

AVS Prairie Chapter Regional Meeting 2005



Northwestern University
Evanston, IL
June 13 - Meeting
June 14 - Short Courses

Oral Abstracts

Northwestern Room A

9:00 am **Elastic properties and bonding of MAX Phases, Jochen M. Schneider** RWTH-Aachen, Aachen, Germany **Invited**

We have investigated the elastic properties of nanolayered M_2AC with $M=Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W,$ and $A=Al, Ga, Ge, Sn$ as well as M_2AN , with $M=Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W,$ and $A=Al, Ga, Ge, Sn$ by *ab initio* calculations. We suggest that M_2AC can be classified into two groups: One where the bulk modulus of the binary MC is conserved and another group where the bulk modulus is decreased. This classification can be understood in terms of coupling between MC and A layers which is defined by the valence electron population. The coupling in the here investigated M_2AN is in general weaker which can be understood based on the DOS. A comparison of the valence electron concentration effect on the bulk modulus and the shear properties is discussed.

9:40 am **Combined Experimental and Computational Study of SPIAD Polymerization of Polythiophene, Sanja Tepavcevic**, University of Illinois at Chicago, *Wen-Dung Hsu, Susan B. Sinnott*, University of Florida *Luke Hanley*, University of Illinois at Chicago

Surface polymerization by ion-assisted deposition (SPIAD) of conducting polymer films is achieved by simultaneous co-deposition of hyperthermal organic ions and neutral organic oligomers onto a substrate surface.¹ Our previous work on the SPIAD mechanism found that polymerization occurs in a defined region of ion/neutral ratio and ion energy space to form a distribution of species, rather than a single oligomer.^{2,3} Experiments are combined here with density functional theory-molecular dynamics simulations (DFT-MD) to further elucidate mechanistic aspects of SPIAD. 25 – 200 eV thiophene ions are co-deposited with evaporated α -terthiophene (3T) onto hydrogen terminated Si(100). Mass-selected ion deposition is used to remove fragment ions, radicals, and photons from the deposition process. X-ray photoelectron and mass spectra of the deposited films indicate polymerization at all ion energies, with the highest mass polymerization products formed at 50 eV. Varying the energy and number of deposited hyperthermal ions shows that a lower ion/neutral ratio is optimal at lower ion energies, due to reduced desorption and sputtering.² The simulations can trace the fate of every atom in the deposited films and clarify several phenomenon observed experimentally. The simulations indicate that the incident thiophene ions dissociate upon impact and react with the adsorbed 3T thin film. C atoms which come from the incident ions or broken 3T rings have energy high enough to abstract hydrogen from another 3T. This process is highly likely to initiate polymerization when it occurs on adjacent 3T species. The simulations also confirm that hyperthermal thiophene ions and their fragments incorporate in the deposited film, behaving as the reagents of surface polymerization as well as catalysts.^{2,3}

References:

1. Tepavcevic, S.; Choi, Y.; Hanley, L. *J. Amer. Chem. Soc.* **2003**, *125*, 2396.
2. Tepavcevic, S.; Choi, Y.; Hanley, L. *Lang.* **2004**, *20*, 8754.
3. Choi, Y.; Zachary, A.; Tepavcevic, S.; Wu, C.; Hanley, L. *Inter. J. Mass Spectrom. Ion Proces.* **2005**, *242*, 139.

10:00 am **Analysis of a Monolayer Model of a Dental Composite Material by Laser Desorption Photoionization Mass Spectrometry, Manshui Zhou, Chunping Wu, Praneeth D. Edirisinghe, James L Drummond, and Luke Hanley** University of Illinois at Chicago

Introduction

One popular dental composite consists of a polymerizable resin matrix bound to reinforcing glass particle fillers by a silane coupling agent. The resin typically contains one or more monomers such as ethylene glycol dimethacrylate (Bis-GMA). These resin-glass composites undergo material property changes during exposure to the oral environment due to biodegradation and erosion. However, study of this degradation in commercial dental composites is severely limited by their complex composition which often includes proprietary additives. This study develops a simplified model system that will be utilized to study degradation mechanisms in these dental composites by mass spectrometry. Laser desorption followed by

118 nm single photon ionization is demonstrated as a superior analytical tool to study this model composite system.

Methods

The model dental polymeric composite system consists of a polymerizable resin matrix compound Bis-GMA covalently bound to oxidized silicon wafers via the silane coupling agent 3-(trimethoxysilyl)propyl methacrylate (MPS). The oxidized silicon wafers are homemade versions of those employed for desorption ionization on oxidized silicon (DIOS). The DIOS substrates are first silanized with MPS resulting in a methacryloyl-terminated monolayer. Next, Bis-GMA is covalently bound to the methacryloyl monolayer by photopolymerization with eosin Y/triethanolamine co-initiator. A home built laser desorption photoionization linear time of flight mass spectrometer (LDPI MS) is used for analysis. 118 nm radiation for single photon ionization is produced by frequency-tripling the Nd:YAG 355 nm output. X-ray photoelectron spectroscopy is performed on the films using a Kratos Axis instrument.

Results

LDPI MS is used to verify the preparation steps of the model dental composite by chemical analysis of the methacryloyl and Bis-GMA monolayers as well as several control surfaces. The methacryloyl monolayer forms a Si-O-Si bond with the DIOS substrate, so LDPI MS displays no parent ion peak for MPS. Rather the highest mass peak with the methacryloyl-terminated monolayer forms by cleavage of the C-Si surface bond during the laser desorption step to form an ion at m/z 127. If MPS is simply physisorbed on the DIOS surface as a control, the parent ion peak at m/z 248 is observed along with the $[\text{Si}(\text{OCH}_3)_3]^+$ peak at m/z 121, but not the m/z 127 fragment peak typical of the chemisorbed layer. If MPS is prepared in aqueous solution as another control, no fragmentation ion peaks display due to the homocondensation of hydrolyzed MPS. The methacryloyl-Bis-GMA monolayer also fragments at the C-Si bond during laser desorption, but now this leads to the formation of a much larger ion at m/z 640, as expected due to the covalently bound Bis-GMA compound. Controls produced by physisorbing Bis-GMA either onto the methacryloyl monolayer or the DIOS substrate, without the photopolymerization required step for covalent bonding, lead only to the formation of m/z 495 during LDPI MS. This m/z 495 peak is due to a major Bis-GMA fragment, whose intact molecular weight is 512 Da. Different conditions of monolayer preparation are also evaluated by LDPI MS. Single laser desorption without separate single photon ionization by a second laser, as is commonly applied in DIOS experiments, did not provide useful spectra for these monolayers. X-ray photoelectron spectroscopy did allow confirmation of the binding process, but it does not provide the chemical specificity available from mass spectrometry.

10:40 am **Toward the Ultimate Tribological Interface: Surface Chemistry and Nanotribology of**

Nanostructured Carbon Thin Films, Anirudha V. Sumant, R. W. Carpick, D. S. Grierson, University of Wisconsin at Madison, *J. E. Gerbi, James Birrell, O. Auciello and J. A. Carlisle,* Argonne National Laboratory, *T. A. Friedmann, J. P. Sullivan,* Sandia National Laboratories

Invited

Fundamental understanding of the surface chemistry and bonding configuration of materials at the molecular level, particularly at tribological interfaces, is of prime importance for developing robust and reliable MEMS and NEMS devices involving rotating and sliding contacts. Nanostructured carbon materials such as ultrananocrystalline diamond (UNCD) and tetrahedral amorphous carbon (ta-C) thin films have demonstrated exceptional physical, chemical and tribological properties at the macro and micro-scale, and therefore are considered promising materials for MEMS and NEMS applications. However, little is known about their surface chemistry and bonding configuration at the tribological interface, and how it changes with different processing conditions. In our earlier studies on UNCD thin films, we have shown that UNCD surfaces can be engineered at the tribological interface using hydrogen termination to achieve extremely low adhesion energies (down to the van der Waals limit) along with low friction. These results will be reviewed, and new results on ta-C will be presented. It is well known that as-deposited ta-C films possess high residual stress, but full stress relief is possible by post-annealing at elevated temperatures (~650 °C). However, no detailed experimental studies have been performed to understand the surface chemistry and bonding configuration of these films after annealing, which most likely will affect the nanotribological properties as well. We present our approach using a combination of synchrotron-based near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM) techniques to understand surface chemistry, bonding configuration and nanotribological properties of these materials. We show that there are subtle and correlated changes in the surface chemistry, the ratio of sp^2 - and sp^3 -bonded carbon, and the local and long-

range order on the surface and in the sub-surface region of ta-C. We also show how it changes with different annealing methods used. We then show how nanoscale friction and adhesion depend on the surface chemistry and local bonding configuration and how it is possible to control nanotribology, to achieve the ultimate tribological interface.

Part of this work was funded by Sandia. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. Part of this work was also supported by the US Department of Energy, BES-Materials Sciences, under Contracts DE-FG02-02ER46016 and W-13-109-ENG-38.

11:20 am **Synthesis of Carbon Films with Ultralow Friction in Dry and Humid Air**, *Christina Freyman, Yanfeng Chen, Yip-Wah Chung*, Northwestern University

In this paper, we present experimental strategies of how one can synthesize smooth carbon films using sulfur doping with ultralow friction coefficients (< 0.01) in dry and humid air, with relative humidity up to 50%. Auger studies show the absence of water adsorption after room temperature water exposure of 100,000 Langmuirs. Thermal desorption studies suggest the formation of water multilayers even at very low exposures, indicating that the surface is hydrophobic, consisting with water contact angle measurements. Results from quartz crystal microbalance studies at ambient pressures will also be discussed.

11:40 am **Morphology and chemical bonding of carbon structures grown on SiC surface via the carbide-derived carbon (CDC) process**, *A.V. Zinovev, J.F. Moore, M.J. Pellin*, Argonne National Laboratory

We investigated the effect of treatment of silicon carbide (single crystals and industrial ceramic) in chlorine-containing gas mixtures at high temperatures and ambient pressure. Due to the more energetically favored reaction of Cl_2 with Si rather than C , selective etching of the SiC surface takes place, leading to the formation of a carbide-derived carbon (CDC) film. The results of X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, Auger electron spectroscopy AES and scanning electron microscopy SEM studies of the chemical conversion on silicon carbide surface, treated at different gas concentrations and different temperatures, are presented. XPS and angle-resolved XPS (ARXPS) analysis of carbon $1s$ and silicon $Si2p$ peaks and the surface conduction band shows that created CDC films cannot be attributed to one of the simple fundamental forms of carbon but correspond to a mixture of components, mainly sp^2 and sp^3 bonded carbon and also small amount of oxycarbide species. A strong difference in the CDC process for different types of substrate SiC materials (single crystal with different surface termination or industrial ceramics) was observed, which is connected with the chemical structure of the topmost surface layers of those materials. *Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

1:00 pm **Sorting Single-Walled Carbon Nanotubes by Diameter in Density Gradients** *Michael S. Arnold, Samuel I. Stupp, Mark C. Hersam*, Northwestern University

The separation of single-walled carbon nanotubes (SWNTs) by their physical and electronic structures is essential for future applications of SWNTs in molecular electronics, opto-electronics, and sensing, where nanotubes more monodisperse in diameter and electronic-character are needed.(1) Here, we demonstrate the bulk enrichment and separation of SWNTs by diameter through ultracentrifugation of DNA wrapped SWNTs in aqueous density gradients.(2) Successful separation is identified after centrifugation by the formation of colored bands of SWNTs in the density range of $1.11-1.17 \text{ g cm}^{-3}$ and by analyzing the optical absorbance spectra of the separated fractions. From the spectra, we infer that SWNTs of increasing diameter and increasingly more buoyant (Fig. 2A). This strategy for sorting SWNTs is scalable and non-destructive and utilizes standard centrifugation equipment already used during the solution based processing of carbon nanotubes. We propose a geometric-based hydration model to describe the unexpected trend of increasing diameter with buoyant density. The effectiveness of the separation is indicated in Fig. 2B, where the optical absorbance spectra of SWNTs grown by the Co-Mo catalyst method are compared before and after separation, selecting for SWNTs 0.76 \AA in diameter. After separation, the amplitudes of absorbance at 929 and 991 nm were enhanced by factors of 5.3 and 3.5, respectively, while other optical transitions were not appreciably enhanced. The quality of the separation is observed to be highly dependent on the single-stranded DNA length and sequence, with

the best separation observed for the sequence (GT) n where n varies from 10-30. For this case, the conformation of the DNA around the nanotubes was probed using atomic force microscopy and by measuring circular dichroism spectra at the DNA absorption band near 260 nm. (1) M. S. Arnold *et al.*, Band Gap Photobleaching in Isolated Single-Walled Carbon Nanotubes, *Nano Lett.*, **2003**, 3, 1549. (2) M. S. Arnold *et al.*, Enrichment of Single-Walled Carbon Nanotubes by Diameter in Density Gradients, *Nano Lett.*, **2005**, 5, 713.

1:20 pm **The Electromechanics of DNA in a Nanopore, Dr. Greg Timp** University of Illinois

Invited

We have explored the electromechanical properties of *DNA* using an electric field to force single molecules through synthetic nanopores in ultra-thin silicon nitride membranes. At low electric fields $E < 200 \text{ mV}/10 \text{ nm}$, we observed that single stranded *DNA* can permeate pores with a radii $\geq 0.5 \text{ nm}$, while double stranded *DNA* only permeates pores with a radius $\geq 1.5 \text{ nm}$ because the diameter of the double helix is about 2nm. For pores $< 1.5 \text{ nm}$ -radius, we find a threshold for permeation of double stranded *DNA* that depends on the electric field and pH. For a 1nm-radius pore, the threshold is $E \cong 3.1 \text{ V}/10 \text{ nm}$ at $\text{pH}=8.5$, which we suppose corresponds to the stretching transition in *DNA*. The threshold field decreases as pH becomes more acidic, consistent with the destabilization of the double helix, implying that double-stranded *DNA melts* during an electric field-driven translocation through a 1nm-radius pore.

2:00 pm **Sub-Micron OLEDs in a Whole New Light: Realizing Individual Addressability, Matthew**

Russell, L. S. C. Pingree, B. J. Scott, M. C. Hersam, T. J. Marks, Northwestern University

Modern micron and sub-micron organic light emitting diode (OLED) arrays have been realized by a variety of techniques, including nanosphere lithography, filtration membranes, zeolites, inkjet printing, and imprint lithography. Although these fabrication techniques allow for relatively simple fabrication of OLED arrays, they do not permit the fabrication of individually addressable OLEDs. The data measured for these structures is therefore the average performance of the array and cannot account for device to device non-uniformities. Therefore, detailed evaluation of the current injection, light emission, and quantum efficiency of *individual* devices is not possible. In order to measure the performance of individual devices we demonstrate fabrication of small-molecule OLEDs utilizing a suspended membrane shadow mask. Using traditional semiconductor processing and E-beam lithography we can fabricate shadow masks with variable patterns and sizes. This masking approach allows for fabrication of *individually addressable* devices ranging in size from microns down to hundreds of nanometers.

To measure these devices, we utilize a modified conductive atomic force microscopy (cAFM) technique called Atomic Force Electroluminescence Microscopy (AFEM) [1]. This technique uses a conductive diamond tip and a light collection stage to address and measure individual diodes. One advantage of the technique is it offers nanometer scale spatial resolution of simultaneously gathered current, topography, and light emission data from functioning OLEDs. Further, we have screened several silver OLED cathode configurations and found a barium-silver bilayer cathode gives optimal performance.

Using AFEM and a suspended membrane shadow mask we have fabricated and characterized individually addressable small-molecule OLEDs as small as $\sim 500 \text{ nm}$. These sub-micron diodes exhibit turn on voltages of 3-5 volts and current densities of 20-50 mA/cm^2 at an applied bias of 20 volts. These values are comparable to previously published millimeter scale OLEDs [2].

[1] L.S.C. Pingree, M.C. Hersam, M.M. Kern, B.J. Scott, and T.J. Marks. *Appl. Phys. Lett.* **85**, 344 (2004).

[2] J. Cui, Q. Huang, J.C.G. Veinot, H. Yan, Q. Wang, G.R. Hutchinson, A. Richter, G. Evmenenko, P. Dutta, T.J. Marks. *Langmuir* **18**, 9958 (2002).

2:40 pm **Dislocation Free Strained-Si/SiGe Free-Standing Membranes, M.M. Roberts, H.-C. Yuan, L. J.**

Klein, D.E. Savage, Z. Q. Ma, M.A. Eriksson, M.G. Lagall, University of Wisconsin-Madison

Engineering strain in the Si/SiGe hetero-system provides control over band offsets and carrier mobility.

The main problem in the Si/SiGe system is that to obtain strained Si layers, SiGe relaxation, typically by dislocation motion, is required. Dislocations extending into the device layer degrade device performance and dislocations that open at the surface create significant surface roughness. We describe a new method to obtain thin strained Si layers on any substrate. SiGe films are grown by chemical vapor deposition (CVD) on ultra-thin Si-on-Insulator (SOI) substrates and then completely released into large continuous membranes of Si/SiGe/Si that achieve their final strain state after removing the buried oxide layer using an HF etch.¹ Membranes as large as 4 mm x 4 mm of Si/SiGe/Si have been released from substrates and

transferred to a variety of substrates. Upon release, the strain in the system becomes distributed elastically between the layers, based on their relative thicknesses. Elastic-strain sharing is demonstrated using a 50 nm Si/130 nm Si_{0.84}Ge_{0.16}/50 nm Si membrane test structure released and transferred to an oxidized Si wafer. High-resolution x-ray diffraction shows transfer to the Si layer of a 0.30% tensile strain following release, as expected based on the mismatch strain and layer thicknesses. We demonstrate that relaxed transferred membranes can then be “wafer bonded” to the new handle wafer with a bond sufficiently strong to survive a standard chemical clean and second growth. Multiple growths and releases allow for increasing the Si strain without exceeding kinetic critical thickness for the membrane layers. Practical limits to the amount of Si strain achievable by our approach will be discussed. We will also highlight two possible device structures that can take advantage of our membranes. The first is a low-temperature two-dimensional electron gas (2DEG) achieved by delta doping SiGe above a thin strained Si layer. Successful implication will be used to make lithographically gated quantum dots. The second will be for room temperature strained Si MOSFETS.

1.) D.E. Savage, M.M. Roberts, and M.G. Lagally, "Fabrication of Silicon/Silicon-Germanium Heterojunction Structures," application #P04286US, filed December 16, 2004. Research supported by NSF, DOE, and AFOSR

3:00 pm **Fabrication of inverted opal ZnO photonic crystals by atomic layer deposition, M. Scharrer, L. Agesen, X. Wu, A. Yamilov, H. Cao, and R. P. H. Chang**, Northwestern University

Atomic layer deposition is a versatile growth technique that allows surface-controlled, layer-by-layer deposition of highly conformal films on substrates with complex geometries. We have fabricated three-dimensional optically active ZnO photonic crystals by infiltrating carboxylate-modified polystyrene opal templates using a low-temperature ALD process. The polystyrene is removed by firing the samples at elevated temperatures, leaving an ordered fcc array of air spheres in the ZnO matrix. The resulting structures have high filling fractions, possess photonic band gaps in the near-UV to visible spectrum, depending on the sphere size, and exhibit efficient photoluminescence. We can utilize the photonic band structure to modify the photoluminescence and lasing properties of ZnO.

3:20 pm **Microstructural Chemical Evolution of Nanoscale Precipitation-Strengthened Aluminum Alloys, Keith E. Knipling, David C. Dunand, David N. Seidman**, Northwestern University

This research is toward developing a new castable and heat-treatable precipitation-strengthened aluminum alloy having coarsening- and creep resistance beyond 400°C. This is higher than the extant commercial age-hardening 2xxx and 7xxx series alloys where the metastable precipitates and GP zones responsible for strengthening dissolve or transform at relatively low temperatures. The intermetallic Al₃Zr precipitates as a semi-coherent tetragonal equilibrium phase or a coherent metastable L1₂ form. Partially substituting Ti for Zr reduces the lattice mismatch of the L1₂ precipitate with the Al matrix, thereby increasing the stability of the L1₂ phase and delaying the transformation to the tetragonal phase.

Understanding how much solute – i.e., the relative amounts of Zr and Ti – incorporated into the Al₃(Zr,Ti) phase during precipitation is essential for understanding the stability of this dispersed phase during prolonged thermal exposure. Furthermore, both Zr and Ti exhibit terminal peritectic phase equilibria with Al, with equilibrium partition coefficients greater than unity. The resulting solute distribution during solidification has a direct bearing on the precipitate distribution, morphology, and chemistry. Two time-of-flight spectrometry techniques – atom-probe tomography (APT) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) – are discussed. ToF-SIMS is utilized to quantify the initial distribution of solute within the alloy and APT examines the nanoscale chemical compositions of the precipitates and their interfaces, and how these compositions change temporally with exposure at elevated temperatures.

3:40 pm **Rare Earth Additions to Precipitation-Strengthened Al-Sc Alloys, Marsha van Dalen**, Northwestern University

Currently, most precipitation-strengthened aluminum alloys are limited to usage at relatively low temperatures, because of the rapid coarsening and/or dissolution of their precipitates. Al-Sc alloys represent an exception, because they contain nanosize, coherent Al₃Sc precipitates (L1₂ structure) with low coarsening rates. In the present study, rare earth (RE) elements (Yb, Sm or Gd) were added as a ternary alloying additions to replace the expensive Sc in Al₃Sc precipitates with less expensive RE elements. Al-Sc-RE alloys are cast, solutionized and aged at temperatures in the range 300 to 350°C to form nanosize, coherent Al₃(Sc,RE) precipitates within coarse aluminum grains. Each RE element increases the hardness

significantly, as compared to Al-Sc alloys, as the size of the precipitates remains small. In the Al-Sc-Yb alloy, the hardness increase occurs at a faster rate than for the binary Al-Sc. Atom-probe tomographic results demonstrate that the initial precipitates nucleating are Al₃Yb precipitates with Sc partitioning to the precipitates at longer aging times. The resulting creep properties of the Al-Sc-RE alloys are also presented.

Northwestern Room B

9:00 am **Grain Boundary Effects on Charge Transport in Epitaxial Cu(In,Ga)Se₂**

Damon Hebert, *Allen Hall, Angus Rockett*, University of Illinois

Cu(In,Ga)Se₂ (CIGS) is the leading choice for the absorber layer in thin film photovoltaic (PV) devices due to its direct gap, high absorption coefficient and excellent thermal stability. Although the reason is yet unknown, PV devices made of *polycrystalline* CIGS absorber layers consistently outperform their single crystal counterparts. This may be due to advanced deposition techniques for the polycrystalline films, but little is known about the effect of grain boundaries on charge transport in CIGS. There is however evidence that suggests that grain boundaries restrict carrier flow, which could degrade device performance. It has also been suggested that grain boundaries are both inactive and vital to the absorber layer. In the past we have looked for modified chemistry at the grain boundaries in CIGS using TEM nanoprobe.

In order to investigate the electrical effect of grain boundaries in more detail, epitaxial CIGS thin films were grown on GaAs bicrystals using a hybrid sputtering and evaporation technique. The substrate consists of two grains separated by a single, easily visible boundary. SEM and XRD has verified the registry of the CIGS to the GaAs bicrystal substrate. This allows us to isolate and electrically characterize individual grains and their boundary. Temperature-dependent Hall effect provides an analysis of both the defect states present in the epitaxial thin film as well as the effects of grain boundaries on the film resistivity, majority carrier concentration and mobility. Properties of intergranular and transgranular charge transport are compared.

9:20 am **Self-Assembly of FePt Nanoparticles on Modified Diblock Copolymer Templates**, **Nataliya Yufa**, The University of Chicago

Combining inorganic and organic components to create functional materials has been an active area of research in recent years. The inorganic components possess useful electric, photonic or magnetic properties while the organic components self-assemble into a variety of morphologies on the nanoscale. We have created a hierarchically self-assembled magnetic nanostructure. Thin (30 nm) films of poly(styrene-block-methacrylate) (PS-PMMA) copolymer were used as a scaffold. Upon annealing PS-PMMA forms lying-down cylinders of PMMA in a matrix of PS. These thin films were modified by exposure to ultraviolet light in vacuum which etched away the PMMA leaving behind a corrugated surface. We find that superparamagnetic FePt nanodots capped with oleic acid deposited on this surface show a very high degree of preference for the etched phase. In the future this hierarchical self-assembly method may prove useful for producing bit-patterned magnetic memory.

9:40 am **Quantum-dot Cellular Automata, a Nanoelectronic Computing Paradigm**, **Dr. Greg Snider**, Notre Dame Univ. **Invited**

An introduction to quantum-dot cellular automata (QCA) will be presented. QCA is a nanoelectronic computing paradigm based on quantum dots instead of conventional transistors. Information is encoded by the position of single electrons within a cell of quantum dots, rather than by currents or voltages. QCA is scalable to molecular dimensions promising tremendous packing density, and the power-delay product of a QCA device is expected to be orders of magnitude smaller than that of conventional devices. An introduction to the theory of QCA devices will be presented, followed by a presentation of experimental results. These experiments are a significant step toward the realization of a nanoelectronic computing architecture. The experimental devices to be presented include a line of QCA cells, which demonstrates the transmission of information from cell to cell, and the basic QCA logic element, a majority gate that is a programmable AND/OR gate. Clocked cells and latching cells will be presented that open the way for synchronous control and pipelining in QCA arrays. A demonstration of power gain in QCA systems will also be presented. Molecules are being explored as a means to implement QCA cells that operate at room

temperature, and experiments will be presented showing controlled switching of electrons within molecules.

10:40 am Local Electrode Atom Probe Investigation of InAs Nanowires, *D. E. Perea, C. K. Sudbrack, J. E. Allen, S. J. May, L. J. Lauhon*, Northwestern University

The Local Electrode Atom Probe (LEAP) Microscope is a revolutionary instrument capable of producing 3D reconstructions with sub-nanometer resolution. In this talk, I will describe the use of the LEAP to investigate the structure of InAs nanowires for the first time. InAs nanowires were grown epitaxially on (111) GaAs as a patterned array with evaporated gold as a catalyst. Data sets of up to 2.5 million atoms were collected from individual nanowires; In, As, and Au were identified in the mass spectra. Three dimensional reconstructions of the evaporated ions reveal atomic planes as well as a sharp compositional interface between the gold catalyst particle and the InAs nanowire. The work presented here clearly demonstrates the unique capabilities of the LEAP to probe the structure of semiconducting materials and lays the foundation to study more complicated materials systems such as semiconductor nanowire heterostructures.

11:00 am Magnetoresistance in p -(In,Mn)As/ n -InAs junctions, *Steven J. May, Bruce W. Wessels* Northwestern University

Motivated by theoretical work on ferromagnetic p - n junctions for spintronic devices, we have measured the electronic and magnetoresistive properties of epitaxial p -(In,Mn)As/ n -InAs junctions. The junctions were formed by depositing ferromagnetic (In,Mn)As films on InAs substrates using metal-organic vapor phase epitaxy. The junction transport mechanisms have been determined from the current-voltage (I-V) characteristics of the junctions. Ohmic leakage, defect-assisted tunneling and diffusion currents dominate conduction at different temperatures and biases. The junction magnetoresistance (MR), defined as

$$\left(\frac{dV(H)}{dI} - \frac{dV(H=0)}{dI} \right) / \left(\frac{dV(H=0)}{dI} \right)$$
, is dependent on the specific junction transport mechanism.

Under high injection conditions, a large positive magnetoresistance is observed. The magnetoresistance does not saturate in fields up to 9 T. At room temperature, the longitudinal magnetoresistance increases linearly with field from 1.5 T (MR = 56 %) to 9 T (MR = 714 %). The measured magnetoresistance is larger at 78 K, where MR = 82 % (1 T) and 822 % (9 T). The large, linear response makes the junctions promising candidates from high field magnetic sensors.

11:20 am The Holidays Are Over: the Emerging Critical Role of Ion Implantation in Advanced Semiconductor Device Manufacturing, *Anne L. Testoni*, Varian Semiconductor **Invited**

1:00 pm Magnetic and structural properties of self-assembled MnAs nanodots on InAs nanowires, *Dinna G. Ramlan, Jian-Guo Zheng, Steven J. May, Jonathan Allen, Bruce W. Wessels, and Lincoln J. Lauhon*, Northwestern University

Magnetic force microscopy (MFM) was used to characterize the magnetic properties of self-assembled MnAs nanodots on InAs nanowires. High-resolution transmission electron microscopy (TEM) showed that the MnAs nanodots grow epitaxially on the InAs nanowires and have hexagonal crystal structure. MFM images exhibited magnetic field-dependent phase contrast that was correlated with small protrusions in the topographic images. The magnetic origin of the contrast was verified by the observation of opposite contrast upon reversal of the tip magnetization. Variable temperature MFM studies showed that the magnetization is approximately constant below 313 K, beyond which it drops abruptly to zero. The MFM data is therefore consistent with a first order phase transformation as is seen in bulk hexagonal α -MnAs.

1:20 pm Rapid Detection of an Anthrax Biomarker by Surface-Enhanced Raman Spectroscopy, *Xiaoyu Zhang, Richard P. Van Duyne*, Northwestern University

A rapid detection protocol suitable for use by first-responders to detect anthrax spores using a low-cost, battery powered, portable Raman spectrometer has been developed. *Bacillus subtilis* spores, harmless simulants for *Bacillus anthracis*, were studied using surface-enhanced Raman spectroscopy (SERS) on silver film over nanosphere (AgFON) substrates. Calcium dipicolinate (CaDPA), a biomarker for bacillus

spores, was efficiently extracted by sonication in nitric acid and rapidly detected by SERS. AgFON surfaces optimized for 750-nm laser excitation have been fabricated and characterized by UV-vis diffuse reflectance spectroscopy and SERS. The SERS signal from extracted CaDPA was measured over the spore concentration range 10^{-14} - 10^{-12} M to determine the saturation binding capacity of the AgFON surface and calculate the adsorption constant ($K_{\text{spore}} = 1.7 \times 10^{13} \text{ M}^{-1}$). At present, an 11-minute procedure is capable of achieving a limit of detection (LOD) of $\sim 2.6 \times 10^3$ spores, below the anthrax infectious dose of 10^4 spores. The data presented herein also demonstrate that the shelf life of pre-fabricated AgFON substrates can be as long as 40 days prior to use. Finally, these sensing capabilities have been successfully transitioned from a laboratory spectrometer to a field-portable instrument. Using this technology, 10^4 bacillus spores were detected with a five-second data acquisition period on a one-month-old AgFON substrate. The speed and sensitivity of this SERS sensor indicate that this technology can be used as a viable option for the field analysis of potentially harmful environmental samples.

1:40 pm **Single Photon Ionization of Derivatized Peptides with a Fluorine Laser**

Praneeth D. Edirisinghe, Luke Hanley University of Illinois at Chicago, Jerry F. Moore, Michael J. Pellin, Argonne National Laboratory

Introduction

Single photon ionization shows great promise for enhancing ionization yields with a minimum of fragmentation. The F_2 excimer laser is an intense laboratory source of vacuum ultraviolet radiation, but the 7.9 eV (157 nm) photons it generates are lower in energy than the ionization potential of many target species. A method is described here whereby chemical labeling of peptides with polycyclic aromatic hydrocarbons (PAH) allows efficient F_2 laser single photon ionization of the entire labeled peptide. PAH-labeling produces parent ion formation in some cases and fragmentation in other cases.

Methods

Naphthalene and anthracene carboxylic acids and aminobenzoic acid are used to derivatize various synthetic peptides. PAH labeled peptides are prepared using the NHS ester of the PAH carboxylic acid. PAH labeled and unlabeled physisorbed peptides as well as various physisorbed amino acids are prepared by drying a solution thereof onto a clean aluminum sample holder. These physisorbed peptides are analyzed by secondary ion (SIMS), direct laser desorption (LDMS), secondary neutral (SNMS) with 157 nm photoionization, and laser desorption photoionization mass spectrometry (LDPI MS) using a N_2 laser for desorption and 157 nm photoionization. Samples are prepared at UIC for mass spectrometry experiments performed on the SPIRIT apparatus located at Argonne National Laboratory. Ab initio calculations are performed using Gaussian 98.

Results

LDPI MS is used to measure various unlabeled and PAH labeled peptides and amino acids, including GAPKSC, GGG, GG, GV, H, and W. LDPI MS with 157 nm photoionization displays representative high mass peaks for the labeled peptides and amino acids, with anthracene labeled peptides displaying intact parent ions. The aminobenzoic acid and naphthalene tags show only high mass fragments of the parent ion, but no parent ion. Unlabeled peptides and amino acids display only low mass ions signal in SIMS, LDMS, SNMS, and LDPI MS. Neither does LDMS of tagged peptides and amino acids show any higher mass peaks. High resolution LDPI MS measurements of GGG, GG, GV, H, and W indicate that at least in these cases, the parent ion is a radical cation rather than protonated. LDPI MS of much larger peptides is also observed, but it is unknown whether the mechanism is direct ionization or proton transfer. The observation of more parent ion signal and less fragmentation with single photon ionization (SNMS and LDPI MS) compared to experiments without (SIMS and LDMS) indicates that the PAH group behaves as an ionization tag for the entire PAH-peptide species (at least for the smaller species). The ionization potentials of these three PAHs are below 7.9 eV, rendering them suitable ionization tags for use with 157 nm photoionization. The extended conjugated structure of these PAHs further serve to stabilize and delocalize the positive charge of their radical cations, reducing postionization fragmentation. Anthracene is the largest ring structure of the three PAHs and it displays the least fragmentation due to greater delocalization of positive charge. Direct single photon ionization via the PAH tag is supported by charge distribution maps and ionization potentials obtained from ab initio calculations.

2:00 pm **Controlled Nanoscale Morphology on the α -Fe $_2$ O $_3$ (0001) Surface** *Steven T. Christensen, Mark E. Greene, Ann N. Chiamonti, Michael J. Bedzyk, Mark C. Hersam* Northwestern University

The ability to control surface morphology at the nanometer scale may enhance several technological applications for α -Fe₂O₃ (0001) including catalysis, photoelectrochemistry, magnetic data storage, and spintronics. In pursuit of this goal, atomic force microscopy is employed to study the nanoscale morphology of α -Fe₂O₃ following annealing treatments in oxygen-rich atmospheres. The α -Fe₂O₃ (0001) crystals were grown via chemical vapor transport using the equilibrium reaction: $\text{Fe}_2\text{O}_3 (s) + 6\text{HCl} (g) \leftrightarrow 2\text{FeCl}_3 (g) + 3\text{H}_2\text{O} (g)$.^{1,2,3} Upon annealing the crystals in oxygen rich atmospheres at 900°C for 2 hours, the originally featureless surface was transformed to one with broad (~100 μm wide) atomically flat terraces separated by narrow (~1 μm wide) regions with dense step bunching. The terraces support two-dimensional circular domains with diameters on the order of hundreds of nanometers and depths of 2.2 ± 0.2 Å. The domains extend across >90% of the surface and can locally coalesce to form layered domains that are multiple unit cell lengths deep. The formation of these circular domain structures are consistent with a theoretical model based on relatively long range repulsive dipole interactions among the domains.^{4,5,6,7} The generality of this model will be discussed by comparing the case of circular domains in α -Fe₂O₃ with similar domain formation observed in other oxide systems (e.g., SrTiO₃ and TiO₂).

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2:40 pm **Improving Nanoscale Impedance Microscopy**, *Liam S. C. Pingree, Mark C. Hersam*, Northwestern University

Nanoscale Impedance Microscopy (NIM) has advanced the ability to assess the complex impedance of individual conductive pathways in a variety of materials. [1] This technique concurrently monitors the magnitude and phase response of the current through a conductive AFM tip in response to an AC bias. By varying the frequency of the driving potential, the resistance and reactance of nanometer scale conductive pathways can be quantitatively determined. We have demonstrated the extreme accuracy of NIM on a variety of control systems, such as a set of gold nanowires connected to a set of series RC circuits, resulting in concurrent current and phase images. In addition, we have performed NIM on 8 μm x 8 μm Organic Light-Emitting Diode (OLED) pixels, which exhibit enhanced negative capacitance.[2]

The application of this technique to other materials systems will also be discussed.

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[2] L. S. C. Pingree, *et al.*, *Appl. Phys. Lett.*, **86**, 073509 (2005).

3:00 pm **Novel Field Emission Source for Electron Microscopy**, *J. W. Lewellen, J.R. Noonan*, Argonne National Laboratory

A novel field emission electron source that combines desirable features of thermionic cathode and photocathode has been designed. Simulations indicate that the electron beam has very small emittance, ~ 2 nm-radian, and high average current. The source uses high gradient radio frequency (RF) fields to extract electrons off of a field emitter tip and accelerate these electrons to ~1.5 MeV energy. The resulting gun design show promise in a number accelerator and non-accelerator applications, such as energy recovery LINACS, TeraHertz radiation sources, high voltage electron microscopy, electron beam welding, and thin film deposition.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under contract No. W-31-109-ENG-38.

3:20 pm **Si(114)-(2x1): A nano chem kit for comparative molecular surface functionalization of silicon**, *D. E. Barlow, A. R. Laracuente, L. J. Whitman, and J. N. Russell, Jr.*, Naval Research Laboratory
Invited

Poster Abstracts

Thermal and Photo-Activation of Bulk Defects in CuIn_{1-x}GaxSe₂ Thin Films, *J. D. Cohen, J. T. Heath, W. N. Shafarman, Eric Tweeten*, University of Oregon

Drive level capacitance profiling (DLCP) is a method which uses the capacitance of the rectifying junction in a solar cell to deduce the concentration of bulk defects in the absorber layer, whose energies lie within the material's band gap. The capacitance is found by applying an AC bias across the junction and using a lock-in amplifier to separate the response into conductive and capacitive components. The capacitance typically shows a quadratic dependence on AC amplitude, and the coefficients of the fit of this curve can be used to calculate the number of donors/acceptors that respond within a certain energy separation from the valence/conduction band edge. This allowed energy separation is determined from the frequency of the AC bias. Defects located deeper in the band gap will not respond at higher frequencies, so varying the frequency can give an energy profile. At low frequencies, this is a quasi-steady state process and time dependence need not be taken into account. The defect density is given at the point at which the defects cross the Fermi energy, so applying a reverse DC bias to the junction gives a spatial profile of defect density. This technique is done in the dark and so the defect states are detected by thermal capture/emission.

Transient photocapacitance (TPC) measures capacitance in the way described above. The junction is placed under a reverse DC bias and is subjected to a train of positive square wave pulses that reduce the reverse bias. This collapses the depletion region by neutralizing donors/acceptors. Capacitance is dependent upon the size of the depletion zone, and hence upon the rate at which these states re-ionize. Therefore, capacitance is measured as a function of time between these pulses. Light-induced transitions will increase the rate of re-ionization. Therefore, the light response of defect states in the band gap can be deduced by comparing transient capacitance curves with and without light exposure. By varying the wavelength of the incident radiation, an energy profile of the band gap defect distribution can be obtained

Highly Substituted Arene Imides as Versatile Organic Semiconductor Materials, *Brooks Jones, Michael J. Abrens, Myung-Han Yoon, Antonio Facchetti, Tobin J. Marks, Michael R. Wasielewski*, Northwestern University

The design and characterization of new classes of arene imide dyes with substitution at both the imide and core positions is detailed. In particular extremely electron-deficient core-cyanated arene imides reveal excellent potential as n-type semiconductors in organic field-effect transistors. Thin film transistors fabricated with these materials exhibit long sought after air-stable n-type operation with mobilities as high as $0.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. While functioning devices can be fabricated from vapor and solution based methods, the structure/function relationships are primarily explored in vapor-deposited polycrystalline films.

Organic Semiconductors, *Joseph Letizia*, Northwestern University

Organic semiconductors are promising materials to replace amorphous silicon in low performance electronics. Their materials properties allow fabrication of large-area and flexible circuits with high production throughput at low cost. A major challenge for these materials is achieving electron mobilities similar to hole mobilities ($\sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Incorporation of electron withdrawing groups into conjugated organic systems can, in some cases, enhance electron (n-type) charge transport and carrier stability in organic semiconductors. A family of molecules is designed and synthesized having an acyl-quaterthiophene core. The molecules are found to have high volatility and favorable solubility allowing vacuum evaporation and solution casting of films. Thin film field effect transistors are fabricated with a fluorinated molecule having n-type mobilities of $0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and drop cast films having a mobility remarkably only one order of magnitude lower than this. A non-fluorinated molecule is found to have a p-type mobility of $0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The crystal structure is obtained for both molecules and shows a nearly planar thiophene core with herringbone packing. Initial DFT calculations are performed to qualitatively assess the Marcus electron transfer rate for these molecules.

Epitaxial Growth Of Multigrain CuInSe₂, *Allen Hall, Changhui Lei, Mark Nowakowski, Angus Rockett*, University of Illinois at Urbana Champaign

Epitaxial copper indium diselenide (CuInSe₂) films were grown on gallium arsenide (GaAs) multigrain wafers using a hybrid sputtering/evaporation growth process. Scanning electron microscopy (SEM) morphology shows epitaxial growth with intimate grain boundary contact. Epitaxial growth across GaAs

twin boundaries is also observed. Electron backscatter detection (EBSD) shows off-axis [001] and off-axis [101] crystal normal directions in the epitaxial layers consistent with the substrate patterns. SEM morphology is compared to [100] and [111] epitaxial films previously grown. Atomic force microscope, transmission electron microscope and high-resolution transmission electron microscope images are presented which demonstrate the surface morphology and the grain boundary structure and nanochemistry. The grain boundary morphologies are compared with grain surfaces and are interpreted in terms of growth mechanisms and surface energies.

The shapes of voids in Cu(InGa)Se₂ solar cells, Changhui Lei, D.X. Liao, Ch Miller, A.A.Rockett, I.M. Robertson, University of Illinois at Urbana Champaign

Voids are found in both epitaxial Cu(InGa)Se₂ films grown on GaAs substrates and polycrystalline films grown for solar cell devices. These voids are Kirkendall voids; their shapes are regular, but strongly depend on the growth process and the orientation of substrates. The voids in CuInSe₂ films grown on (001), (110) and (111)A and (111)B orientated GaAs substrates, are substrate-dependent, located at the interfaces and extend into GaAs substrates. Large voids of micron size are also found in the Cu(In_{1-x}Ga_x)Se₂ (0 < x < 0.5) films grown by the metalorganic vapor phase epitaxy (MOVPE) at 570°C. The voids in the epitaxial films are produced during the out-diffusion of Ga from GaAs into the CuInSe₂ films. The bilayer process, in which two layers, the first highly Cu-rich and the second highly In-rich or pure In₂Se₃ mix during growth and are found to result in void formation in the polycrystalline films. These voids are usually located at grain boundaries, and are the consequence of fast-diffusion of Cu during the mixture of CuSe₂ and (InGa)₂Se₃ precursors. All of these voids show good facets on the {112} planes of chalcopyrite structure, indicating the low energy of {112} planes

Nanoscale studies of coarsening in a Ni-Cr-Al-Re model superalloy, Kevin Yoon, David N. Seidman, Northwestern University, Ronald D. Noebe, NASA Glenn Research Center

The addition of refractory elements, such as W, Mo, Ta, and/or Re, have improved significantly the high-temperature properties of Ni-based superalloys. The optimum mechanical properties and operating temperature of single-crystal blades are achieved by increasing the total amounts of refractory elements. Recent third generation Ni-based superalloys, such as CMSX-10 and René N6, have higher Re concentrations to obtain higher operating temperatures of about 85% of the absolute melting temperature, even though large amounts of the heavy refractory elements increases the densities of alloys. In spite of the improvement of mechanical properties of Ni-based superalloys utilizing the addition of refractory elements, their effects on the microstructure of superalloys are mostly unidentified at the subnano- to nanoscale.

Rhenium (2 at.%) was added to a model ternary Ni-8.5 at.% Cr-10 at.% Al superalloy to study its effects on the temporal evolution. The temporal evolution of gamma-prime (L1₂) precipitates in a Ni-Cr-Al-Re FCC alloy, aged at 1073 K from 0.25 to 264 hours, is investigated by transmission electron microscopy and atom-probe tomography. The number density, mean radius, and volume fraction of gamma-prime precipitates are measured, as well as the supersaturations of alloying elements in both matrix and precipitate phases as functions of time. The experimental results are compared with coarsening models and the coarsening kinetics do not obey the time dependencies predicted by the models. The coagulation and coalescence of γ'-precipitates and slow-diffusing Re are suggested to be the reason for the deviations. In addition, experimental results are compared with *PrecipiCalc* simulations to test the applicability of the simulations, and they are in reasonable agreement.

Sorting Single-Walled Carbon Nanotubes by Diameter in Density Gradients, Michael Arnold, Northwestern University

See oral abstracts

Self-Assembly of FePt Nanoparticles on Modified Diblock Copolymer Templates, Nataliya Yufa, The University of Chicago.

See oral abstracts

Preparation and characterization of hydroxyapatite thin films produced by radio frequency facing magnetron sputtering, Zhendong Hong, L.Luan, B.Deng, J.B.Ketterson, D.Ellis,, A.Rossi, A.Mello, J.Eon, Northwestern University

Hydroxyapatite coatings on implant materials have been continuously investigated since the 1980's. The plasma spraying technique is the most widely used commercial method to prepare such coatings in dentistry

and orthopaedics. RF sputtering in the conventional geometry has shown promise for application, with however, some problems. This paper focuses on the improvement of the method by using a specially-designed right-angle geometry. This setup was observed to approximately keep the stoichiometry of the sputtered targets in our experiments. We have demonstrated the influence of various sputtering parameters and post deposition treatment on the quality of films. Our preliminary results show that our preparation method may produce better HA coatings than plasma spraying and convention sputtering method. However biocompatibility tests still need to be performed.

Confinement and the Glass Transition Temperature in Supported Polymer Films: Molecular Weight, Repeat Unit Modification, Composition, Induced Stresses and Cooperative Length Scale Investigation, Manish Mundra, John M. Torkelson, Northwestern University

Numerous experimental and theoretical modelling studies have established that the glass transition temperature (T_g) of supported polystyrene (PS) films decreases dramatically with decreasing film thickness below 50 - 70 nm. However, a detailed understanding of the cause of this effect is lacking. This behavior has implications in applications ranging from photoresists technology, sensors, separation via membranes, disk drive lubricants, and nanocomposites, among others. A number of postulates have been offered regarding the origin of these effects in systems lacking attractive polymer-substrate interactions such as, internal stresses caused by film preparation methods, finite size effect with the thickness approaching the fundamental length scale, segregation of chain ends to the free surface, radius of gyration (R_g) approaching film thickness, impact of polymer-air free surface, among others. It is noteworthy that these “ T_g -nanoconfinement” effects are “tunable” to various degrees by modifying different parameters such as polymer-substrate interactions, addition of diluents, variation in composition etc. This investigation focuses on the tunability aspect of T_g -nanoconfinement as well as addresses some key questions and disagreements in this area.

Improved Transparent Conducting Oxides Through Modulation Doping, David Cohen, Scott Barnett, Northwestern University

Transparent conducting oxides (TCO's) are utilized as electrodes in technologically important applications such as flat panel displays and solar cells. Recent attempts to decrease the resistivity $\rho = (ne\mu)^{-1}$ have typically focused on increasing the mobility μ rather than the carrier concentration n (e is the electron charge). The mobility $\mu = e\tau/m^*$ can be increased by increasing the relaxation time τ or by decreasing the effective mass m^* . One proposed method for increasing τ in TCO's is by using modulation-doped multilayer films. In this method, donor atoms are placed in wider band gap layers and the resulting conduction-band electrons transfer across the heterojunction interfaces to undoped, smaller band gap layers.

In order to produce modulation-doped ZnO/ZnMgO films it was first necessary to effectively donor dope the ZnMgO layers. To this end, $Zn_{1-x}Mg_xO:Al$ thin films were grown epitaxially on c-plane sapphire substrates by direct current reactive magnetron sputtering. Post deposition annealing with *in situ* indium doping was done at 415°C for 4 hours in H_2/Ar mixtures, resulting in improved electrical properties. Increasing the Mg content from 0 to 20 at% increased the band gap but decreased the conductivity, mobility, and electron density in annealed films. Increasing the Al dopant content in ZnMgO had similar effects as in pure ZnO, increasing the carrier density and optical band gap but decreasing the mobility.

A one-dimensional Poisson/Schrödinger program was used to investigate the effect of layer thicknesses, donor concentration, and band gap offset on the electrical properties of transparent conducting modulation-doped ZnO/ZnMgO multilayer structures. Mobilities as high as 145 cm^2/Vs are predicted for a structure with average carrier density $8 \times 10^{18} cm^{-3}$ and resistivity $1 \times 10^{-2} \Omega cm$; for a comparable resistivity in monolithic ZnO, the mobility would be lower $\sim 30 cm^2/Vs$, and the carrier density higher leading to higher optical absorption.

Chemical Vapor Deposition of Transition Metal Diborides from Single Source Precursors,, Sreenivas Jayaraman, Yu Yang, Jeniffer E. Gerbi, Do Young Kim, Gregory S. Girolami, John R. Abelson, University of Illinois at Urbana Champaign

Transition metal diborides are very useful engineering materials due to their attractive properties like high melting points, high hardnesses and low electrical resistivities. However, they have been largely overlooked in thin film science and technology which can be attributed to the difficulties associated the available deposition methods. For example, the stoichiometry control of diborides is crucial as the material properties degrade severely with stoichiometry deviation. And the halogenated precursor based CVD

requires high deposition temperature and corrosive gas handling. We will show a simple CVD route toward transition metal diborides from a class of single source, impurity-free precursors – the metal boron hydrides. Very high quality CrB_2 , ZrB_2 and HfB_2 thin films can be grown at deposition temperature 200°C and above. The growth kinetics, microstructures, and crystallinity of the films will be presented. A few applications that are currently under development will also be given. The low temperature deposited films are dense and extremely conformal, and has been initially tested as diffusion barrier for copper metallization. The Nanocrystalline HfB_2 films obtained by post annealing the amorphous films provide a very respectable hardness of 40GPa. At 950°C and above, ZrB_2 and HfB_2 can be grown epitaxially on $\text{Si}(111)$ and $\text{Si}(100)$ substrates, thus can serve as a buffer layer for GaN growth on Si due to their close lattice-match with GaN.

X-Ray standing wave imaging of submonolayer vanadium oxides on the $\alpha\text{-Fe}_2\text{O}_3(0001)$ surface,

Chang-Yong Kim, Anthony Escudro, Michael Bedzyk, Northwestern University

Using x-ray photoemission spectroscopy (XPS) and x-ray standing wave (XSW) measurements, we have studied the electronic and atomic structure of submonolayer vanadium on $\alpha\text{-Fe}_2\text{O}_3(0001)$ as a function of the vanadium oxidation state. The XSW data is used to generate a direct-space, model-independent image of the vanadium distribution, both before and after the vanadium is oxidized and reduced using atomic oxygen and hydrogen. The direct-space atomic density profile shows the vanadium adatoms occupy bulk-like Fe substitutional sites when 0.51 ML of vanadium is deposited on the $\alpha\text{-Fe}_2\text{O}_3(0001)$ surface at room temperature. After the vanadium is oxidized, the average adsorption height of the vanadium atoms increases by 0.5 \AA ; furthermore, some of the vanadium migrates upward to occupy an additional Fe-bulk like atomic site. A lateral shift of the vanadium may also accompany these vertical shifts. This structural change can be understood in light of our recent findings regarding the electronic structure of the $\text{V}/\text{Fe}_2\text{O}_3(0001)$ system. In this study, XPS results suggest the exposure of a vanadium film to atomic oxygen converts the vanadium into a V_2O_5 film and re-oxidizes the hematite at the film-substrate interface. Our current XSW results also suggest the oxidation of the supported vanadium is a reversible process, by demonstrating the ability of the atomic hydrogen to reduce the submonolayer vanadium oxide and recover the as-deposited surface geometry.