Tuesday Morning, October 21, 2008

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).

Graphene Topical Conference
Room: 306 - Session GR+EM+NC-TuM

Graphene and Carbon Electronics
Moderator: B.D. Schultz, International Technology Center

8:00am **GR+EM+NC-TuM1 Two Dimensional Plasmon Behavior in Graphene Sheets on SiC(0001)**, ***Y. Liu***, The Pennsylvania State University, *K.V. Emtsev, Th. Seyller,* University Erlangen-Nurnberg, Germany, *R.F. Willis*, The Pennsylvania State University

Using High Resolution Energy Loss Spectroscopy (HREELS), we compare experimental results for the wavevector-dependent behavior of plasmons in a graphene sheet on SiC(0001), with that due to a filled band of surface states on semiconducting silicon. There are significant diffences in behavior between the two systems, and the behavior predicted for a classical two-dimensional sheet of electrons. In particular, the damping increases with wavevector beyond the critical momentum for Landau damping by electron-hole pairs. This unusual behavior is compared with that due to the filling of two dimensional surface states on a metallized silicon surface. The graphene results are a consequence of the unusual collective behavior of Dirac fermions. The effect of adding additional graphene layers is discussed.

8:20am **GR+EM+NC-TuM2 Furnace Growth of High Quality Epitaxial Graphene on 4H-SiC(000-1)**, ***M. Sprinkle***, *F. Ming,* Georgia Institute of Technology, *D. Martinotti,* CEA Saclay, France, *P.G. Soukiassian,* Université de Paris-Sud/Orsay and CEA Saclay, France, *C. Berger, E.H. Conrad, W.A. de Heer*, Georgia Institute of Technology

Multi-layer graphene grown epitaxially on the C-terminated (000-1) surface of 4H-SiC in a high vacuum (~10^{-5} Torr), high temperature (~1420 °C) induction furnace environment has been shown to be of extremely high quality[1,2] and mobility.[3,4] Though multi-layered, the material exhibits electronic properties similar to those of isolated graphene.[1,3,4,5] Here, we characterize the material by atomic force microscopy (AFM), low energy electron microscopy (LEEM), and ellipsometry, and gain insight into growth mechanisms, highlighting growth on 4H-SiC(000-1) in comparison to 4H-SiC(0001), 6H-SiC(000-1), and 6H-SiC(0001). AFM and LEEM images demonstrate µm-scale graphene terraces. Ellipsometry and LEEM data show that graphene thickness is quite uniform over mm and µm scales.

[1] J. Hass et al., Phys. Rev. Lett. 100, 125504 (2008).
[2] J. Hass et al., J. Phys. Cond. Matt. 80, (in press)
[3] C. Berger et al., Science 3012, 1191 (2006).
[4] W. A. de Heer et al., Solid State Comm. 143, 92-100 (2007).
[5] M. Sadowski et al., Phys. Rev. Lett. 97, 266405 (2006).

8:40am **GR+EM+NC-TuM3 Toward Carbon Based Electronics**, ***K. Bolotin***, Columbia University **INVITED**

Carbon based graphitic nanomaterials such as carbon nanotubes and grpahene have been provided us opportunities to explore exotic transport effect in low-energy condensed matter systems and the potential of carbon based novel device applications. The unique electronic band structure of graphene lattice provides a linear dispersion relation where the Fermi velocity replaces the role of the speed of light in usual Dirac Fermion spectrum. In this presentation I will discuss experimental consequence of charged Dirac Fermion spectrum in two representative low dimensional graphitic carbon systems: 1-dimensional carbon nanotubes and 2-dimensional graphene. Combined with semiconductor device fabrication techniques and the development of new methods of nanoscaled material synthesis/manipulation enables us to investigate mesoscopic transport phenomena in these materials. The exotic quantum transport behavior discovered in these materials, such as ballistic charge transport and unusual half-integer quantum Hall effect both of which appear even at room temperature. In addition, I will discuss electronic transport measurements in patterned locally gated graphene nanoconstrictions with tunable transmission and bipolar heterojunctions. We observe various unusual transport phenomena, such as energy gap formation in confined graphene structures which promise novel electronic device applications based on graphitic carbon nanostructures.

9:20am **GR+EM+NC-TuM5 Spectro-Microscopy of Single and Multi-Layer Graphene Supported by a Weakly Interacting Substrate**, ***K.R. Knox**, S. Wang,* Columbia University, *A. Morgante, D. Cvetko,* Laboratorio TASC-INFM, Italy, *A. Locatelli, T.O. Mentes, M.A. Niño,* Elettra - Sincrotrone Trieste S.C.p.A., Italy, *P. Kim, R.M. Osgood*, Columbia University

While graphene's distinctive Dirac-cone electronic structure and simple 2D atomic structure have attracted major interest in the physics community, inherent limitations in the size of available exfoliated graphene samples have made it difficult to study this system with conventional UHV probes such as photoemission and low energy electron diffraction (LEED). Thus, previous photoemission and LEED studies of graphene have probed films grown on SiC.[1,2,3] While graphene grown on SiC can form large area sheets, exfoliated graphene on SiO_2 continues to be the system of choice for transport experiments as it is relatively easy to gate and has shown the most interesting and impressive electrical properties.[4,5] Using the high spatial resolution of the Nanospectroscopy beamline at the Elettra synchrotron light source, we have overcome these size limitations by utilizing micro-spot low energy electron diffraction (μLEED) and micro-spot angle resolved photoemission (μARPES) to study exfoliated graphene. In this talk, we will discuss our measurements of the electronic structure and surface morphology of exfoliated graphene using low energy electron microscopy (LEEM), μLEED and μARPES. Our LEEM data can be used to unambiguously determine the film thickness of graphene sheets by means of a quantum size contrast effect; a well understood effect in which modulations in the electron reflectivity arise due to quantum well resonances above the vacuum level.[6] Our diffraction measurements provide information about the surface morphology of monolayer and multilayer graphene sheets, which are not atomically flat, but microscopically corrugated. This corrugation increases with decreasing film thickness, reaching a maximum for monolayer graphene. Our photoemission measurements probe the unique massless fermionic dispersion of monolayer graphene, to confirm that the electronic structure of the valence band is well described by the one-orbital tight binding model.

[1] T. Ohta et al., Science 313, 951 (2006).
[2] A. Bostwick et al., Nature Phys. 3, 36 (2007).
[3] S.Y. Zhou et al., Nature Phys. 2, 595 (2006).
[4] K.S. Novoselov et al., Science 306, 666 (2004).
[5] Y.B. Zhang et al., Nature 438, 201 (2005).
[6] M.S. Altman, et al. App. Surf. Sci. 169, 82 (2001).

9:40am **GR+EM+NC-TuM6 Intercalation and Ultrasonic Treatment of Graphite – a New Synthetic Route to Graphene**, ***E. Widenkvist,*** Uppsala University, Sweden, *R.A. Quinlan,* The College of William and Mary, *S. Akhtar, S. Rubino,* Uppsala University, Sweden, *D.W. Boukhvalov, M.I. Katsnelson,* Radboud University of Nijmegen, the Netherlands, *B. Sanyal, O. Eriksson, K. Leifer, H. Grennberg, U. Jansson*, Uppsala University, Sweden

We will demonstrate that ultrasonic treatment of a graphite crystal in water can lead to the formation of small graphene-like flakes in solution. The delamination of the graphite can be increased dramatically by intercalation of bromine from a Br_2-saturated water solution. After ultrasonic treatment, large amounts of graphene-like flakes with varying thickness are observed in SEM and TEM. They can be adsorbed onto a surface of a suitable substrate by a simple dipping technique. The effect of polar and non-polar solvents as well as adsorption of the graphene on hydrophobic and hydrophilic substrates will be demonstrated and compared. DFT calculations of the intercalation process have been carried out using the SIESTA package and the effect of bromine intercalation on cohesive energy and electronic structure will be discussed and compared with experimental data. Finally, the general approach of using ultrasonic treatment and intercalation as a facile route to graphene synthesis compared to other methods will be discussed.

10:40am **GR+EM+NC-TuM9 Graphene: Exploring Carbon Flatland**, *E.W. Hill,* ***A.K. Geim***, University of Manchester, UK **INVITED**

Graphene is now a bright and still rapidly rising star on the horizon of materials science and condensed matter physics, revealing a cornucopia of new physics and potential applications. We will overview our experimental work on graphene concentrating on its exotic electronic properties and speculate about potential applications.

11:20am **GR+EM+NC-TuM11 The Mechanism of Graphene Growth on Metal Surfaces**, ***E. Loginova***, *N.C. Bartelt, K.F. McCarty, P.J. Feibelman*, Sandia National Laboratories

The structure and defects of graphene sheets have been characterized on many different surfaces, but the mechanisms of graphene growth largely remain unknown. Although simulations have been reported, how carbon atoms attach to the edge of a graphene sheet has not been experimentally determined, owing to limitations of the available experimental techniques. We have used low-energy electron microscopy (LEEM) to study the epitaxial growth of graphene on a representative metal, Ru(0001). The unique capabilities of LEEM allow us to measure simultaneously the growth rate of individual graphene islands and of the local, absolute concentration of vapor-deposited, mobile carbon adatoms. Combining this information, we have learned what controls the nucleation and growth rate of graphene on Ru(0001), and what species transport carbon over the metal surface. Graphene growth differs strikingly from the well-studied case of metal epitaxy: 1) the growth rate is limited by C-atom attachment, not by C-atom diffusion, and 2) the absolute value of the supersaturation required for appreciable growth rates is comparable to that required to nucleate new islands. Thus, a large barrier must exist for monomers to attach to the graphene step edge. We have also discovered that the growth rate as a function of supersaturation is highly nonlinear. Such behavior can be explained if carbon clusters must form, as precursors to carbon attachment. As experiment and theory reveal, this could arise from strong bonding of individual monomers to the metal substrate. We will discuss a model that explains all these observations, and thus provides insight into the molecular processes by which graphene grows. Lastly, we will show that our understanding and ability to monitor the carbon supersaturation allow the shape and position of the growing graphene sheets to be controlled. This research is supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U. S. Department of Energy under Contract No. DE-AC04-94AL85000.

11:40am **GR+EM+NC-TuM12 Conformal Dielectric Layers Deposited by ALD (Atomic Layer Deposition) for Graphene-based Nanoelectronics**, ***B. Lee***, *S.Y. Park, H.Y. Kim, K.J. Cho, E.M. Vogel, M.J. Kim, R.M. Wallace, J. Kim*, The University of Texas at Dallas

To make use of top-gated graphene devices, uniform and thin dielectrics on top of graphene is required. However, the chemically inert nature of graphene basal planes inhibits deposition of high quality and atomically uniform gate dielectric films. Here, we present characteristics of dielectrics employed by atomic layer deposition on top of a highly oriented pyrolytic graphite (HOPG) surface for localized gate applications. It was found that TMA/H_2O process shows selective deposition of Al_2O_3 only along with step edges which have high chemical reactivity. Therefore, it is critical to provide uniform and dense nucleation sites on the basal plane in order to achieve conformal deposition of dielectric. In this presentation, we will demonstrate a facile route providing atomically smooth and uniform Al_2O_3 layers on top of a HOPG by atomic layer deposition (ALD). The physical properties of the deposited Al_2O_3 layer will be also studied using various characterization techniques including HR-TEM, XPS, and AFM. Acknowledgements: We acknowledge financial supports by KETI through the international collaboration program of COSAR (funded by MKE in Korea) and the SWAN program funded by the GRC-NRI.

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

Complex and Multifunctional Oxides
Moderator: A. Herrera-Gomez, Cinvestav-Unidad Queretaro, Mexico

1:40pm **EM-TuA1 Understanding Metastable Structures in Sputter Deposited Hafnia-Alumina, Hafnia-Zirconia, and Hafnia-Titania Nanolaminates**, ***C.R. Aita***, *E.E. Hoppe, M.C. Cisneros-Morales*, University of Wisconsin-Milwaukee

The formation of metastable nanocrystalline phases during reactive sputter deposition of HfO_2-Al_2O_3, HfO_2-ZrO_2, and HfO_2-TiO_2 nanolaminates on unheated substrates is discussed. In addition to being technologically useful, these nanolaminates are archetypical because their bulk pseudobinary phase diagrams predict three different modes of interfacial mixing: complete immiscibility (HfO_2-Al_2O_3), complete miscibility (HfO_2-ZrO_2) and limited miscibility without a common end-member lattice (HfO_2-TiO_2). Of these individual constituents, all but Al_2O_3 (which has structural complexity) form both intralayer and interfacial nanocrystalline phases. However, these are often not bulk equilibrium phases and are termed here metastable. This paper addresses two questions: (1) By what mechanisms do these metastable phases arise? (2) How thermally stable are they at temperatures that a device may see during routine processing? We discuss metastable phases resulting from finite crystal size effects (tetragonal and orthorhombic HfO_2 in HfO_2-Al_2O_3) and heteroepitaxy (tetragonal $Hf_{1-x}Zr_xO_2$ in HfO_2-ZrO_2). We discuss the formation of a complex interface in HfO_2-TiO_2 nanolaminates that includes monoclinic $Hf_{1-x}Ti_xO_2$, a metastable phase which here results from a second order phase transition of orthorhombic $HfTiO_2$ (a stable interfacial phase) to accommodate the larger Hf atom at aHfO_2-on-TiO_2 interface. In all cases, these metastable structures represent self-assembly into the lowest possible energy structures in the absence of long-range diffusion.

2:00pm **EM-TuA2 Band Edge Engineering of Barium Strontium Titanate Thin Films by Ni-doping Driven Changes in Bonding Symmetry of Ti and O**, ***H. Seo***, North Carolina State University, *Y.B. Kim*, Hanyang University, Korea, *G. Lucovsky*, North Carolina State University

Suppression of the transition from direct to trap-assisted Fowler-Nordheim tunneling in metal-insulator-metal (MIM) capacitors is reported when approximately one percent Ni-doped barium strontium titanate (BST) thin film dielectrics are substituted for undoped BST. A significant leakage current reduction and improved breakdown resistance are observed for Ni-doped BST compared to undoped BST. The origin of such a large reliability enhancement of Ni-doped BST was investigated by spectroscopic studies includng spectroscopic ellipsometry (SE) and synchrotron X-ray absorption spectroscopy (XAS) measurements. For Ni-doping at the one percent level, the spectral dependence of the imaginary part of the complex dielectric constant,ε_2, obtained from SE shows significant differences in the band edge trap depth and density relative to undoped BST revealing defect states 0.2 eV shallower in energy and seven-fold reduced in density. This change in the defect state energy in Ni-doped BST is accompanied by a change in symmetry of the Ti atom empty t_{2g} states from either monoclinic/orthorhombic to tetragonal: the two t_{2g} states higher lying in the undoped BST O K1 edge and spectroscopic ellipsomtery ε_2 spectra are merged into to a single state in Ni-doped BST, while preserving the average t_{2g} d-state energy. The physical origin of these changes in the band edge defects is the substitution of divalent Ni^{2+} for tetravalent Ti^{4+} in band edge divacancy defects. Electrical measurements of J-V traces for Ni-doped BST show a symmetric direct tunneling process while undoped BST revealed asymmetric trap assistant tunneling/Fowler-Nordheim conduction process responsible for a rapid current rise. The results on improved Ni-doped BST suggest an approach for BST MIM capacitor in gigabit dynamic random access memory as well as identify a novel band edge state engineering approach based on transition metal doping which should be applied to other oxides with perovskite structures, e.g., $PbTiO_3$ and $PbZrO_3$.

2:20pm **EM-TuA3 Growth and Properties on Multifunctional Epitaxial Oxide Structures**, ***C.H. Ahn***, Yale University INVITED

Complex oxides exhibit a wide range of phenomena, including magnetism, ferroelectricity, superconductivity, and colossal magnetoresistance. The epitaxial growth of these complex oxides in crystalline heterostructure form allows these functionalities to be combined and utilized for fundamental science and technical applications. The ability to integrate this class of materials with others, and silicon in particular, multiply these research and technical opportunities. To fully realize this potential, the interfaces between materials must be understood, controlled, and optimized on the atomic level. We have developed techniques for the determination of such interface structures with sub-Angstrom accuracy, and informed by first-principles calculations, we have developed real-space models for complex oxide heteroepitaxy.

3:00pm **EM-TuA5 Structure and Properties of Polar Oxide Hetero-Interfaces: Hematite on Magnesia (111) and Alumina (0001)**, ***M. Gajdardziska-Josifovska***, *P. Dey, K. Pande, A. Celik-Aktas, S.H. Cheung, M. Weinert,* University of Wisconsin – Milwaukee, *S.A. Chambers*, Pacific Northwest National Laboratory

The most fundamental differences between oxide surfaces and those of metals and elemental semiconductors arise from the strong ionic character of the metal-oxygen bond, presenting opportunities to use polarity in design of novel oxide hetero-interfaces. For example, controlled growth of hematite and magnetite films has been a subject of intense studies inspired by their many technological applications in catalysis, gas sensing, sequestration of toxic metals, and magnetic devices. Surface and interface polarities add novel and desirable properties to these complex multi-functional oxide materials. In this work we integrate experimental and theoretical methods to study the atomic structure and electronic properties of hematite films grown on unreconstructed hydrogen-stabilized and on reconstruction stabilized polar oxide surfaces. We find that different modes of polar surface stabilization have profound effects on the growth mode, phase composition and magnetic properties of polar hematite films grown by OPA-MBE on magnesia and alumina single crystal substrates. Growth on reconstruction stabilized magnesia results in formation of an interfacial magnetite-like phase that offers a new way to create materials of interest in spintronics. This polarity-induced self-organized magnetite buffer persists after growth, in contrast to the transient maghemite detected by recent in-situ studies of the early stage of growth on unreconstructed sapphire surfaces. Indeed, pure phase Fe_2O_3 (0001) that is macroscopically antiferromagnetic is obtained on the hydrogen stabilized unreconstructed MgO(111) and Al_2O_3(0001) substrates. Theoretical modeling by DFT predicts unusual ferrimagnetic properties at the atomically abrupt α-Fe_2O_3 (0001)/MgO(111)-(1x1) interfaces.

4:00pm **EM-TuA8 The Metal-Insulator Transition in Vanadium Dioxide: A View at Bulk and Surface Contributions for Thin Films and the Effect of Annealing**, *W. Yin, K. West, J. Lu,* University of Virginia, *Y. Sun,* Stanford University, *S.A. Wolf*, ***P. Reinke***, University of Virginia

Vanadium dioxide is investigated as potential oxide barrier in spin switches, and undergoes a first order metal-to-insulator (MIT) transition at 340 K, which will provide an actively switchable interlayer as a critical element in the device. In order to incorporate VO2 layers in a complex multi-layer devices it is necessary to understand the relation between bulk and surface/interface properties in order to optimize device performance. Our study focuses on the comparison of the MIT in the bulk and at the surface of thin VO2 layers, and establishes an irreversible modification of the crystallite structure and surface for temperatures exceeding the MIT. The surface modification impacts on the strategies which are employed to build the magnetic contact on a VO2 layer. Highly oriented VO2 thin films were grown on (0001) sapphire single crystal substrates with a novel growth technique called reactive bias target ion beam deposition. In the analysis of the VO2 films we employed bulk-sensitive methods (x-ray diffraction, transport measurements) and surface sensitive techniques (photoelectron spectroscopy, STM). The samples were subjected to a heating cycle with repeated cycling through the MIT, and annealing to at least 100 K above the MIT. The VO2 films exhibit the the transition from the monoclinic to the tetragonal phase, with the concurrent change in conductivity by 10-3. The cycling across the MIT temperature and annealing have no impact on the abruptness and magnitude of the transition, and the bulk-dominated process exhibits therefore the requisite long-term stability. The stability of the surface with respect to annealing is dramatically lower, and electronic and structural changes occur. The observation of the valence band with PES as the film transits through the MIT temperature and the subsequent annealing clearly show that the surface partially retains its high-temperature metallic character. The onset of oxygen depletion at the surface is held responsible for this behavior, and a critical issue in tailoring the interface to the top contact. In addition to the changes on an atomic level, the annealing triggers a rearrangement in the orientation and shape of the crystallites, which is shown in a quantitative analysis of the STM images of the VO2 surface. The in-situ observation of the temperature-induced changes of the surface with STM will provide additional information on the oxygen-depletion and morphological changes in the VO2 surface.

4:20pm **EM-TuA9 Some High k Potential for MIM or RRAM Applications**, ***C. Vallee***, *P. Gonon, E. Gourvest, C. Jorel, M. Mougenot, M. Bonvalot,* CNRS - France, *V. Jousseaume,* CEA/LETI/D2NT - France, *O. Joubert*, CNRS - France

Metal Insulator Metal (MIM) capacitors in silicon analog circuit applications have attracted great attention due to their high conductive electrodes and low parasitic capacitance. Silicon oxide and nitride were commonly used in conventional MIM capacitors. Though they can provide good-voltage linearity and low temperature coefficients, their capacitance density are limited due to their low dielectric permittivity. In order to increase the surface density of MIM capacitors, several technological ways are investigated: realization of capacitors according to 3D architectures and integrating high or medium k materials. First MIM high k investigations dealt with Ta_2O_5. Among various high k dielectric materials, medium k such has HfO_2, ZrO_2 and rare earth oxides should give better performances owing to larger band gap than Ta_2O_5 and higher permittivity than silicon nitride. Flash technology is expected to reach its limits by the beginning of the next decade. In this context, existing research efforts are exploring a variety of novel memory concepts including: i) FeRAMs (Ferroelectric RAMs), ii) MRAMs (Magnetic RAMs), iii) PCRAMs (Phase Change RAMs). More recently, the semiconductor research community has shown a growing interest for RRAM (Resistive RAM) which exploits the resistive switching properties of oxides (mainly NiO) to store information. Its main advantages are good compatibility with current CMOS technology, high speed, and low power switching and good temperature stability of the data retention. A PVD process is usually used for the deposition of the oxide. Hence, for both applications (MIM capacitors and RRAM devices) high k dielectrics deposited with a low thermal budget should be a solution. This study is then focused on the deposition and characterization of several high k dielectrics such as HfO_2 or Y_2O_3 on different metallic electrodes (Pt,TiN,…) for MIM capacitors or RRAM devices. These materials are deposited by ALD or PE-MOCVD processes. The electrical behavior of the structures will be presented and discussed in terms of capacitance density, capacitance linearity and current-voltage characteristics with a special care to the switching mechanism of the high k RRAM. They will be correlated to chemical analysis results (XPS, ATR and FUV-SE), with special attention devoted to metal/oxide interface investigations.

5:00pm **EM-TuA11 Study of Luminescence and Epitaxy of Green Light Emitting ZnO Thin Films Prepared by MOCVD**, ***J.H. Liang***, *Y.J. Chen, J.H. Du, H.Y. Lai*, National Dong Hwa University, Taiwan

ZnO is one of the potential candidates for application on the green light LED, since ZnO has a broad PL peak in the green light region. Since the green light emission is caused by defect level transition in ZnO, epitaxial relationship could affect the behavior of green light emission due to the formation of different types of defects. Therefore, we studied intensively the dependence of luminescence of the ZnO film on the epitaxial relationship between film and substrate in order to get high intensity of green light emission. In our experiment, we prepared ZnO thin films on sapphire substrates by metal organic chemical vapor deposition (MOCVD), using dimethylzinc (DMZn) and oxygen, respectively, as zinc and oxygen source. We changed the Ⅵ-Ⅱ ratios and the growth temperature, and annealed the ZnO thin film at various temperature of 600°C - 1000°C in three kinds of atmospheres (Argon, nitrogen and oxygen). We used XRD to analyze the crystal structure, PL to analyze light emission, FESEM to observe the morphology and TEM to observe the epitaxial relationship between the film and the substrate. We reported the successful growth of dense (002)-oriented ZnO thin films with nearly 100 nm of grain size. We found that the XRD intensity of (002) and the grain size of ZnO grown under all three kinds of atmospheres increase with increasing temperature. We also found that the intensity of UV and green light emission were the highest at 1000°C in oxygen atmosphere, and the improvement of the intensity of green light emission was even more significant. We suggested that the defects of oxygen dominate the intensity of green light emission. We will show the TEM results about epitaxial relation between the film and the substrate to prove that there are 30-degree rotated epitaxial relationship between the film and the substrate. We will discuss about how the epitaxial relationship may affect the green light luminescence.

5:20pm **EM-TuA12 Investigation of Conductive Channel on GaInZnO Surface**, ***J. Lee***, *J. Chung, H.I. Lee, E. Lee, T. Kim, D. Kang,* Samsung Advanced Institute of Technology, Korea, *H.J. Kang*, Chungbuk National University, Korea

GaInZnO (GIZO) is a promising material for oxide thin film transistor which has transparent and high electric mobility. However GIZO has very sensitive to ambient environment. To understand the surface sensitive electrical property of GIZO, the physical properties of GIZO surfaces such as energy band gap, work function, and surface composition were investigated at the GIZO (70nm thick) fabricated by radio frequency sputter deposition on Si(100) and Glass substrate. The energy band gap of GIZO was measured using electron energy loss spectroscopy (EELS) against the energy of primary electron beam. The energy band gap of GIZO (Ga:In:Zn=3:2:1) was increased from 3.0eV to 3.5eV when the energy of primary electron beam increased from 300eV to 2000eV. Because of lower the primary electron beam energy of EELS, more sensitive to of surface, the result says that the energy band gap of surface is about 0.5eV lower than that of bulk of GIZO. When the Ga concentration in the GIZO increased from Ga:In:Zn=2:2:1 to 4:2:1, the energy band gap slightly increased from 3.3eV to 3.6eV. A depth profiling analysis of GIZO by Secondary Ion Mass Spectrometry (SIMS) indicated that GIZO was divided by 4 layers such as Zn+Ga rich, Ga rich, In rich, and balanced GIZO layers. The thickness of altered layer was about 3nm. The concentration of Zn at the surface was higher when the oxygen partial pressure during sputter deposition was higher. The Zn+Ga rich layer was just top monolayer (~0.2nm thickness). The thickness of Ga rich layer was about 0.45nm. The thickness of altered layer of GIZO was well agreement with that of estimated by EELS results. The previous results suggest the existence of a conductive channel on GIZO surface. The characteristics of GIZO based thin film transistor are strongly influenced by the conductive channel which formed near surface. In this report, the existence of conductive channel on GIZO surface will be discussed in detail.

Energy Science and Technology Focus Topic
Room: 203 - Session EN+EM+NS+PS-TuA

Photovoltaics
Moderator: B.J. Stanbery, Helio Volt Corporation, J. Xue, University of Florida

1:40pm **EN+EM+NS+PS-TuA1 Thin films, Plasmas and Solar Cells**, ***M.C.M. van de Sanden***, Eindhoven University of Technology, The Netherlands **INVITED**

Solar cells, devices which can convert sunlight directly into electricity by the photovoltaic (PV) effect, is now recognized as one of the options to provide a significant fraction of the energy mix in 2050 to power the world. Presently the PV industry is booming and two important challenges lie ahead: increasing the efficiency of conversion of sunlight into electricity and obtaining the required scale in terms of the surface area produced. The latter requires high throughput processing of solar cells in all its aspects. Increasing the efficiency is scientifically attaining the most attention, but history has shown that more cost reduction can be obtained by improving processes and increasing the scale of the industry. This talk will address both challenges by discussing the role of thin film and plasma technology. Presently the solar cell market is dominated by solar cells based on crystalline silicon. In this solar cell technology, where the photo-active material is wafer based silicon, thin films still play an important role to increase efficiency by effectively passivating bulk and surface defects and enhancing light trapping in the solar cell. The high rate deposition of a-SiNx:H as passivation and anti-reflection coating, by means of the expanding thermal plasma technique, will be shortly reviewed. Possible combinations with novel concepts to convert the solar spectrum will be addressed. Recently, we also introduced plasma assisted atomic layer deposition of Al_2O_3, a high k dielectric containing a large amount of negative charge, to passivate future p-type emitters on n-type silicon based solar cells. Demonstration of improved performance of n-type solar cells using this type of passivation layer with an efficiency as high 23.2 % will be discussed. To obtain the required large scale by 2050 further improvement of thin film solar cell technology will be essential, both in terms of materials as well as in terms of processes. Apart from the need for high throughput deposition of the photo-active materials, additional thin film technologies will be needed for barrier layers on substrates to limit impurity transport, for efficient light trapping (textured surfaces and anti-reflection layers) and last but not least encapsulation layers to guarantee the lifetime of the thin film solar cell. Apart from the further development of improved materials and device concepts, process monitoring and control to improve quality and throughput becomes more and more important. I will discuss here the monitoring of high rate deposition of microcrystalline silicon by means of optical emission spectroscopy. This optical probing method also enables the in situ detection of the crystallinity of the material deposited as well as fundamental insights in the growth mechanism.

2:20pm **EN+EM+NS+PS-TuA3 Effects of Nanostructures formed by Plasma Etching on Reflectance of Solar Cells**, ***S.H. Ryu***, *C. Yang, W.J. Yoo,* Sungkyunkwan University, Korea, *D.-H. Kim, T. Kim*, Samsung Advanced Institute of Technology, Korea

We investigated the lithography-free plasma etching methods to modify surface of single crystalline Si which was widely used for manufacturing of

solar cells. Experiments were performed using SF6/O2 gases dry etching for the purpose of reducing the reflectivity at the Si surface. Upon inductively coupled plasma etching in SF6/O2 pillar-shaped nanostructures were formed on the surface which changed to black in color. The absorption factor was estimated by measuring reflection and transmission on the surface across near UV to near IR. Before etching, reflectance of Si wafer was ~ 35% in the wavelength range of 600-1000 nm and > 50% in the wavelength range of 200-400nm, whereas it decreased to < 5% after performing SF6/O2 plasma etching. The absorption factor of Si wafer after etching was increased up to ~ 90% from 65% compared to that without etching, in the wavelength range of 600-1000 nm. Furthermore, various etching methods and conditions to suppress reflectivity in a broad spectral range were investigated for optimization of the surface property of the solar cells, ie, enhancement of solar cell efficiency. We investigated the effects of various processing parameters on surface property by changing gas ratio, bias power and etching time. The current-voltage characteristics on the surface textured solar cells showed that short circuit current (Isc) and open circuit voltage (Voc) changed sensitively depending on the surface treatment. The relation between the surface morphology and the absorption factor was analyzed.

2:40pm **EN+EM+NS+PS-TuA4 Nanoscale Heterojunction Engineering to Grow High-Quality Ge on Si for Multijunction Solar Cells**, ***D. Leonhardt****, J. Sheng, T.E. Vandervelde,* University of New Mexico*, J.G. Cederberg, M.S. Carroll,* Sandia National Laboratories*, S.M. Han*, University of New Mexico

In an effort to reduce the manufacturing cost of multijunction solar cells, we have scaled up a process to grow low-defect-density Ge films on 2-inch-diameter Si substrates. This growth technique makes use of nanoscale heterojunction engineering to minimize the interfacial strain density. The engineered substrates may potentially replace the Ge wafers that are currently used in multijunction solar cell fabrication, if the Ge film's bulk and surface quality can match that of the epi-ready Ge wafers. We will present results for the scaled-up process of Ge film production, including key aspects of the nucleation process and film characterization, using transmission electron microscopy and etch pit counting. Next, we present our efforts to produce a high-quality surface finish, using chemical-mechanical planarization, and method for cleaning and passivating the Ge surface. Additionally, results of GaAs film growth on our engineered substrates will be presented and compared to growth on Ge and GaAs wafers, both offcut and nominal. We find that the offcut wafers effectively eliminate anti-phase domains in the GaAs. We also observe room-temperature photoluminescence from GaAs epilayers grown on our engineered Ge/Si substrates. Lastly, future work and directions will be discussed in light of our findings.

3:00pm **EN+EM+NS+PS-TuA5 On a New Concept of Tandem Photovoltaic Cells Based on III-V Semiconductor Materials**, ***M. Emziane****,* Masdar Institute of Science and Technology, UAE*, R.J. Nicholas*, University of Oxford, UK

We have investigated single-junction and double-junction photovoltaic devices using ternary and quaternary InGaAs(P) semiconductor materials. These were designed and optimized for potential applications in conventional photovoltaics, thermophotovoltaics and concentrator photovoltaics.Different bandgaps were considered for single-junctions, and various bandgap combinations were simulated for the top and bottom cells of the tandem devices where the structure comprises two single-junction cells connected back to back and separated by a middle common contact. For both single and double-junctions, the device structures were modeled and optimized as a function of the doping concentration and thickness of the active layers, and the simulations show that optimum device performance can be achieved by using relatively thin structures and low doping concentrations in the emitter and base layers. The variation of the device performance with the black-body source temperature, incident intensity and operating temperature was also simulated and discussed. Due to the split of the incident spectrum, the bottom cell response is found to be different from that expected for a single-junction cell having the same bandgap. The optimal bandgap combination that delivers the best total efficiency for the tandem device was also determined and the data discussed.

4:00pm **EN+EM+NS+PS-TuA8 Thin Film Preparation of Chalcopyrites for Solar Cells and Fundamental Material Physics**, ***S. Siebentritt***, University of Luxembourg **INVITED**

Thin film solar modules are expected to be the next generation of photovoltaics technologies. Their cost reduction potential has been estimated much higher than that of Si wafer technologies. Among the various thin film technologies solar cells based on chalcopyrite ($CuInGaSe_2$, CIGS) absorbers show the highest efficiencies, reaching 19.9% in the lab. These record solar cells are prepared by a high vacuum co-evaporation process that proceeds in three stages with different composition. A simplified two stage co-evaporation process is used in the first mass production of chalcopyrite solar modules. Further industrial processes are the sputter deposition of metallic precursors which are reacted in an annealing process to the semiconductor compound. Recently electrochemical deposition has appeared as a low cost approach to the precursor deposition. In all cases the knowledge on fundamental growth processes, nucleation behaviour and detailed reaction is limited. The details of the processes and their advantages and disadvantages for solar module production will be discussed. The afore mentioned deposition processes result in polycrystalline films with grain sizes of approximately 1 micrometer. For the investigation of the fundamental material physics it is necessary to obtain grain boundary free material. The lattice mismatch between $CuInSe_2$ and $CuGaSe_2$ on one side and GaAs on the other side is between 2.2 and -0.7% and allows epitaxy of chalcopyrite films on GaAs. Several methods for the epitaxy have been developed: metal organic vapour phase epitaxy (MOVPE), molecular beam epitaxy (MBE) and a hybrid sputter/evaporation process. The specifics of these processes will be briefly discussed and some results of epitaxial films will be presented.

4:40pm **EN+EM+NS+PS-TuA10 Influence of a Single Grain Boundary on Epitaxial $CuInSe_2$ Film Growth**, ***A.J. Hall****, D. Hebert, A. Rockett*, University of Illinois at Urbana-Champaign

Very large multigrain copper indium diselenide (CuInSe2) films were grown on gallium arsenide (GaAs) multigrain wafers using a hybrid sputtering/effusion growth process. Scanning electrom microscopy (SEM) morphology shows excellent epitaxial grain growth on the substrate with intimate grain boundary contact. Electron backscatter diffraction analysis shows a crystal misorientation common axis and misorientation angle for a high-angle, non-twin, boundary. Atomic force microscope and transmission electron microscope images are presented which confirm the surface morphology and the atomic intimacy of the grain interface. Kelvin probe force microscopy shows that the grain-boundary has little electrical influence on the film in comparison to other features present in the crystallites. Growth of large multicrystalline or bicrystalline CuInSe2 films allows more careful study of both physical and electrical influence of grain-boundaries on film properties. Current work on the physical influence of a single boundary on film growth is discussed.

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

High-K Oxides and High Mobility Substrates
Moderator: R.M. Wallace, University of Texas at Dallas

8:00am **EM-WeM1 Spectroscopic Detection of Conduction Band Edge Defects in HfO_2, Hf Si Oxynitride and Stacked Hf Si Oxynitride/HfO_2 High-k Dielectrics: Extraction of Defect States from O K Edge NEXAS Spectra**, ***K.B. Chung***, *H. Seo, J.P. Long, G. Lucovsky*, North Carolina State University

A novel approach for eliminating Ge-N bonding at Ge-high-k dielectric interfaces from sacrificial Ge nitride interfacial transition regions (ITRs) used to passivate the Ge substrate against oxidation during film deposition. The GeN ITRs can be effectively eliminated during an 800°C post-deposition one minute anneal in Ar leaving the HfO_2 films in direct bonding contact with Ge(100) or Ge(111) substrates. This paper presents a study of band edge electronic structure, including band edge defects as function of annealing temperature by comparing near edge X-ray absorption spectra (NEXAS), O K_1 and N K_1 edges, for films deposited on a ~0.6-0.8 nm interfacial Ge-N layer, and after partial and complete removal of interfacial Ge-N and/or Ge-O bonding for anneals up to 800°C in Ar. Three types of dielectrics have been addressed: i) HfO_2, ii) high Si_3N_4 content Hf Si oxynitride alloys, and iii) stacked dielectrics comprised of high Si_3N_4 content Hf Si oxynitride alloy/HfO_2. One of the primary sources of defects in the HfO_2 films is associated with the incorporation of Ge, which has been detected in SXPS/UPS spectra. Finally defects identified in HfO_2 spectroscopically, explain large differences in the tunneling currents.

8:20am **EM-WeM2 ARXPS Study of the Early Stages of the Formation of the HfO_2/Si and HfO_2/SiO_2 Interfaces**, *M.D. Morales-Acosta,* ***A. Herrera-Gomez,*** Cinvestav-Unidad Queretaro, Mexico*, F.S. Aguirre-Tostado, J. Kim, R.M. Wallace*, The University of Texas at Dallas

The interfacial layer that is formed as hafnium oxide is deposited on silicon affects the performance of hafnium-based C-MOS devices. Although the composition of the interfacial layer could be evaluated from electrical measurements,[1] a more direct approach is desirable. The ideal technique for this type of studies is ARXPS because of its unparallel chemical and depth resolution. We performed high resolution ARXPS studies on ALD HfO2 film grown on H-terminated and 1nm SiO2-terminated Si(001) surfaces employing 5 and 30 cycles (H2O and TEMA-Hf). The deconvolution of the peaks was done robustly. Since surface potentials could also cause "chemical" shifts on the binding energies, the physical origin of the different peaks was assigned not only from the peak position but also from the detailed analysis of the take-off angle dependence of the peak area. It was possible to learn about the early stages of the HfO2/SiO2 interface formation since the thickness of the hafnium oxide layer for the samples with 5 ALD cycles were less than one monolayer. Although the 30 cycle ALD growth resulted in stoichiometric 2nm HfO2 films for both surfaces, in the early stages the growth of the HfO2 was more efficient for the SiO2-terminated sample. The first ALD cycles in the H-terminated samples caused the formation of 1.5ML of oxidized silicon. The Si 2p binding energy was 102.9eV, 0.4eV smaller than for the SiO2-terminated samples. Our analysis shows that this difference could be associated to the known dependence of the Si 2p binding energy on the oxide growing process, and not to the formation of a hafnium silicate layer for the H-terminated surfaces. As reported elsewhere,[2] there is a component (Hf*) with Hf 4f binding energy 0.6eV higher than for hafnium oxide. The analysis strongly suggests that Hf* could be associated to the first layer of HfO2 in contact with the SiO2, and not to a hafnium silicate layer. We concluded that the ALD process produced an abrupt SiO2/HfO2 interface, even for the H-terminated samples. A clear description of the self-consistent ARXPS analysis will be presented. This work was supported by the Semiconductor Research Corporation and the Texas Enterprise Fund.

[1]S. K. Dey, A. Das, M. Tsai, D. Gu, M. Floyd, R. W. Carpenter, H. De Waard, C. Werkhoven, and S. Marcus. J. Appl. Phys. 95, p. 5042 (2004).

[2]N. Barrett, O. Renault, J.F. Damlencourt, and F. Martin. J. Appl. Phys. 96, p. 6362 (2004).

8:40am **EM-WeM3 Characterization of High-k Dielectric and Metal Gate Film Stack by AR-XPS**, ***G. Conti****, Y. Uritsky, C. Lazik, S. Hung, N. Yoshida, M. Agustin, X. Tang, R. Wang*, Applied Materials Inc.

The implementation of a higher-k hafnium-based dielectric coupled with an atomically engineered oxynitride interface addresses gate leakage while maintaining high mobility. In conjunction with the new dielectric stack, metal gates are replacing polysilicon gate electrodes for material compatibility and performance. Devices made with high-k/metal gates can achieve >100x improvement in gate leakage, with significantly greater switching speed. The desirable properties of the dielectric High-K layer are : high dielectric constant; low leakage current; and thermal stability against reaction or diffusion to ensure sharp interfaces with both the substrate Si and the gate metal . Extensive characterization of such materials in thin-film form is crucial not only for the selection of alternative gate dielectrics and processes, but also for the development of an appropriate metrology of the high-k films on Si. This paper will report recent results on structural and compositional properties of Al2O3 deposited on 20A ALD HfO2 / 8A SiO2 . This stack was capped with 20A TiN . Angle-resolved XPS showed that after the high temperature anneal Al diffused into the dielectric stack with its concentration peaking at the HfO2/SiO2 interface and some remaining at the HfO2 surface. No Al was detected near the Si substrate interface suggesting that the insertion of Al2O3 cap layer at the high-k/metal gate interface and subsequent high temperature process should not degrade the device channel mobility. The AR-XPS and the TEM results are compared to the electrical data.

9:00am **EM-WeM4 Density-Functional Theory Molecular Dynamics Simulations of a-Al_2O_3/Ge(100)(2x1), a-Al_2O_3/$In_{0.5}Ga_{0.5}As$, a-Al_2O_3/$In_{0.5}Al_{0.5}As$/$In_{0.5}Ga_{0.5}As$**, *E. Chagarov,* ***A.C. Kummel***, University of California, San Diego

Amorphous oxide-semiconductor interfaces are keys to the performance of all metal-oxide field effect transistors (MOSFETs), but little is known about the exact bonding geometry at the interface. In this study, the bonding of a single amorphous oxide onto three semiconductors is compared to understand selective bond formation and intermixing since interfaces with non-polar bonds, no intermixing, and no half-filled dangling bonds are optimal for MOSFET devices. The local atomic and electronic structure of a-Al_2O_3/Ge(100)(2x1), a-Al_2O_3/$In_{0.5}Ga_{0.5}As$, and a-Al_2O_3/$In_{0.5}Al_{0.5}As$/$In_{0.5}Ga_{0.5}As$ interfaces were investigated by density-functional theory (DFT) molecular dynamics (MD) simulations. Realistic amorphous a-Al_2O_3 samples were generated using a hybrid approach including classical and DFT molecular dynamics. Each amorphous oxide/semiconductor interface was formed by placing an amorphous oxide sample on a slab of one of the semiconductors and annealing the stack at 700K / 800K and 1100K; subsequently, the stack was cooled and relaxed to get the final oxide-semiconductor interfacial bonding structure. The a-Al_2O_3/Ge interface demonstrates strong chemical selectivity with Al atoms migrating out of interface into the oxide bulk and O atoms migrating into the interface region resulting in interface bonding exclusively through Al-O-Ge bonds creating a large interface dipole; this exclusive Al-O-Ge bonding is due to Al-O bonds being more energetically favorable than Al-G bonds. During annealing of a-Al_2O_3/$In_{0.5}Al_{0.5}As$/$In_{0.5}Ga_{0.5}As$, Al migrates from InAlAs to a-Al_2O_3, demonstrating interfacial mixing; the intermixing is driven by the high energy of formation for Al-O bonds. The a-Al_2O_3/$In_{0.5}Ga_{0.5}As$ interface has polar As-Al bonds and In/Ga-O bonds of opposite dipole direction, low lattice distortion, and no intermixing. The formation of two types of bonds with opposite dipoles is driven by electronegativity: Al, an electron donor, bonds to As an electron acceptor while O, an electron acceptor bonds to In/Ga, electron donor.

9:20am **EM-WeM5 Atomic Layer Deposition (ALD) of Amorphous High-k Dielectric Films of $La_{(1-x)}M_xO_{3/2}$, M = Al, Sc, Lu, Y and La**, ***H. Wang****, M. Coulter, Y. Liu, J.J. Wang, R.G. Gordon,* Harvard University*, J.S. Lehn, H. Li, D.V. Shenai*, Rohm and Haas Electronic Materials

ALD was used to deposit films containing lanthanum and other trivalent elements aluminum, scandium, lutetium and yttrium. The precursors are N,N'-dialkylformamidinates or acetamidinates, except for aluminum, for which trimethylaluminum was used. The oxygen source was water vapor, which was sometimes supplemented with molecular oxygen to eliminate oxygen vacancies. Substrates used include silicon, germanium, gallium arsenide, ruthenium and titanium nitride. The films are amorphous as deposited, and have no interfacial layer between the dielectric an silicon. The films remain amorphous after rapid thermal annealing to temperatures as high as 1000 °C. High dielectric constants and very low leakage currents were measured. Dielectric constants remain the same even when the film thickness is reduced to ~ 5 nm, leading to EOT values < 1 nm with leakage currents < 10^{-3} A cm^{-2}.

9:40am **EM-WeM6 Boron Oxynitride as Gate Dielectric Films for Future CMOS Technology**, ***N. Badi****, S. Vijayaraghavan, A. Bensaoula,* University of Houston*, A. Tempez, P. Chapon,* Horiba Jobin Yvon, France*, N. Tuccitto, A. Licciardello*, University of Catania, Italy

Existing silicon oxynitride dielectric can only provide a very near term solution for the CMOS technology. The emerging high-k materials have a limited thermal stability and are prone to electrical behavior degradation

which is associated with unwanted chemical reactions with silicon. We investigate here applicability of amorphous boron oxynitride (BO_xN_{1-x}) thin films as an emerging high temperature gate dielectric. (BO_xN_{1-x}) samples of thickness varying from 10 nm down to 1 nm were deposited in a high vacuum reactor using filamentless ion source assisted physical vapor deposition technique. The (BO_xN_{1-x}) dielectric structural and mechanical properties were investigated as a function of thickness and O/N composition. B10 implanted (BO_xN_{1-x}) /Si heterostructures and (BO_xN_{1-x}) layers deposited on B10 implanted Si substrates were post annealed at high temperatures up to 1000°C. Depth profiling of these layers were performed to evaluate the stability of the dielectric layers and their efficacy against B dopant diffusion simulating processes occurring in activated polySi-based devices. Elemental composition along with chemical and electronic states analysis of the layers were carried out using Secondary Ion Mass Spectrometry (SIMS), Glow Discharge Optical Emission Spectroscopy (GDOES), Glow Discharge Time of Flight Mass Spectrometry (GD-TOFMS) and X-ray Photo-Electron Spectroscopy techniques. Preliminary results show that (BO_xN_{1-x}) dielectric constant ranges from 4 – 6 and that capacitance change with temperature (25°C- 400°C) and frequency (10 KHz-2 MHz) is about 10% and 2%, respectively. Our conclusions on suitability of (BO_xN_{1-x}) for advanced energy storage devices and gate dielectric for future CMOS technology will be presented.

This research was supported in part by USDOE grant # DE-FG02-05ER84325 to Integrated Micro Sensors, Inc.

10:40am **EM-WeM9 Electrical and Physical Properties of High-k Gate Dielectrics on III-V Semiconductors**, ***E.M. Vogel***, *C.L. Hinkle, A. Sonnet, F.S. Aguirre-Tostado, M. Milojevic, K.J. Choi, H.C. Kim, J.G. Wang, H.C. Floresca, J. Kim, M.J. Kim, R.M. Wallace*, The University of Texas at Dallas **INVITED**

Because of a significantly higher electron mobility compared to silicon, III-V semiconductors (e.g. GaAs, InGaAs) with high-k gate dielectrics (e.g. Al_2O_3, HfO_2) are being considered for future Metal Oxide Semiconductor Field Effect Transistors (MOSFETs). However, device performance has been limited by high electrically active interfacial defect density. Various physical characterization techniques including monochromatic x-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM) are used to study the physical properties of atomic-layer-deposited Al_2O_3 and HfO_2 dielectrics with various interlayers (e.g. silicon), precursors and surface treatments. Characterization and modeling of the electrical properties of MOS capacitors and MOSFETs is correlated to the details of the bonding arrangements and physical properties of the dielectric stacks. The results suggest that proper selection of interlayer, ALD precursors, and surface treatment can result in selective interfacial bonding arrangements and associated device electrical properties.

11:20am **EM-WeM11 Surface Structure and Fermi Level Determination of Oxides/III-V Interface**, ***J. Shen***, *A.C. Kummel*, University of California, San Diego

We have used scanning tunneling microscopy (STM) and density functional theory (DFT) calculations to both identify the group III rich III-V surface reconstruction and to identify the bonding structure for oxide on these surfaces. In-rich InAs(001)-(4×2) can readily be prepared by decapping of As2 capped InAs(001) wafers. STM results reveal that In-rich InAs(001)-(4×2) has a very different atomic structure than Ga-rich GaAs(001)-ζ(4×2) structure even though the surfaces have similar symmetry. The InAs(001)-(4×2) is denoted as the β3(4×2) and has a unit cell consisting of two undimerized group III atoms on the row and two group III dimers in the trough. STM results showed that the initial deposited In2O molecules bond to the edges of the rows and most likely form new In-As bonds to the surface without any disruption of the clean surface structure. Annealing the In2O/InAs(001)-(4×2) surface at 400˚C results in formation of flat order monolayer rectangular islands onto which oxide grows in a layer-by-layer mechanisms with amorphous structure. In0.53Ga0.47As is a good candidate for a III-V MOSFET due to its high carrier mobility, low density of thermal carriers, and ability to be grown lattice matched on semi-insulator InP substrates. STM images of the clean surface indicate that the In0.53Ga0.47As(001)-(4×2) surface reconstruction is similar to the InAs(001)-(4×2) structure. The DFT calculations reveal that the some of the trough dimers are buckled, which is consistent with the STM images showing that the trough has poor order. Ga2O was deposited on the surface to determine how oxide adsorbates bond to In0.53Ga0.47As(001)-(4×2) clean surface. The bonding structure of the annealed Ga2O/In0.53Ga0.47As(001)-(4×2) is similar to that of In2O/InAs(001)-(4×2); however, the Ga2O/ In0.53Ga0.47As(001)-(4×2) islands are more weakly ordered than the In2O/InAs(001)-(4×2) islands. For both In2O/InAs(001)-(4×2) islands and Ga2O/ In0.53Ga0.47As(001)-(4×2), the oxide adsorbates never cause the abstraction of any surface atoms on the InAs and In0.53Ga0.47As(001)-(4×2) surfaces; furthermore, for monolayer oxide films, the oxide molecules only occupied specific sites. After high temperature annealing, the oxide desorbs from the surface and the clean (4×2) surface is restored. This is consistent with the formation of a smooth interface between the oxide and the semiconductor.

11:40am **EM-WeM12 High-K Dielectrics/High Mobility Channel Interface Optimization for Future CMOS Technology**, ***L. Yu***, *T. Feng, Q. Jiang, H.D. Lee, C.L. Hsueh, A.S. Wan, D.D.T. Mastrogiovanni, Y. Xu, T. Gustafsson, E. Garfunkel*, Rutgers, The State University of New Jersey

High-k dielectrics have been adapted as gate oxide in order to prolong the Moore's law of CMOS transistor scaling to a critical length of 45 nm and beyond. Also, replacing Si with a higher mobility material (for example, Ge and III-Vs) as transistor channel is expected to further enhance the transistor performance. Thus, the idea of combining those two advances in one process has attracted many research efforts from both academia and industry. However, the task has been difficult due to the lack of proper treatment to the oxide/channel interface. The defect states at the interface or inside dielectrics can enhance carrier scattering and degrade device threshold voltage. Further more, the chemical instability and compatibility at the interface are often detrimental to device performance. Several studies, including ours, showed that chemical cleaning and subsequent passivation (for example, with ammonium sulfide) prior to dielectrics deposition on both Ge and GaAs channels can greatly reduce the interface state density (Dit). We have established tools that enable ALD and sputtering deposition of the CMOS gate stacks along with in.situ. characterization by MEIS (Medium Energy Ion Scattering) and XPS. It allows us to determine, with high spatial resolution, the composition, structure and thermal stability of gate stacks on various channels. We will present the in. situ. characterization results of Al2O3 and HfO2 based gate stacks on chemically treated Ge and GaAs surface. These results will be directly correlated with studies of gate stack electrical properties and electronic structure.

Energy Science and Technology Focus Topic
Room: 203 - Session EN+AS+EM+TF-WeM

Electrochemical Storage
Moderator: S. Haile, Caltech, K. Thornton, University of Michigan

8:00am **EN+AS+EM+TF-WeM1 Molybdenum Oxide Nanoparticles for Improved Lithium Ion Battery Technologies**, ***A.C. Dillon***, National Renewable Energy Lab., *S.-H. Lee*, University of Colorado, *Y.-H. Kim*, National Renewable Energy Lab., *R. Deshpande*, Lam Research, *P.A. Parilla, D.T. Gillaspie, E. Whitney*, National Renewable Energy Lab., *S.B. Zhang*, Rensselaer Polytechnic Institute, *A.H. Mahan*, National Renewable Energy Lab. **INVITED**

Lithium-ion batteries are current power sources of choice for portable electronics. Further improvement of performance and simultaneous reduction in cost could allow for the deployment in hybrid electric vehicles or plug-in hybrid electric vehicles (PHEVs). The development of PHEVs will enable reduced oil consumption in the transportation sector. Importantly, PHEVs will also enable increased use of intermittent renewable energy resources such as solar and wind. By charging PHEVs during peak solar generation times, the load on the grid is effectively "leveled", and the average output of coal-fired power plants will be decreased. Recent efforts for electric vehicle applications are focused on new anode materials with slightly more positive insertion voltages to minimize any risks of high-surface-area Li plating while charging at high rates, a major safety concern. The state-of-the-art anode is graphite with a reversible capacity of ~ 350 mAh/g and a potential of 0.1 V relative to lithium metal. Metal oxides have long been known as Li-insertion compounds and typically operate at higher potential than graphite. Unfortunately they suffer from poor kinetics and/or capacity fade with cycling, especially at higher rates. Hot-wire chemical vapor deposition has been employed as a scalable method for the deposition of crystalline metal oxide nanoparticles at high density. Under optimal synthesis conditions, only crystalline nanostructures with a smallest dimension of ~ 10 - 40 nm are observed. Anodes fabricated from crystalline MoO3 nanoparticles display both an unprecedented reversible capacity of ~ 630 mAh/g and durable high rate capability. Porous thin film nanoparticle anodes, deposited by a simple electrophoresis technique, show no degradation in capacity for 150 cycles when cycled at high rate (C/2 corresponding to one discharge in 2 hrs.). Micron sized MoO3 particles are shown to fail after several cycles, under the same conditions. Both x-ray diffraction and in situ Raman spectroscopy studies reveal that upon Li-ion insertion the crystalline nanoparticles become highly disordered. Density functional theory calculations elucidate the complex Li-ion insertion process and reveal a novel mechanism confirming the nanoscale, high-rate, reversible capacity

despite the loss of structural order. The synthesis of these novel nanostructured materials and their potential for improving lithium-ion battery technologies will be discussed in detail.

8:40am **EN+AS+EM+TF-WeM3 Boron Oxynitride: An Emerging Dielectric for High Temperature Capacitor Applications**, *N. Badi, **S. Vijayaraghavan**, A. Bensaoula,* University of Houston*, A. Tempez, P. Chapon,* Horiba Jobin Yvon, France*, N. Tuccitto, A. Licciardello*, University of Catania, Italy

Among the many technical challenges encountered in the development of high temperature electronics, the role of a passive component like capacitor is very important. Dielectric integrity at temperatures greater than 250 °C has however, up till now, been one of the major impediments to bringing out a capacitor with suitable performance characteristics at these high temperatures. In this work, we investigate applicability of boron oxynitride (BO_xN_{1-x}) thin films to fabricate capacitors for high temperature applications. Deposited BO_xN_{1-x} layers by a filamentless ion source assisted physical vapor deposition technique show a high thermal stability up to 400 °C and a very high breakdown voltage (BDV) above 400 V/µm. BO_xN_{1-x} samples of thickness varying from 70nm – 200nm were grown in a high vacuum reactor. Prototype capacitors with boron oxynitride dielectric and titanium metal electrodes have been fabricated on 3" Si wafers followed by electrical and thermal characterization. Preliminary results indicate a very small variation (~3%) of capacitance over the frequency range of 10 KHz – 2 MHz and <10% variation in capacitance for the temperature range of 25 °C-400 °C. The device electrical characteristics studies (capacitance, leakage current, breakdown voltage), as a function of temperature and frequency for (BO_xN_{1-x}) dielectrics with varying oxygen to nitrogen ratio, are currently underway and their results will be presented at the conference.

This research was supported in part by USDOE grant # DE-FG02-05ER84325 to Integrated Micro Sensors, Inc.

9:00am **EN+AS+EM+TF-WeM4 Improving Efficiencies of Electrochemical Systems Through Microstructure Optimization**, *H.Y. Chen,* University of Michigan*, J.R. Wilson, P.W. Voorhees,* Northwestern University*, S.B. Adler,* University of Washington*, S.A. Barnett,* Northwestern University*, **K. Thornton***, University of Michigan

The properties and performance of a wide range of materials depend on their microstructures. This is especially true in multifunctional, multiphase or composite materials in which different phases perform different functions. Therefore, controlling microstructures in these materials is one of the main routes for materials design to achieve optimal performance. Various simulation methods that can be applied to examine processing, property, and degradation during operation, including the phase-field simulations and finite element modeling, will be discussed. Through coupling of simulations of microstructural evolution and transport that use realistic microstructures, microstructural design for optimized performance is investigated. Specific examples will include microstructures found in solid oxide fuel cell electrodes and those resulting from phase separation.

9:20am **EN+AS+EM+TF-WeM5 Layer-By-Layer Approaches to Electrochemical Energy and Storage**, ***P.T. Hammond***, MIT **INVITED**

New advances in multilayer assembly have involved the development of ionically conductive multilayer thin films and the introduction of electrochemical functionality. These systems have allowed the formation of a range of ultrathin electrochemical devices including electrochromic displays, proton exchange membranes in fuel cells, and the use of these multilayers in other power and micropower devices. The use of this water based electrostatic assembly method has enabled the use of simple processing conditions, such as salt content and solution pH, to act as tools for the manipulation of ion and electron transport characteristics in the film, as well as the morphology of these unique nano-assemblies. Examples of this approach include the ability to integrate highly water soluble polymers with large sulfonic acid content into mechanically stable ultrathin films has led to new membranes with ionic conductivity approaching that of Nafion, and methanol permeability two orders lower, thus lowering fuel crossover and leading to large enhancements in methanol fuel cell performance with the application of nanometer thick thin films. On the other hand, the incorporation of both organic and inorganic nanoscale objects using the electrostatic assembly approach has enabled the incorporation of genetically engineering virus biotemplates in collaborations with the Belcher research group that have resulted in new developments in battery electrodes, and the integration of titania and other materials systems for reactive electrodes. Ultimately, the use of layer-by-layer systems have led to a range of organic and inorganic materials systems that have incorporated metal oxide nanoparticles, semiconducting carbon elements, and organic polymers to yield systems of interest for solar cells, capacitor/battery and electrochemical energy electrode and separator applications.

10:40am **EN+AS+EM+TF-WeM9 Material Solutions for Solid State Energy Storage**, ***L.F. Nazar***, University of Waterloo, Canada **INVITED**

The increasing demand for energy world-wide and inherent pressing environmental needs, have jump-started efforts to develop energy storage systems that can be coupled to renewable sources, and/or viable energy conversion systems. Traditional electrode materials for lithium-ion storage cells are typically crystalline, single-phase layered structures such as metal oxides, and graphitic carbons. These materials power billions of portable electronic devices in today's society. However, large-scale, high-capacity storage devices capable of powering hybrid electric vehicles (HEV's) or their plug-in versions (PHEV's and EV's) have much more demanding requirements. This in turn, means that demands are on chemists to create novel materials, and address fundamental scientific issues relating to mass (ion) and electron transport at rapid rates. Recently, nanostructured solid state materials comprised of two more compositions, are being increasingly exploited. These can take the form of "surface modified nanocrystallites", or stuffed nanoporous materials. For example, we employ porous frameworks as electrically conductive scaffolds to encapsulate active electrode materials, where both components play a role in controlling the electrochemical performance. This presentation will provide an overview of how the nanostructured approach provides benefit over the bulk, using selected examples from a range of promising new solid state materials with targeted, and tuneable structures.

11:20am **EN+AS+EM+TF-WeM11 Platinum Nanorods as PEM Fuel Cell Electrodes**, ***M. Gasda**, R. Teki, T.-M. Lu, N. Koratkar, G. Eisman, D. Gall*, Rensselaer Polytechnic Institute

Platinum catalyst layers were deposited by magnetron sputtering from a variable deposition angle α onto gas diffusion layer (GDL) substrates and were tested as cathode electrodes in polymer electrolyte membrane (PEM) fuel cells. Layers deposited at normal incidence (α = 0°) are continuous, and approximately replicate the rough surface morphology of the underlying GDL. In contrast, glancing angle deposition (GLAD) with α = 85° and continuously rotating substrates yields highly porous layers consisting of vertical Pt nanorods. At 0.40 mg/cm^2 total Pt loading, the rods are 100-500 nm long and ~300 nm wide, separated by 20-100 nm wide voids. The dramatic difference in microstructure is due to atomic shadowing during GLAD that causes Pt flux from highly oblique angles to preferentially deposit on surface protrusions, leading to nucleation and columnar growth on substrate mounds while surface depressions remain uncoated. Fuel cell testing at 70°C using Nafion 1135 membranes, Teflon-bonded Pt-black electrodes (TBPBE) at the anode, and atmospheric pressure hydrogen and air reactants shows a monotonic increase in performance of GLAD cathodes from 0.05 to 0.40 mg/cm^2 total Pt loading. Nanorod cells exhibit approximately 2x higher mass activity than continuous layers at 0.50V (corrected for iR, shorting, and gas crossover); for example, GLAD and continuous layers with approximately the same Pt loading (0.18 and 0.25 mg/cm^2, respectively) show 1.7 and 0.8 A/mg. In contrast, at low current density of 0.10 A/cm^2, the continuous layers (0.70 V with 0.25 mg/cm^2 Pt) outperform GLAD cells even with relatively high Pt loadings (0.65 V with 0.40 mg/cm^2 Pt). The GLAD cells' higher mass-specific performance at high current densities is due to their high porosity which facilitates reactant transport, while the low-current performance of the continuous layer is attributed to a higher active Pt surface area. The sputter-deposited electrodes exhibit a higher platinum utilization in comparison to TBPBE reference cathodes, with GLAD cells (1.7 A/mg) performing better than TBPBE (0.75 A/mg) at high current densities (0.50 V), while continuous layers (0.07 A/mg) outperform TBPBE (0.035 A/mg) at 0.80 V. These results indicate the promise of nanoengineering to boost catalyst utilization in PEM fuel cells.

Electronic Materials and Processing
Room: 210 - Session EM+NC-WeA

Molecular and Organic Electronics
Moderator: L.M. Porter, Carnegie Mellon University

1:40pm **EM+NC-WeA1 Metal-Molecule-Semiconductor Devices: Accurate Extraction of Device Parameters from Transport Measurements**, ***A. Scott***, *D. Janes*, Purdue University

In recent years there has been considerable interest in integrating molecular components into solid-state electronic devices for high-density memory, nanoelectronic, and sensing applications. Molecular devices directly grafted to semiconductors are of particular interest due to the electrically tunable nature and technological relevance of the substrates. Considerable experimental efforts have been invested in the fabrication and electrical characterization of metal-molecule-semiconductor (MMS) devices. When moderately-doped semiconductors are used in MMS structures, the devices exhibit Schottky diode-like behavior. Typically, current-voltage or capacitance-voltage characteristics of the devices are measured at room temperature and the results are analyzed by using well-known ideal Schottky diode relationships.[1] The Schottky barrier height, Φ_B, is experimentally determined assuming that the electronic and structural properties of the interfaced are not significantly modified by the presence of the molecular layer. Although this approach has been used to offer valuable qualitative insights about effects such as the influence molecular dipole on Φ_B,[2] it does not consider the detailed structural and electronic properties of the interface. Additional experimental and theoretical tools are needed to capture the interfacial physics introduced by the molecular electronic structure as well as non-idealities which are present at such hybrid interfaces. We present a MMS device model which considers the molecular electronic structure, semiconductor interface states, junction non-uniformity, and other important physical phenomena which are not present in the ideal Schottky diode model. The influence of various effects on current-voltage and capacitance-voltage characteristics are illustrated. Theoretical and experimental evidence is presented to show that temperature dependent transport allows for more accurate extraction of device parameters with fewer assumptions. The improved description MMS devices will shed additional light on the transport mechanisms that dominate these structures as the substrate and molecular properties are varied, leading to improved device design and characterization.

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2:00pm **EM+NC-WeA2 Silicon-on-Insulator based sub 10 nm Spaced Metal Electrodes for Hybrid Molecular Electronics**, *S. Strobel,* Technische Universität München, Germany*, R. Sondergaard,* Technical University of Denmark*, R. Murcia Hernandez,* Technische Universität München, Germany*, A. Hansen, F. Krebs,* Technical University of Denmark*, P. Lugli,* Technische Universität München, Germany*,* ***M. Tornow***, Technische Universität Braunschweig, Germany

In future microelectronic circuits a partial replacement of certain electronic functions by organic molecule junctions may become feasible. For such “hybrid” integration the fabrication of nanoscale contacts on the same semiconductor wafer using existing microelectronic process technology, only, will be advantageous. We investigated the fabrication of nanogap electrode devices based on silicon-on-insulator, by using optical lithography, a combination of dry and wet etching techniques and thin-film metal deposition. The prepared, smooth metallic contact pairs are separated by predetermined distances down to below 10 nm, and feature a well tailored material layer structure, as characterized by cross-sectional scanning TEM analysis. We studied the electronic transport properties of molecular wires based on conjugated organic molecules and molecule-nanoparticle hybrid systems. In the case of approx. 12 nm long dithiolated, oligo-phenylene-vinylene derivatives we observed a pronounced non-linear current-voltage characteristic at 4.2 K. The electronic states of the molecule have been studied by Density Functional Theory (DFT) in order to show the effect of the ligands and of the gold contacts. By using the results of the DFT calculations in a Non Equilibrium Green Function model, the current-voltage characteristics of OPVs have been analyzed, showing a good agreement with the experimental data. Low temperature transport through 30 nm gold nanoparticles positioned onto electrodes coated by a self-assembled monolayer of mercaptohexanol features a distinct Coulomb staircase behavior. These measurements are in excellent agreement with classical Coulomb blockade theory for an asymmetric double barrier tunneling system.

2:20pm **EM+NC-WeA3 Single Molecule Electronics and Sensors**, ***N.J. Tao***, Arizona State University **INVITED**

The ability to measure and control current through a single molecule is a basic requirement towards the ultimate goal of building an electronic device using single molecules. It also allows one to read the chemical and biological information of the molecule electronically, which opens the door to chemical and biological sensor applications based on electrical measurement of individually wired molecules. To reliably measure the current, one must: 1) provide a reproducible contact between the molecule and two probing electrodes; 2) find a signature to identify that the measured conductance is due to not only the sample molecules but also a single sample molecule; 3) provide a third gate electrode to control the current; and 4) carry out the measurement in aqueous solutions for biologically relevant molecules in order to preserve their native conformations. We will describe methods to attach a single molecule to two electrodes via covalent bonds and control the current through the molecule with an electrochemical gate, and report on sensor applications of the molecular junctions. We will also discuss unresolved issues in the attempt to measure and control electron transport in single molecules.

3:00pm **EM+NC-WeA5 Spectroscopic Observation of Conductance Switching with Inelastic Electron Tunneling Spectroscopy**, ***B.G. Willis***, University of Delaware

Molecular electronics is a promising area of research for creating electronic devices that can be integrated with semiconductor based nanoelectronics for novel capabilities such as molecular sensors. Recent literature data has shown that the electrical transport properties of molecules can be tuned through chemistry, and the long term expectation is that useful devices can be engineered through a combination of chemistry and electrical transport properties. It is also known that the electrical contact between a molecule and an electrode has a significant influence on electrical transport measurements, and these contact effects complicate the interpretation and design of molecular electronics devices. The contact effects become increasingly important as the number of molecules in the molecular transport junction is reduced toward the limit of a single molecule, and there is an urgent need to investigate contact effects in transport measurements. This is difficult due to the inherent nanoscopic nature of the experiments and the general lack of appropriate experimental tools. In this paper, we present an approach using inelastic electron tunneling spectroscopy (IETS) to investigate the chemistry and chemical bonding in electrode-molecule-electrode tunnel junctions. We present IETS spectroscopic observation of conductance switching for carbon monoxide bonded to a Cu/Pd bimetallic surface in a nanoelectrode junction. It is shown that the conductance switching is caused by the formation of an adatom on the surface that leads to an abrupt increase in the current of almost an order of magnitude. The new bonding arrangement leads to intense IETS features including the metal-CO bond stretch that has not previously been observed in related scanning tunneling microscopy IETS experiments. This work demonstrates that conductance changes in molecular electronics junctions can be studied and understood using IETS as a spectroscopic probe of the chemistry and bonding in the junction. Furthermore, it is shown that small molecules such as CO may be useful for characterizing electrode structure in molecular electronics measurements.

4:00pm **EM+NC-WeA8 Nanocontacts Inducing Surface Initiated Polymerization of Nanowires on Molybdenum Carbide**, ***I. Temprano***, Université Laval, Canada

The ability to develop new methods to enhance electrical contact between organic molecules and electrodes is fundamental to the design of devices that require electron flow between an organic and a metallic component. Metal-organic contacts using double and triple bonds is a promising approach in that it combines three advantages. First it offers a transmission coeficient not yet seen way ahead of any other molecular linkages yet known,[1,2] second they have enhanced thermal stability[3,9-10] over 900 K, and they show activity for olefin-metathesis add-on chemistry.[1] The dissociative adsorption of carbonyl compounds leads to the formation of C=Mo double bonds on the surface of molybdenum carbide.[3-6] These metal alkylidenes are mimics of well defined homogeneous metathesis catalysts, and present similar activity face to transalkylidenation and ring-openining polymerization (ROMP)[8] reaction. The data presented will show this breaktrhough catalytic system and its performance, paying especial attention to the formation and characterization of surface initiated metathesis polymerization of polyacetylene,[9] the simplest of the conjugated polymers, and an ideal candidate to study the special properties this system can developpe. This study opens a whole new era in which a very controllable reaction as olefin-metathesis may be used to grow

technologically very interesting conjugated polymers, directly from a metallic surface, and hence, to interconnect electrodes, as nanowires, in nanodevices with great control and precission. Self-assembly of conjugated polymers may allow their targeted insertion into electronic and electrooptical devices.

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4:20pm **EM+NC-WeA9 Spatially Resolved Conductance Measurements of Novel Porphyrin-Chromophore Molecular Assemblies**, ***S.U. Nanayakkara**, L. Kraya,* University of Pennsylvania*, T.-H. Park, J.T. Stecher, M.J. Therien,* Duke University*, D.A. Bonnell*, University of Pennsylvania

We have measured charge transport in individual porphyrin-chromophore molecules using an ultra-high vacuum scanning tunneling microscope. This class of fully conjugated molecules can include a mono- or multi-chromophoric center and a linker-group that terminates with a thiol or dithioate functionality. These functionalities facilitate attachment to a gold substrate. Therefore, in order to isolate individual and small groups of molecules we have utilized self- and directed-assembly using alkanethiolate self-assembled monolayers (SAMs) on Au(111). The alkanethiolate SAMs provide a support matrix confining the porphyrin-chromophore molecules into precise assemblies for charge transport measurements. We have further coupled a laser to the tunneling junction in order to record photo-induced single molecule charge transport measurements. We aim to understand the conductance pathways of these molecules with and without illumination, and as a function of its chemical structure and the molecule-substrate interface.

4:40pm **EM+NC-WeA10 Phase Selection in TiOPc/Ag (111) Molecular Films: Combined STM:STS Investigations***, ***Y.Y Wei**,* University of Maryland, College Park*, S.W. Robey,* National Institute of Standards and Technology*, J.E. Reutt-Robey*, University of Maryland, College Park

Titanyl phthalocyanine (TiOPc) has emerged as an important molecular component in building organic electronic devices. Its broad optical absorption spans the near infrared - visible region and high photoconductivity are most promising features, yet a tendency for polymorphism may limit TiOPc applications. Understanding how to control the molecular architecture in thin TiOPc films, and relate structure to electronic properties, is thus an important scientific goal. We present STM/STS studies of growth and two-dimensional crystallization of TiOPc films prepared by vapor deposition on Ag (111). We show how three distinctive TiOPc monolayer phases can be fabricated via flux control. At lowest TiOPc fluxes, a honeycomb phase forms, in which molecules organize into interlocked pairs. This phase optimizes quadrupole attraction and minimizes lateral dipole repulsion between TiOPc neighbors. At medium fluxes, a higher-energy hexagonal phase, stabilized by partly overlapped Pc rings between neighboring molecules emerges. At yet higher fluxes, a triangular network of misfit dislocations, with a characteristic domain size of ca. 14 nm is produced. We present molecular models of these three distinctive phases and describe how the film architecture is controlled primarily by electrostatic TiOPc-TiOPc interactions. Comparative STS Studies of the honeycomb and hexagonal monolayers reveal a metallic-like conductivity for both films. Finally, we show how these different TiOPc phases, employed as substrates for sequential C_{60} deposition, yield distinctive donor-acceptor heterostructures with unique electronic characteristics.

*This work has been supported by the Department of Commerce through the Nanomanufacturing Center of NIST, the Nanotechnolgy Fund of NASA, and the National Science Foundation under Surface Analytical Chemistry grant CHE0750203.

5:00pm **EM+NC-WeA11 Spin Polarized Electron Tunneling Through Conjugated Molecules**, ***P. LeClair**, W. Xu, G. Szulczewski, A. Gupta*, University of Alabama

Electron tunneling across organic/inorganic interfaces is important to the performance of organic based electronic devices, such as organic light emitting diodes and organic field effect transistors. However, spin dependent electron tunneling across organic/inorganic interfaces is not well understood.[1] In this presentation we will demonstrate the injection, transport, and detection of a spin-polarized current through pi-conjugated molecules. Specifically we highlight the results for tetraphenyl porphyrin (TPP), but the results are similar for other conjugated organic semiconductors.[2] Tunnel junctions were made by depositing TPP between $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) and Co electrodes. At cryogenic temperatures the devices show a negative magnetoresistance of 15-25%. A tunneling model that explains the temperature, bias voltage and sign of the magnetoresistance will be presented. In addition, we have directly measured the spin polarization (~37%) for electrons tunneling from Co through TPP monolayers using superconductor Al films as the spin detector. Collectively these results clearly demonstrate that spin polarized electrons tunnel through conjugated organic semiconductors with negligible spin-flipping and suggest that such molecules may find use in spintronic applications. For comparison, we will also present recent results utilizing halogen-substituted benzoic acid self-assembled monolayers as a "model" system. In this case, the presence or abscence of spin-flip scattering during tunneling is highly dependent on the choice of the halogen substituent.

[1] T. S. Santos, J. S. Lee, P. Migdal, I. C. Lekshmi, B. Satpati, and J. S. Moodera, Physical Review Letters 98, 016601 (2007).
[2] W. Xu, G. J. Szulczewski, P. LeClair, I. Navarrete, R. Schad, G. Miao, H. Guo, and A. Gupta, Applied Physics Letters 90,072506 (2007).

5:20pm **EM+NC-WeA12 Influence of Structural Ordering on Conductivity of Pentathiophene Based Langmuir-Blodgett Monolayers**, ***Y. Qi*,** University of California, Berkeley and Lawrence Berkeley National Laboratory*, B.L.M. Hendriksen, F. Martin, D.F. Ogletree,* Lawrence Berkeley National Laboratory*, C. Mauldin, J.M.J. Frechet,* University of California, Berkeley*, M. Salmeron*, Lawrence Berkeley National Laboratory

Good understanding of the mechanisms responsible for electrical conduction in organic molecules is essential for the development of organic and molecular electronics. In this study we correlate structural and electrical conduction properties of decyl-pentathiophenyl butyric acid monolayers using a conductance atomic force microscope (C-AFM). We used the Langmuir-Blodgett technique to prepare monolayers on heavily doped p-type Si, mica and flat Au substrates. For all substrates we find that two types of structures coexist in the monolayers: one consisting of compact and crystalline islands; the other phase is poorly packed and contains many holes. The magnitude of the friction on crystalline islands is significantly lower than on the poorly packed structure, while the current is at least an order of magnitude higher on the crystalline islands. Scanning on the well-order phase at high loads destroys the lateral order and reduces the conductivity. Our data show that there is a lateral, structural component to the conduction perpendicularly through the monolayer.

Tribology Focus Topic
Room: 205 - Session TR+NS+EM+NC-WeA

Nanotribology and Nanomechanics
Moderator: S.J. Bull, Newcastle University, UK

1:40pm **TR+NS+EM+NC-WeA1 Frictional and Transverse Shear Forces as Probes of Disorder and Anisotropy in Organic Semiconductors**, ***G. Haugstad**, V. Kalahari, C.D. Frisbie*, University of Minnesota **INVITED**

The condensed matter properties of conjugated organic systems are critically important to thin-film transistors for flexible electronics. As with conventional (inorganic) semiconductors, crystallinity is expected to strongly impact electronic transport. But unlike inorganic semiconductors, details of intermolecular coupling also are important. It is well known from friction force microscopy on alkane-chain films (self-assembled monolayers) that sliding friction is exceedingly sensitive to disorder and molecular coupling. Friction anisotropy also has been observed on Langmuir-Blodgett and liquid crystal films, as relates to the crystallographic axes and molecular packing. This suggests that nanotribological phenomenology can be targeted towards the analysis of crystalline organic systems whose principal technological application resides outside of tribology. Recently we discovered that the presence of defects in the form of line dislocations (revealed via etching) within a given micron-scale grain of pentacene correlates with elevated friction. Moreover we discovered that images of shear force transverse to the fast-scan axis reveal the crystallographic orientation of pentacene grains.[1] We report more detailed investigations into these novel tribological phenomena, expanded to additional conjugated crystalline organic thin films as well as surfaces of bulk single crystals. We also broaden our methodology to include shear modulation force microscopy, to isolate purely elastic effects under a pinned contact from dissipative effects under a sliding contact. We compare tribological/nanomechanical observations of crystal anisotropy to electronic transport measurements, uncovering systematic relationships. Our findings establish a highly reproducible phenomenology across a family of similar systems, but with some interesting differences related to crystal structure. We expect these findings to be important to both electronic transport in organic thin-film semiconductors and to the fundamentals of tribology on crystalline organic systems.

[1] K. Puntambekar, J. Dong, G. Haugstad and C. D. Frisbie, Adv. Funct. Mater. 16, 879 (2006).

2:20pm **TR+NS+EM+NC-WeA3 Load Dependence of Interfacial Friction Analyzed by Nanoparticle Manipulation**, ***D. Dietzel***, University of Muenster and Forschungszentrum Karlsruhe, Germany, *A. Schirmeisen*, University of Muenster, Germany

By analyzing the friction between an atomic force microscopy (AFM) cantilever tip and the sample surface, friction force microscopy (FFM) has proven to be a powerful tool for nanotribology. Unfortunately, FFM has some limitations inherent to the experimental configuration. For example it is extremely difficult to measure friction as a function of the normal force applied to the interface, since any quantitative interpretation is complicated by the simultaneous variation of the contact area. In order to address the important problem of load dependence of nanoscale friction, a technique for measurements under well defined interface conditions is required. Well-defined interfaces can be investigated by friction force analysis during nanoparticle manipulation.[1] However, the aspect of load dependence can not be analyzed as long as the cantilever is just pushing the particles from the side. In this work, a new approach for load dependent friction measurements by particle manipulation is presented. The AFM tip is used for pushing the nanoparticle while exerting a defined normal force simultaneously. For this approach the AFM-tip is centered on top of a highly mobile nanoparticle. Depending on the scanning conditions, the tip is either scanned on top of the particle or the particle moves together with the tip on the surface. In the latter case, the cantilever torsion during particle movement represents the interfacial friction between particle and surface. Thermally evaporated Sb-islands on HOPG substrate were used as a model system for the manipulation experiments. To ensure clean interface conditions and high mobility of the particles, all measurements have been performed under UHV conditions. When scanning the tip on top of the Sb-particle, the cantilever normal force is used to control the manipulation. Low normal forces usually result in scanning the tip on top of the particle, whereas higher normal forces can overcome the particle's static friction and induce the switch to simultaneously moving the particle with the tip. Once the particle is moving, the normal force can be further increased, making load dependent friction measurements possible. In contrast to conventional FFM, the measured friction originates from a well defined interface of constant size and can thus unambiguously be interpreted with respect to the load dependence of the interfacial shear stress.

[1]Dietzel et al., J. Appl. Phys. 102, 084306 (2007).

2:40pm **TR+NS+EM+NC-WeA4 Atomistic Simulations of Tribology at Sliding Surfaces**, *P. Barry, P. Chiu, T. Liang, S.S. Perry, W.G. Sawyer, S.R. Phillpot,* ***S.B. Sinnott***, University of Florida

Friction is of tremendous technological importance and has, consequently, been under study for centuries. This research has led to the development of classical theories of friction that have successfully solved several tribological problems. However, these classical theories do less well at describing the behavior of advanced materials that operate under extreme environments. Here, we describe integrated experimental and computational studies of atomic-scale friction and wear at solid-solid interfaces across length and time scales. The influence of molecular orientation in the case of polymer films of polytetrafluoroethylene and polyethylene, on friction and wear are discussed. In addition, the tribological behavior of polycrystalline molybdenum disulfide is elucidated in a combination of atomic-force microscopy and classical molecular dynamics simulations. These results provide new insights into how classical theories of friction may be modified to better describe advanced materials under extreme environments. This work is supported by a MURI from the Air Force Office of Scientific Research through grant FA9550-04-1-0367.

3:00pm **TR+NS+EM+NC-WeA5 Local Thermomechanical Characterization of Phase Transitions in Polymers using Band Excitation Atomic Force Acoustic Microscopy with Heated Probe**, *M.P. Nikiforov,* ***S. Jesse,*** Oak Ridge National Laboratory, *L. Germinario,* Eastman Kodak, *S.V. Kalinin*, Oak Ridge National Laboratory

Nanoscale confinement effects strongly affect thermomechanical properties of materials and composites, including surface- and interface-induced changes in melting and glass temperatures, temperature-dependent interface bonding, and local viscoelastic properties. Probing these behaviors locally overcomes the challenge of non-destructive characterization of thermomechanical behaviors in small volumes. Here we demonstrated that phase transitions in polymeric materials induced by the heated probe can be detected by band excitation acoustic force microscopy. Phase transition can be detected using any of the 3 independently determined parameters, such as oscillation amplitude, resonance frequency, and Q factor. Glass transition as well as melting in polymers can be efficiently differentiated using this technique. We developed the heating protocol to maintain contact area and effective force constant during the heating cycle, thus allowing for reproducible measurements and potentially for quantitative extraction of local thermomechnical properties. The contact mechanics models for tip indenting the surface are discussed. These models provide a framework connecting viscoelastic properties of the surface and oscillation parameters measured in the experiment. Currently, the major limitation of thermal probe techniques, such as Wollastone probe, is large indentation footprint (~ 10 um) of the probe on the surface after the experiment. Our method overcomes this problem. In the best case scenario, development of the band excitation acoustic force microscopy combined with a heated-probe approach will provide us a tool for non-destructive measurements of the glass transition and melting temperatures with sub-100 nm spatial resolution. Research was sponsored by the Center for Nanophase Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

4:00pm **TR+NS+EM+NC-WeA8 Effects of Structure, Doping, & Environment on the Tribochemistry of DLC**, ***J.A. Harrison***, *J.D. Schall, G. Gao, M.T. Knippenberg, P.T. Mikulski*, United States Naval Academy

The classical reactive empirical bond-order potentials have been used to model a wide range physical and chemical processes in covalent materials. Despite the many successes of these potentials, they are not able to model all properties of materials equally well nor are they able to model systems where intermolecular interactions are important. For hydrocarbons, intermolecular forces can be modeled using an adaptive algorithm as is used in the AIREBO potential. We will briefly discuss our recent efforts to add additional elements, such as Si, to the second-generation REBO formalism, thereby extending the types of materials which can be modeled with these potentials. In addition, we will also briefly discuss the parameterization of additional atom types for the AIREBO formalism. The majority of the talk will focus on recent simulations that have examined atomic-scale friction and wear of diamondlike carbon (DLC) and doped DLC. Work supported by The Office of Naval Research and The Air Force Office of Scientific Research as part of the Extreme Friction MURI & the Tribology Program.

4:20pm **TR+NS+EM+NC-WeA9 Low-Wear Variable-Slope Method of Lateral Force Calibration**, ***S. Chakraborty***, *D. Eggiman, C. DeGraf, K. Stevens, D.-L. Liu, N.A. Burnham*, Worcester Polytechnic Institute

Dozens of publications address the confounding problem of lateral force calibration. The existing techniques suffer from limitations including: i) repeated measurements are necessary, thereby causing wear to the tip, ii) calibration is done on another cantilever other than the one that will be used in the experiment, iii) specialized or expensive equipment is required, iv) the method is time consuming, v) the calibration is performed ex-situ, vi) a form for the frictional dependence on load is assumed, and vii) the equilibrium diagrams of the forces acting on the tip are incorrect. We describe a method[1,2] that overcomes all of these problems; it uses an easily available test sample with a continuously variable slope. The theory and proof-of-concept experimental data will be shown. If confirmed as a robust approach, lateral forces will at last be tamed by simple, quick, and potentially accurate calibration.

[1] D. Eggimand, senior thesis, Physics Department, Worcester Polytechnic Institute, 2007.

[2] C. DeGraf and K. Stevens, senior thesis, Physics Department, Worcester Polytechnic Institute, 2006.

4:40pm **TR+NS+EM+NC-WeA10 The Effect of Tip Size on Frictional Forces in Self-Assembled Monolayers**, ***M.T. Knippenberg***, United States Naval Academy

Molecular dynamics simulations have been used to investigate the differences in molecular forces between a nominally flat tip, which is infinite in extent, and a spherical tip when both tips are in sliding contact with a self-assembled monolayer. The simulation technique used provides a method for evaluating contact forces of individual atoms, which are defined as the force between single atoms and the sliding tip. From this, atoms can be described as either contributing forces that push the tip forward, or resist the forward movement of the tip. Multiple loads are applied to both tip shapes during sliding, providing the opportunity to investigate force propagation as a dependence on load. Additionally, geometrical information such as the occurrence of gauche defects during sliding is investigated.

5:00pm **TR+NS+EM+NC-WeA11 Microscale Tribology of Nanostructured Coatings**, ***K.J. Wahl***, U.S. Naval Research Laboratory, *E. So,* U.S. Naval Research Laboratory and PSU, *M.C. Demirel*, Pennsylvania State University

Novel nanostructured architectures are being explored for a wide range of applications including mimicking bioadhesive pads on insects and geckos, RF-microelectronics switches with robust compliant carbon nanotube films, and energy harvesting from friction by rubbing nanostructured piezoelectric coated fibers together. Developing an understanding of how these collections of nanostructured materials behave collectively requires experimental approaches at micron length scales. Experimental examination of the mechanics and tribology of materials in this intermediate regime can be influenced by macroscale phenomena (such as wear and interfacial

transfer film formation during sliding) as well as phenomena more often associated with nanoscale contacts (such as significant adhesion contributions). In this talk, we will present tribological and mechanical analysis of columnar nanostructured poly-(p-xylylene) (PPX) thin films. Experiments are performed using nanoindentation and microtribology tools to examine the effects of load, counterface material, roughness, and transfer film formation on microscale tribological response. The PPX films are structurally anisotropic, consisting of nanowires oriented at various angles with respect to the surface normal. Sliding friction experiments performed at discrete angles with respect to the nanowire orientation resulted in relatively uniform friction behavior but significant differences in deformation response of the films. A simple mechanical model is proposed to explain the observed depth anisotropy. The value of monitoring both friction and contact depth simultaneously will be discussed and evaluated in context of materials exhibiting highly anisotropic mechanical properties.

5:20pm **TR+NS+EM+NC-WeA12 Characterization of the Al/Si Interfaces under Dry Wear Conditions**, ***J.F. Su***, *X. Nie, V. Stoilov*, University of Windsor, Canada

Plastic deformation and damage accumulation at the contact surface are two important aspects of sliding wear of metal-matrix composite(MMC) materials such as AlSi alloys. The particular topography of the surfaces of the AlSi alloys has triggered the idea that the silicon particles form a load-bearing surface over which the counter surfaces are sliding. Therefore the wear resistance of AlSi surface is thought to originate from the high hardness of the silicon surface formed by the primary Si particles(inclusions). On the other hand the mechanical strength of the reinforcement(Si)/matrix(Al) interface in a MMC is the primary factor determining the strength on the load bearing Si formation. In this work we have developed a hybrid method to characterize the interface strength of an MMC, combining a nano/micro indentation experiment and an atomistic analysis. The nano/micro indentation experiment was carried out by indenting individual reinforcement particles on a free surface with a nano/microindenter. The dependence of indentation response on the interface properties was systematically studied and the interface strength was extracted from the threshold stress for the sink-in of the Si particles. With this method, the shear strength of an Al/Si interface was measured approximately 330MPa which compares well with the lower bound of an atomistic simulation with a modified embedded atom method (MEAM) potential.

Biological, Organic, and Soft Materials Focus Topic
Room: 201 - Session BO+EM+BI+NC-ThM

Semiconducting Biointerfaces and Sensors
Moderator: L.J. Brillson, Ohio State University

8:00am **BO+EM+BI+NC-ThM1 AlGaN/GaN HEMT And ZnO Nanorod Based Sensors for Chemical and Bio Applications**, *B.S. Kang, H.T. Wang, K.C. Chen, Y.L. Wang, T. Lele, J. Lin, S.J. Pearton,* ***F. Ren***, University of Florida

AlGaN/GaN high electron mobility transistor based sensors are good candidates for low cost, handheld, and wireless chemical and biomedical sensor due to their excellent thermal as well as chemical stability and sensitivity to the changes of ambient. The electrons in the AlGaN/GaN HEMT two-dimensional electron gas (2DEG) channel are induced by piezoelectric and spontaneous polarization effects and there is no dopant needed. There are positive counter charges at the AlGaN surface layer induced by the 2DEG. Any slight changes in the ambient of the AlGaN/GaN HEMT affect the surface charges of the AlGaN/GaN HEMT. These changes in the surface charge are transduced into a change in the concentration of the 2DEG in the AlGaN/GaN HEMTs. We have demonstrated AlGaN/GaN HEMT based individual sensors for protein, DNA, kidney injury molecules, prostate cancer, pH values of the solutions, pH in the exhaled breath condensate, and mercury ions with specific surface functionalizations. We have also demonstrated ZnO nanorod based sensors to detect UV, hydrogen, carbon monoxide and ammonium. Recently, we integrated ZnO nanorods with AlGaN/GaN HEMT to detect glucose in the breath condensate. This approach makes a possibility of integrating AlGaN/GaN HEMT based sensors with ZnO nanorod sensors on a single "smart sensor chip" with the techniques of selective area functionalization and mircofluidic device approaches. This smart sensor chip can be mounted on a handheld, portable, wireless transmitter circuit board.

8:20am **BO+EM+BI+NC-ThM2 Label-Free Dual Sensing of DNA-Molecules using GaN Nanowires**, ***A. Ganguly***, *C.-P. Chen,* National Taiwan University, *K.H. Chen,* Academia Sinica, Taiwan, *L.C. Chen*, National Taiwan University

GaN, a leading optoelectronic material, is also known to be non-toxic and bio-compatible. Interestingly, this material in the form of nanowires (NWs), with the advantages of large surface-to-volume ratio and direct electrical-path due to surface-induced spatial-separation of charge-carriers, could possess high sensitivity to the local environment, hence to the surface-immobilized biomolecules. Here, we report the GaN NWs possess high bio-binding efficiency and provide a platform for in situ, label-free, and rapid (assay-time within 2 hours) detection of DNA-molecules with dual-sensing capability (electrochemical and optical). Both electrochemical (EC) and optical (photoluminescence, PL) measurements showed clear distinction of pristine GaN NWs with probe-DNA (pLF) immobilization, and after further hybridization, employing a popular target-DNA with anthrax lethal factor sequence (LF). In label-free condition, both EC and PL-based techniques exhibited high sensitivity, without any little effort to optimize the sensing-condition, up to nM and pM of concentrations, respectively for the recognition of LF, with very low assay-time. Furthermore, successful application for detection of "hotspot"-mutations, related to human p53 tumor-suppressor gene, revealed excellent selectivity and specificity towards the fully-complementary targets, down to pM concentration, even in presence of mutations and non-complementary strands, suggesting the potential pragmatic application in complex clinical samples. The simplicity in detection-method, without any requirement of extra step/modification in both probe and target-systems, and simultaneously, the unique label-free dual-detection capability of GaN NWs, with excellent selectivity and sensitivity, can make them a promising choice of transducers, even in clinical application.

8:40am **BO+EM+BI+NC-ThM3 GaN Field Effect Transistors for Biosensor Applications**, ***W. Lu***, The Ohio State University **INVITED**

Biosensors based on electrical field effect transistors (FETs) are of great research interests due to their properties of label free, low cost, small size, and easy integration to external circuitry electronics. Such biosensors have been fabricated on many semiconductor materials including Si, silicon on oxide, carbon nanotube, ZnO, etc. Si-based such biologically FETs (bioFETs) suffer from various difficulties such as limited sensitivity and current drift caused by degradation of gate dielectrics and chemical instability. Due to the chemical inertness and the high concentration of two dimensional electron gas (2DEG) at the AlGaN/GaN interface, AlGaN/GaN heterojunction FETs have great potentials for detection of bioagents in biological buffers with high ionic strengths. In this paper, we will give an overview of recent research progress on GaN FET biosensors. The process and characterization of functionalization of AlGaN surface for biosensing applications will be discussed. The detection of streptavidin (STA) and monokine induced by interferon γ (MIG) proteins and hybridization process of single strand DNAs by AlGaN/GaN HFETs will be presented. Specifically, for STA detection, at different ionic strengths, the effect of Debye length on detection sensitivity has been demonstrated. No current change is observed for fully biotinylated STA, indicating that there is no non-specific binding. Furthermore, we have used open binding pockets of specifically-bound STA on the biotinylated surface as receptors for detection of biotinylated MIG proteins. The results show that the devices are capable of detecting of biotinylated MIGs at pathological concentrations even at physiological ion strengths. In part, this is due to the superior stability of the AlGaN/GaN HFET platform in buffer, which results in sensor noise being sufficiently low to allow reproducible detection of protein analyte binding. For comparison, regular unbiotinylated MIG proteins gave no current change, indicating that there is no non-specific binding and the change of current is due to the charges transferred from charged analytes.

9:20am **BO+EM+BI+NC-ThM5 Surface Functionalization of ZnO Nanoparticles and Thin Films for Sensor Applications**, ***L. Selegard***, *C. Vahlberg, F. Söderlind, V. Khranovskii, A. Lloyd Spetz, R. Yakimova, P.-O. Käll, K. Uvdal*, Linköping University, Sweden

A new procedure has been developed for functionalization of electrochemically produced ZnO nanoparticles. The core of the particles was characterized using TEM, PEEM and LEEM. Single crystal nanoparticles, with uniform spherical morphology with a size of approximately 50Å were obtained. The first aims of ZnO nanoparticle functionalization were to make a stabilizing molecular layer at the surface and to prepare for further linking possibilities, for use in different types of sensing applications. The functionalization process was investigated and the molecular layer was verifyed by XPS and FT-IR. Parallel studies on biofunctionalization of plane ZnO thin films were performed to obtain a suitable reference system. One of the molecules used for functionalization of the nanoparticle surface was (3-Mercaptopropyl)triethoxysilane (MPTS) as it enables further functionalization on the thiol part and as it has the possibility to form a stable network around the particles. The MPTS linking was investigated by XPS and NEXAFS. The XPS spectra of the functionalized particles showed significant signal from both Si and S verifying the presence of MPTS. XPS core level S2p spectrum further showed presence of SH groups, indicating that thiols was available for further linking processes. Another molecule of interest for nanoparticle functionalization is oleic acid. The strategy is then to coordinate the carboxyl groups to the surface and further linking will be based on hydrofobic interactions. The TEM and PEEM results, so far, indicated that the particles were not fully dispersed but the use of oleic acid showed a much smaller extent of agglomerated particles than for example MPTS. PEEM also showed that the oleic acid capped particles was much more heat stable then MPTS capped once. ZnO nanoparticles show two emission peaks, one band gap related UV-emission and one visible emission arising from oxygen vacancies. In this work fluorescence spectroscopy was used to study the emitted, visible light of the particles as a function of different surface modifications.

9:40am **BO+EM+BI+NC-ThM6 Surface Functionalization and Micropatterning of Ta_2O_5 Films Using Organo-silane and Atom Transfer Radical Polymerization(ATRP) Methods**, ***W. Kulisch***, *D. Gilliland, G. Ceccone, L. Sirghi, F. Rossi, H. Rauscher*, European Commission Joint Research Center, Italy

Optical waveguide biosensors frequently require the use high refractive index thin films such as tantalum pentoxide to act as both as a light guide and as a surface on which active biomolecules can be covalently immobilized. In this work, a process for the room temperature deposition of Ta_2O_5 films onto silicon/silica and thermoplast substrates by reactive ion beam sputtering from a tantalum target has been developed. The resultant high refractive index films have been chemically and optically characterized and methods examined for the wet chemical modification of the oxide film to produce either reactive amino groups or low protein fouling polyethylene glycol (PEG) layers. In both cases the first step toward the functionalization of the as-grown films used either an oxygen plasma or to an UV/O_3 treatment to produce a clean and fully oxidized surface. Using these clean, active surfaces-NH_2 terminated SAMs could be routinely produced using a conventional silanization process using 3-aminopropyl trimethoxysilane (APTMS). To produce high density, low protein binding (anti-fouling)

layers a more sophisticated procedure based on surface initiated atom transfer radical polymerization (SI-ATRP) of poly(ethylenglycol)methacrylate (PEGMA) has been used. In this method the oxide surface is firstly modified using a combination of poly(glycidylmethacrylate) (PGMA) and α-bromoisobutyryl bromide (BIB) to produce a surface rich in tethered α-bromoisobutyryl groups. These BIB groups can then used as initiation sites for the growth of dense PEG films using the copper complex catalysed ATRP of PEGMA macromonomers. To characterize the final surfaces and to assist in the optimization of process, time-of-flight secondary ion mass spectrometry (TOF-SIMS), X-ray photoelectron spectroscopy (XPS), contact angle measurements and atomic force microscopy (AFM) have been applied to samples after each step of the different processes. The effectiveness of the two processes will be demonstrated and examples given of methods by which the two methods have been combined for the production of fouling/non-fouling micropatterned surfaces.

10:40am **BO+EM+BI+NC-ThM9 Designing the Interfaces between Biomolecules and Semiconductor Substrates: From the C60 Buckyball Model System to Shape-Restricted DNA Molecules**, ***X. Zhang***, *A.V. Teplyakov*, University of Delaware

A well-characterized interface based upon covalent binding between biomolecules and semiconductor surface was designed using the functionalized self-assembled monolayers (SAM) on Si(111) surface and specific shaped-restricted DNA molecules. This type of interface can serve as a prototype for the future devices in biosensing and single molecule spectroscopy. The spectroscopic and microscopic benchmarks were initially tested using fullerene C60 as a model to understand the attachment chemistry of large molecules with amine-terminated SAM on Si(111) surface. X-ray photoelectron spectroscopy (XPS) and Infrared spectroscopic (IR) studies, supported by computational investigation, verified the covalent attachment of C60 to the amine-terminated SAM on Si(111) surface. The atomic force microscopy (AFM) revealed the topography of the C60-modied surface with molecular resolution. The biomolecule/semiconductor interface was tailored with the same amine-terminated SAM on Si(111) surface and thiol-DNA molecules, which is achieved via a sulfo-succinimidyl 4-(N-maleimidomethyl)-cyclohexane-1-carboxylate (SSMCC) crosslinker molecule. The shape-restricted thiol-DNA is anchored to the surface through the formation of covalent bonds as confirmed by XPS and time-of-flight secondary ion mass spectroscopy (ToF-SIMS). The AFM is used to visualize the well-defined and selective covalent binding of thiol-DNA molecules on SAM-covered Si(111). In addition, AFM and contact angle measurement are employed to study the change of the surface topography and the change of the surface hydrophilicity following each step of the DNA attachment chemistry on silicon.

11:00am **BO+EM+BI+NC-ThM10 The Effect of a Spacer Thiol on the Orientation and Hybridization Properties of 40mer DNA SAMs on Gold**, ***L.J. Gamble***, *P.-C. Nguyen*, *T. Weidner*, University of Washington, *D.W. Grainger*, University of Utah, *D.G. Castner*, University of Washington

Methods for surface-immobilizing single-strand nucleic acids while preserving their original hybridization specificity with minimal non-specific interactions remain an important goal for improving the performance of surface bound DNA microarray and biosensor applications. Before the full potential of DNA microarrays can be realized, fundamental issues must be better understood, including how the crowding, conformation and orientation of immobilized DNA impacts DNA target hybridization efficiency. For detection of small amounts of DNA in a target solution, the coverage and orientation of DNA probes should be optimized for the capture of low concentrations of DNA via hybridization. In this study the effect of backfill of mercaptohexanol (MCH) on 40mer thiolated single stranded DNA (SH-ssDNA) sequence orientation and hybridization efficiency is studied with X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, sum frequency generation (SFG) vibrational spectroscopy, and surface plasmon resonance (SPR). While XPS and NEXAFS are both ultra-high vacuum techniques, SPR is a real-time solution based technique and SFG spectroscopy can be acquired both at the solid-air interface as well as the solid-liquid interface. While the 40mer DNA is longer and expected to be more disordered, the NEXAFS N k-edge spectra showed increased the polarization dependence of the peaks at 401eV and 399eV for the 40mer sequence increased with an MCH backfill time of 1 hour. SFG spectroscopy results showed that incorporation of the MCH into the DNA monolayer resulted in an increase of the nucleotide related peaks at 2961 cm^{-1} and 3045 cm^{-1} which maximized at 1 hour MCH backfill. This evidence of orientation changes in the surface bound 40mer DNA will be correlated with hybridization data from SPR.

11:20am **BO+EM+BI+NC-ThM11 Anchoring and LT-STM/STS Characterization of Single Organic Molecules at Semiconducting and Insulating Surfaces**, ***M. Szymonski***, *A. Tekiel*, *S. Godlewski*, *G. Goryl*, *J. Prauzner-Bechcicki*, *J. Budzioch*, Jagiellonian University, Poland

In recent years self-assembling of organic molecules deposited onto different surfaces have attracted considerable attention because of important applications in organic electronic technologies and prospects for development of single molecule computing devices. In this presentation we will report on our recent studies of initial stages of growth and organization of several organic molecules on reconstructed (001) surface of InSb, (011) and (110) surfaces of TiO2, and on ultrathin KBr layers grown epitaxially on InSb(001). Among different organic molecules the perylene derivative - 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA), often regarded as a model system for planar-stacking molecules, copper phthalocyanine (CuPc), violet landers (VL), and chiral helicene[11] molecules were studied by means of scanning tunneling microscopy (STM) at room and liquid nitrogen temperatures, nc-AFM at room temperature and low energy electron diffraction (LEED). It is shown that during initial stages of growth on InSb molecules often form chains parallel to [110] crystallographic direction of the c(8x2) reconstructed substrate. They are frequently attached to the lower terrace step edge, or some defects on the surface, indicating surprisingly weak interaction between the molecules and the substrate and their high mobility along [110] diffusion channel. Geometrical orientation of the molecules with respect to the reconstruction rows of the substrate will be discussed. We will present the images acquired with submolecular resolution, as well as images demonstrating the pinning effect of the molecular chains by surface charge density waves, and incorporation of the molecules into overall electronic structure of the system.

11:40am **BO+EM+BI+NC-ThM12 Molecular Self-Assembly of Funtionalized Fullerenes on a Closed Packed Metal Surface**, ***B. Diaconescu***, University of New Hampshire, *T. Yang*, *S. Berber*, Michigan State University, *M. Jazdzyk*, *G. Miller*, University of New Hampshire, *D. Tomanek*, Michigan State University, *K. Pohl*, University of New Hampshire

Self-assembled organic thin films have a great number of practical applications, ranging from sensors and biological interfaces in medical implants to organic electronics and photovoltaics. Generally speaking, self-assembled monolayers (SAMs) form as a result of a delicate balance between competing molecule–substrate and intermolecular interactions. Therefore, to control such self-assembly processes in a useful way, it is mandatory to understand how this balance reflects onto the SAM's final structure. Here, we present a combined STM and DFT study of the self-assembly of C60 molecules functionalized with long alkane chains, F-C60, on the (111) surface of silver. We find that F-C60 molecules lay down on the Ag surface and form a complex zigzag like pattern with an oblique unit cell of 4 nm by 2.5 nm and two molecules per basis. The C60s are placed at a larger than van der Waals distance. The symmetry of the functionalized C60 self-assembled monolayer is dictated by the alkane–surface interaction while the size of the unit cell is a consequence of the in-plane intermolecular interactions. These results show that C60s can be assembled in a two-dimensional and non-compact molecular array and suggest a way to control their surface density via appropriate chemical functionalization.

*This work was supported by the Nanoscale Science and Engineering Center for High-rate Nanomanufacturing (NSF NSEC-425826). Partial support has been provided by the NSF-NIRT grant ECS-0506309."

Electronic Materials and Processing
Room: 210 - Session EM+NC-ThM

Contacts, Interfaces, and Defects in Semiconductors
Moderator: F. Ren, University of Florida

8:40am **EM+NC-ThM3 Point-probe Tunneling Measurements of Sheet Conductance of Metallized Silicon Surfaces**, ***H. Won***, *R.F. Willis*, The Pennsylvania State University

We report measurements of the sheet conductance of Si(111) 7x7 reconstructed surface and its metallization with Ag-overlayer. The experiment employs a STM-tip point tunneling probe coupled to a second spring-contact electrode to evaluate charge-carrier injection and transport via surface states prepared in-situ in UHV. The measurements distinguish a surface-states contribution, a Schottky diode contribution, and a metallic-overlayers dependence on thickness, ranging from submonolayer coverage to 10 monolayers. The thin film conductance shows a dependence on the interface conductance of the semiconductor, which is a function of the surface electron density.

9:00am **EM+NC-ThM4 Photoluminescece Spectroscopy on Near Surface InAs Quantum Dots and Wetting Layers**, ***I. Kamiya***, *K. Fukui*, Toyota Technological Institute, Japan

The electronic and optical properties of self-assembled (SA) InAs quantum dots (QDs) prepared by MBE or MOCVD have been one of the key topics of quantum nanostructures during the past few decades. In contrast to colloidal quantum dots such as CdSe with tri-octylphosphine oxide where the ligands plays a major role in passivating the surface,[1] SA InAs QDs are usually investigated without much concern on their surface/interface properties. However, we have shown that capping on the InAs QDs strongly influence their photoluminescence (PL)[2] or that the conductivity of surface InAs QDs strongly depends on their size.[3] More recently, it has been shown that surface and near surface InAs QDs exhibit features different from those of the well-buried.[4] Here, we have performed PL and PL excitation (PLE) spectroscopies on near surface InAs QDs and wetting layer (WL) to further investigate the influence of surface and interfaces of such structures. While we observed PL features similar to those reported in ref. 4, we have also found those that are different. PL and PLE measurements reveal that the carrier dynamics are stongly influenced by the surfaces and interface structures of the QDs and WL. We will discuss the mechanisms that could be governing such observations.

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[2] I. Kamiya, I. Tanaka, and H. Sakaki, Physica E2, 637 (1998).

[3] I. Tanaka, I. Kamiya, H. Sakaki, N. Qureshi, S. J. Allen, and P. M. Petroff, Appl. Phys. Lett. 74, 844 (1999).

[4] B. L. Liang, Zh. M. Wang, Y. I. Mazur, G. J. Salamo, E. A. DeCuir, and M. O. Manasreh, Appl. Phys. Lett. 89, 043125 (2006).

9:20am **EM+NC-ThM5 Barrier Formation and Transport in Metal Contacts to Nanotubes and Nanowires**, ***A. Talin***, *F. Leonard, B.S. Swartzentruber*, Sandia National Laboratories **INVITED**

The technology of metal-semiconductor contacts has progressed tremendously over the past fifty years. However, as device dimensions shrink well below 100 nm, and as new materials with novel composition and geometry are explored for 'next generation' electronic components, the underlying physics of metal-semiconductor contacts departs substantially from the early models of Schottky, Mott, and Bardeen. Single wall carbon nanotubes, for example, have a quasi-one-dimensional density of states and a relatively inert surface which results in less Fermi level pinning and a strong dependence of the contact barrier height on the metal workfunction. Nevertheless, the simple Schottky model fails to correctly predict the barrier height dependence on the nanotube band gap. The Schottky model is also inadequate for describing metal-nanowire contacts, even in the absence of strong one dimensional character in the band structure. In my talk, I will review recent experimental results for metal contacts to nanotubes and nanowires, and discuss how the dimensions and geometry of these nanostructures affect barrier formation. I will also discuss situations where bulk-limited transport in nanowires leads to non-linear current-voltage characteristics, and which is often, incorrectly, ascribed to contact effects.

10:40am **EM+NC-ThM9 Reliability of III-N Electronic Devices**, ***M. Shur***, Rensselaer Polytechnic Institute **INVITED**

III-N materials system has a much larger dislocation and defect densities than more conventional semiconductors, such as silicon or III-V materials, and III-N field effect transistors operate at much higher voltages and/or current densities. As a consequence, device reliability is one of major concerns for III-N semiconductor technology. In GaN-based field effect transistors, reliability mechanisms are linked to hot electron trapping, trap creation in high electric fields at the gate edges (especially at the gate edge closer to the drain), and to the gate leakage current. The electric field activated carrier trapping in the gate-to-drain spacing of AlGaN/GaN HFET is primarily responsible for the current reduction at RF frequencies (so-called current collapse, or RF dispersion. The defect states creation at the gate edges and in the drain-to-gate spacing depends on the device temperature. At relatively low temperatures, these defect states are created due to impurity anneal. At higher temperatures, crack and dislocation creation becomes the dominant mechanism leading to the permanent device failure. As a consequence, an extrapolation of high temperature accelerated reliability tests to lower temperatures might be inaccurate. Except for the failure mechanism related to the gate leakage current, other failure and performance degradation mechanisms are related to a high electric field at the drain edge of the device channel and in the drain-to-gate spacing adjacent to the gate. (Therefore, GaN-based RF switches operating at zero DC drain bias and having insulated gate structure (MOSHFETs and MISHFETs) do not have reliability problems.) Field plates and dual field plates diminish the maximum electric field in the device channel improving reliability. Another approach, still to be explored, is based on using Field Controlled Electrode at the drain, which a kind of a field plate attached to the drain, rather than to the gate or source. Leaky passivation helps discharging the trapped charge diminishing the current collapse. Optimization of buffer doping also improves reliability. These design approaches, using better quality substrates, and improving materials quality of III-N epitaxial films will allow to achieve long life times and stable performance for high power and high frequency GaN-based field effect transistors.

11:20am **EM+NC-ThM11 The SiC Surface: A Surface of Growing Technological Importance**, ***C.R. Eddy, Jr.***, *D.K. Gaskill, M.A. Mastro, R.T. Holm, B.L. VanMil, R.L. Myers-Ward, M.E. Twigg, Y.N. Picard,* U.S. Naval Research Laboratory, *P.G. Neudeck, A.J. Trunek, J.A. Powell*, NASA Glenn Research Center

Silicon carbide has become a highly versatile substrate providing a foundation for device technologies based on III-V nitrides, silicon carbide and graphene materials. In each of these systems, the starting silicon carbide surface plays a pivotal role in determining the properties and qualities of the material. The importance of surface orientation and preparation to each materials system will be discussed in terms of step morphology and contributions of extended defects in the substrate. For III-V nitride heteroepitaxy, basal plane SiC is preferred and surface morphology plays a critical role in the defectivity of films. Engineered SiC substrate surfaces are used to create localized regions of the surface with widely varying step densities including areas nearly free of surface steps. Experiments show that surface steps are directly responsible for extended defects in the heteroepitaxial layers. Nearly step-free surfaces are used to demonstrate drastically reduced extended defect concentrations ($\leq 10^7$ cm^{-2}) in GaN epilayers. In regard to SiC homoepitaxy, the key elements are the control of polytype deposition, the removal of surface imperfections arising from the substrate, and the reduction or elimination of extended defects arising from the substrate or during the epitaxial nucleation process. Substrates are prepared oriented slightly away from the basal plane to promote single polytype epitaxy and off-cut toward <11-20> to promote the smoothest films. Although modification of the surface is an unavoidable first step to epitaxy due to the reactive nature of hydrogen at growth temperatures near 1600°C, the best epitaxy occurs when the surface is controllably etched to remove unwanted polishing damage. And with the desire to fully exploit the properties of SiC for high power devices, it is necessary to initiate the epitaxy in such a way as to greatly reduce or eliminate extended defects. In the new field of graphene formation through sublimation of SiC surfaces, key elements are the removal of surface imperfections from the substrate and the control of surface properties, i.e., steps that may be used advantageously for specialized devices. Key aspects of surface properties and preparation will be discussed in terms of surface structure and extended defect intersection with the surface as characterized by atomic force microscopy, electron channeling contrast imaging, and transmission electron microscopy.

11:40am **EM+NC-ThM12 Investigation of Negative Electron Affinity in Hydrogen Complex Deactivated Surface of InP:Zn (100)**, ***M.D. Williams***, Clark Atlanta University

Ultraviolet photoemission spectroscopy is used to investigate the development of negative electron affinity at the surface of hydrogenated Zn doped InP (100). Hydrogen injected into the material electronically passivates the local carrier concentration. Reverse-biased anneals of the InP under ultra-high vacuum show a dramatic change in the work function of the material within a set annealing temperature range suggesting the establishment of negative electron affinity at the surface. The strength of the negative electron affinity is 1.08 eV for a reverse bias field strength of approximately 1875 V/m . This value is consistent with the deactivation energy of the H-Zn complex (1.14 eV) determined previously. Spectral features are also shown to be sensitive to sample temperature. Hydrogen retrapping at the surface limits the effect and it is dependent on surface conditions.

Nanomanufacturing Focus Topic
Room: 309 - Session NM+EM+PS+NS+NC-ThM

Printable Lithography and Processing
Moderator: D. Janes, Purdue University

8:00am **NM+EM+PS+NS+NC-ThM1 Techniques for Three Dimensional and Molecular Scale Nanofabrication**, *J. Rogers*, ***D. Shir***, University of Illinois, Urbana-Champaign **INVITED**

Progress in nanoscience and technology relies critically on the ability to build structures with nanometer dimensions. This talk describes unconventional lithographic methods based on (i) advanced forms of soft nanoimprint lithography for 2D patterning with resolution that extends to molecular (~1 nm) length scales, and (ii) conformable phase mask optics for single step formation of fully three dimensional (3D) nanostructures. The

first method relies on optimized polymers for molds and mold materials that, together, enable lithographic fidelity at the ~1-2 nm scale, as demonstrated by the replication of relief structures defined by individual single walled carbon nanotubes with diameters down to ~0.7 nm. The use of this method to form alignment layers for liquid crystal devices illustrates a realistic application and a simple example of the broader notion of molded molecular structures for chemical and biological surface recognition. The second method exploits an unusual class of optical element – an elastomeric, sub-wavelength phase mask – in a contact mode exposure geometry to generate 3D structures in photopolymers and other materials in a single patterning step. Aspects such as the self-imaging, Talbot effect optics of this approach, its capabilities for creating periodic, aperiodic and quasi-crystalline 3D nanostructures and selected applications in microfluidics, laser fusion targets and photonic crystals will be discussed. This work was supported by the NSF and the Department of Energy.

8:40am **NM+EM+PS+NS+NC-ThM3 Preparation of 25-nm-spaced PdAu Metal Electrodes on Silicon by Direct Nanotransfer Printing**, ***S. Strobel****, S. Harrer, G. Penso-Blanco, G. Scarpa, G. Abstreiter, P. Lugli,* Technische Universität München, Germany*, M. Tornow*, Technische Universität Braunschweig, Germany

Nanometer scale metallic contacts which can be directly deposited on planar substrates are of growing importance in view of future applications involving the integration of molecular electronics with current silicon technology. Here, a method which may provide well defined nanogap electrodes of predetermined spacing in a reproducible manner, without the need of sequential direct writing techniques, would be highly advantegous. We present a novel technique using direct high-resolution metal nanotransfer printing and demonstrate its capability to fabricate nanogap electrodes of predetermined spacing on a solid substrate such as silicon. The one-step transfer process is economical, simple and fast, and preserves the mold for manifold transfer. Using molecular beam epitaxy (MBE) a sandwich-like structure is grown with monolayer precision, comprising few nanometer thick GaAs layers embedded in AlGaAs. This structure is cleaved atomically flat perpendicular to the <110> crystallographic direction. Subsequently, the exposed GaAs layers are wet chemically etched thereby generating a 3D grating structure with nanometer-resolution at their edges. This structure serves as mold for nanotransfer printing: By coating the grating surface with a metallic thin film of PdAu/Ti (7/5 nm) and pressing the mold against a Si/SiO_2 substrate the patterned PdAu/Ti sandwich structure is directly transferred onto the surface. This one-step process does not require any flexible buffer layer or additional organic adhesion promoters. We report on a series of successful transfer experiments using different multi-line molds with varying aspect ratios and linewidths down to below 10 nm. In particular, we demonstrate electrically functional PdAu metal electrode pairs with separations down to 25 nm, featuring lead resistances of the order of kΩ and gap isolation in excess of 50 GΩ up to 2 Volts.

9:00am **NM+EM+PS+NS+NC-ThM4 Adhesion Enhancement using Plasma Processing in the Printing of Carbon-based and Organic Flexible Electronics**, ***D.R. Hines****,* University of Maryland*, V.W. Ballarotto, C. Hull,* Laboratory for Physical Sciences*, G.S. Oehrlein, D.Y. Lee,* University of Maryland*, C.M. Stafford, C.L. Soles, E.K. Lin, J. Liu, J.-Y. Chung,* National Institute of Standards and Technology*, S.G. Walton, E.H. Lock*, US Naval Research Laboratory

High quality organic & carbon-based thin-film transistors (TFT) have been successfully fabricated onto plastic substrates using transfer printing. With this printing process, each device component (conducting electrodes, polymer dielectric layer and semiconductor layer) was printed using only pressure and temperature, eliminating all chemical processing on the plastic device substrates. Pentacene (Pn), poly(3-hexylthiophene) (P3HT), carbon nanotube mats (CNTM) and graphene TFTs were all fabricated on polyethylene terephthalate (PET) substrates. Bottom gate, bottom source/drain devices yielded mobilities of 0.237 cm^2/Vs for Pn and 0.04 cm^2/Vs for P3HT. Bottom-gate CNTM TFTs exhibited p-type behavior, mobilities of 13.7 cm^2/Vs, on/off ratio of 10^3 and minimal hysteresis. Top-gate graphene TFTs exhibited mobilities of $1.0x10^4$ cm^2/Vs for holes and $4x10^3$ cm^2/Vs for electrons. The organic TFT devices were fabricated using a variety of polymer dielectric layers including poly(hydroxystyrene) (PHS), polystyrene (PS), polycarbonate (PC) and poly(methylmethacrylate) (PMMA). The resulting TFTs showed little variation in mobility, but strong variation in threshold voltage for different dielectric layers. The transfer printing process relies primarily on differential adhesion for the assembly of both patterned and unpatterned films onto a common flexible, plastic substrate. It is a simple and robust process that is compatible with a wide range of materials. Plasma processing techniques are being adapted to control the surface energy of polymer and plastic surfaces in order to increase adhesion forces at the interface between polymer dielectric layers and plastic substrates. The printability and surface characterization of plasma treated polymer/plastic surfaces will be discussed. One goal of this work is to enable the incorporation of many different dielectric materials (including 10 test polymer dielectric films) and substrate materials (including 11 test plastic substrate sheets) into the fabrication of flexible electronics. This work partially supported by the Office of Naval Research and the Laboratory for Physical Sciences. *E.H. Lock, NRC/NRL Postdoctoral Research Associate.

9:20am **NM+EM+PS+NS+NC-ThM5 Fabrication of Microarrays with Nanoscale Chemical Contrast by Nanoimprint-Assisted Lift-Off**, ***A. Ruiz****,* JRC, European Commission*, C.A. Mills,* Inst. for Bioeng. of Catalonia, Barcelona Sci. Park*, A. Valsesia,* JRC, European Commission*, E. Martinez,* Inst. for Bioeng. of Catalonia, Barcelona Sci. Park*, P. Colpo,* JRC, European Commission*, J. Samitier,* Inst. for Bioeng. of Catalonia, Barcelona Sci. Park*, F. Rossi*, JRC, European Commission

The fabrication of ordered microstructures of colloidal crystals is increasingly attracting interest due to their potential applications as sensing, optical and photonic band-gap materials. Depending on the application (i.e. chemical or biochemical sensors, photonic chips), specific microstructured configurations of the colloidal crystal are needed. Most of the methodologies reported so far for the production of colloidal crystals are based on the directed self-assembly of micro or nanospheres, in which patterning and formation take place simultaneously in a template created beforehand, normally by the modification of the surface chemical or topographic properties. However, methods for patterning the colloidal film after it has been formed are scarce. The interest in such methods lies in the fact that they allow fine control over the microstructure of the colloidal film by selective removal of a single layer of close-packed nanospheres. Recent top-down approaches to the micropatterning of nano-beads are based on soft lithography lift-off processes using PDMS stamps. Removal of nano-beads strongly adhering to the substrate is however hard to realize and limitations related to the PDMS structural properties, i.e. deformation, appear. Normally, the beads have to be loosely attached so that bead transfer or removal is not inhibited. In this work, a new soft-lithographic method for micro-patterning nano-bead arrays, based on structured poly(methyl methacrylate) (PMMA) and using a nanoimprinter apparatus, is described. The properties of the PMMA, with respect to hardness and flexibility, are promising for resolving sub-micron patterns of nanoparticles. The use of the nanoimprinter allows careful control of the temperature and pressure during the contact-stripping operation; this ensures accurate removal of nanoparticles over large areas even when they are strongly attached to the substrate. Patterns of polystyrene nano-beads in several micro-scale configurations have been obtained using beads of different diameters (100 ~ 500 nm) and with different levels of adherence to the substrate. The micropatterning of nanobeads thus achieved has been then used to create surfaces with nanoscale chemical contrast inside the micro-patterns. Having structured regions separated by flat, unstructured regions is advantageous for many applications, such as sensing platforms for parallel detection or cell culture platforms for examining cell-surface interactions at the nanoscale.

9:40am **NM+EM+PS+NS+NC-ThM6 Inkless Deposition of Microparticles by Electrostatic Acceleration for Materials Processing**, *I. Eu, L. Musinski, T. Liu,* University of Michigan*, D. Morris,* ElectroDynamic Applications, Inc.*, **J.M. Millunchick**, B. Gilchrist, A.D. Gallimore*, University of Michigan

We have developed a particle accelerator that electro-statically charges nanometer- to micron-sized conductive particles that are then accelerated through grids with bias voltages up to roughly 10kV, allowing for the deposition of particles without using a carrier solution or “ink”. By carefully controlling the energy of the particles, various regimes of materials processing may be achieved. For example, high energy high mass particles are expected to etch a substrate, while decreasing either the mass or velocity will result in deposition of the particles. A prototype device has been fabricated based on transporting the particles to and through an ultrafine “sieve” via back pressure and acoustic and/or mechanical vibration. The pressure and vibration moves the particles through the sieve apertures, allowing for electrostatic acceleration of the particles one at a time for maximum impulse. The experimental data shows a roughly Gaussian distribution of 50 micron Ag-coated glass spheres extracted at a mean electric field of about 1.9 MV/m with a standard deviation of approximately 0.4 MV/m. The data agrees well with the analytical model for required extraction fields determined using calculated Van der Waal’s forces and a Lipshitz constant of 0.6 eV. The variance likely attributable to electrode surface roughness and manufacturing imperfections in particle shape. Initial feasibility tests have been conducted in which this system has been used to impact aluminum spheres of size 5-20 microns on glass slides. Scanning Electron Micrographs show that at a charging field of approximately 1.3 MV/m and an acceleration voltage of roughly 10kV, the glass slides are uniformly coated with individually isolated Al particles. The

particle isolation and deposition control implies the potential for very high vertical and horizontal resolution in target applications. Now that the proof of concept has been established, we are scaling down the technology so that submicron particles may be deposited, with the long-term goal to deposit individual particles on the order of tens of nanometers.

10:40am **NM+EM+PS+NS+NC-ThM9 Plasma-Lithography Interactions for Advanced CMOS Manufacturing (45nm and Beyond)**, ***K. Kumar***, International Business Machines **INVITED**

The advent of 45nm saw the introduction of immersion lithography with up to 1.20 NA exposure conditions. The need for higher fidelity lithography printing gave rise to new resist, which in turn necessitated closer interactions with the plasma etch conditions. An overall synergistic model between litho and plasma etch was crucial for overall pattern fidelity. With the near horizons of the lithographic tooling window being limited to 1.35NA, and with EUV looking distant for prime time use, more emphasis is being placed on plasma etch pattern transfer for overall patterning fidelity. Added to scenario, is increased complexity in the form of "Double Expose Double Etch" which has helped increase the overall fidelity and density in the printing of the final structures in 32nm. In order to accomplish these tasks, engineering tools were developed or modified, that methodically studied the interactions between lithography and plasma etch. Strategy and results from Lithography – Plasma Etch interaction will be presented.

11:20am **NM+EM+PS+NS+NC-ThM11 Etching Development and Characterization for a Novel Nano-Imprint Lithography Technology**, ***J. Chiaroni***, *Y. Le Cunff, C. Charpin,* Minatec/Cea-Leti, France*, M.P. Clement,* St Microelect., France*, H. Denis,* Minatec/Cea-Leti, France*, G. Medico, M.L. Villani,* St Microelect., France*, N. Rochat, A. Fanton, L. Lachal, P. Brianceau, S. Barnola, F. Perrin, E. Vermande, P. Lavios,* Minatec/Cea-Leti, France*, N. Khusnatdinov, D. Labrake,* Molecular Imprint Inc.*, J.P. Gouy,* Minatec/Cea-Leti, France*, P. Gubbini*, Molecular Imprint Inc.

Nano-Imprint Lithography (NIL) is one of the most promising candidates (ITRS road map 2007) to address the 32 nm node and below thanks to a high resolution capability (templates are manufactured with E-Beam Lithography), a compatibility with CMOS technology and a lower COO as a simpler technology. The method is based on stamping out patterns on a specific polymer and then transferring into the underneath materials. SFIL/R® is an innovative NIL technology proposed by Molecular Imprint Inc, which uses a stack of three materials: 1. TranSpinTM for initial planarization; 2. MonoMatTM in which pattern is printed; 3. SilSpinTM which planarizes MonoMatTM material. Then, two specific dry etching processes are required to generate the polymer mask: 1. Imprint features opening (SilSpinTM dry etch back with stop on MonoMatTM); 2. Polymers mask opening (TranSpinTM and MonoMatTM dry etching with high selectivity on SilSpinTM Hard Mask and CD control). One of the main challenges is to obtain a good etching selectivity between these three materials which are polymer based and very similar one to the other. SilSpinTM characterization has been performed with XPS and SIMS analysis in order to determine etching orientation. According to these results, imprint features opening was achieved with fluorinated chemistry (CHF3/O2/Ar) and Polymer mask opening with HBr/O2 or Cl2/O2 based chemistry. Study of plasma impact on SilSpinTM with XPS and FTIR analysis has shown a clear impact of chlorine due to its higher efficiency to break SilSpinTM characteristic bonding. So, HBr/O2 plasma has been preferred to perform the polymer mask opening. A Design Of Experiments was achieved with HBr/O2 based chemistry in order to determine the most effective input parameters and get the optimized selectivities. By adjusting HBr/O2 ratio and bias power, a selectivity of seven was obtained between SilSpinTM and pure organic materials, which is consider as high enough. Then, Vias and Lines applications were studied with cross section SEM and CD bias measurement. This work has been carried out within the frame of European program MEDEA+ 2T305 "«Fantastic».

11:40am **NM+EM+PS+NS+NC-ThM12 Influence of Polymer Structure on Dry Etch Behavior of Resists in Soft Lithography**, ***R.L. Bruce***, *F. Weilnboeck, S. Engelmann, T.C. Lin, R. Phaneuf, G.S. Oehrlein,* University of Maryland, College Park*, B. Long, G. Willson,* University of Texas, Austin*, D.G. Nest, J.J. Vegh, D.B. Graves,* University of California, Berkeley*, A. Alizadeh*, GE Global Research Center

For the realization of sub-10 nm resolution, soft lithography alternatives to conventional photolithography are being considered. In soft lithography, the imprint material is used for pattern definition and also as a mask for pattern transfer into underlying layers. For successful nanoscale pattern transfer, a rational design of polymer resists and an atomistic understanding of plasma-polymer interactions are required. In this study, the effect of different species of the plasma (ions, UV, neutrals) on model polymers with distinct chemical structure (styrene-, acrylate-, methacrylate-, and vinylpyridine-based) was investigated. Model polymers were exposed to Ar and C_4F_8/Ar plasmas. Modification of the polymer surface was characterized using in situ ellipsometry, X-ray photoelectron spectroscopy, and atomic force microscopy (AFM). The effect of crosslinking and chain scission reactions, as well as oxygen containing functional groups, is considered. Mechanisms of plasma-polymer interactions for the different polymer structures are proposed. Finally, select polymers (poly(styrene), poly(α-methylstyrene), and poly(4-vinylpyridine)) were used as imprint materials, patterned, and plasma processed. The top and sidewall profiles and morphologies were examined by AFM and secondary electron microscopy before and after exposure. The importance of polymer structure and plasma species on pattern transfer in soft lithography is discussed.

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

Organic Electronics
Moderator: R.L. Opila, University of Delaware

2:00pm **EM-ThA1 Dependence of Contact Resistance and Field-Effect Mobility on Morphology in Poly(3-hexylthiophene based Field-Effect Transistors**, ***K.A. Singh***, *G. Sauvé, R. Zhang, T. Kowalewski, R.D. McCullough, L.M. Porter*, Carnegie Mellon University

The field-effect mobility and the contact resistance (Rc) of field effect transistors (FETs) based on regioregular poly(3-hexylthiophene) (P3HT) were investigated as a function of the molecular weight (Mw). Bottom-contact FETs were fabricated having Pt or Au contacts with the channel lengths varying from 3 to 40 µm. Our electrical measurements show an initial increase (decrease) of the mobility (contact resistance) with Mw followed by a saturation of the values. For example, at a gate voltage of -80V and for Mw between 5.5 and 11 kDa in FETs with Pt contacts, the mobility increased from 0.05 to 0.16 $cm^2V^{-1}s^{-1}$, whereas the contact resistance decreased from 1.7 to 0.5 MΩ. However, above 11 kDa, the values remained relatively constant. Devices with Au contacts displayed a similar trend, although the mobilities were lower and the contact resistances were higher, as expected due to the lower work function of Au. The inverse relationship between mobility and Rc is attributed to the dependence of Rc on bulk transport through a depletion region associated with defects near the contacts.[1] Atomic force microscopy (AFM) images indicate that P3HT self assembles in a nanofibrilar morphology.[2] It is also evident that an increase in Mw leads to an increase in the width of the self-assembled nanofibrils and, at the highest molecular weights, to a simultaneous disruption arising from folding of the polymer chains. An associated loss in conjugation within the polymer chains, along with a possible disruption in the π-π stacking that occurs concurrently with the increase in nanofibril size, would account for the saturation of the mobility and the contact resistance at higher molecular weights. In summary, our results show that mobility and contact resistance in P3HT-based FETs depend strongly on the polymer nanomorphology and display an inverse relationship with each other, supporting the theory that the contact resistance is affected by the bulk transport properties of P3HT. Future experiments including X-ray scattering studies are planned to further quantify the structure within the P3HT films.

[1] L. Bürgi, T. J. Richards, R. H. Friend, and H. Sirringhaus, J. Appl. Phys. 94[9], 6129(2003).

[2] R. Zhang, B. Li, M.C. Iovu, M. Jeffries-EL, G. Sauvé, J. Cooper, S. Jia, S. Tristram-Nagle, D.M. Smilgies, D.N. Lambeth, R.D. McCullough, and T. Kowalewski, J. Am. Chem. Soc. 128[11], 3480(2006).

2:20pm **EM-ThA2 In-Situ Characterization of the Thermal Transformations of High Performance Polymer Semiconductors**, ***L.J. Richter***, *A.J. Moad, D.M. DeLongchamp, R.J. Kline, D.A. Fischer, D.J. Gundlach, B.H. Hamadani,* National Institute of Science and Technology, *M. Heeney, I. McCulloch*, Imperial College London, UK

Polymer semiconductors are inexpensive solution processable alternatives to amorphous silicon for applications in flexible large area electronics. Recently, thin films of spun-cast poly(2,5-bis(3-alkylthiophen-2yl)thieno[3,2-b]thiophene) (pBTTT) have been demonstrated to exhibit exceptional hole mobilities in thin film transistors (TFTs) after heating into a low temperature (~ 150 °C) mesophase. This mild thermal cycle results in high level of crystalline order in the annealed film with a morphology exhibiting single molecular layer terraces. Recently we have discovered that heating into a second, higher temperature (~240°C) phase results in a distinct ribbon morphology. The ribbon phase can be oriented over large (cm^2) areas by a simple flow coating process. We have applied polarized optical spectroscopies: spectroscopic ellipsometry and FTIR, along with x-ray diffraction and NEXAFS to the in-situ study of the structural evolution in the two high temperature phases. The first mesophase is a well ordered liquid crystal characterized by melted side chains, but excellent vertical lamella order. The second, high temperature phase appears to be an isotropic melt. The behavior of pBTTT is contrasted with that of poly(dialkylthieno[3,2-b]thiophene-2,5-bithiophene) (pTTBT), a newly synthesized isomer of pBTTT with side chains attached to the thienothiophene rather than the bithiophene unit. This subtle structural change results in distinct thermal behavior. The structural transitions of the isomers are generally similar; however, the side chain melting transition Tm occurs about 50°C lower in pTTBT than in pBTTT. The significant drop in Tm appears to correlate with a subtle decrease in main chain packing interactions. Both materials exhibit high hole mobility, even in their respective liquid crystal mesophases. The slight overall higher order in pBTTT is reflected in the annealed device performance.

2:40pm **EM-ThA3 Advances in Plexcore™ Active Layer Technology Systems for Organic Solar Cells**, ***S.P. Williams***, *D.W. Laird, S. Li, J. Bernkopf, S. Jia*, Plextronics, Inc.

Abstract: Plextronics designs and develops active layer technology for printed electronics devices - OLED displays and lighting, polymer solar cells and plastic circuitry. Active layer technology is the printed semiconductors and conductors that drive device performance. Plextronics has robust control of polymer design and ink formulation, as well as an intimate understanding of device physics and its impact on device performance. This knowledge is applied to the creation of Plexcore™ technology. Plexcore technology is designed to maximize the efficiency, lifetime and stability of printed electronic devices. This talk will emphasize advances to our Plexcore™ PV technology system for Organic Solar Cells. This active layer system includes the hole-transport layer (HTL), and the p-type and n-type semiconductors. To date, Plexcore™ PV has achieved world-class NREL certified efficiency for an all-organic solar cell at 5.4%. In addition, we will discuss both advances in both materials and device properties/performance, OPV cell lifetime measurement and performance, and our trajectory toward commercialization.

3:00pm **EM-ThA4 Isolation of Aging Components in Organic Transistors**, ***J.E. Royer***, *J. Park, C.N. Colesniuc, F. Bohrer, A. Sharoni, I.K. Schuller, W.C. Trogler, A.C. Kummel*, University of California, San Diego

A systematic approach to isolating the cause of device degradation ("aging") in copper phthalocyanine (CuPc) organic thin film transistors (OTFTs) is presented. Aging is one of the primary impediments to the widespread deployments of OTFTs in gas sensors and as drivers for OLEDs. Exposure of 1000ML thick CuPc OTFTs to a sequence of environments including ambient air, clean dry air (20% O_2/N_2), water vapor and N_2 isolated the causes of device degradation in thick CuPc OTFTs. Initial exposure to ambient air increases conductivity of the CuPc film but also causes rapid device aging characterized by increased threshold voltage and loss of saturation behavior consistent with a loss of control of the channel conductivity by the gate. Exposure of the thick CuPc OTFTs to clean dry air, H_2O/N_2 mixture, or clean air/H_2O mixture not only prevents aging but can counter the aging effect of ambient air. This suggests that O_2, H_2O and O_2/H_2O products are not responsible for the aging process in ambient air. The data is consistent with trace strong oxidants in ambient air (e.g. O_3 and NO_x) being responsible for OTFT aging via formation of fixed charge. The aging effect is only present in thick films and is attributed to strong oxidants dissociative chemisorbing in grain boundaries to form fixed charges which degrade the control of the OTFT conductivity by the gate.

3:20pm **EM-ThA5 Modification of Transport Levels of Organic Single Crystals Functionalized with Self Assembled Monolayers**, ***A.S. Wan***, *S. Rangan, D.D.T. Mastrogiovanni, E. Bersch, B. Lee, S. Katalinic, M. Connors, E. Garfunkel, R.A. Bartynski, V. Podzorov*, Rutgers University

We present the first detailed study of energy level modification of single crystal organic semiconductors by functionalization with self-assembled monolayers (SAMs) deposited from the vapor phase by combined photoemission and inverse photoemission spectroscopy (PES-IPES). Large changes in conductivity in organic crystal transistors are observed between pristine and functionalized surfaces. For example, in the case of rubrene functionalized with fluorinated trichlorosilane (FTS) SAMs the conductivity increases almost 6 orders of magnitude at full coverage.[1] Preliminary evidence suggests that the presence of electron-withdrawing SAM on the organic crystals acts to p-type dope the surface, which could lead to the observed energy level and conductivity changes. X-ray photoemission (XPS) results examining both the band bending in the bulk of the organic crystals as well as interface chemistry, as well as scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) will also be discussed.

[1] M. F. Calhoun, J. Sanchez, D. Olaya, M. E. Gershenson, and V. Podzorov. Nat. Materials 7, 84 (2008).

4:00pm **EM-ThA7 Ion Scattering Studies of Self-Assembled Monolayers Grown on Organic Molecular Single Crystals and Polymers**, ***L.S. Wielunski***, *S. Katalinic, B. Lee, V. Podzorov, E. Garfunkel, L.C. Feldman*, Rutgers University

It has been recently observed that electrical conductivity of small-molecule organic semiconductors (such as Rubrene) can be strongly enhanced in the presence of fluorinated silane SAM at the surface.[1] In order to understand the microscopic origin of this large electronic effect and to resolve the exact SAM composition, we have performed Rutherford Backscattering Spectrometry (RBS) of SAM-rubrene and SAM-polymer systems using 2

MeV He ions. RBS allows a determination of the fluorine and silicon concentrations in a monolayer-thick film formed at the surface of organic crystals and polymers. Preliminary results indicate a modified SAM composition upon adsorption, possibly due to new interfacial chemistry or possibly due to beam induced effects. The analytical results will be compared with electrical measurements of SAM-induced conductivity in organic semiconductors.

[1] M. F. Calhoun, J. Sanchez, D. Olaya, M. E. Gershenson and V. Podzorov, Nature Mat. 7, 84 (2008).

4:20pm **EM-ThA8 Soft X-Ray Spectroscopic Studies of the Electronic Structure of Cu(tfacac)$_2$en (TFAC)**, ***A. DeMasi***, *L.F.J. Piper, R. Allenbaugh, L. Doerrer, K.E. Smith*, Boston University

The valence and core level electronic structure of the organic molecule Cu(tfacac)$_2$en, or TFAC, has been measured using synchrotron radiation-excited resonant x-ray emission spectroscopy (RXES) and x-ray photoelectron spectroscopy (XPS). Samples were in the form of thin films, grown in-situ in an organic molecular beam deposition chamber attached to the spectrometer system. The thin films were characterized with scanning electron microscopy (SEM) after growth, and ordering is observed that is consistent with expectations for molecular beam deposition. The films were found to be sensitive to photon induced beam damage, but this problem could be alleviated by continuous translation of the films during measurement. Our measurements indicate that TFAC potentially has semiconducting properties, and may compare favorably with copper phthalocyanine as an organic semiconductor. Work supported in part by the AFOSR.

Electronic Materials and Processing
Room: Hall D - Session EM-ThP

Electronic Materials and Processing Poster Session

EM-ThP1 Effect of Water Immersion and Surface Compositional Profile of Photoacid Generator Molecules in Photoresist Materials, ***S. Sambasivan***, Suffolk Community College, *V.M. Prabhu, D.A. Fischer,* National Institute of Standards and Technology, *L.K. Sundberg, R.D. Allen*, IBM Almaden Research Center

Near-edge x-ray absorption fine structure (NEXAFS) spectroscopy was used to quantify the surface composition and depth profiling in the top 2 to 6 nm range of photoacid generators (PAG) in thin film photoresist materials. By considering model compositional profiles, NEXAFS distinguishes the surface molar excess within the top 6 nm from the bulk. A surface enriched system, triphenylsulfonium perfluorooctanesulfonate (TPS-PFOS), is contrasted with a perfluorobutanesulfonate (TPS-PFBS) photoacid generator, which displays an appreciable surface profile within a 6 nm segregation length scale. A comparative study of the surface composition of PAG (TPS-PFOS, TPS-PFBS and TPS-Triflate) in photoresist system before and water immersion was monitored via NEXAFS. Results reveal that the loss of PAG occurs after the water immersion in all the three different PAG system examined. Detailed quantification of the PAG loss due to water immersion was seen to critically depend on the size of the PAG and its solubility in water. TPS-PFOS photoacid generator largest in size despite its least solubility in water showed the maximum loss after water immersion followed by TPS-PFBS and TPS-Triflate. These results, while applied to 193-nm photoresist materials, highlight a general approach to quantifying NEXAFS partial electron yield data and find application to immersion lithography fundamentals.

EM-ThP2 Direct Evidence for Post-Crystallization Germanium Precipitation in Thin Films of Phase-Change Material $Ge_{15}Sb_{85}$, ***C. Cabral, Jr.***, *L. Krusin-Elbaum,* IBM T.J. Watson Research Center, *S. Raoux, V.R. Deline,* IBM Almaden Research Center, *J. Bruley, A Madan, T.L. Pinto*, IBM Hudson Valley Research Park

We present evidence for the instability in the crystalline metallic phase of eutectic phase-change $Ge_{15}Sb_{85}$ thin films considered for integration into nonvolatile embedded memory cells. Te-free phase-change materials, owing to a combination of higher crystallization temperatures and the absence of easily diffusing chalcogen atoms, offer an advantage over the ternary chalcogenides, provided that the material is stable throughout the switching process. We find that while the amorphous (semiconducting) phase is robust until $Ge_{15}Sb_{85}$ film's crystallization into a rhombohedral structure at 240°C, at 350°C, Ge rapidly precipitates out, aggregating at the film's grain boundaries and interfaces. Ge precipitation, visualized directly with transmission electron microscopy and in-situ x-ray diffraction, is found to be exothermic by differential scanning calorimetry, and is found to affect films' reflectivity, resistance, and stress. Such changes could impact switching reliability, with additional doping required to minimize the precipitation process.

EM-ThP3 Development of a Polycrystalline Zinc Oxide Scintillator for Radiation Detection, ***D.M. DeVito***, *J.S. Neal, B.L. Armstrong,* Oak Ridge National Laboratory, *M. Hong,* University of California - Davis, *B. Kesanli, J.O. Ramey, J.Y. Howe,* Oak Ridge National Laboratory, *X. Yang, N.C. Giles,* West Virginia University, *Z.A. Munir,* University of California - Davis, *L.A. Boatner*, Oak Ridge National Laboratory

N-type doped ZnO is an ideal scintillator for use as an alpha particle detector due to its high light output, chemical stability, and sub-nanosecond decay times. ZnO, being a non-cubic material, has seen little success in producing the highly transparent polycrystalline bodies needed for scintillator applications. In this work, ZnO:Ga and ZnO powders were pressed into high density (>98%) polycrystalline bodies by hot uniaxial pressing and spark plasma sintering. These samples showed both photoluminescence and emission under alpha particle exposure. Investigation of the sample microstructure showed substantial grain growth. Samples also showed a high degree of translucency after post-sintering heat treatments. Additional processing results will also be included.

EM-ThP4 Structure and Optical Behavior of Sputter Deposited Hafnia-Alumina Nanolaminate Films, ***E.E. Hoppe***, *M. AlMomani, C.R. Aita*, University of Wisconsin-Milwaukee

Nanolaminate films of polycrystalline HfO_2 and amorphous Al_2O_3 were grown by reactive sputter deposition on unheated fused SiO_2 and the nascent oxide of <111> Si. Many different bilayer architectures were examined. The films were air annealed at 573 K to 1273 K, and analyzed by double angle x-ray diffraction and ultraviolet-visible spectrophometry. X-ray diffraction showed the amount of monoclinic HfO_2 (the bulk equilibrium phase) decreased with decreasing HfO_2 layer thickness. Previous high resolution transmission electron microscopy results[1] showed that the initial HfO_2 phases present in ultrathin layers were tetragonal and orthorhombic, consistent with a finite crystal size effect. Annealing of the as-grown nonmonoclinic structure at temperature up to 973 K produced no gross structural change. Annealing at 1173 K produced a metastable mixed cation tetragonal phase, $Hf_{1-x}Al_xO_{2-z}$, that is isomorphous with tetragonal HfO_2. This mixed cation phase became unstable at 1273 K and phase-separated into monoclinic HfO_2 and amorphous Al_2O_3. In all cases, the fundamental optical absorption edge was found to consist of two distinct regions with respect to incident photon energy. Significant O 2p -> Hf 5d interband absorption occurred at energy $E \geq 6.2$ eV. For $E < 6.2$ eV, films with nonmonoclinc structure retained a (desirable) featureless optical absorption edge despite further (nano)crystallization, including the formation of $Hf_{1-x}Al_xO_{2-z}$. Films with a monoclinic structure developed a pre-gap absorption band found to be characteristic of the seven-fold Hf-O coordination in the single layer monoclinic HfO_2.[2] We relate this undesirable pre-gap absorption band to self-trapped excitons that can form in the monoclinic structure.[3]

[1] E.E. Hoppe, M. Gajdardziska-Josifovska, and C.R. Aita, Appl. Phys. Lett. 91, 203105 (2007).
[2] E.E. Hoppe, R.S. Sorbello, C.R. Aita, J. Appl. Phys. 101, 123534 (2007).
[3] D. Muñoz Ramo et al. PRL 99, 155504 (2007).

EM-ThP5 Properties of Mn Doped ZnO Hollow Nanosphere Structures, ***D.-R. Liu***, *C.-C. Kei, C.-Y. Su, W.-C. Chen*, National Applied Research Laboratories, Taiwan

Diluted magnetic semiconductors (DMS) have recently attracted considerable attention due to their potential applications for spintronic devices, such as spin-valve transistors, nonvolatile memory, and magneto-optical switches. ZnMnO is one of the most promising DMS materials due to its predicted above room temperature ferromagnetism. In this study, Al2O3 layer was conformally deposited on the surface of polystyrene (PS) nanoshpere by atomic layer deposition (ALD). After removal of PS nanosphere by heating, alumina hollow nanospheres were formed. Then the (1-x)Zn(x)MnO hollow nanosphere were grown by Nd:YAG pulsed laser deposition(PLD). Atomic force microscopy (AFM) and magnetic force microscopy (MFM) were employed to characterize the surface properties of these samples. The high-resolution x-ray diffraction was used to evaluate the crystal quality. The magnetic properties of the (1-x)Zn(x)MnO hollow nanosphere were measured by a superconducting quantum interference device (SQUID) magnetometer. Photoluminescence (PL) spectroscopy and spectrometer were used to characterize the optical properties. The results show that the properties of Mn doped ZnO hollow nanosphere strongly depend on the size of nanosphere.

EM-ThP6 Electrical Properties of Atomic Layer Deposited ZnO Thin Film Transistor with Various Channel Layer Thickness, ***W. Jeong***, *S. Bang, S. Lee, S. Jeon, S. Kwon, H.T. Jeon*, Hanyang University, Korea

Wide band gap II-VI compound semiconductors have attracted much attention because of many potential applications for optoelectronic devices. Among these, ZnO thin films have been particularly interesting due to their potential applications in optoelectric devices, such as light-emitting diodes, laser diodes, and transparent thin film transistor. Especially, ZnO-based thin film transistors (TFTs) have been intensively studied for flexible electronics, replacing conventional amorphous-Si TFT. Recently, there have been several reports on the fabrication of ZnO TFTs by means of rf magnetron sputtering, pulsed laser deposition, and chemical solution process. These methods need high process temperature or additional annealing process to obtain good transistor properties such as high mobility, low operation voltage. However, high temperature process is not suitable to apply for flexible substrates or organic dielectrics. Hence, we choose atomic layer deposition (ALD) method because ALD offers several advantages over the other techniques such as large area capability and good growth control in terms of homogeneity, composition, and thickness. Moreover, ALD process can be performed at low temperature. These merits are fundamental for a wide variety of applications requiring low thermal budgets. However, atomic layer deposited ZnO films exhibit high carrier

concentration (n ~ 10^{18} cm^{-3}). The high channel carrier concentration in the oxide semiconductors is not suitable for TFT applications. Therefore, it is necessary to control the carrier concentration in order to build good quality ZnO-TFT. In this study, we varied thickness of ZnO in order to find optimal condition for thin film transistor. ZnO film on SiO_2/p-type Si substrate was deposited by ALD method using diethylzinc (DEZn) and H2O at 110 °C and the thickness of ZnO film were varied from 40 nm to 70 nm as a function of ALD cycles. The crystallographic orientation of the ZnO films was determined by an X-ray diffractometer (XRD) with Cu Ka radiation and the film morphology was analyzed by Atomic force microscopy (AFM) measurements. Device characterization was carried out at room temperature in the dark using an Agilent B1500A Semiconductor Analyzer. As a result, Ion/Ioff ratio was observed in 10^2~10^6, saturation mobility was observed in 0.02 ~ 1.4cm^2/Vsec.

EM-ThP7 Characterization of P-Si/SiO$_2$/N+Si Devices with Various Thickness of SiO$_2$, ***S.M. Lee***, *B.I. Son, K.H. Eum, I.S. Chung*, Sungkyunkwan University, Korea

We attempted to evaluate n+Si/SiO2/p-Si devices as a function of the thickness of SiO2. The thickness of SiO2 were varied from 2 nm to 5 nm. The breakdown of SiO2 layer in n+Si/SiO2/p-Si structure cause the device appears as pn+ junction diode. The simulated results using Silvaco TCAD also indicate that the currents of n+Si/SiO2/p-Si structures increase exponentially with respect to the applied voltage in the forward bias region. In addition, as the SiO2 breakdown is getting serious, the current-voltage curve moves toward the that obtained from ideal pn+ junction diode. The ratio in the current at 1.5 V between the breakdown device and the non-breakdown device reveals higher than 10000. The off state current in n+Si/SiO2/p-Si structure was simulated based on the direct tunneling model. The fabricated devices reveals similar characteristics. However, as the thickness of SiO2 layer decreases, the breakdown distribution and reliability tends to show worse results.

EM-ThP8 Role of Adsorbates in Surface Electron Accumulation on InN Films, *R.P. Bhatta, A.R. Acharya,* ***B.D. Thoms****, M. Alevli, N. Dietz*, Georgia State University

The presence of surface electron accumulation on a semiconductor has been shown to affect the properties of metallic contacts and may be important in determining other properties of devices. Adsorbates have been shown to affect the electron density on InAs surfaces, however, the effects on the surface electron concentration for InN have not been established. In this work, the effects of adsorbates on surface electron accumulation for N-polar InN have been studied by high resolution electron energy loss spectroscopy (HREELS). By varying the energy of the incident electrons the probing depth can be varied. Shifts in the energy of the conduction band plasmon indicate differences in plasma frequency and therefore differences in free carrier concentration as a function of depth from the surface. By this method it is shown that hydrogen-terminated N-polar InN exhibits surface electron accumulation. Heating InN for 15 minutes at 425°C desorbs the surface hydrogen without surface damage or film decomposition. HREELS of bare N-polar InN indicates the presence of surface electron accumulation and confirms that no surface indium is present. These results indicate that surface electron accumulation is not due to indium-indium bonding and is not affected by the presence or absence of surface hydrogen, but may instead be intrinsic to the N-polar InN surface. The effects of other adsorbates, such as oxygen, will also be discussed.

EM-ThP9 Effect of TCO Buffer Layer on the Growth of InN Film by MOMBE, ***W.-C. Chen***, National Applied Research Laboratories, Taiwan, *S.-Y. Kuo,* Chang Gung University, Taiwan, *H.-C. Pan,* Gintech Energy Corporation, Taiwan, *F.-I. Lai,* Yuan Ze University, Taiwan, *C.-N. Hsiao*, National Applied Research Laboratories, Taiwan

In this paper, wurtzite structure Indium nitride films on TCO layer was examined. InN films were grown on highly-quality of TCO buffer layer by UHV-plasma assisted metal-organic molecule beam epitaxy system. We have studied influence of to growth temperature by their structure, surface morphology and optical properties. The InN films has been characterized in detail using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), Transmittance electron microscopy(TEM),Hall effect. The surface roughness was obtained from SEM measurements with increased growth temperature. Furthermore, a pronounced two-dimensional growth mode was observed at the growth temperature of 500 ℃, and InN films highly oriented to the c-axis were obtained by optimizing growth conditions in the direct growth on TCO buffer layer. TEM images show these InN films are single phase wurtzite crystals with preferred orientation along the c axis. Our results indicated that the growth temperatures of 500-550 ℃ were beat to achieve high quality InN films.

EM-ThP10 Synthesis of Ordered Arrays of (Ba$_{0.6}$,Sr$_{0.4}$)TiO$_3$ Nanotubes, ***G.H. Kim****, K.T. Kim, C.I. Kim,* Chungang University, Korea*, Y.K. Yoon*, University at Buffalo, the State University of New York

(Ba_x,Sr_{1-x})TiO_3 (BST) ferroelectrics exhibit high dielectric permittivity and have been widely investigated both in films and ceramics. Using BST ferroelectric structures, manufacturing highly integrated memory device is possible. Recently, one dimensional nanostructures, such as nanotube and nanofiber, have been intensively studied because of their unique structure and properties. However, the BST nanotube arrays have not been widely studied yet because of fabrication difficulty and its properties are not reported. The main aim of this work includes the fabrication and investigation of structural BST nanotube arrays prepared using the sol-gel method in an anodized nanoporous aluminum oxide template. The perovskite phase has been obtained as a function of the annealing temperature from 450 to 700 ºC for 1h. The crystalline structures of the BST nanotubes arrays have been analyzed by X-ray diffraction. The surface and cross-sectional microstructures of BST nanotubes arrays are examined using scanning electron microscopy and transmission electron microscopy. The electrical P-E curve (hysteresis loop) of the BST nanotube array are illustrated.

EM-ThP11 Fabrication of Cerium Oxide Nanopillars for Oxygen Gas Sensor by Nanosphere Lithography, ***P.-J. Ko****, J.-S. Park, H.-Y. Na,* Chosun University, Korea*, N.-H. Kim,* Chonnam National University, Korea*, W.-S. Lee*, Chosun University, Korea

Cerium oxide (CeO_2) is one of the most widely used materials for the oxygen gas sensors. Sensing properties of CeO_2 is required to be improved by the fabrication to nanometer-scaled structure. The well-arrayed nanopillars of CeO_2 in a large area were fabricated by nanosphere lithography and oxygen plasma etching process. The spin coated CeO_2 thin films on silicon substrates by Sol-Gel method were prepared. Polystyrene beads of 100 nm were arrayed orderly on CeO_2 thin films and they were ashed by oxygen plasma for decreasing the size of well-arrayed polystyrene beads. Plasma etching of CeO_2 thin films was performed by inductively coupled plasmas (ICP) with the ashed polystyrene beads as a mask. The high-density nanometer-scaled pillars of CeO_2 were successfully fabricated with a diameter of 50 nm and the distance of 50 nm between the neighboring beads. The effects of the fabrication of CeO_2 nanopillar on the sensing properties were also investigated. The improved sensing properties of CeO_2 for oxygen sensors were obtained after fabrication of nanopillar of CeO_2 by the nanosphere lithography of polystyrene beads. Acknowledgement: This work was supported by Korea Research Foundation Grant (KRF-2007-412-J02003).

EM-ThP12 Influence of Acid Etching of MgAl$_2$O$_4$ (111) Substrate on the Deposition of ZnO Thin Film by MOCVD, ***G.Y. Jhan****, Y.J. Chen, H.Y. Lai, J.H. Du, J.H. Liang*, National Dong Hwa University, Taiwan

$MgAl_2O_4$ (111) has lower lattice mismatch than c-plane sapphire with ZnO epilayer, so it is possible for ZnO film deposited on $MgAl_2O_4$ to obtain better quality than on c-plane sapphire. However, $MgAl_2O_4$ (111) has two kinds of sublattice of oxygen layer. Although surface energies of two kinds of sublattice of oxygen layer are similar, the sublattice constants of oxygen layers are different. Since the difference of oxygen sublattice constant could affect ZnO film epitaxy quality on $MgAl_2O_4$ (111), we should control surface of $MgAl_2O_4$ (111) to expose the proper oxygen sublattices for ZnO film growth. In this research, we studied influence of H_2SO_4 and H_3PO_4 etching of $MgAl_2O_4$ (111) substrate on the deposition of ZnO thin film by MOCVD. The chemical etching of $MgAl_2O_4$ was performed with H_2SO_4 and H_3PO_4 respectively to obtain different surfaces of $MgAl_2O_4$ (111). The ZnO film was deposited on pretreated $MgAl_2O_4$ (111) at the growth temperature of 350°C. By SEM、XRD and PL analysis, the specimen of H_3PO_4 etching has better quality than specimen of H_2SO_4 etching at the growth temperature of about 350°C. These results imply that different surfaces were created by using H_3PO_4 and H_2SO_4. We proved that ZnO film has good quality on H_3PO_4 etched $MgAl_2O_4$ (111) substrate.

EM-ThP13 Self-Limiting Growth of Semiconductor Grade Zinc Oxide at Low Temperature by Pulsed Pecvd and Plasma-Enhanced Atomic Layer Deposition, ***P. Rowlette****, C.G. Allen, O. Bromley, D.N. Richards, A. Dubetz, C.A. Wolden*, Colorado School of Mines

Self-limiting growth of ZnO was accomplished using both pulsed plasma-enhanced chemical vapor deposition (PECVD) and plasma-enhanced atomic layer deposition (PE-ALD) at temperatures ranging from 25–155 ºC. This work explored the suitability of dimethyl zinc (DMZ, Zn(CH3)2) as an alternative to the commonly used diethyl zinc (DEZ, Zn(C2H5)2) precursor. Mass spectrometry shows that DMZ is less reactive than DEZ, which may be advantageous for self-limiting growth of semiconductor grade ZnO. In pulsed PECVD DMZ and O2 were both supplied continuously, while in PE-ALD the DMZ was delivered in pulses separated by purge steps. Films were characterized using spectroscopic ellipsometry, Fourier transform infrared

(FTIR) spectroscopy, photoluminescence (PL), Hall measurements, energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD), atomic force microscopy (AFM), and field emission scanning electron microcopy (FE-SEM). Deposition rates scaled with DMZ exposure during pulsed PECVD films, and could be tuned over a large range (1.5 – 6.0 Å/pulse). The PE-ALD growth rate saturated at 2.9 Å/cycle for DMZ exposures >50 mTorr*s. Deposition rates increased exponentially for pulsed PECVD films as a function of substrate temperature, while PE-ALD displayed a constant rate within a temperature window of 85 to 120 ºC. With the substrate temperatures elevated above 70 ºC, impurities related to carbon and hydroxyl groups were attenuated below the detection limit of FTIR for both deposition modes. EDS analysis showed that all films were stoichiometric. At low temperatures pulsed PECVD films were amorphous, and became polycrystalline at higher temperatures with a preferred orientation in the (100) direction. PE-ALD produced polycrystalline films with a (100) texture at room temperature, with the preferred orientation switching to the (002) direction as the substrate temperature was increased. Changes in orientation were accompanied by alterations in surface morphology. The as-deposited films were semiconductor grade, with resistivity values ranging from of 1 – 20 W-cm. The high quality of the films was confirmed by strong band edge emission in room temperature PL experiments. Films deposited at room temperature also showed strong emission from oxygen vacancies, however emission from these defects was attenuated for substrate temperatures ? 120 ºC.

Surface Science
Room: 208 - Session SS+EM+NC-FrM

Semiconductor Surfaces
Moderator: V.M. Bermudez, Naval Research Laboratory

8:20am **SS+EM+NC-FrM1 From Nanochemistry to Active Nano-Objects at Semiconductor Surfaces**, ***P.G. Soukiassian***, Commissariat à l'Energie Atomique and Université de Paris-Sud/Orsay, France **INVITED**

Silicon carbide (SiC) surfaces/interfaces are studied by atom-resolved scanning tunneling microscopy and spectroscopy (STM/STS) using electrons and/or photons, synchrotron radiation-based photoelectron spectroscopies (XPS, UPS, µ-spot XPS) and/or diffraction, low energy electron microscopy (LEEM) experimental techniques and density functional theory. Such important issues as self-organized active metal nano-objects, defects and an amazing nanochemistry will be presented and discussed. It includes: The 1st example of H/D-induced clean/pre-oxidized semiconductor surface metallization, with an isotopic effect occurring using D; Selective formation of ultra-thin nitride layer at Si-SiC interface; Atomic crack defects developing at SiC surfaces; Anisotropic metal diffusion, metal atom pairs, chains and wires formation; Massively parallel active architecture based on metal/Si nanowires exhibiting a negative differential resistance behavior. These findings impact some important issues such as i) metallization of wide band-gap chemically passive semiconductor surfaces which is of particular interest in interfacing with biology, ii) selective SiC interface passivation especially useful in limiting dopant diffusion, iii) identifying and understanding some unusual defects most likely involved in the high density of interface states recurrent at SiC interfaces, and iv) achieving a massively parallel active architecture in the solid state.

9:00am **SS+EM+NC-FrM3 Chemistry of the Si-rich β-SiC(100) Surface Compared to the Si(100) Surface**, ***S.M. Casey***, *L.N. Adhikari*, University of Nevada, Reno

The chemistry of the Si-rich β-SiC(100) surface has been studied using density functional theory (DFT) computational methods and small clusters to model the surface reactivity. Results for the reactions of the cluster models of the silicon carbide surface with ammonia and small alcohols and amines will be presented and the energetics compared to the corresponding pathways on the Si(100) surface. The computational results generally show that the silicon-rich silicon carbide surface exhibits stronger interactions with these types of adsorbates by 5-10 kJ/mol relative to the clean silicon surface. The major difference is that the silicon carbide surface has no closely bordering reactive silicon surface dimers, and, thus, the "intrinsic" reactivity of the silicon surface dimer can be examined without complicating multi-dimer reactions. The computational results will also be compared to experimental thermal desorption studies on these surfaces. The thermal desorption results are in general agreement with the DFT results.

9:20am **SS+EM+NC-FrM4 Surface Band Bending in GaN**, *M. Ruchala, M. Foussekis, H. Morkoc, M.A. Reshchikov,* ***A.A. Baski***, Virginia Commonwealth University

In spite of tremendous progress in the development of nitride semiconductors, the detrimental effects of surfaces and interfaces on the electrical and optical properties of devices based on these semiconductors is often underestimated. We have investigated band bending at the surface of undoped GaN and its change caused by illumination (photovoltage) with scanning Kelvin probe microscopy (SKPM) in ambient and with a Kelvin probe attached to an optical cryostat in high vacuum. In the microscopy set-up, we charged the surface and increased band bending by several eV using conductive atomic force microscopy (CAFM), and then used SKPM to observe discharge transients of the surface band bending in dark from room temperature (RT) to 35 °C, as well as under sub-bandgap illumination. In the Kelvin probe set-up, we measured the photovoltage spectrum and its transients after UV illumination at temperatures from RT to 125 °C in vacuum and air ambient. These two complementary techniques provide independent information about surface band bending and its transient behavior after charge injection or illumination. The rate of restoration of the initial band bending in dark for both experiments (after CAFM charging or after flattening of band bending due to illumination) increased at higher temperatures and typically exhibited a quasi-logarithmic time dependence. The results indicate that the restoration of band bending disturbed from equilibrium occurs primarily by means of adsorption of some species from air, and not by thermionic emission of electrons over the surface potential barrier. Indeed, transients of the photovoltage (PV) caused by UV illumination in the Kelvin probe strongly depended on the ambient. In air ambient under illumination, the PV signal increased to its maximum of 0.65 V in a few seconds and then gradually decayed by 0.3 V over 3 h, whereas in vacuum the signal quickly increased to 0.55 V and then slowly increased by 0.1 V over 3 h. This behavior indicates the photo-induced adsorption of negatively charged species in ambient or the photo-induced desorption of such species in vacuum. With regard to temperature, the initial band bending increased by 0.2 V from RT to 125 °C due to more bulk electrons overcoming the surface barrier and becoming trapped at surface states. Experiments are now in progress in the Kelvin probe to investigate the band bending behavior as a function of introduced gas species such as oxygen or water vapor.

9:40am **SS+EM+NC-FrM5 An Accelerated Molecular Dynamics Study of Diffusion on the GaAs (001) β2(2x4) Reconstruction**, ***M.H. Mignogna***, *K.A. Fichthorn*, The Pennsylvania State University

The GaAs (001) β2(2x4) reconstruction is the most commonly used substrate for growth in GaAs homoepitaxy by molecular beam epitaxy. Kinetic Monte Carlo (KMC) simulations based on first-principles calculations[1] have illuminated the mechanisms for recovering this reconstruction during growth. However, the KMC simulations are based on rates of processes that occur on perfect β2(2x4) unit cells. In experimental studies with reflection high-energy electron diffraction and scanning-tunneling microscopy, the surface is observed to exhibit domains of perfect β2(2x4) unit cells, but long-range disorder persists and a possible origin is out-of-phase β2(2x4) domains.[2] To examine the atomic-scale processes that lead to long-range disorder, as well as to characterize diffusion and the early stages of homoepitaxy on this surface, we employ accelerated molecular dynamics (MD). Our simulations are based on a semi-empirical, Tersoff-type potential that exhibits good agreement with a variety of bulk and surface properties of GaAs. Using accelerated MD we can probe long time scales, extending into the microsecond range and beyond. On the bare surface, we observe breaking, re-forming, and shifting of As row and trench dimers, that promotes the formation of out-of-phase domains of β2(2x4) unit cells and leads to long-range disorder of the surface. The kinetic processes of the As dimers affect the surface diffusion of Ga adatoms, as well as the initial morphologies that occur during growth.

[1] P. Kratzer, E. Penev, M. Scheffler, Appl. Phys. A 75, 79 (2002)
[2] D.W. Pashley, J.H. Neave, B.A. Joyce, Surf. Sci., 582, 189 (2005).

10:00am **SS+EM+NC-FrM6 First Principles Investigation of Dimer Ordering on III-V Semiconductor Surfaces**, ***J.C. Thomas***, *J.E. Bickel, J.M. Millunchick, A. Van der Ven*, University of Michigan

Surface disorder can contribute significantly to optoelectronic, thermodynamic, kinetic and interfacial properties of epitaxial thin films, especially at the nano-scale. Surface reconstructions, which decrease surface free energy relative to bulk configurations via a reduction in unfavorable bonding and increase in configurational entropy, play a vital role in the determination of these properties. In this work, the effect of finite temperature on the free energy of surface reconstructions is investigated in order to determine the role of entropy in surface dimer concentration and ordering. As a model system, we consider the α2(2x4) and β2(2x4) reconstructions on the (001) surface of homoepitaxial InAs, as these reconstructions are not only well studied, but are also stable within a continuous interval of chemical potential. A first principles model Hamiltonian is developed within the cluster expansion formalism and applied to equilibrium Monte Carlo simulations to obtain accurate thermodynamic quantities, as well as configurational trends. For example, fitting to energies for seven different dimer configurations of these 2x4 reconstructions, calculated via density functional theory show that there is an energetic preference for third nearest neighbor pairing (along the diagonal), giving rise to a "zig-zag" ordering of dimers, referred to as the z(4x4). Evidence of this structure has been previously reported. Monte Carlo simulations show the α2(2x4) to be stable within an intermediate range of chemical potentials, giving way to the β2(2x4) at higher chemical potential. The transition between configurations shows a step-like behavior at low temperatures, smoothing out at higher temperatures. The fraction of the α2(2x4) that posseses the z(4x4) ordering was determined from averaged correlations. The coverage is about 60% at room temperature, and decreases to approximately 50% at typical growth temperatures, in reasonable agreement with published results. We show that size mismatch strain in ternary III-V alloys drives In surface segregation in GaAs and locks in a zig-zag ordering of As surface dimers.

10:20am **SS+EM+NC-FrM7 Hydroxyl Termination and Passivation of the Group III-rich (4x2)/c(8x2) Surfaces of InAs(001) and InGaAs(001) Surface Studied by STM, STS, and DFT**, ***J.B. Clemens**, T. Song, A.C. Kummel*, University of California, San Diego

Atomic Layer Deposition requires the substrate to have a chemical passivation/termination layer consisting of reactive groups that initiate the ALD reaction. A suitable passivation/termination layer would have ligands that mimic the surface during growth, such as hydroxyl (OH^-).[1,2] Scanning tunneling microscopy was used to study the initial bonding configuration of hydroxyl onto the group III-rich InAs(001)-(4x2)/c(8x2) surface, which is almost identical to the InGaAs(001)-(4x2)/c(8x2) surface. These surfaces are more resistant to oxidation than group V-rich surfaces, which is true of many III-arsenide semiconductors, and therefore is a better starting template for ALD.[3] Aqueous (30%) hydrogen peroxide vapour is used as the OH source. After annealing, the surface reaction forms well-ordered interfaces that terminate at about one ML indicating that this process is self-limiting. Substrate lattice disruption is minimal following OH desorption after annealing at 350° C. If pure water vapour is used as a control dose, less surface reaction occurs and it centers at surface defect sites. Density functional theory was used to model the interaction of InGaAs(001)-(4x2) with OH, H, and H_2O. Energies and kinetics of adsorption and desorption of OH, H, and H_2O are presented, which compares the stability of the HOOH/H_2O vs the H_2O only termination/passivation methods. DFT results show that the OH passivation method using HOOH is stable at high temperatures that are typically found under ALD growth conditions, while the passivation method using only water is not. The electronic structure was probed using scanning tunneling spectroscopy. On the clean as-prepared substrates, both n- and p-type InAs(001)-(4x2)/c(8x2) show n-type behavior, consistent with literature.[4,5] Upon OH termination, both surfaces exhibit n-type behavior, with the Fermi level about 0.1 eV below the CB minimum. This shows no evidence for midgap Fermi level pinning, suggesting that this method has potential for high-κ gate oxide ALD on III-V semiconductor surfaces.

[1] K. Kukli, et.al., J. Appl. Phys., 92, 1833 (2002).

[2] J. Aarik, et.al., Appl. Surf. Sci., 161, 385 (2000).

[3] D. Winn, et.al., J. Chem. Phys., 127, 134705 (2007).

[4] L. Olsson, et.al., Phys. Rev. Lett., 76, 3626 (1996).

[5] P. De Padova, et.al., Surf. Sci., 482-485, 587 (2001).

10:40am **SS+EM+NC-FrM8 Pit Nucleation in the Presence of (nx3) and β2(2x4) Surface Reconstructions on $In_{.81}Ga_{.19}As$/InP Films**, ***L.E. Sears**, A. Riposan, J.M. Millunchick*, University of Michigan - Ann Arbor

The growth of heteroepitaxial films with high misfit strains on the crystallographic surface such as InGaAs/GaAs usually occurs in the Stranski-Krastanov mode, whereby coherent islands form on a planar wetting layer as a way to relieve strain due to a lattice mismatch. Theory has shown that both islands and pits can relieve strain on high misfit, low temperature films,[1] but experimentally only islands are typically observed as the initial mechanism of strain relief. We have discovered a growth regime in which pits relieve strain rather than islands due to a decrease in surface energy with increasing indium content. Models have predicted that altering the growth conditions, such as growth rate and temperature, or materials properties, such as surface energy or lattice mismatch, can lead to the nucleation of pits initially on the surface instead of islands,[1,2] but little experimental data exists to support those claims. We examine the growth of $In_{0.27}Ga_{0.73}As$/GaAs(001) and $In_{0.81}Ga_{0.19}As$/InP(001), which both have the same lattice mismatch strain, and show that In composition is important in determining the type of 3D features that nucleate on the surface. As the critical thickness is exceeded, low indium composition films have a tendency to form 3D islands as the primary strain relief mechanism. On the other hand, pits are the preferred strain relief mechanism in high In composition films grown with the same growth conditions and lattice mismatch. Increasing the indium content results in a more metallic surface that has a lower surface energy (γ) and models have predicted that at sufficiently low γ pit nucleation is favored over islands as the initial strain relief mechanism.[2] Models have suggested that the presence of β2(2x4) reconstructions may also act as strain relief mechanism in $In_{0.81}Ga_{0.19}As$/InP(001) films.[3] Analysis of the atomic surface structure of these films using scanning tunneling microscopy show that the reconstructions are also affected by the presence of pits, lending more evidence to surface reconstructions as a mechanism for strain relief.

[1] Lung MT, Lam CH, and Sander LM, Phys. Rev. Lett. 95 (086102) AUG 18 2005

[2] Bouville M, Millunchick JM, Falk ML, Phys. Rev. B 70 (235312) DEC 10 2004

[3] Riposan A, C. Pearson, and JM Millunchick, J. Vac. Sci. Technol. A 24 (2041) OCT 10 2006.

11:00am **SS+EM+NC-FrM9 In-situ ALD Studies of Al- and La-oxide on $In_{0.53}Ga_{0.47}As$**, ***M. Milojevic**, University of Texas at Dallas, B. Brennan,* Dublin City University, Ireland*, H.C. Kim,* University of Texas at Dallas*, F.S. Aguirre-Tostado,* The University of Texas at Dallas*, J. Kim, R.M. Wallace,* University of Texas at Dallas*, G. Hughes*, Dublin City University, Ireland

The combination of high k dielectric materials on high mobility III-V semiconductors offers the potential for MOSFETs with larger transconductance at lower operating voltages than are currently achievable with silicon based devices. Arsenic and gallium oxidation states are suspected to be the cause of Fermi level pinning, and therefore the removal or minimization of such states is required in order to develop practical devices. This study investigates the atomic layer deposition (ALD) of aluminium and lanthanum oxide based high-k dielectrics on the ammonium sulphide $(NH_4)_2S$ and ammonium hydroxide NH_4OH treated $In_{0.53}Ga_{0.47}As$ surface grown by metal organic vapour phase epitaxy (MOVPE) on lattice matched InP substrates using in-situ surface chemical analysis. Monochromatic, in-situ X-ray photoelectron spectroscopy (XPS) and ex-situ atomic force microscopy (AFM) were used to determine optimal $(NH_4)_2S$ conditions based on varying the sulphur concentration, temperature and treatment time. The ALD of the high-k films carried out at 300°C consists of a metal precursor pulse followed by a water pulse with an high purity N_2 carrier gas and was sequentially examined with in-situ XPS after every half cycle of the deposition process to determine the initial interfacial oxide and substrate reactions taking place during the growth. A 'clean up' effect, whereby the ALD process reduces native oxides at the surface during high-k deposition, is well known for thin dielectric films. In the case of TMA/water based deposition of Al_2O_3, we have found that the first TMA pulse is responsible for the removal of virtually all of the arsenic oxide left on the surface after the pre-treatments, especially with $(NH_4)_2S$, to within the detection limits of XPS. Gallium oxide bonding is reduced to approximately a monolayer consistent with a Ga-O-Al bond at the interface. Similar results for La-based precursor reactions will also be presented. Capacitance-voltage measurements were also carried out on metal oxide semiconductor MOS devices formed after the high-k dielectric growth. Supported by MARCO MSD Focus Center, Science Foundation Ireland, and FUSION.

11:20am **SS+EM+NC-FrM10 Atomic Scale Investigation of Mn Impurities on the InAs(110) Surface**, ***Y.J. Song**,* University of Maryland, College Park and NIST*, G.M. Rutter, P.N. First,* Georgia Institute of Technology*, N. Zhitenev, J.A. Stroscio*, National Institute of Standards and Technology

Increased interest in spin-based electronics as a replacement for charge-based electronics has led to significant scientific attention to dilute magnetic semiconductors (DMS). One of the main dilute magnetic semiconductors involves doping III-V semiconductors with Mn acceptors with the aim of achieving high Curie temperatures. In the present work, we studied Mn deposited on the InAs(110) surface with low temperature scanning tunneling microscopy and spectroscopy (STM/STS). Single Mn atoms were deposited onto a cleaved n-InAs(110) surface at cryogenic temperatures. The as-deposited Mn adatoms were found to be in two distinct configurations. About 10% of the Mn adatoms appear in the topographic images to be positively charged. The other 90% appear to be in a neutral configuration. Both types of adatoms can undergo an exchange process whereby the surface Mn atom substitutes for an In atom in the top surface layer. This process involves raising the sample tunneling voltage beyond a certain threshold voltage of approximately -0.6 eV for both types of Mn adatoms. This process is similar to that seen in the Mn/GaAs system.[1] And we also studied that in-situ deposition of Mn onto a cleaved n-doped InAs(110) substrate at low temperature produces an adsorbate-induced 2DEG at the InAs surface. Spatial properties of Landau level quantization[2] in high magnetic fields of both the 2D sub-bands and 3D conduction bands were studied in relation to the configuration of Mn atoms on the surface.

[1] D. Kitchen et al, Nature 442, 436 (2006)

[2] M. Morgestern et al, Phys. Rev. Lett. 90, 56804 (2003).

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Kim, H.C.: EM-WeM9, 8; SS+EM+NC-FrM9, 25
Kim, H.Y.: GR+EM+NC-TuM12, 3
Kim, J.: EM-WeM2, 7; EM-WeM9, 8; GR+EM+NC-TuM12, 3; SS+EM+NC-FrM9, 25
Kim, K.T.: EM-ThP10, 22
Kim, M.J.: EM-WeM9, 8; GR+EM+NC-TuM12, 3
Kim, N.-H.: EM-ThP11, 22
Kim, P.: GR+EM+NC-TuM5, 3
Kim, T.: EM-TuA12, 5; EN+EM+NS+PS-TuA3, 5
Kim, Y.B.: EM-TuA2, 4
Kim, Y.-H.: EN+AS+EM+TF-WeM1, 8
King, P.D.C.: EM-TuM5, 1
Kline, R.J.: EM-ThA2, 19
Knippenberg, M.T.: TR+NS+EM+NC-WeA10, **12**; TR+NS+EM+NC-WeA8, 12
Knox, K.R.: GR+EM+NC-TuM5, **3**
Ko, P.-J.: EM-ThP11, **22**
Koratkar, N.: EN+AS+EM+TF-WeM11, 9
Kowalewski, T.: EM-ThA1, 19
Kraya, L.: EM+NC-WeA9, 11
Krebs, F.: EM+NC-WeA2, 10
Krusin-Elbaum, L.: EM-ThP2, 21
Kulisch, W.: BO+EM+BI+NC-ThM6, **14**
Kumar, K.: NM+EM+PS+NS+NC-ThM9, **18**
Kummel, A.C.: EM-ThA4, 19; EM-WeM11, 8; EM-WeM4, **7**; SS+EM+NC-FrM7, 25
Kuo, S.-Y.: EM-ThP9, 22
Kwon, S.: EM-ThP6, 21; EM-TuM9, 2

— L —

Labrake, D.: NM+EM+PS+NS+NC-ThM11, 18
Lachal, L.: NM+EM+PS+NS+NC-ThM11, 18
Lai, F.-I.: EM-ThP9, 22
Lai, H.Y.: EM-ThP12, 22; EM-TuA11, 5
Laird, D.W.: EM-ThA3, 19
Lavios, P.: NM+EM+PS+NS+NC-ThM11, 18
Lazik, C.: EM-WeM3, 7
Le Cunff, Y.: NM+EM+PS+NS+NC-ThM11, 18
LeClair, P.: EM+NC-WeA11, **11**
Lee, B.: EM-ThA5, 19; EM-ThA7, 19; GR+EM+NC-TuM12, **3**
Lee, D.Y.: NM+EM+PS+NS+NC-ThM4, 17
Lee, E.: EM-TuA12, 5
Lee, H.D.: EM-WeM12, 8
Lee, H.I.: EM-TuA12, 5
Lee, J.: EM-TuA12, **5**
Lee, S.: EM-ThP6, 21
Lee, S.-H.: EN+AS+EM+TF-WeM1, 8
Lee, S.M.: EM-ThP7, **22**
Lee, W.-S.: EM-ThP11, 22
Lehn, J.S.: EM-WeM5, 7
Leifer, K.: GR+EM+NC-TuM6, 3
Lele, T.: BO+EM+BI+NC-ThM1, 14
Leonard, F.: EM+NC-ThM5, 16
Leonhardt, D.: EN+EM+NS+PS-TuA4, **6**
Li, H.: EM-WeM5, 7
Li, S.: EM-ThA3, 19
Liang, J.H.: EM-ThP12, 22; EM-TuA11, **5**
Liang, T.: TR+NS+EM+NC-WeA4, 12
Licciardello, A.: EM-WeM6, 7; EN+AS+EM+TF-WeM3, 9
Lim, S.J.: EM-TuM9, **2**
Lin, E.K.: NM+EM+PS+NS+NC-ThM4, 17
Lin, J.: BO+EM+BI+NC-ThM1, 14
Lin, T.C.: NM+EM+PS+NS+NC-ThM12, 18
Liu, D.-L.: TR+NS+EM+NC-WeA9, 12
Liu, D.-R.: EM-ThP5, **21**
Liu, J.: NM+EM+PS+NS+NC-ThM4, 17
Liu, T.: NM+EM+PS+NS+NC-ThM6, 17
Liu, Y.: EM-WeM5, 7; GR+EM+NC-TuM1, **2**
Lloyd Spetz, A.: BO+EM+BI+NC-ThM5, 14
Locatelli, A.: GR+EM+NC-TuM5, 3
Lock, E.H.: NM+EM+PS+NS+NC-ThM4, 17
Loginova, E.: GR+EM+NC-TuM11, **3**
Long, B.: NM+EM+PS+NS+NC-ThM12, 18
Long, J.P.: EM-WeM1, 7
Look, D.C.: EM-TuM4, 1
Lu, J.: EM-TuA8, 4
Lu, T.-M.: EN+AS+EM+TF-WeM11, 9
Lu, W.: BO+EM+BI+NC-ThM3, **14**
Lucovsky, G.: EM-TuA2, 4; EM-WeM1, 7
Lugli, P.: EM+NC-WeA2, 10; NM+EM+PS+NS+NC-ThM3, 17

— M —

Madan, A: EM-ThP2, 21
Mahan, A.H.: EN+AS+EM+TF-WeM1, 8
Martel, B.: EM-TuM5, 1
Martin, F.: EM+NC-WeA12, 11
Martinez, E.: NM+EM+PS+NS+NC-ThM5, 17
Martinotti, D.: GR+EM+NC-TuM2, 2
Mastro, M.A.: EM+NC-ThM11, 16
Mastrogiovanni, D.D.T.: EM-ThA5, 19; EM-WeM12, 8
Mauldin, C.: EM+NC-WeA12, 11
McCarty, K.F.: GR+EM+NC-TuM11, 3
McConville, C.F.: EM-TuM5, **1**
McCulloch, I.: EM-ThA2, 19
McCullough, R.D.: EM-ThA1, 19
Medico, G.: NM+EM+PS+NS+NC-ThM11, 18
Mentes, T.O.: GR+EM+NC-TuM5, 3
Mignogna, M.H.: SS+EM+NC-FrM5, **24**
Mikulski, P.T.: TR+NS+EM+NC-WeA8, 12
Miller, G.: BO+EM+BI+NC-ThM12, 15
Mills, C.A.: NM+EM+PS+NS+NC-ThM5, 17
Millunchick, J.M.: NM+EM+PS+NS+NC-ThM6, **17**; SS+EM+NC-FrM6, 24; SS+EM+NC-FrM8, 25
Milojevic, M.: EM-WeM9, 8; SS+EM+NC-FrM9, **25**
Ming, F.: GR+EM+NC-TuM2, 2
Moad, A.J.: EM-ThA2, 19
Morales-Acosta, M.D.: EM-WeM2, 7
Morgante, A.: GR+EM+NC-TuM5, 3
Morkoc, H.: SS+EM+NC-FrM4, 24
Morris, D.: NM+EM+PS+NS+NC-ThM6, 17
Mosbacker, H.L.: EM-TuM4, 1
Mougenot, M.: EM-TuA9, 5
Munir, Z.A.: EM-ThP3, 21
Munoz-Sanjose, V.: EM-TuM5, 1
Murcia Hernandez, R.: EM+NC-WeA2, 10
Musinski, L.: NM+EM+PS+NS+NC-ThM6, 17
Myers-Ward, R.L.: EM+NC-ThM11, 16

— N —

Na, H.-Y.: EM-ThP11, 22
Nanayakkara, S.U.: EM+NC-WeA9, **11**
Nazar, L.F.: EN+AS+EM+TF-WeM9, **9**
Neal, J.S.: EM-ThP3, 21
Nest, D.G.: NM+EM+PS+NS+NC-ThM12, 18
Neudeck, P.G.: EM+NC-ThM11, 16
Nguyen, P.-C.: BO+EM+BI+NC-ThM10, 15
Nicholas, R.J.: EN+EM+NS+PS-TuA5, 6
Nie, X.: TR+NS+EM+NC-WeA12, 13
Nikiforov, M.P.: TR+NS+EM+NC-WeA5, 12
Niño, M.A.: GR+EM+NC-TuM5, 3

— O —

Oehrlein, G.S.: NM+EM+PS+NS+NC-ThM12, 18; NM+EM+PS+NS+NC-ThM4, 17
Ogletree, D.F.: EM+NC-WeA12, 11
Osgood, R.M.: GR+EM+NC-TuM5, 3

— P —

Pan, H.-C.: EM-ThP9, 22
Pande, K.: EM-TuA5, 4
Parilla, P.A.: EN+AS+EM+TF-WeM1, 8
Park, J.: EM-ThA4, 19
Park, J.-S.: EM-ThP11, 22
Park, S.Y.: GR+EM+NC-TuM12, 3
Park, T.-H.: EM+NC-WeA9, 11
Pearton, S.J.: BO+EM+BI+NC-ThM1, 14
Penso-Blanco, G.: NM+EM+PS+NS+NC-ThM3, 17
Perrin, F.: NM+EM+PS+NS+NC-ThM11, 18
Perry, S.S.: TR+NS+EM+NC-WeA4, 12
Phaneuf, R.: NM+EM+PS+NS+NC-ThM12, 18
Phillpot, S.R.: TR+NS+EM+NC-WeA4, 12
Picard, Y.N.: EM+NC-ThM11, 16
Pinto, T.L.: EM-ThP2, 21
Piper, L.F.J.: EM-ThA8, 20; EM-TuM1, **1**
Podzorov, V.: EM-ThA5, 19; EM-ThA7, 19
Pohl, K.: BO+EM+BI+NC-ThM12, 15
Porter, L.M.: EM-ThA1, 19
Powell, J.A.: EM+NC-ThM11, 16
Prabhu, V.M.: EM-ThP1, 21
Prauzner-Bechcicki, J.: BO+EM+BI+NC-ThM11, 15
Preston, A.R.H.: EM-TuM1, 1

— Q —

Qi, Y.: EM+NC-WeA12, **11**
Quinlan, R.A.: GR+EM+NC-TuM6, 3

— R —

Ramey, J.O.: EM-ThP3, 21
Rangan, S.: EM-ThA5, 19
Raoux, S.: EM-ThP2, 21
Rauscher, H.: BO+EM+BI+NC-ThM6, 14
Reinke, P.: EM-TuA8, **4**
Ren, F.: BO+EM+BI+NC-ThM1, **14**
Reshchikov, M.A.: SS+EM+NC-FrM4, 24
Reutt-Robey, J.E.: EM+NC-WeA10, 11
Richards, D.N.: EM-ThP13, 22
Richter, L.J.: EM-ThA2, **19**
Riposan, A.: SS+EM+NC-FrM8, 25
Robey, S.W.: EM+NC-WeA10, 11
Rochat, N.: NM+EM+PS+NS+NC-ThM11, 18
Rockett, A.: EN+EM+NS+PS-TuA10, 6
Rogers, J.: NM+EM+PS+NS+NC-ThM1, 16
Rossi, F.: BO+EM+BI+NC-ThM6, 14; NM+EM+PS+NS+NC-ThM5, 17
Rowlette, P.: EM-ThP13, **22**
Royer, J.E.: EM-ThA4, **19**
Rubino, S.: GR+EM+NC-TuM6, 3
Ruchala, M.: SS+EM+NC-FrM4, 24
Ruck, B.J.: EM-TuM1, 1
Ruiz, A.: NM+EM+PS+NS+NC-ThM5, **17**
Rutter, G.M.: SS+EM+NC-FrM10, 25
Ryu, S.H.: EN+EM+NS+PS-TuA3, **5**

— S —

Salmeron, M.: EM+NC-WeA12, 11
Sambasivan, S.: EM-ThP1, **21**
Samitier, J.: NM+EM+PS+NS+NC-ThM5, 17
Sanyal, B.: GR+EM+NC-TuM6, 3
Sauvé, G.: EM-ThA1, 19
Sawyer, W.G.: TR+NS+EM+NC-WeA4, 12
Scarpa, G.: NM+EM+PS+NS+NC-ThM3, 17
Schall, J.D.: TR+NS+EM+NC-WeA8, 12
Schirmeisen, A.: TR+NS+EM+NC-WeA3, 12
Schleife, A.: EM-TuM1, 1
Schuller, I.K.: EM-ThA4, 19
Scott, A.: EM+NC-WeA1, **10**
Sears, L.E.: SS+EM+NC-FrM8, **25**
Selegard, L.: BO+EM+BI+NC-ThM5, **14**

Seo, H.: EM-TuA2, **4**; EM-WeM1, 7
Seyller, Th.: GR+EM+NC-TuM1, 2
Sharoni, A.: EM-ThA4, 19
Shen, J.: EM-WeM11, **8**
Shenai, D.V.: EM-WeM5, 7
Sheng, J.: EN+EM+NS+PS-TuA4, 6
Shir, D.: NM+EM+PS+NS+NC-ThM1, **16**
Shur, M.: EM+NC-ThM9, **16**
Siebentritt, S.: EN+EM+NS+PS-TuA8, **6**
Singh, J.: EM-TuM2, 1
Singh, K.A.: EM-ThA1, **19**
Sinnott, S.B.: TR+NS+EM+NC-WeA4, **12**
Sirghi, L.: BO+EM+BI+NC-ThM6, 14
Smith, K.E.: EM-ThA8, 20; EM-TuM1, 1
So, E.: TR+NS+EM+NC-WeA11, 12
Soares, J.W.: EM-TuM2, 1
Söderlind, F.: BO+EM+BI+NC-ThM5, 14
Soles, C.L.: NM+EM+PS+NS+NC-ThM4, 17
Son, B.I.: EM-ThP7, 22
Sondergaard, R.: EM+NC-WeA2, 10
Song, T.: SS+EM+NC-FrM7, 25
Song, Y.J.: SS+EM+NC-FrM10, **25**
Sonnet, A.: EM-WeM9, 8
Soukiassian, P.G.: GR+EM+NC-TuM2, 2; SS+EM+NC-FrM1, **24**
Sprinkle, M.: GR+EM+NC-TuM2, **2**
Stafford, C.M.: NM+EM+PS+NS+NC-ThM4, 17
Stecher, J.T.: EM+NC-WeA9, 11
Steeves, D.M.: EM-TuM2, 1
Stevens, K.: TR+NS+EM+NC-WeA9, 12
Stoilov, V.: TR+NS+EM+NC-WeA12, 13
Strobel, S.: EM+NC-WeA2, 10; NM+EM+PS+NS+NC-ThM3, **17**
Stroscio, J.A.: SS+EM+NC-FrM10, 25
Su, C.-Y.: EM-ThP5, 21
Su, J.F.: TR+NS+EM+NC-WeA12, **13**
Sun, Y.: EM-TuA8, 4
Sundberg, L.K.: EM-ThP1, 21
Swartzentruber, B.S.: EM+NC-ThM5, 16
Szulczewski, G.: EM+NC-WeA11, 11
Szymonski, M.: BO+EM+BI+NC-ThM11, **15**

— T —

Talin, A.: EM+NC-ThM5, **16**
Tang, X.: EM-WeM3, 7
Tao, N.J.: EM+NC-WeA3, **10**
Teki, R.: EN+AS+EM+TF-WeM11, 9
Tekiel, A.: BO+EM+BI+NC-ThM11, 15
Tempez, A.: EM-WeM6, 7; EN+AS+EM+TF-WeM3, 9
Temprano, I.: EM+NC-WeA8, **10**
Teplyakov, A.V.: BO+EM+BI+NC-ThM9, 15
Therien, M.J.: EM+NC-WeA9, 11
Thomas, J.C.: SS+EM+NC-FrM6, **24**
Thoms, B.D.: EM-ThP8, **22**
Thornton, K.: EN+AS+EM+TF-WeM4, **9**
Tomanek, D.: BO+EM+BI+NC-ThM12, 15
Tornow, M.: EM+NC-WeA2, **10**; NM+EM+PS+NS+NC-ThM3, 17
Trogler, W.C.: EM-ThA4, 19
Trunek, A.J.: EM+NC-ThM11, 16
Tuccitto, N.: EM-WeM6, 7; EN+AS+EM+TF-WeM3, 9
Twigg, M.E.: EM+NC-ThM11, 16

— U —

Uritsky, Y.: EM-WeM3, 7
Uvdal, K.: BO+EM+BI+NC-ThM5, 14

— V —

Vahlberg, C.: BO+EM+BI+NC-ThM5, 14
Vallee, C.: EM-TuA9, **5**
Valsesia, A.: NM+EM+PS+NS+NC-ThM5, 17
van de Sanden, M.C.M.: EN+EM+NS+PS-TuA1, **5**
Van der Ven, A.: SS+EM+NC-FrM6, 24
Vandervelde, T.E.: EN+EM+NS+PS-TuA4, 6
VanMil, B.L.: EM+NC-ThM11, 16
Veal, T.D.: EM-TuM5, 1
Vegh, J.J.: NM+EM+PS+NS+NC-ThM12, 18
Vermande, E.: NM+EM+PS+NS+NC-ThM11, 18
Vijayaraghavan, S.: EM-WeM6, 7; EN+AS+EM+TF-WeM3, **9**
Villani, M.L.: NM+EM+PS+NS+NC-ThM11, 18
Vogel, E.M.: EM-WeM9, **8**; GR+EM+NC-TuM12, 3
Voorhees, P.W.: EN+AS+EM+TF-WeM4, 9

— W —

Wahl, K.J.: TR+NS+EM+NC-WeA11, **12**
Wallace, R.M.: EM-WeM2, 7; EM-WeM9, 8; GR+EM+NC-TuM12, 3; SS+EM+NC-FrM9, 25
Walton, S.G.: NM+EM+PS+NS+NC-ThM4, 17
Wan, A.S.: EM-ThA5, **19**; EM-WeM12, 8
Wang, H.: EM-WeM5, **7**
Wang, H.T.: BO+EM+BI+NC-ThM1, 14
Wang, J.G.: EM-WeM9, 8
Wang, J.J.: EM-WeM5, 7
Wang, R.: EM-WeM3, 7
Wang, S.: GR+EM+NC-TuM5, 3
Wang, Y.L.: BO+EM+BI+NC-ThM1, 14
Wei, Y.Y: EM+NC-WeA10, **11**
Weidner, T.: BO+EM+BI+NC-ThM10, 15
Weilnboeck, F.: NM+EM+PS+NS+NC-ThM12, 18
Weinert, M.: EM-TuA5, 4
West, K.: EM-TuA8, 4
Whitney, E.: EN+AS+EM+TF-WeM1, 8
Whitten, J.E.: EM-TuM2, **1**
Widenkvist, E.: GR+EM+NC-TuM6, **3**
Wielunski, L.S.: EM-ThA7, **19**
Williams, M.D.: EM+NC-ThM12, **16**
Williams, S.P.: EM-ThA3, **19**
Willis, B.G.: EM+NC-WeA5, **10**
Willis, R.F.: EM+NC-ThM3, 15; GR+EM+NC-TuM1, 2
Willson, G.: NM+EM+PS+NS+NC-ThM12, 18
Wilson, J.R.: EN+AS+EM+TF-WeM4, 9
Wolden, C.A.: EM-ThP13, 22
Wolf, S.A.: EM-TuA8, 4
Won, H.: EM+NC-ThM3, **15**

— X —

Xu, W.: EM+NC-WeA11, 11
Xu, Y.: EM-WeM12, 8

— Y —

Yakimova, R.: BO+EM+BI+NC-ThM5, 14
Yang, C.: EN+EM+NS+PS-TuA3, 5
Yang, T.: BO+EM+BI+NC-ThM12, 15
Yang, X.: EM-ThP3, 21
Yin, W.: EM-TuA8, 4
Yoo, W.J.: EN+EM+NS+PS-TuA3, 5
Yoon, Y.K.: EM-ThP10, 22
Yoshida, N.: EM-WeM3, 7
Yu, L.: EM-WeM12, **8**

— Z —

Zhang, R.: EM-ThA1, 19
Zhang, S.B.: EN+AS+EM+TF-WeM1, 8
Zhang, X.: BO+EM+BI+NC-ThM9, **15**
Zhitenev, N.: SS+EM+NC-FrM10, 25
Zuniga-Perez, J.: EM-TuM5, 1