F. McConville***, *T.D. Veal, P.D.C. King, S.A. Hatfield,* University of Warwick, UK, *B. Martel,* CNRS, France, *J. Chai, M.W. Allen, S.M. Durbin,* Univ. of Canterbury, New Zealand, *J. Zuniga-Perez,* CNRS, France, *V. Munoz-Sanjose*, Valencia University, Spain **INVITED**

The surface and interface electronic properties of ZnO have been investigated using high-resolution x-ray photoemission spectroscopy (XPS). Understanding the surface and interface electronic properties of ZnO is vital for the realisation of its potential in applications as diverse as gas, chemical and biological sensors, Schottky diodes, light emitters and transparent electrodes. A wide range of ZnO bulk and epi-samples grown by different techniques and with different surface orientations and bulk carrier densities have been studied. These include m-plane and Zn- and O-polarity c-plane hydrothermally-grown bulk ZnO, a-plane and c-plane ZnO grown by metal organic vapour phase epitaxy and c-plane ZnO grown by plasma-assisted molecular-beam epitaxy (MBE). Valence-band XPS indicates that the surface Fermi level is significantly above the conduction band minimum for all of the samples studied, with small variations observed as a function of surface orientation. These results are explained in terms of the band structure of ZnO with its low Gamma-point conduction band minimum, significantly below the charge neutrality level. The results are further discussed in the context of a wide range of previous results on ZnO surface

electronic properties, particularly surface conductivity data. Additionally, the first steps towards the development of hybrid oxide/nitride heterostructures have been taken with the MBE growth of ZnO on AlN. XPS has been used to determine the valence band offset of the ZnO/AlN heterojunction. Using the transitivity rule, and our measurements of the III-nitride band offsets, this has enabled all the ZnO/III-N band offsets to be determined. The band offset measurements enable an experimental estimation of the location of the charge neutrality level in ZnO to be made which is found to be consistent with both the observed surface electronic properties and the predictions of band structure calculations.

10:40am **EM-TuM9 Control of Electrical Properties of Atomic Layer Deposition ZnO Channel Layer for Thin Film Transistor: In-Situ Nitrogen Doping and Post-deposition Ultra-violet Treatments**, ***S.J. Lim***, *S. Kwon, H. Kim*, POSTECH, Republic of Korea

For emerging transparent flexible display, ZnO is considered as a promising material for channel layer of thin film transistors (TFTs). For the application, the control of key electrical parameters for the ZnO thin films are required to improve off current (IOFF), on-off current ratio, mobility, and threshold voltage (VTH) etc for ZnO TFT. Atomic layer deposition is one of the promising deposition techniques for the ZnO active layer due to its low growth temperature and good uniformity over large area. However, the control of electrical properties of ALD ZnO for the application of TFT active layer has not been widely studied. In this study, we fabricated the ALD ZnO based TFTs with controlled electrical properties by two ways with low process temperature. First, the in situ nitrogen doping using NH4OH as a reactant was employed to control the electrical properties of thermal ALD ZnO. We effectively reduced the high carrier concentration in ALD ZnO thin films (as high as 1018 cm-3) by nitrogen doping, and obtained low carrier concentration down to 1013 cm-3. High performance inverted staggered type TFTs was fabricated using these nitrogen doped ZnO thin films at low growth temperature (<150 °C), with saturation mobility (µsat) = 6.7 cm2/Vs, on-off current ratio (ION/OFF) = 9.46 × 107, IOFF = 2.03×10-12 A, and subthreshold swing = 0.67 V/dec. In addition, VTH values were controlled by changing the amount of nitrogen incorporation. Second, for plasma-enhanced ALD (PE-ALD) ZnO films has too small carrier concentration in contrary to thermal ALD using oxygen plasma as a reactant. As a result PEALD ZnO TFT does not turn on within voltage sweep range, thus postdeposition ultra-violet (UV) treatments were employed to reduce the carrier concentration. As a result, we obtained proper device properties after UV treatment in vacuum. Additionally VTH of PEALD ZnO TFTs decreased with increasing UV exposure time due to the increment of carrier concentration. We will discuss the effects of nitrogen incorporation and UV treatments on ZnO film properties. Especially, we will focused on demonstrate of the production of ZnO TFTs either depletion mode or enhancement mode controllably.

11:20am **EM-TuM11 ZnO PEALD TFTs and Hybrid ZnO/Organic CMOS Circuits**, ***T.N. Jackson***, Penn State University **INVITED**

ZnO and similar metal oxide semiconductors are of interest because of their wide band gap, transparency, and good electrical transport properties. ZnO thin-film transistors (TFTs) have potential as a higher performance, more stable alternative to amorphous silicon for use in displays and other large area electronics applications. Using ZnO semiconductor and Al_2O_3 dielectric layers deposited at 200 °C by plasma enhanced atomic layer deposition (PEALD) we have fabricated n-channel TFTs with field effect mobility > 15 cm^2/V-s, subthreshold slope < 100 mV/decade, and current on/off ratio > 10^8. Seven stage ring oscillators fabricated with 4 µm channel length ZnO PEALD TFTs have propagation delay < 40 nsec/stage for 15 V supply voltage (1.8 MHz oscillation frequency) and oscillate for supply voltage as low as 2 V. CMOS circuits are also of interest, but both p-type doping and p-channel TFTs have been problematic for ZnO. Hybrid inorganic/organic circuits using n-channel ZnO TFTs and p-channel organic thin film transistors provide an alternative path to CMOS circuits. Using Ti/Au contacts treated with a pentafluorobenzenethiol (PFBT) self-assembled monolayer as dual use contacts for both ZnO inorganic TFTs and spin cast difluoro 5,11-bis(triethylsilylethynyl) anthradithiophene (diF TES-ADT, synthesized by J. Anthony, U. Kentucky) organic TFTs, we have fabricated simple CMOS circuits. The diF TES-ADT is simply spin cast onto ZnO devices and Ti/Au contacts in a single step to complete the CMOS circuits. The diF TES-ADT develops a differential microstructure on and near PFBT-treated Au electrodes[1] and allows circuit operation with no direct patterning of the organic semiconductor layer and a simple, four mask CMOS process. The ZnO and diF TES-ADT TFTs used in the hybrid circuits have field effect mobility of 15 and 0.2 cm^2/V-s, respectively, and hybrid seven stage ring oscillators with 3 µm channel length have propagation delay less than 200 nsec/stage for 30 V supply voltage. The low temperature processing and good performance of PEALD ZnO TFTs, and the ease of integration with organic TFTs and other devices, make these devices attractive candidates for large area electronic applications.

[1] D. Gundlach et al. Nature Materials, 7, 216–221 (2008).

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