

## *Oral Presentations*

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### **Surface Characterization of Drug Delivery Systems**

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Controlled drug delivery focuses drugs to diseased sites in the human body which helps minimize side effects. Surface characterization methods provide critical chemical and microstructure information useful in the development of drug delivery systems such as microspheres, implants, and drug coatings on medical devices. In this presentation, the degree of mixing between drug and excipient, type of drug polymorph present (amorphous and crystalline forms), and the mechanisms by which the drug elutes from the delivery system are revealed using a variety of methods such as Raman imaging, atomic force microscopy (AFM) and x-ray diffraction.

In one example, an ophthalmic device was coated with the steroid triamcinolone acetonide (TA) blended with polymers. Depending upon the preparation method, the steroid TA can exist in three forms: anhydrous or hydrate crystals, or the amorphous form. Raman imaging shows the spatial distribution of the up to five components, and indicated that upon exposure to buffer, water is absorbed into the polymer, the crystals of drug shrink and eventually dissolve, amorphous drug appears, and drug diffuses out of the matrix. In another example, highly loaded coatings of amorphous dexamethasone in polymer exhibit 100 nm diameter nanostructures according to AFM. From adhesion and stiffness measurements, the nanostructures are identified as domains of amorphous dexamethasone. Upon exposure to water, a sub-population of the nanostructures pop off the surface quickly, while another population slowly erodes away, leaving small pits in the polymer coating surface. In this way Raman and AFM show how the microstructure of drug delivery systems evolve upon elution of drug.

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### **Is There a Future for TOF-SIMS in Biological Imaging?**

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There has been growing interest in tools that utilize hyperthermal ion/solid interactions for the characterization of molecular solids by mass spectrometry. These techniques are generally distinguished by electrospray ionization (ESI) where the sample is interrogated in an ambient environment, and interest in them is further driven by low cost, diminutive size, and ease-of-use. In practice, the mass range and sensitivity of the ambient ionization techniques is limited, as is the lateral resolution; however, there is great potential for the study of surface chemistry as a result of the low energy density, e.g. soft landing. There is an additional benefit in that most specimens may be analyzed without the need for an applied ionization matrix which stands in contrast to a widely used mass spectrometry method known as matrix-assisted laser desorption-ionization (MALDI). The energy density within the MALDI excitation zone is such that large molecules, e.g. intact proteins, may be characterized. Analysis is carried out in a vacuum environment, and various detection schemes may be connected to the MALDI front-end to achieve useful mass resolutions. However, large sample volumes are consumed during the analysis, and the distribution of the analyte(s) is affected by the applied ionization matrix in a way that is not well understood.

Situated between the aforementioned mass spectrometry methods is time-of-flight secondary ion mass spectrometry (TOF-SIMS). The energy density is such that the mass range is limited to small molecule (< 3 kDa) analysis and the sample is interrogated in a vacuum environment which presents challenges for certain analyses; however, there is no inexorable need for an applied ionization matrix. The analytical volume of TOF-SIMS is quite small and, when normalized by volume, the sensitivity of TOF-SIMS is  $\gg 10^3$  times larger than the aforementioned methods. A further asset of TOF-SIMS lies in the ability to simultaneously achieve high mass resolution and

high lateral resolution. Hence, TOF-SIMS plays a vital role, and should have a vibrant future, in the characterization and imaging of molecular and biological specimens.

The mass range, sensitivity, mass resolution, and lateral resolution of TOF-SIMS will be illustrated in a number of applications. Mass range and sensitivity are demonstrated by full protein sequencing and identification using a classic proteomics workflow. In addition to the advantage of sensitivity, the TOF-SIMS method carries the benefit of sample re-usability following analysis. The capacity for analysis at high mass resolution and high lateral resolution together, i.e. HR<sup>2</sup> analysis, will be illustrated with biological examples which include tissue sections of various studies. Finally, we will explore the difficulties associated with the analysis of topographically rough, intact specimens and demonstrate that the ion energy distributions arising from topography may be adequately counteracted within the TOF-SIMS mass analyzer to achieve HR<sup>2</sup> imaging.

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### **Analysis of PdSn nanoparticles by Auger, XPS and TEM**

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Nanoparticles of Pd and PdSn are important as catalysts for chemical reactions and metallization of polymeric materials. Metallization applications include nano-circuitry and automotive plating on plastic. Catalytic applications include the Heck and Suzuki reactions and a variety of other coupling reactions (hydrogenation, dehydrogenization and petroleum cracking). A common synthesis route for Pd nanoparticles is reduction of PdCl<sub>2</sub> with stannous compounds. The structure and purity of the resulting particles is critical to their performance. TEM has been used to examine PdSn nanoparticles for their compositional structure. For very small particles, EDS and EELS analyses become difficult due to the expanded excitation volume. Surface sensitive methods have utility for effective characterization of materials of this type.

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### **Engineering film composition for efficient, single-layer organic light-emitting devices**

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Organic light-emitting devices (OLEDs) have received considerable attention for application in both displays and solid-state lighting. These devices are attractive for their compatibility with low-cost processing techniques, their broad spectral tunability, and their exceptionally high electroluminescence efficiencies. Most frequently, high efficiency is realized through the use of complex, multilayered device architectures. Here, the focus is instead on realizing high efficiency in OLEDs comprising only a single active-layer whose composition is spatially engineered to realize effective charge and exciton confinement. In a graded-emissive layer (G-EML) OLED, the composition consists of nearly 100% hole-transporting material (HTM) at the anode and nearly 100% electron-transport material (ETM) at the cathode, with a continuously varying HTM:ETM composition across the active layer. Complementary depth-profiling using X-ray photoelectron spectroscopy is used to probe film composition and confirm the presence of a gradient. Electroluminescence comes from a phosphorescent guest that is uniformly doped throughout the G-EML. In this work we demonstrate red-, green-, and blue-emitting G-EML OLEDs which show high efficiency comparable to more complex, multilayered structures. We also demonstrate how charge confinement in a G-EML OLED is realized through a spatial variation in the electron and hole mobilities across the active layer. This leads to a natural confinement of both charge carriers and excitons, without the need for any additional active layers. Consequently, variations in the composition gradient offer a new handle for device design and the realization of high efficiency in a single-layer device.

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## Surface Analysis of Chalcopyrite Semiconductors for Photovoltaic Applications

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Urbana, Illinois

This talk reviews our work on surface analysis of chalcopyrite semiconductors used in solar cells (photovoltaics). The (Ag,Cu)(In,Ga)(S,Se)<sub>2</sub> compound semiconductor family forms a range of chalcopyrite alloys with high solubility and high performances in photovoltaic devices. The current record performance small devices exceeds 20% while active and manufacturable modules exceed 17% efficiency in 900 cm<sup>2</sup> areas and 15% in 6000 cm<sup>2</sup> areas. These results have spurred development of commercial products around the world. Much remains to learn about the operating principles of the devices, what limits their performance, and how the energy gap can be increased without loss of performance. To develop this understanding we have been analyzing the materials and their associated heterojunctions with CdS (the structure used in all commercial devices) by a range of microanalysis techniques. This has included dynamic and static photoelectron spectroscopy, low energy ion scattering, scanning tunneling microscopy, atomic force microscopy, secondary ion mass spectrometry, and more; as well as bulk analysis methods such as transmission electron microscopy.

## Poster Presentations

(S) Denotes student poster

P1 (S)

### Thermal Boundary Conductance Measurements of the Germanium-Silicon Interface with Ultrafast Transmission Electron Microscopy

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Heteroepitaxial and amorphous growth of germanium on silicon to create Ge-on-Si (GOS) devices is an area of intense research due to the advantageous optical and electronic properties of germanium for use in photodetectors<sup>1</sup>, semiconductor lasers<sup>2</sup>, photovoltaics<sup>3</sup>, and a host of other optoelectronic applications. Understanding the interfacial composition and structure, as well as how the silicon/germanium interface affects heat transport through the system, is vital to designing and fabricating next-generation GOS devices.

Thermal boundary conductance (TBC) describes the heat transfer characteristics of an interface based on the heat flux and a finite temperature difference. Ultrafast transmission electron microscopy (UTEM) offers unique capabilities in measuring local lattice temperature through a combination of ultrafast (i.e., femtosecond) temporal resolution and nanometer spatial resolution. By combining finite difference modeling with ultrafast diffraction experiments, an interface can be characterized structurally and compositionally, and the thermal boundary conductance at any point along the interface can be extracted.

In order to determine the effects of a well-characterized silicon/germanium interface on heat transport, we use a combination of specimen preparation, ultrafast convergent-beam electron diffraction, and thermal modelling. We have fabricated and structurally characterized epitaxial germanium films hundreds of nanometers to several microns thick grown on single crystalline silicon substrates. These films are then made into cross-sectional transmission electron microscopy specimens allowing for diffraction information to be obtained across as well as along the interface.

We introduce a thermal gradient across our silicon-germanium interface through selective ultrafast laser heating of the germanium film. This is accomplished by selecting a laser wavelength that is strongly absorbed by germanium but at which silicon is essentially transparent – in our case 1030 nm. By varying the time delay between the arrival of the excitation pulse (pump pulse) and electron packet (probe pulse), a temporal profile of the excitation and decay back to equilibrium can be developed. We then use the Debye-Waller Effect – which relates diffraction spot intensity to localized effective lattice temperature<sup>4</sup> – to build a transient temperature profile of our region of interest with nanometer spatial resolution. Once the experimental transient temperature profile is determined, the interface thermal conductance can be extracted by fitting the spot intensity decay to a thermal model of the system using finite differences to solve the one-dimensional heat equation under appropriate interface boundary conditions. As such, one of the overall goals of this work is to establish UTEM as a powerful method for exploring experimental parameter space surrounding interfacial thermal transport at unprecedented combined spatial and temporal resolutions.

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2. Liu, J. F.; Sun, X. C.; Kimerling, L. C.; Michel, J. Direct-Gap Optical Gain of Ge on Si at Room Temperature. *Opt. Lett.* **2009**, *34*, 1738-1740.

3. Ginige, R.; Corbett, B.; Modreanu, M.; Barrett, C.; Hilgarth, J.; Isella, G.; Chrastina, D.; von Kanel, H. Characterization of Ge-on-Si Virtual Substrates and Single Junction GaAs Solar Cells. *Semicond. Sci. Technol.* **2006**, *21*, 775-780.

4. Yurtsever, A.; Zewail, A. H. 4d Nanoscale Diffraction Observed by Convergent-Beam Ultrafast Electron Microscopy. *Science* **2009**, *326*, 708-712.

P2 (S)

### Direct Observation of a Crystallographic Phase Transition in Undoped LaFeAsO with *In Situ* Transmission Electron Microscopy

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Recent discovery of the iron-based superconductor LaFeAs[O<sub>1-x</sub>F<sub>x</sub>] with a high transition temperature ( $T_c$ ) of 26 K has triggered extensive activity focused on elucidating the fundamental properties of the parent compound LaFeAsO and its doped counterparts.<sup>1,2</sup> Undoped LaFeAsO has a layered structure and belongs to the large family of LnT<sub>M</sub>PnO compounds, where Ln represents a 4f rare-earth element, T<sub>M</sub> a transition-metal element having a more than half-filled 3d shell, and Pn a pnictogen (i.e., nitrogen family) element.<sup>3</sup> The layered structure consists of alternating stacks of electrically charged (LnO)<sup>+□□</sup> and (T<sub>M</sub>Pn)<sup>□□</sup> layers which form a tetragonal crystal structure (space group *P4/nmm*) between 160 K and room temperature.<sup>1,4</sup>

The electronic and magnetic properties of LnT<sub>M</sub>PnO compounds are highly dependent upon the nature of the T<sub>M</sub> component. For example, when T<sub>M</sub> = Mn, Fe or Ni, or Co, the material behaves as an antiferromagnetic insulator, a superconductor, or a ferromagnetic

metal, respectively.<sup>3</sup> Moreover, exchanging La with Ce, Nd, Pr, or Sm results in the coexistence of superconductivity and antiferromagnetism. Importantly, rare-earth elements with decreasing ionic radii elevate  $T_c$  to as much as 56 K due to the decreasing lattice constant. High- $T_c$  superconductivity in LnFeAsO materials is induced by substituting  $O^{2\ominus}$  ions with  $F^\ominus$  or by creating oxygen vacancies. The complex relationships between electronic and magnetic properties and crystal structure, bond distance, and doping make this class of materials interesting from a fundamental physics perspective. Despite intense study, however, the behavior of these materials is still not fully understood, especially at the atomic level.

Here, we describe our initial studies of the crystallographic phase transition of undoped LaFeAsO using *in situ* transmission electron microscopy (TEM). These initial efforts include temperature-dependent parallel-beam electron diffraction, bright-field high-resolution imaging, and spectroscopy supported by detailed analysis meant to elucidate the crystal structure of LaFeAsO below 160 K. At 160 K, LaFeAsO shows anomalies in both resistivity and magnetic susceptibility,<sup>1</sup> and this behavior has been attributed to the combined effect of an abrupt crystallographic phase transition and an antiferromagnetic ordering of the electron spins on the Fe centers. With parallel-beam electron diffraction along the [001] zone axis, we observe a disappearance of Bragg spots corresponding to a symmetry lowering of the crystal structure from tetragonal to either monoclinic or orthorhombic. Analysis of spot positions supported by simulations provides a means to quantify the lattice parameters, which is supported by high-resolution images. In addition to structural studies, we discuss our efforts on probing the temperature-dependent electronic and magnetic properties,<sup>5</sup> especially across the phase transition region, via spectroscopy and Fresnel imaging.

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3. Nomura, T.; Kim, S. W.; Kamihara, Y.; Hirano, M.; Sushko, P. V.; Kato, K.; Takata, M.; Shluger, A. L.; Hosono, H. Crystallographic Phase Transition and High- $T_c$  Superconductivity in  $LaFeAsO:F$ . *Supercond. Sci. Technol.* **2008**, *21*, 125028. (and references therein)
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5. McElroy, C. A.; Hamlin, J. J.; White, B. D.; McGuire, M. A.; Sales, B. C.; Maple, M. B. Magnetotransport Properties of Single-Crystalline  $LaFeAsO$ . *Phys. Rev. B* **2013**, *88*, 134513.

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P3 (S)

### Label-Free DNA Sensing Platform with Low-Voltage Electrolyte-Gated Transistors

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We have developed a sensor that presents a new, electronic strategy for label-free detection of DNA hybridization. Our work is the first to incorporate a floating-gate electrode with an electrolyte-gated transistor (EGT) so that the analyte-containing solution is physically separated from the electronic materials. The fabrication method, ease of use, and compatibility with flexible substrates make this a promising approach for DNA detection in field applications such as forensics, biothreat detection, and pathogen screening.

The key component of the sensor is an EGT that utilizes the high capacitance of mobile ions to modulate the current through an organic semiconductor under the application of low input voltages. The source of mobile ions is the ion-gel dielectric layer formed by gelating a block copolymer in an ionic liquid. Due to their solution-processability, high ionic conductivity, and high capacitance, ion-gels have been successfully used as dielectric layers in organic electronic transistors, circuits, and displays but this our lab's first work to carry them over to DNA sensors. To facilitate interaction with DNA, a novel floating gate geometry is implemented to decouple the electronic materials from an aqueous solution containing target molecules for detection. Hybridization of ssDNA bound to the aqueous arm of the floating gate shifts the voltage through the EGT by altering the work function of the functionalized electrode.

The origin of the voltage offset is thought to be a combination of many molecular changes between ssDNA and dsDNA such as an altered dipole, dielectric constant, thickness, and charge. These in turn affect the interfacial capacitance at the floating-gate/aqueous interface, the electrostatic charge bound to the floating-gate, and the magnitude of the immobilized dipole. The precise operating mechanism is still under investigation, but the sensor has demonstrated favorable responses to fully complementary and mismatched DNA in terms of sensitivity and selectivity. Additionally, the device can be readily integrated with a microfluidic system in a large area array where many EGTs are functionalized and tested in parallel to characterize a DNA mixture in a high-throughput, label-free manner.

Device fabrication begins with gold contacts photolithographically patterned on a silicon wafer. Next, the benchmark semiconducting polymer, poly(3-hexylthiophene) or P3HT, and the ion-gel are deposited from solution at room temperature using an aerosol-jet printing technique. The side-gated EGT is then interfaced with an aqueous electrolyte contained by a rubber well made from poly(dimethylsiloxane) or PDMS. Figure 1 shows a device schematic and a working prototype. The ssDNA probes are attached to the aqueous arm of the floating gate electrode using a thiol/gold bond.

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P4

### **Spectral Chemical State Imaging with High Spatial Resolution Scanning Auger**

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Recent improvements of field emission scanning Auger instruments have led to the ability to provide elemental imaging of surfaces with a spatial resolution better than 8 nm. The PHI 710 now provides the capability to combine high energy resolution spectra with high spatial resolution chemical state imaging with a CMA analyzer. The system software also provides LLS separation of different chemical states from the Auger imaging data.

A semiconductor structure with multiple silicon chemical states will be presented. The 0.1% energy resolution spectra for silicide, silicon, and silicon oxynitride are extracted from the scanning Auger image. These basis spectra are then used to create the different chemical state images. The resulting image overlays demonstrate the ability of the CMA analyzer to image different chemical states at high energy resolution without topographical artifacts.

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P5 (S)

### **Growth, Structure and Electronic Properties of Complex Oxide Thin Films and Heterostructures Grown via Advanced Molecular Beam Epitaxy Approach**

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Utilizing the hybrid molecular beam epitaxy approach for the growth of interfaces between NdTiO<sub>3</sub>/SrTiO<sub>3</sub> - a polar/nonpolar system sharing many similarities with LaAlO<sub>3</sub>/SrTiO<sub>3</sub> and with an added functionality of NdTiO<sub>3</sub> being an antiferromagnetic Mott insulator - we will present a detailed film growth and transport study as a function of cation stoichiometry in NdTiO<sub>3</sub>. Irrespective of the cation stoichiometry (measured in high resolution x-ray diffraction and x-ray photo electron spectroscopy), films grew in an atomic layer-by-layer fashion as evidenced by the reflection high-energy electron diffraction intensity oscillations, and films showed a temperature dependent metal-to-insulator (M-I) type behavior. Remarkably,  $T_{MI}$  was found to increase irrespective of whether films were Nd- or Ti-rich. Furthermore, hall measurement of a ~3.5 nm NdTiO<sub>3</sub> film grown on 3 nm SrTiO<sub>3</sub> layer on LSAT substrate revealed n type carrier density, ~  $3.3 \times 10^{14} \text{ cm}^{-2}$  for stoichiometric samples, which would be consistent with the interface conduction due to an interfacial electronic reconstruction effect. Using detailed growth and temperature dependent magneto-transport measurements, we will present a comprehensive study of correlation between film stoichiometry, interface conduction, and transport mechanisms.

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P6 (S)

### **Intense Pulsed Light Annealing of Copper Zinc Tin Sulfide Nanocrystal Coatings**

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Rapid annealing of coatings cast from nanocrystal dispersions to form polycrystalline thin films has the potential to decrease the production cost of thin film solar cells by both increasing throughput and by enabling manufacturing on flexible substrates. Intense pulsed light (IPL) annealing is one possible alternative to current thermal processes which typically require heating to high temperatures (> 500 °C) for 30 to 60 minutes. IPL annealing utilizes high intensity electromagnetic radiation pulses produced by a xenon flash lamp and range from the ultraviolet to visible wavelengths. In IPL, energy fluences are adjustable from 3 to 15 J/cm<sup>2</sup> with flash durations less than 4 milliseconds. We used IPL to heat coatings cast from copper zinc tin sulfide (Cu<sub>2</sub>ZnSnS<sub>4</sub> or CZTS) nanocrystal dispersions onto molybdenum coated soda lime glass. CZTS is emerging as a potential solar absorber comprised of earth-abundant elements for low cost sustainable solar cell production. Currently, little is known about the effect of IPL annealing on the coating integrity, microstructure development, and chemical stability of CZTS nanocrystal coatings. To advance our understanding of IPL annealing of CZTS, we studied the effects of flash intensity and time on the structural integrity and microstructure of CZTS coatings comprised of 35 nm diameter nanocrystals. Specifically, we varied the number of flashes while maintaining the flash duration constant at 3.5 ms. The CZTS coatings on molybdenum coated soda lime glass were sealed in evacuated quartz ampoules. At low flash intensities (4 J/cm<sup>2</sup>), cracks developed throughout the coating with no noticeable physical changes. The coating developed “blisters”, raised areas of coating, as the flash intensity was increased (9-13 J/cm<sup>2</sup>). The blisters were accompanied by extensive

cracking, localized coating delamination, and material decomposition. Moreover, there was no significant CZTS grain growth when the coatings were sealed and IPL annealed in evacuated ampoules ( $\sim 10^{-6}$  Torr). In contrast annealing in 50 Torr of sulfur vapor decreased the frequency of the blisters and increased grain growth.

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P7

### **Probing the morphology, viscoelasticity and lubriciousness of crosslinked hydrophilic biomedical coatings with environmental AFM**

Greg Haugstad<sup>1</sup>, Maggie Zeng<sup>2</sup>, Connor Collings<sup>1</sup>, Alon McCormick<sup>1</sup> and Klaus Wormuth<sup>1</sup>

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We explore the morphology and tribo-mechanical properties of polyacrylate catheter coatings variably UV-crosslinked (1,4-butanediol diacrylate) and following variable tribological history, mimicking shear stresses during surgery (to assess lubricity and durability of coatings). A rich surface morphology is revealed over micro- to nano-scales, strongly dependent on both the extent of crosslinking and subsequent macrotribological processes under aqueous immersion. Submicron defect structures resulting from the sponge-coating deposition process include shallow (nm's) circular depressions hundreds of nanometers across ("cheetah spots") and much deeper/narrower "pinholes"; from the UV curing we find deep but larger in diameter "craters" plus "fissures" running between the deep holes and craters. The deepest defects exhibit modified behavior, as sensed in multiple AFM modes sensitive to dissipative properties (friction, adhesion, phase), consistent with these defects extending to the substrate, the Pebax catheter tube. Differences in contact-mode rippling propensities track differences in coating behavior versus curing time and tribo-history.

Mapped AFM-nanoindentation measurements are used to interrogate both elastic and dissipative property changes of the coatings as a function of UV curing and macrotribological history. Force-penetration responses are further explored under variable humidity and temperature (heated sample, heated tip). A highly reproducible solvent-induced glass-rubber transition is identified over a narrow range of relative humidity, and found to be shifted to higher humidity on coatings that are "over cured" (50 seconds compared to 5- and 10-second curings). These 50 second UV coatings are also found to be nonlubricious in the macrotribological tests. In the process of exploring humidity cycles, dramatic irreversible transformations in coating morphology were discovered, whereby many of the defects present from sponge coating and UV curing are largely "healed".

Broadly, this study exemplifies (1) technologically important and scientifically rich phenomenology over scales ranging from tens of microns to tens of nanometers; (2) connections of nanoscale behavior to macroscale properties; and (3) the complementarity that multiple AFM methodologies[1] afford in assessing the performance of thin film coatings for biomedical device technologies, here lubricious but also drug eluting[2].

[1] G. Haugstad, *AFM: Understanding Basic Modes and Advanced Applications* (Wiley, 2012).

[2] G. Haugstad and K. Wormuth, "Nanomechanical Characterization of Biomaterial Surfaces: Polymer Coatings that Elute Drugs", in *Industrial Applications of Scanning Probe Microscopy*, ed. D. Yablon, (Wiley, 2013).

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P8 (S)

### **Modeling the migration of second-phase particles in cadmium zinc telluride (CZT) via temperature gradient zone melting (TGZM)**

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Crystals of cadmium zinc telluride (CZT) typically exhibit significant populations of large (10 micron and above) tellurium-rich particles that are deleterious to the performance of semiconductor radiation detectors. It is well understood that melt growth of CZT produces crystalline material that is supersaturated with tellurium, providing a thermodynamic basis for the existence of these second-phase particles. While their specific formation mechanisms are not well understood, their presence is unavoidable.

As an alternative to preventing particle formation during the growth process (which may not be possible), an interesting post-growth treatment may provide a means to higher-quality crystals. Namely, these large, tellurium-enriched, secondary-phase particles can be induced to move away from a region of grown crystal and accumulate elsewhere, leaving higher-quality regions that contain far fewer particles. This accomplished by heating the sample to slightly above the eutectic temperature (the melting point of the second-phase particles) and engineering a temperature gradient across the sample. Under such conditions, the now-liquid particle dissolves on the hot side and re-solidifies on the cool side, with a net effect of migrating toward the hotter region. This process is termed "temperature gradient zone melting," or TGZM.

We present the formulation of mathematical models for particle migration via TGZM. We demonstrate that an approximate analytical solution to this model in one spatial dimension well describes the general behavior of particle migration. The analytical solution shows that steady-state migration is not possible, and that, under a constant thermal gradient, the particle velocity and size increase continually with time. Experimental observations are consistent with these predictions. We also describe the implementation of a moving-boundary, finite-element method that solves the model equations with no simplifying assumptions about mechanistic interactions. Initial results are presented to verify the numerical model, identify the dominant physical interactions involved in this process, and demonstrate reasonably quantitative predictions of particle migration in CZT.

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P9 (S)

### **Microwave-Assisted Low Temperature Synthesis of Abundant Metal Sulfides**

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Abundant metal sulfides are promising materials for photovoltaic and photocatalytic materials. Synthesis techniques need to be developed to produce novel phase-pure materials with desired crystallite size to meet the cost and sustainability goals of the future. Employing microwave heating allows for a low cost alternative to conventional thermal methods. The materials synthesized have been thoroughly analyzed by Raman spectroscopy, X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy.

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P10 (S)

### **Structural and Electronic Transport Properties of BaSnO<sub>3,δ</sub> Deposited via High Pressure Oxygen Sputtering**

Koustav Ganguly, Palak Ambwani, Jong Seok Jeong, K. Andre Mkhoyan, Peng Xu, C. Leighton, and Bharat Jalan  
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The recent discovery of high electron mobility ( $320 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) at 300 K in Ba<sub>1-x</sub>La<sub>x</sub>SnO<sub>3</sub> single crystals provides a great motivation for establishing similar property in thin films [1]. From theory it is now well understood that the conduction band in BaSnO<sub>3</sub> is dominated by highly delocalized tin 5s states, leading to low electron effective mass and high electron mobility, while maintaining epitaxial compatibility with functional transition metal complex oxides [2]. This makes the alkaline earth stannate family (ASnO<sub>3</sub>, A = Ca, Sr, and Ba) ideal candidates for all-perovskite oxide heterostructures with multi-functionalities.

In this work, we focus on structural and electronic transport properties of oxygen vacancy doped BaSnO<sub>3</sub> films grown on SrTiO<sub>3</sub>(001) and MgO(001) using high pressure oxygen sputtering technique. High-resolution x-ray diffraction confirms phase-pure, epitaxial BaSnO<sub>3</sub> with (001) orientation on SrTiO<sub>3</sub>(001) and MgO(001). The out-of-plane lattice parameter obtained from wide angle x-ray diffraction is used as a sensitive probe for stoichiometry and mismatch strain. Thickness dependence of the out-of-plane lattice parameter and Scherrer length are used to understand strain relaxation of the films. High temperature, vacuum annealing of as-grown, insulating BaSnO<sub>3</sub> resulted in n-type conduction with remarkably high electron density of  $2 \times 10^{19} \text{ cm}^{-3}$ , and a maximum room temperature hall mobility of  $8 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ . The temperature dependence of resistivity and electron density suggest degenerately doped semiconducting behavior. Temperature dependent transport and magnetotransport studies will be described in detail as a function of annealing conditions, and will be correlated to the strain relaxation of BaSnO<sub>3-x</sub> films.

This work is supported by NSF through the UMN MRSEC.

[1] H. J. Kim *et al.*, Applied Physics Express **5**, 061102 (2012)

[2] H. R. Liu *et al.*, Applied Physics Letters **102**, 112105 (2013)

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P11 (S)

### **Development of the Hybrid Molecular Beam Epitaxy Approach for Stannate Oxides**

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In this presentation, we will present a detailed molecular beam epitaxy (MBE) growth study of SnO<sub>2</sub> films on r-plane sapphire as a function of tin precursor flux, oxygen pressure and substrate temperature. High-resolution x-ray diffraction and atomic force microscopy revealed single phase, epitaxial (101) SnO<sub>2</sub> films and atomically smooth surfaces (rms roughness value between 0.3 – 0.9 nm) respectively between substrate temperatures of 300 to 900 °C. Three growth regimes were identified as a function of temperature where films grew in reaction-, flux- and desorption-limited regime with increasing temperature. Further growth exploration at constant substrate temperature revealed that the growth rate first increases and then becomes constant with increasing tin precursor flux (i.e. any excess tin flux desorbs). We will discuss its implication on the growth, and structural quality of ternary stannate oxides by presenting a comprehensive growth study of SrSnO<sub>3</sub>.

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P12 (S)

**Understanding exciton energy transfer across complex interfaces using the Monte Carlo technique**

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Power conversion from solar energy in an organic photovoltaic requires photogenerated excitons to be dissociated. Exciton dissociation further requires excitons to migrate from the point of photogeneration to a donor-acceptor heterojunction where an energetic level offset provides an energy favorable dissociation mechanism. In many fluorescent organic semiconducting materials, excitons migrate to the heterojunction by a series of Förster energy transfer events. Describing the net motion of excitons with the diffusion equation is generally sufficient, but there are emerging photovoltaic architectures having complex interfaces which deny such an analytical approach. We demonstrate how an implementation of the Kinetic Monte Carlo method can model these systems with remarkable agreement. Further this agreement is obtained using in-house measured rates with zero fitted parameters. From these models we explain how the clever use of interfaces can transition exciton motion from the diffusive regime into a super-diffusive regime; excitons are dissociated faster and with greater efficiency. These benefits lead to next generation devices where exciton motion is engineered and power conversion efficiencies are enhanced.

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P13 (S)

**Highly-Stoichiometric Epitaxial SrTiO<sub>3</sub> via High Pressure Oxygen Sputter Deposition**

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SrTiO<sub>3</sub> is a wide band-gap perovskite oxide semiconductor that is widely investigated in bulk form, in part due to its remarkable electronic properties when doped. These properties arise from its quantum paraelectric nature which enables such unique features as a high-mobility low-density metallic state, quantum transport in an unusual limit, and the most dilute superconducting state thus reported. Recent progress with thin films and heterostructures of doped SrTiO<sub>3</sub> has further demonstrated record high mobilities, 2D electron gases at interfaces, and even simultaneous observation of quantum oscillations and superconductivity. Such progress has been possible only by precise control of stoichiometry and defect density in SrTiO<sub>3</sub> using techniques such as oxide/LASER MBE or high-temperature PLD. In this work, we demonstrate that high pressure oxygen RF sputtering from a ceramic target is similarly capable of growth of high-quality, precisely stoichiometric thin films of SrTiO<sub>3</sub>. By employing homoepitaxy on SrTiO<sub>3</sub>(001) substrates, we show that optimization of deposition temperature (above 750 °C), oxygen pressure (above 2.5 mBar) and deposition rate (below 2 Å/min) leads to films that are indistinguishable from the substrate *via* grazing incidence, wide-angle x-ray scattering and high-resolution transmission electron microscopy. We reiterate the importance of pre-annealing of substrates in oxygen above 900 °C to obtain such properties and eliminate interfacial scattering contrast. Detailed transport measurements on reduced films grown on a variety of substrates will be discussed, particularly for the insight they provide into the interplay between carrier mobility and structural perfection.

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P14 (S)

**Size Control of Inert Gas Condensed Iron Nanoclusters**

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Nanoclusters are an important focus of study in the scientific field because they are a step between bulk materials and the atomic scale. Nanoclusters often display size dependent properties; among these properties are a size dependent core-shell structure, and an increase in crystallinity that have been seen in previous studies. The purpose of this experiment was to determine the parameters essential to controlling the size of iron nanoclusters formed by inert gas condensation. Inert gas condensation of nanoclusters utilizes

plasma in a vacuum chamber that evaporates the iron off of a sputtering target and condenses it with an inert mixture of argon and helium. The clusters are deposited onto the substrate. This method usually produces clusters with a narrow size distribution and an average size around eight nanometers. Variable parameters include the flow rate of the argon gas, the power of the electric arc, and the pressure in source chamber. This project looked at the various production factors of the nanoclusters to try to increase the average size, while maintaining a narrow size distribution. It was concluded that higher powers and lower deposition rates produced the narrowest size distributions. A reduction of the pressure ratio between chambers was achieved by changing apertures, but there was no observable relationship between dwell time and average particle size. There was an increasing trend towards crystallinity with longer dwell times induced by the reduced pressure ratio.

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P15

**Characterization of Electro-Nanosprayed Drug Particles Suspended in a Polymer Matrix**

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Poor water solubility of drug agents is a major problem for the pharmaceutical industry. Increasing solubility is possible, however, via drug suspension in a suitable polymer. Nanocopia's patented ElectroNanospray™ (ENS) process has shown promise as a method of controlling the crystallinity and size of the drug particles in the drug-polymer blend, thereby enhancing bioavailability. Atomic Force Microscopy (AFM) is used to investigate the sprayed particles' response to humidity and localized temperature ramping. The ability to locally vary the temperature is due to the addition of a new nano-TA2 local thermal imaging and analysis package.