

Monday Morning, October 31, 2011

Nanomanufacturing Science and Technology Focus

Topic

Room: 207 - Session NM+MS+NS+TF-MoM

ALD for Nanomanufacturing

Moderator: B. Lu, AIXTRON Inc.

9:00am **NM+MS+NS+TF-MoM3 Industrialization of Atomic Layer Deposition: From Design to Deposition**, J.S. Becker, A. Bertuch, R. Bhatia, L. Lecordier, G. Liu, M. Sershen, M. Sowa, R. Coutu, G.M. Sundaram, Cambridge NanoTech, Inc. **INVITED**

The demonstrated benefits provided by Atomic Layer Deposition (ALD) in producing films of exceptional uniformity, and conformality, has set the stage for its use in large area, batch processing, and Roll-to-Roll applications. In this work we discuss the use of Computational Fluid Dynamics (CFD) as a means of gaining insight into the system performance of such industrial instruments, but also as a technique for refining system design. Additionally we describe the basic underpinnings of design for ALD systems operated under atmospheric conditions, (for Roll-to-Roll use), along with the design factors which must be considered for zone separated ALD methods. Finally we will present film results taken from a zone-separated ALD system, and discuss the salient aspects of the deposition process.

9:40am **NM+MS+NS+TF-MoM5 Improved MOS Characteristics of CeO₂/La₂O₃ and MgO/La₂O₃ Gate Stacks Prepared by ALD**, T. Suzuki, M. Kouda, Tokyo Institute of Technology and AIST, Japan, K. Kakushima, P. Ahmet, H. Iwai, Tokyo Institute of Technology, Japan, T. Yasuda, AIST, Japan

La₂O₃ is one of the candidate materials for the next-generation high-k gate stacks because it can achieve sub-1 nm EOT by forming direct-contact La silicate with Si. There have been many ALD studies for La₂O₃, however, the performance of the MOSFETs incorporating ALD-La₂O₃ needs much improvement. Our previous studies using EB evaporation showed that capping the La₂O₃ dielectrics with an ultrathin layer of CeO₂ or metallic Mg (~1 nm) effectively improved the channel mobility [1,2]. In this paper, we report fabrication of CeO₂/La₂O₃ and MgO/La₂O₃ gate stacks by ALD/CVD for the first time, and demonstrate that these stacks show improved electrical properties (k value, channel mobility, etc.) as compared to single-layer ALD-La₂O₃.

The experiments were carried out using a multi-chamber ALD/CVD system which was capable of in-situ metallization and RTA. The CeO₂/La₂O₃ and MgO/La₂O₃ gate stacks were formed on H-terminated Si(100) using Ce[OCEt₂Me]₄, La(PrCp)₃, and Mg(EtCp)₂ metal sources. La₂O₃ and MgO films were formed by ALD using H₂O as an oxidant. The ALD temperature was set at a relatively low temperature of 175°C in order to ensure the self-limiting growth [3]. CeO₂ films were formed in the CVD mode via thermal decomposition of Ce[OCEt₂Me]₄ at 350°C. The gate electrodes were formed by sputtering of W. MOSFETs were fabricated by the gate-last process.

The effective k values for the CeO₂(1nm)/La₂O₃(3nm) and MgO(0.8nm)/La₂O₃(4nm) stack capacitors were approximately 16, which was significantly larger than those for La silicate without any capping layer (k=10~12). The k-value improvement by the CeO₂ capping is presumably due to the higher k value of CeO₂ (~23), whereas the improvement by the MgO capping is ascribed to suppression of excessive La-silicate formation.

We have also found that the CeO₂/La₂O₃ gate stack leads to excellent mobility characteristics. The mobility for the MOSFET with 1.43 nm EOT was 214 cm²/Vs at an effective field of 1.0 MV/cm, which was 85% of the Si universal mobility. The mobility improvement by the CeO₂ capping is attributed to the reduced fixed-charge density, since V_{th} approached to the ideal values by the CeO₂ capping. On the other hand, the MgO capping induced a negative shift in V_{th} and consistently degraded the mobility. These effects of ALD-MgO capping are qualitatively different from those observed for EB-evaporated Mg [2]. The mechanisms causing such a difference between EB evaporation and ALD are now under investigation.

This work was carried out in Leading Research Project for Development of Innovative Energy Conservation Technologies supported by NEDO.

References: [1] T. Koyanagi, et al., JJAP, **48**, 05DC02 (2009); [2] M. Kouda, et al., 2009 VLSI Symp., p. 200; [3] K. Ozawa, et al., 2010 ICSICT, p. 932.

10:00am **NM+MS+NS+TF-MoM6 Highly Uniform and Conformal Thin Film Metallization with Thermal and Plasma-Enhanced Atomic Layer Deposition**, M. Toivola, J. Kostamo, T. Malinen, T. Pilvi, T. Lehto, C. Dezelah, Picosun Oy, Finland

Ultra-thin, nanometer-scale metal or metallic films are a crucial component in e.g. several applications of modern MEMS/NEMS (Micro/NanoElectroMechanical Systems) and other advanced IC technologies, sensors, optical devices and catalyst manufacturing. When the component sizes keep diminishing and at the same time, the level of system integration increasing (for example the so-called "System-in-a-Package" multifunctional chip devices), it creates a drive from "conventional" 2D device architecture to 3D component integration. Through Silicon Vias (TSV) are a central structure in these 3D-stacked devices and there's often a need to produce highly uniform and conformal thin films of metals or otherwise conducting materials on the insides of the vias. Due to the often very high aspect ratio (AR) of the TSV structures, Atomic Layer Deposition (ALD) is one of the only methods with which reliably uniform and conformal material layers can be deposited on the via walls.

Industrially upscalable ALD processes were developed for several metals and metallic compounds, i.e. Pt, Ir, Ru, Cu, Ag, Au, TiN and TiAlCN. Deposition of metals can be done with thermal ALD and plasma-enhanced (PEALD). The main benefits of the PEALD technique are the possibility to use reductive processes instead of oxygen, lower deposition temperatures which decreases the thermal stress on the substrates, and a wider variety of precursor chemicals.

Inductively coupled remote plasma source system was further developed to reduce any possibility of plasma damage, which can often happen in the more conventionally designed, direct plasma devices. Instead of direct ion bombardment, our plasma system utilizes highly reactive radicals. Protective flows and separating metal precursor inlets shield the plasma source from getting short-circuited by films from precursor back-diffusion. E.g. N₂/H₂, H₂/Ar, O₂ and mixed gas plasmas can be generated with the system.

Structural design solutions were optimized for ALD reactors. Top flow delivery of the precursor gases ensures even distribution of reactive molecules inside the reactor vessel. This is beneficial especially in the case of non-optimal processes with precursor decomposition or etching or poisoning of reactive sites by reaction by-products. Less impurity and thickness gradient can be achieved with the top flow, compared to the side-flow (cross-flow) design since all the area reacts at the same time leaving less reactive sites left for reaction with the by-products. Therefore, it is possible to get more challenging reaction chemistries working with the top-flow design, and also a forced flow for through-porous samples is possible. With modified stopped flow design, extended reaction time inside the chamber can be reached while still keeping the protective flows from the inlets on to prevent any back-diffusion of precursor and subsequent particle formation in the inlet lines.

Upscalable structure was specifically designed to bridge the gap between R&D and production. Smaller ALD tools can be used for process and chemical precursor development at for universities and research labs, whereas the larger, ALD tools can be fully automatized, upscaled and clustered into full scale high volume throughput industrial production unit capable of coating even several thousands of wafers per hour.

10:40am **NM+MS+NS+TF-MoM8 Atomic Layer Deposition for Continuous Roll-to-Roll Processing**, S.M. George, P.R. P. Ryan Fitzpatrick, University of Colorado at Boulder **INVITED**

Atomic layer deposition (ALD) is currently being developed for continuous roll-to-roll processing. This development is significant because roll-to-roll processing would allow ALD to address many applications in a cost effective manner. This talk overviews the approaches and progress to date. The original idea of ALD with moving substrates and constant precursor flows was presented in a patent by Suntola and Antson in 1977. This scheme involved rotating the substrate between alternating precursor sources and vacuum pumping regions. One current approach under development is based on moving the substrate close to a gas source head. The ALD precursors continuously flow through slits in the gas source head that are separated and isolated by inert gas purging. A second version of this design involves using a gas bearing to set the gap spacing between the gas source head and substrate. Another ongoing approach is based on moving the substrate through separate regions of precursor pressure and inert gas purging. Limited conductance between the regions prevents the gas phase reaction of the ALD precursors. The talk examines the issues and prospects for achieving ALD for continuous roll-to-roll processing. Additional details

are presented for the dependence of precursor isolation on reactor parameters for a substrate under a model gas source head.

11:20am **NM+MS+NS+TF-MoM10 High Rate Continuous Roll-to-Roll Atomic Layer Deposition**, *E. Dickey*, Lotus Applied Technology **INVITED**

Atomic Layer Deposition (ALD) is a unique thin film deposition process, capable of producing coatings with unmatched quality and performance. Its unique attributes include high conformality and outstanding thickness precision, enabling the deposition of dense, continuous pinhole-free films, even when extremely thin, and even on highly imperfect substrate surfaces. These qualities have made the process attractive for applications on flexible substrates, including dielectrics and semiconductors for flexible electronics devices, and high performance gas diffusion barriers to encapsulate and protect environmentally sensitive devices such as OLED displays and lighting, and CIGS photovoltaic modules.

Until recently, ALD films have generally been deposited using conventional static processing, in which the individual precursors are sequentially introduced into and purged from a common volume containing the stationary substrate. This sequence, commonly called an ALD cycle, typically requires at least several seconds and results in the growth of approximately 0.1nm thickness. As a result, the time required to deposit films of reasonable thickness can be quite long. Furthermore, the static nature of the process makes roll-to-roll processing impractical. In this presentation, we discuss the development of a new ALD process based on substrate translation, with the ALD cycle elements enabled by transport of the flexible substrate back and forth between the precursor zones. Because no time is required for introducing, saturating, and removing precursors for each cycle, the deposition speed is dramatically increased. In addition, this configuration naturally provides the unique feature of film deposition only on the substrate itself, as it is the only surface which is exposed to both precursors. In turn, this allows the use of steady-state plasma as the oxygen source, enabling a new technique of precursor isolation; "precursor separation by radical deactivation", in which the oxygen gas precursor actually mixes with the metal precursor, but is only reactive in the region of the plasma source. Together, this technology set has allowed the deposition of high quality ALD films on polymer substrates, including ultra-barrier films, at substrate speeds in excess of one meter per second.

Nanometer-scale Science and Technology Division

Room: 203 - Session NS+EM-MoM

Nanowires and Nanoparticles I: Assembly and Devices

Moderator: M. Hines, Cornell University

8:20am **NS+EM-MoM1 ZnO Nanowire Logic Inverter with the Difference of Two Gate Electrode**, *J.K. Kim, Y.T. Lee, R. Ha, H.J. Choi, S.I. Im*, Yonsei University, Republic of Korea

Recently, zinc oxide nanowires (ZnO NWs) have attracted much attention for high mobility and sensing properties. These advantageous give us strong possibility to use nanostructures as nanoelectronic device application; such as field effect transistors (FETs), diodes, and logic circuit devices.[1] In this work, we fabricated the logic circuit inverter using difference of gate electrodes which have the different work function.[2]

In order to fabricate the inverter devices, grown ZnO NWs were dispersed to the SiO₂/Si substrate by using a drop-and-dry method. The Ni/Ti source and drain electrodes were deposited by e-beam evaporator with a combination of photo-lithography and lift-off process. To make 30nm-thick Al₂O₃ gate insulator layer, we used Atomic Layer Deposition (ALD) system. And then, Pd and Ni/Ti top gate electrodes were deposited and these two devices were connected by wire bonding technique.

The threshold voltage of the Pd top gate ZnO NWs FET shows more positive value (~ 0 V) than that of the other FET (~ -1 V) with Ni/Ti top gate, and these transistors are able to be used as a driver and a load, respectively. The linear mobility of the driver shows about 119 cm²/Vs at V_D = 0.6 V and the inverter device has high gain value of ~15 at V_{DD} = 5 V. Furthermore, the dynamic property of the logic inverter was measured under the 5 V square input voltages.

More details will be discussed in the meeting.

References

1. G.J, W. K. Hong, J.S. Maeng, M.H. Choe, W.J. Park, and T. K. Lee, *Appl. Phys. Lett.* **94** 173118 (2009)
2. K.M. Lee, J.H. Kim and S.I. Im, *Appl. Phys. Lett.* **88**, 023504 (2006)

8:40am **NS+EM-MoM2 Control of Growth Kinetics for Three-Dimensional III-nitride Nano-Heterostructures Towards Nanowire Devices**, *S.D. Carnevale, P.J. Phillips, T.F. Kent, J. Yang, M.J. Mills, R.C. Myers*, Ohio State University

The geometry of semiconductor nanowires (NWs) allows for both vertical and coaxial heterostructures, while only vertical heterostructures can be formed using planar structures. This is especially important for III-nitride NWs because crystallographic directions in which heterostructures are formed largely determine the magnitude of internal electric fields due to polarization. Here we describe a method to control the relative vertical and coaxial growth rates in catalyst-free GaN/AlN NW heterostructures grown on Si(111) substrates by plasma-assisted molecular beam epitaxy*.

A growth phase diagram is established relating NW density to substrate temperature and III/V ratio. This diagram reveals a reduction in effective growth rate and an increase in nucleation time caused by GaN decomposition. Using this information, a two-step method is developed to independently control NW density from NW deposition time. To begin we nucleate NWs until a small but appreciable density is reached. If deposition continues under these conditions, density will increase over time until reaching a saturation point. To suppress this increase, substrate temperature is increased upon completion of the initial nucleation time. NWs already nucleated continue to grow, but there is no new nucleation, thus controlling density. Additionally, the change in conditions alters growth kinetics, leading to purely vertical NW growth, which allows for the formation of NWs with arbitrarily large aspect ratios and small diameters (~20 nm). Kinetics that favor coaxial growth are also achieved. A low density, high aspect ratio NW array is prepared using the method described above then material is deposited at a lower substrate temperature. The relative coaxial growth rate increases due to lower Ga ad-atom mobility at the lower substrate temperature. Using this dynamic method, we demonstrate multiple period GaN/AlN (2 nm / 2 nm) superlattices along either the vertical or coaxial NW axis, which exhibit atomically sharp compositional profiles. A coaxial, AlN/GaN resonant tunneling diode structure is presented. Large areas of nanowires are processed for electrical measurements without removing them from the Si(111) substrate. Preliminary electrical measurements are provided for both room temperature and low temperature conditions. This work is supported by the ONR under grant N00014-09-1-1153.

* S.D. Carnevale, J. Yang, P.J. Phillips, M.J. Mills, and R.C. Myers. "Three-Dimensional GaN/AlN Nanowire Heterostructures by Separating Nucleation and Growth Processes". *Nano Letters* 11, 2, pp. 866-871, Jan. 2011.

9:00am **NS+EM-MoM3 III-V Nanowire MOSFETs**, *L-E. Wernersson*, Lund University, Sweden **INVITED**

III-V Nanowire transistors are considered possible candidates to extend the transistor scaling roadmap. The improved electrostatic control in the cylindrical geometry provides benefits for scaling and the advantageous transport properties of the III-V materials may be used to increase the drive current. Besides heterostructure design may be used to tailor the properties in the transistor channel.

In this talk, we will review some of the efforts made in Lund to realize high-performance III-V nanowire transistors using vertical nanowires grown by MOVPE. We will show how bottom-up technologies can be combined with top-down processing to realize nanowire-based RF-devices on Si 2" wafers. We use CV techniques to characterize the properties of the high-k material in vertical nanowire capacitors and compare the data to the 1/f-noise characteristics of scaled transistors to evaluate the influence of the high-k material on the transistor performance. We also show that the transistor channel may be reduced down to a diameter of 15 nm without degradation of the transport properties. Finally, we explore the use of novel materials in the transistor structures as we developed GaSb/InAs heterostructures with excellent Esaki diode characteristics to be used for TFET implementations.

9:40am **NS+EM-MoM5 Optimizing Quantum Efficiency in Quantum Dot Display**, *S.J. Lim, J. Kwon, Y. Oh*, Seoul National University, Republic of Korea, *B.L. Choi, K. Cho*, Samsung Advanced Institute of Technology, Republic of Korea, *Y. Kuk*, Seoul National University, Republic of Korea

In our previous study, we were able to fabricate full-color, 4-inch display made of colloidal quantum dot (QD). Despite such a demonstration of QD light emitting device which is one of candidates for next-generation display, understanding the interface characteristics between QD layer and electron (or hole) accumulation layer is still lacking and further study for improvement of quantum efficiency is essential. Here, we report on a study

of scanning tunneling microscopy (STM), spectroscopy (STS) and cathode luminescence induced by tunneling current, performed on individually manipulated QD. We control the distance between two QDs using STM to reveal the mechanism of interaction between QDs. STS measurement showed shift of energy levels as manipulating the distance between two QDs. This result suggests that there exists the optimal distance between QDs for efficient light emission. Besides by making contacts between separated QDs and organic molecules, we simulated contacts between QD layer and electron (or hole) accumulation layer. From these experiments, we could understand excitonic behavior and carrier hopping from QD to QD or surrounding materials. Our findings thus suggest optimal configuration for QD application in display.

10:00am **NS+EM-MoM6 Polarization Engineered 1-Dimensional Electron Gas**, *D.N. Nath, P.S. Park, M. Esposito*, Ohio State University, *D. Brown, S. Keller, U.K. Mishra*, University of California Santa Barbara, *S. Rajan*, Ohio State University

One-dimensional electron gas (nanowire) based devices are of great interest due to their promise in high-performance electronics and other future device applications. However, synthesis and patterning of arrays of nanowires is a challenge in all material systems since both bottom-up and top-down approaches have their own merits and demerits.

Here we report on the demonstration of pure 1-dimensional arrays of electrons with current density up to 130 mA/mm and carrier confinement greater than 100 meV using lateral polarization engineering in N-polar vicinal AlGaIn/GaN heterostructures. The width of the atomic terraces characteristic of vicinal surfaces defines the dimensions of the nanowires which are found to exhibit sharp and clear signatures of 1-dimensionality at room temperature making them promising for novel device applications.

We report on devices fabricated on MOCVD grown N-polar AlGaIn/GaN HEMT structures on vicinal sapphire substrate (4° miscut towards a-plane) with anisotropy in current and channel pinch-off voltages. Channels parallel to the miscut direction pinched off at higher negative gate biases than those perpendicular to the steps and carried more charge as measured by direction-dependent C-V profiling. An electrostatic model which predicts a saw-tooth energy band profile in the lateral direction has been proposed to explain the charge anisotropy. Each atomic terrace characteristic of the surface morphology of vicinal GaN with its corresponding saw-tooth energy profile is proposed to exhibit quasi-1D confinement. We will discuss the heterostructure/polarization design of structures demonstrating pure 1-D transport in direction parallel to steps.

Gated structures were fabricated to investigate the physics of the system as the Fermi occupation function is varied by varying gate bias. To confirm that the carriers are indeed 1-dimensional, we used direction-dependent small-signal capacitance voltage measurements to probe the density of state function and hence dimensionality of electrons as a function of gate bias. We developed a 2-band model consisting of one 1-D and one 2-D subband to describe the behavior of these wires at room temperatures. The variation of capacitance as well as charge density for a pure 1-D and a pure 2-D system as a function of applied gate bias as predicted by our 2-band model based on density of states matches very well with the data measured experimentally for 1-D and 2DEG respectively. This confirms that the channels created are indeed 1-dimensional in nature. Since 1-D channels are atomic terrace defined, they are promising for eliminating the disadvantages of both bottom-up and top-down approaches.

10:40am **NS+EM-MoM8 Adding New Capabilities to Silicon CMOS via Deterministic Nanowire Assembly**, *T.S. Mayer, M. Li, T. Morrow, J. Kim, B. Won, K. Sun, X. Zhong, K. Liddell, J.S. Mayer, C.D. Keating*, Penn State University

INVITED

Integrating functionalized nanowires directly onto Si CMOS chips has the potential to combine highly selective and sensitive chemical and/or biological sensing capabilities with electronic signal processing in a single ultra compact, low power platform. Conventional integrated circuit manufacturing methods place considerable limits on the range of and number of different materials and molecules that can be incorporated onto Si chips, making it difficult to realize this goal. This talk provide an overview a new deterministic assembly approach that uses electric field forces to direct many different types of bioprobe-coated nanowires to specific regions of the chip and to provide accurate registration between each individual nanowire and a specific transistor on the chip. This is achieved by synchronizing sequential injections of nanowires carrying different bioprobe molecules with a programmed spatially-confined electric field profile that directs nanowire assembly. Subsequent back-end lithographic and metal deposition processes are then used to electrically and mechanically connect all of the nanowire devices to the Si chip at the same time. Using this technique, individual nanowire device integration yields exceeding 90% have been demonstrated with a less than 1% mismatch across three populations of DNA-coated nanowires for arrays with densities

of 106 cm⁻². The nanowire-bound DNA retained its ability to selectively bind complementary target strands following assembly and device fabrication showing that this process is compatible with these back-end manufacturing steps. The uniformity in the electrical properties of nanowire device arrays that were fabricated using this hybrid integration strategy will also be discussed.

11:20am **NS+EM-MoM10 Solid-State Dewetting of Direct Nanoimprinted Metallic Thin Films**, *R. Clearfield*, North Carolina State University, *J.D. Fowlkes*, Oak Ridge National Laboratory, *P.D. Rack*, University of Tennessee Knoxville, *N. Samatova*, Oak Ridge National Laboratory, *A.V. Melechko*, North Carolina State University

Heat applied to thin films below a critical thickness will generally cause transformation of the film into isolated particles. This process is known as dewetting. Solid state dewetting occurs below the melting temperature of the film and is governed by diffusive mass transport. Currently two mechanisms of dewetting are distinguished: hole nucleation and growth, and spinodal dewetting. Spinodal dewetting proceeds via film surface undulations that have characteristic wavelengths related to the thickness of the film. Lithographic patterning of thin films has been utilized to direct the dewetting instability development toward designed nanostructured geometry of nanoparticle arrays. Tailoring the geometry of thin film edge have been shown to affect both heterogeneous nucleation and spinodal dewetting regimes. Nanoimprint lithography, conventionally used for definition of the edges of thin films, is a fabrication method where a stamp is pressed into a thin normally monomer or polymer film at elevated temperatures. Nanoimprinting can also be conducted in direct mode where the stamp is pressed into a metallic film. Surface undulations characteristic for spinodal dewetting will be used to direct the stamp design. Such imprinting allows setting initial conditions, programming instability, in the thin metallic film that is linked to the spinodal surface instability. In this work we are presenting the results of the investigation into behavior of thin films in which a 3D structure has been imprinted. We present observations on the effect of direct nanoimprint lithography on nanoscale Au and Ni films using periodic arrays of cylinders. Our focus is on the spatial distribution of the particles produced from dewetting of the nanoimprinted films. Particles in patterned regions are characterized in terms of their spacing, periodicity and size, and shape. The geometry of the dewetted patterns is compared to that of the 3D features created after direct nanoimprinting of the films. Analysis of spatial correlation of the final dewetted patterns to stamp patterns is presented.

Monday Afternoon, October 31, 2011

Electronic Materials and Processing Division

Room: 209 - Session EM1-MoA

Group III-Nitrides and Hybrid Devices

Moderator: K. Kavanagh, Simon Fraser University, L.

Porter, Carnegie Mellon University

2:00pm **EM1-MoA1 Electrically-Monitored Gate-Recess for Normally-Off AlGaIn/GaN High-Electron Mobility Transistors**, *H. Kim, M. Schuette, W. Lu*, The Ohio State University

GaN-based power devices have been intensively investigated for high power switching applications as well as high power microwave applications. Particularly, high breakdown voltage and high saturation velocity of GaN-based heterostructures facilitate reduction in on-state loss and switching loss compared to currently dominant Si-based power devices. Moreover, normally-off GaN-based power field-effect transistors (FETs) offer their inherent safety, reduced power consumption, and diverse circuit functionality with normally-on ones. Recently, we developed a zero-bias Cl-based dry etching process to thin AlGaIn barrier with a minimal damage for enhancement-mode AlGaIn/GaN FETs. However, it has been difficult to control gate-recess process for normally-off GaN-based FETs due to strong polarization effects. Namely, 1 nm under- or over-etchings near the critical AlGaIn barrier thickness where the channel is pinch-off result in a negative threshold voltage (V_T) or a degraded transconductance (G_m), respectively. In this work, we report a methodology to control our Cl-based gate-recess for both positive V_T and high $G_{m,MAX}$ by relating electrical properties of the gate-recessed area before gate metallization to V_T and G_m in AlGaIn/GaN FETs.

Gate-recessed AlGaIn/GaN FETs were fabricated through fast etching with BCl_3 and slow etching with $\text{Cl}_2/\text{N}_2/10\%-\text{O}_2$ to thin AlGaIn barrier. The slow etching runs under inductively-coupled plasma mode only to minimize the damage. For monitoring purpose, resistance at 0 V (R_{0V}) and drain-to-source current ($I_{D,SAT}$) at 10 V between source and drain contacts were measured before gate metallization to correlate with V_T and G_m after gate metal deposition.

I_D-V_{GS} , G_m-V_{GS} , and capacitance-voltage characteristics of gate-recessed FETs with different AlGaIn thicknesses by doing $\text{Cl}_2/\text{N}_2/10\%-\text{O}_2$ etching for different times were measured and V_T values were extracted by linear extrapolation at $G_{m,MAX}$. V_T and $G_{m,MAX}$ were correlated with the monitoring parameters of R_{0V} or $I_{D,SAT}$. V_T and $G_{m,MAX}$ distributions with R_{0V} or $I_{D,SAT}$ guide us for monitoring as well as design of gate-recess process. For example, a recessed FET showing $R_{0V} = 1700 \text{ W}$ with 7 nm AlGaIn barrier exhibits V_T of 0.56 V and $G_{m,MAX}$ of 300 mS/mm. In addition, our recess process offers sufficiently long monitoring time (at least 4 minutes) to tune the gate recess for target V_T together with high $G_{m,MAX}$. Based on the distribution, the necessity of tuning process is determined and its progress is monitored by R_{0V} or $I_{D,SAT}$ before gate metallization until target R_{0V} or $I_{D,SAT}$ is met. Our electrically monitoring method allows gate recess process to be well-controlled for target V_T and $G_{m,MAX}$.

2:20pm **EM1-MoA2 Atom Probe Tomography Studies on Green Light Emitting InGaIn/GaN Multi Quantum Wells Grown on GaN Substrates**, *F. Liu, L. Huang*, Carnegie Mellon University, *S.V.N.T. Kuchibhatla, D.K. Schreiber*, Pacific Northwest National Laboratory, *M. Zhang*, University of Michigan, *E.A. Preble, T. Paskova, K.R. Evans*, Kyma Technologies, Inc., *L. Porter, R.F. Davis*, Carnegie Mellon University

Carrier delocalization in InGaIn/GaN multi-quantum wells (MQW) contained within green light-emitting diodes (LEDs) has been proposed as a contributor to LED efficiency droop. By contrast, interface roughness and fluctuations in composition within the MQWs may act to localize and confine carriers¹. In this study, InGaIn/GaN MQWs were grown on both (0001)GaN layers and on $\text{In}_x\text{Ga}_{1-x}\text{N}$ buffer layer with graded In mole fractions from 0 to 10%. Both heterostructures were grown on chemomechanically polished (0001)GaN substrates. Calculations using temperature-dependent photoluminescence spectra revealed a four-fold increase in the internal quantum efficiency (IQE) in the latter structure. A LEAP 4000X HRTM pulsed UV laser (355 nm at 200 kHz) atom probe tomograph was used to investigate the elemental and spatial characteristics of the interface of the $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$ MQWs. To establish consistent atom probe operation parameters for reliable comparison among different samples, a systematic study was conducted to optimize the evaporation rate and laser energy. The concentration profile of $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$ MQW showed slightly varied In fraction among different QWs, ranging from $x=0.21$ to $x=0.27$, while the XRD results showed an average In fraction in all QWs of $x=0.25$. Furthermore, based on isoconcentration surface analysis and proximity histograms the upper surfaces of InGaIn QWs appear to be

more diffuse than the lower surfaces. These results indicate surface roughening of the InGaIn layer. A detailed comparison of the two structures will be presented and the ability of 3-D atom probe tomography for such an analysis and the impact of the results on next generation LED technologies will be discussed.

1. J. Hader, J. V. Moloney and S. W. Koch, Appl. Phys. Lett. **96** (22), 221106 (2010).

2:40pm **EM1-MoA3 Local Surface Electrical Characterization of Polar GaN Surfaces**, *J.D. Ferguson, M.A. Reshchikov, A.A. Baski*, Virginia Commonwealth University

While GaN is a widely-used material in optoelectronic devices, localized surface-related electrical properties are not well-understood. These properties affect the operational performance and lifetimes of GaN-based devices. Here, several atomic force microscopy (AFM) techniques were used to characterize the Ga-polar, +c [0001], and N-polar, -c [0001bar], surfaces of free-standing bulk GaN. Samples were prepared by either a chemical-mechanical polish (CMP) or mechanical polish (MP) of HVPE-grown GaN. AFM data showed that the Ga-polar surfaces (MP and CMP) were uniformly flat with rms roughness of less than 1 nm over a 5x5 micron image. In contrast, the N-polar surfaces were significantly rougher (~5 nm rms) with scratch-like features (100 nm wide, microns long), where the CMP treatment resulted in the presence of surface protrusions (~100 nm dia.) in proximity of the scratches. We then examined the local electrical properties using conducting AFM (C-AFM) to map surface conductivity and to obtain I-V spectra. C-AFM images at forward-bias (<6V) showed small contrast variations for all samples except the N-polar CMP surface. In that case, we observed less conducting behavior on the protrusions as compared to the surrounding surface. Local I-V data also revealed a higher forward-bias, turn-on voltage for the N-polar vs. Ga-polar samples. To investigate the local surface charging behavior, we used a two-step technique. First, a metallized AFM tip was used to locally charge the surface by applying a DC voltage, and then the resulting change in surface potential was monitored as a function of time with scanning Kelvin probe microscopy (SKPM). These surface charging data showed a smaller change in surface potential for the N- vs. Ga-polar samples, which appears to be consistent with the lower onset of conduction for the N-polar orientation. Finally, we measured the photo-induced changes in surface potential under UV light exposure (100W Hg lamp), otherwise known as the surface photovoltage effect (SPV). The N-polar samples had a smaller SPV compared to Ga-polar, which indicates a smaller amount of band bending at the surface. Additionally, N-polar GaN restored to dark-state conditions at a much faster rate, regardless of CMP or MP treatment. In summary, we observed differences in morphology and electrical behavior for the two polar, c-plane GaN surfaces, as well as differences in behavior due to CMP and MP treatments. These data suggest a less pronounced surface charging behavior on N-polar vs. Ga-polar GaN.

3:00pm **EM1-MoA4 The Effect of Ammonia - TMI Pulse Separation on the Structural Properties of InN Epilayers**, *R. Atalay*, Georgia State University, *M. Buegler*, Technische Universität Berlin, Germany, *S. Gamage, I. Senevirathna, A.G.U. Perera*, Georgia State University, *J.S. Tweedie, R. Collazo*, North Carolina State University, *N. Dietz*, Georgia State University

Over the last decade, significant research efforts have been devoted to understand and improve the properties of InN epilayers. However, even today, there is a significant lack of an understanding of the InN surface and growth chemistry and its affect on the physical bulk properties. Crucial challenges in the growth of InN epilayers are the vast different partial pressures between indium and nitrogen and associated fragments of the utilized precursors trimethylindium (TMI) and ammonia (NH₃).

In this work, high-pressure chemical vapor deposition (HPCVD) is employed and explored in order to control and suppress the disassociation of InN alloys at higher growth temperatures. In order to reduce gas phase reactions and to control the surface chemistry, a pulsed precursor injection approach has been implemented, which provides additional process control parameters for the optimization of the physical epilayers properties.

In the pulsed precursor injection approach, the precursor separation times between the metal organic (MO) sources (TMI and TMG) and ammonia (S1), and ammonia and MO (S2) are two critical process parameters.

This contribution will present results on how the precursor separation times between the TMI and ammonia (S1) and ammonia and TMI (S2) affect the structural and optical properties of InN epilayers grown on GaN/sapphire

templates and/or sapphire substrates. In this study, the separation times S1 and S2 have been varied from 1000 to 2500 ms and 250 to 500 ms, respectively. The results show that a longer S1 separation of around 1700 ms and short S2 separation of around 360 ms provide the best structural properties of InN epilayers.

The InN epilayers have been analyzed by Raman scattering, X-ray diffraction, IR reflection, and transmission spectroscopy. The Raman studies showed that the lowest FWHM of E2(high) vibrational mode with about 8 cm⁻¹ for a S2 separation time of 358 ms. XRD 2 θ - ω scans on these InN epilayers and the analysis of the InN (0002) Bragg reflex confirm the improved structural properties for the optimized S2 separation.

3:40pm EM1-MoA6 Neutron Scattering Provides a New Model for Optimal Morphologies in Organic Photovoltaics: Rivers and Streams, M. Dadmun, W. Yin, University of Tennessee, J. Ankner, K. Xiao, Oak Ridge National Laboratory

Organic Photovoltaics (OPVs) have attracted increasing interest as a lightweight, low-cost and easy to process replacement for inorganic solar cells. Moreover, the morphology of the OPV active layer is crucial to its performance, where a bicontinuous, interconnected, phase-separated morphology of pure electron donor and acceptor phases is currently believed to be optimal. In this work, we use neutron scattering to investigate the morphology of a model OPV conjugated polymer bulk heterojunction, poly[3-hexylthiophene] (P3HT) and surface-functionalized fullerene 1-(3-methyloxycarbonyl) propyl(1-phenyl [6,6]) C₆₀ (PCBM). These results show that P3HT and PCBM form a homogeneous structure containing crystalline P3HT and an amorphous P3HT/PCBM matrix, up to ca. 20 vol% PCBM. At 50 vol% PCBM, the samples exhibit a complex structure containing at least P3HT crystals, PCBM crystals, and a homogeneous mixture of the two. The 20 vol% PCBM samples exhibit behavior consistent with the onset of phase separation after 6 hours of thermal annealing at 150 °C, but appears to be miscible at shorter annealing times. This suggests that the miscibility limit of PCBM in P3HT is near 20%. Moreover, for the 50 vol% PCBM sample, the interface roughens under thermal annealing possibly owing to the growth of PCBM crystals. These observations suggest a different morphology than is commonly presented in the literature for optimal bulk heterojunctions. We propose a novel 'rivers and streams' morphology to describe this system, which is consistent with these scattering results and previously reported photovoltaic functionality of P3HT/PCBM bulk heterojunctions.

4:20pm EM1-MoA8 Novel Boron Carbide-Based Semiconducting Polymers for Enhanced Electronic Properties, F. Pasquale, J. Kelber, University of North Texas

We report the controlled modification of valence band electronic structure of semiconducting boron carbides with sharply narrowed band gap, by combination of 1,4-diaminobenzene (DAB) with orthocarboranes to form a novel boron-carbide based semiconducting film. Semiconducting boron carbide films (B₁₀C₂H_x) and related materials formed from crosslinking of carborane icosahedra are of rapidly increasing interest in neutron detection, nanoelectronics, spintronics, and even conventional CMOS ULSI applications. The ability to modify the material's electronic structure in a controlled manner is of obvious interest in all these areas. We report x-ray and ultraviolet photoelectron spectra (XPS, UPS), demonstrating that electron-induced cross-linking of carborane and DAB results in a novel semiconductor with a significantly enhanced valence band density of states near the Fermi level, resulting in a shift, as determined by UPS, in the valence band maximum from ~ 4.3 eV to ~ 1.7 eV below the Fermi level. Importantly, this effect is relatively insensitive to total film thickness and for DAB/orthocarborane atomic ratios (determined by XPS) ranging from 1:4 to 1:1. Films were formed by condensation and cross-linking of alternating layers of orthocarborane and DAB precursors under ultrahigh vacuum (UHV) conditions, allowing precise control of relative DAB and carborane concentrations. This procedure also yielded films of systematically varied DAB/carborane concentration and film thicknesses between 20 Å and 100 Å average thickness, as determined by attenuation of Cu(2p_{3/2}) photoemission intensity from the substrate. The films exhibited shifts in the valence band spectra of ~ 0.2 eV to lower binding energies upon cross-linking, indicating a surface photovoltage effect, and the formation of a true *p*-type semiconducting film. The results demonstrate formation of a new semiconducting material based on carborane icosahedra but modified by the addition of an organic species. These data further indicate the potential for the development of a broad range of novel boron carbide-based polymers using carboranes and other organic additives, with film formation by a variety of methods, including photon or electron bombardment, or plasma-enhanced chemical vapor deposition.

4:40pm EM1-MoA9 Analysis and Application of Hybrid Electronic Structures Formed by Nanoscale Conductive Coatings on Textiles, J.S. Jur, W. Sweet, C.J. Oldham, G.N. Parsons, North Carolina State University

Electronic functionalization of complex fibrous systems is of interest for developing new hybrid electronic systems geared toward integrating biological detection and energy harvesting devices in textile materials. Reliable methods to evaluate the electrical properties of these textiles are necessary for future device design and performance improvement. This work investigates conformal, nanoscale coatings of zinc oxide and tungsten produced by atomic layer deposition (ALD) on natural and synthetic fibers structures, resulting in novel hybrid-based electronic structures. A modified 4-probe test method is introduced to evaluate the effective conductivity of these coatings. An applied normal force orthogonal to the current and field direction improves the fiber/fiber contact, resulting in consistent evaluation of the effective conductivity of the coatings across fiber systems and is a unique method of evaluating the mechanical behavior of these coated fiber structures. Optimization of the coatings has resulted in conductivity values as high as 40 S cm⁻¹ for zinc oxide coatings (~75 nm) on polypropylene and cotton fiber, as well as 1150 S cm⁻¹ for ALD tungsten (~50 nm) on quartz fiber matrices. Device application of these coated fiber matrices are benefited by their "all-fiber" structure, with characteristic high porosity and surface area. For example, a textile-based flow-through metal-insulator-metal capacitors fabricated from tungsten-coated quartz fibers is shown as an application in liquid chemical sensing. The mechanisms related to electron transport in a surface-coated textile fabric and implications on device fabrication and improvement will be discussed.

5:00pm EM1-MoA10 Quantum Dot Transfer using Patterned Self-Assembled Monolayers, S. Miller, A.J. Muscat, University of Arizona

Nano particles such as light emitting quantum dots offer many exciting new possibilities for device manufacturing. Along with the potential for low cost manufacturing, the ability to make quantum dot based solar cells and LEDs, has lead to the potential to make arrays of light detectors and nanometer scale patterned LEDs. Using two such devices together results in an optical switch, which may be employed in computer processing as a fast memory readout device. In addition ROM memories can be created using direct patterning of light emitting quantum dots on a disk. Because quantum dots of different size emit different wavelengths it is possible to code data in several wavelengths allowing the data from each wavelength to be written in the size limited area of focused light, dramatically increasing data storage. Many of the potential devices which can be made using nano particles require precise control over nano particle placement and layer thickness. We have found that it is possible to control quantum dot placement using a patterned self-assembled monolayer (SAM). Due to the hydrophobic properties of octadecyltrichlorosilane (OTS) it is possible to form an OTS SAM on which quantum dots will not deposit. This SAM layer can then be patterned using one of several methods. One approach is to use direct UV light exposure in air through a shadow mask, this will remove the OTS SAM in the open areas of the mask, allowing for quantum dot deposition to occur only in the open areas. OTS SAMs can also be formed on pre-made chemical patterns. Ultra high resolution patterns can be formed using nano-lithography including conductive atomic force microscopy, STM, and EBL. Arrays of conductive atomic force microscope tips can be used to pattern repeated patterns such as those required for detectors. Quantum dots or an alternate SAM can then be deposited directly into the open pattern areas. However, because of the time required for nano-lithography, it is desirable to use the patterned OTS SAM as a nano particle master stamp, where the quantum dots are transferred from the patterned OTS surface to a surface which chemically binds them. A self-assembled monolayer such as APTMS can be used to bind the quantum dots and remove them from the master patterned stamp, allowing the patterned OTS SAM to be repeatedly filled with quantum dots and stamped. This has been demonstrated using CdTe quantum dots with TGA ligands; however, there are a variety of nano particles with which this technique will work. Therefore by creating a patterned SAM and utilizing selective deposition and appropriate transfer chemistry it is possible to open a new realm of potential device manufacturing.

5:20pm EM1-MoA11 Solution Processed Quantum Dots for Infrared Imaging, J. Lewis, E.J.D. Klem, C. Gregory, G. Cunningham, D. Temple, RTI International

While InGaAs-based focal plane arrays (FPAs) provide excellent detectivity and low noise for short wave infrared (SWIR) imaging applications, wider scale adoption of systems capable of working in this spectral range are limited by high costs, limited spectral response, and costly integration with Si readout circuits (ROICs). RTI has demonstrated a novel photodiode technology based on a heterojunction between IR-absorbing, solution-processed PbS colloidal quantum dots (CQD) and C₆₀ fullerenes that can overcome these limitations of InGaAs FPAs. We have fabricated devices with quantum efficiencies exceeding 50%, and detectivities greater than

10¹² Jones, that are competitive with the performance of InGaAs photodiodes. Dark currents of ~2 nA/cm² were measured at temperatures compatible with solid state cooling. Additionally, by processing these devices entirely at room temperature we find them to be compatible with monolithic integration onto ROICs, thereby removing any limitation on device size. We will show early efforts towards demonstrating a direct integration of this sensor technology onto a Si ROIC IC and describe a path towards fabricating sensors sensitive from the visible to 1700 nm at a cost comparable to that of CMOS based devices. This combination of high performance, dramatic cost reduction, and multispectral sensitivity is ideally suited to expand the use of SWIR imaging in current applications, as well as to address applications which require a multispectral sensitivity not met by existing technologies.

Energy Frontiers Focus Topic

Room: 103 - Session EN+EM+NS-MoA

Nanostructured Materials for Third Generation Solar Cells

Moderator: W.A. Tisdale, Massachusetts Institute of Technology

2:00pm EN+EM+NS-MoA1 **Fabrication of Two-dimensional Array of Sub-10nm GaAs Nanodisk using Bio-template Neutral Beam Etching Process.** S.-H. Lin, X.-Y. Wang, C.-H. Huang, Y. Ohno, M. Igarashi, Tohoku University, Japan, A. Murayama, Hokkaido University, Japan, S. Samukawa, Tohoku University, Japan

Recently, 3-dimensional (3D) or 2-dimensional (2D) quantum dot superlattice are widely investigated to develop the new generation devices, such as quantum dot solar cell. Quantum dot superlattice consists of quantum dots with lower band gap energy in the matrix with higher band gap energy. For the device application, the structure requires high QD density, periodic QD array and uniform dot size and inter-dot spacing. Molecular beam epitaxy (MBE) and Metal-organic chemical vapor deposition (MOCVD) are two attractive methods among various bottom-up fabrication methods to fabricate quantum dots. However, there is limitation of bottom-up process to control the size, spacing and density of quantum dots. To breakthrough these problems, we have proposed the ultimate top-down process by combination of bio-template and damage-free neutral beam etching (NBE) for fabricating defect-free 2D array of quantum dots.

In this study, we developed a series of novel process for fabricating uniform size and high density 2D array of GaAs nanodisk with uniform inter-dot-spacing. Firstly, the hydrogen-radical treatment was used to remove the native oxide on GaAs surface. To utilize two-dimensional array of ferritin (protein including 7-nm-diameter iron core) as an etching mask, the formation of a hydrophilic 1-nm thick GaAs neutral beam oxidation film is key point. It is found that protein shell can be removed with oxygen-radical treatment at a low temperature of 280°C without thermal damage to GaAs. After protein shell removal, the iron oxide cores inside the ferritins remained on the surface. Then, using the iron core as an etching mask, neutral beam could etch the defect-free nanodisk structure of GaAs. Finally, we developed that iron oxide core was removed by wet etching with diluted hydrogen chloride and completed a fabrication process without inflicting any damage to GaAs. The result shows the quantum dot superlattice structure with a two-dimensional array of GaAs quantum dots with a diameter of ~7-nm, a height of ~10-nm, and a quantum dot density of more than 7×10¹¹cm⁻² was successfully demonstrated without any damage to GaAs.

This work is supported by the Core Research of Evolutional Science and Technology (CREST) of Japan Science and Technology Agency (JST).

2:40pm EN+EM+NS-MoA3 **Solution Processed Quantum Dots for Low Cost Photovoltaics.** E.J.D. Klem, J. Lewis, C. Gregory, G. Cunningham, D. Temple, RTI International

INVITED

For solar energy to be a significant component of our energy supply new technologies are needed that enable the fabrication of low cost, high efficiency solar cells. Research into solar energy devices which incorporate carbon fullerenes and semiconducting polymers represent one such technology. One factor limiting their further advance is their lack of absorption in the infrared (IR). As half the sun's energy lies beyond 700 nm and one third beyond 1000 nm, low-cost device technologies are needed which capture this lost infrared potential. An additional factor limiting the further advance of these devices is the relatively poor electrical transport properties of most semiconducting polymers.

The use of solution processed quantum dots provides a potential route towards overcoming both of these limitations. Solution processed quantum

dots can be tuned to absorb light well into the infrared, and quantum dot composite thin films have been shown to have charge carrier mobilities approaching that of amorphous silicon.

In this presentation we will present a brief overview of colloidal quantum dots and the field of quantum dot photovoltaics. We will discuss a range of device architectures and material systems that have been explored experimentally. This includes quantum dot-metal Schottky junctions, quantum dot heterojunctions, and quantum dot-metal oxide junctions.

We will also present a device architecture which is based on the heterojunction formed between infrared-sensitive PbS quantum dots and C₆₀ fullerenes. In this device pre- and post-deposition treatments are used to passivate carrier traps and increase the conductivity of the quantum dot films. A device stack is presented that is designed to steer photo-excited charge carriers to the charge-separating interface, reducing recombination pathways and improving carrier extraction efficiency. Under simulated solar illumination the devices exhibit short circuit current densities greater than 20 mA/cm², power conversion efficiencies greater than 5%, and spectral sensitivity out to 1500 nm. This represents a significant step towards demonstrating the commercial viability of solution processed quantum dot technology

3:40pm EN+EM+NS-MoA6 **Role of Quantized and Mid-Gap States in "Dark" Charge Transport and Photoconductivity in Semiconductor Nanocrystal Films.** P. Nagpal, Los Alamos National Laboratory

Colloidal semiconductor nanocrystals (NCs) have attracted significant interest for applications in solution-processable devices such as light-emitting diodes and solar cells. However, poor understanding of charge transport in NC assemblies, specifically the relation between electrical conductance in dark and under light illumination, hinders their technological applicability. Here, we simultaneously address the issues of "dark" transport and photoconductivity in films of PbS NCs by incorporating them into optical field-effect transistors (OFETs), in which the channel conductance is controlled by both gate voltage and incident radiation. Spectrally resolved photoresponses of OFETs reveal a weakly conductive mid-gap band (MGB) which is responsible for charge transport in dark. The mechanism for conductance, however, changes under illumination when it becomes dominated by band-edge quantized states. In this case, the MGB still plays an important role as its occupancy (tuned by the gate voltage) controls the dynamics of band-edge charges. Our study has broad implications for NC-based electronics and optoelectronics, and specifically, suggests that design guidelines for NC devices might be different depending on whether they are intended for operation in dark (diodes and transistors) or under illumination (photodetectors and solar cells).

4:00pm EN+EM+NS-MoA7 **Using Surface Chemistry to Modulate the Bandgap of Ge Nanowires.** S. Sivaram, M.A. Filler, Georgia Institute of Technology

Small-diameter semiconductor nanowires are highly attractive building blocks for next generation photovoltaic devices because they exhibit highly tunable optoelectronic properties as a result of quantum confinement. Bottom up approaches, such as the vapor-liquid-solid (VLS) growth mechanism, are controllable down to ~20 nanometers but significant challenges exist at smaller length scales where property tuning is maximized. Furthermore, it is expected that the optoelectronic properties of quantum-confined nanowires will be heavily dependent on surface chemistry, yet there are no experimental studies that fundamentally probe this relationship. Germanium is an ideal system to study because of its large Bohr exciton radius, low rate of oxidation, and chemical similarity to silicon. In this work we controllably synthesize germanium nanowires with diameters from 5 to 20 nanometers using gold catalyst particles with a narrow size distribution. To obtain epitaxial Ge nanowires with uniform diameters and lengths, a two-step growth process is employed that includes a brief, high-temperature nucleation (390°C) above the Au-Ge eutectic point, followed by elongation at various process conditions, generally below the eutectic point (280 – 340°C, 1×10⁻⁷ – 1×10⁻⁴ Torr). To limit catalyst diffusion and formation of the √3 × √3 Au/Si reconstruction on the Si(111) surface, a key problem for controllable sub-20 nm growth, the substrate is passivated with -CH₃ groups prior to nanowire synthesis by introducing small quantities of methylgermane. Nanowire surface chemistry is probed with *in-situ* transmission infrared (IR) spectroscopy both during and after growth. We introduced different adsorbates (-H and -CH₃) and monitored their influence on the band gap as a function of surface coverage. We show that the band gap of Ge nanowires blue shifts with H passivation and red shifts with CH₃ termination.

4:20pm **EN+EM+NS-MoA8 Production of Multi-milligram Yields of Ternary II-VI Semiconductor Nanocrystals Under Non-coordinating Amine Activated Synthesis**, *M. Plaisant, P.H. Holloway*, University of Florida

Thermolysis of Zn and Cd precursors under a non-coordinating one-pot wet-chemical synthesis has successfully produced a heterogeneous ternary $Cd_xZn_{1-x}Se$ alloy with an extensive spectral red shift of 200nm in the visible range. Large yields of twenty milligram of the $Cd_xZn_{1-x}Se$ alloy are minimally required for inclusion of the material in the active layer of an inorganic/organic photovoltaic device. The facile synthesis of such large yields of ternary semiconductor nanocrystal alloys has not commonly been reported in the literature. Herein we discuss first the thermolytic synthesis of the material beginning from the ZnSe core through the inclusion of the Cd-precursor. We then discuss the production of the ternary II-VI semiconductor $Cd_xZn_{1-x}Se$ material through a process of non-coordinating synthesis with amine-activation to produce the high multi-milligram yields required for device inclusion.

4:40pm **EN+EM+NS-MoA9 Type-II ZnTe/ZnSe Quantum Dots for Intermediate Band Solar Energy Conversion**, *C. Chen, B. Juang, J. Hwang, S. Kim, X. Pan, J. Phillips*, University of Michigan

Intermediate band solar cells and impurity photovoltaics have been proposed to achieve high efficiency solar energy conversion by introducing electronic states within the bandgap of the host material. The intermediate electronic states provide enhanced photocurrent through the addition of sub-bandgap optical transitions while maintaining a voltage that follows the host material. Approaches to realize these solar cells include the incorporation of dopants/impurities, dilute alloys, and nanostructures such as quantum dots. Self-assembled quantum dots such as InAs/GaAs possess excellent optical properties and have been applied to numerous optoelectronic devices including demonstration of the intermediate band solar cell concept. The highly radiative transitions in these type-I materials result in short radiative carrier lifetimes – a feature that is desirable for light emitters, but can be problematic for photodetectors and solar cells. Semiconductor nanostructures with type-II band alignment result in spatially separated electron and hole wavefunctions, resulting in reduced oscillator strength and corresponding reduction in optical absorption, spontaneous radiative recombination rate, and increased radiative carrier lifetime. The tradeoff between carrier lifetime and optical absorption may be effectively used to provide a closer match to the generation-recombination rates desired for intermediate band solar energy conversion. In this work, ZnTe/ZnSe type-II quantum dots are proposed for intermediate band solar energy conversion. The theory of intermediate band solar energy conversion in this material system will be presented along with initial experimental results on the epitaxial growth, structural properties, and optoelectronic response of the materials. The ZnTe/ZnSe quantum dots were grown by molecular beam epitaxy, where three-dimensional island formation is observed via strained layer growth in the Stranski-Krastanow growth mode. Low temperature photoluminescence spectra reveal optical transitions from ZnSe (2.8eV), Te_{Se} isoelectronic centers (2.6eV), and broad emission in the range of 2.0-2.4eV attributed to type-II quantum dots.

Nanometer-scale Science and Technology Division

Room: 203 - Session NS-MoA

Frontiers in Nanophotonics and Plasmonics

Moderator: N. Camillone III, Brookhaven National Laboratory

2:00pm **NS-MoA1 Probing the Metal-Insulator Transition of Vanadium Dioxide using Gold Nanoantennas**, *D.W. Ferrara, J. Nag, E.R. MacQuarrie, R.F. Haglund*, Vanderbilt University

Vanadium dioxide (VO_2) films and nanostructures in contact with gold (Au) or silver nanostructures can form the building blocks of active metamaterials that can be modulated in response to various stimuli such as the presence of chemical agents, changes in temperature, or irradiation. The semiconducting-to-metal phase transition (SMT) of VO_2 , — which can be induced thermally ($T_c = 68^\circ C$), optically, or electrically — leads to a change in the dielectric function of the film. Since the localized surface plasmon resonance (LSPR) of the metal nanoantenna is sensitive to the local dielectric environment, the SMT allows the optical response of the metal: VO_2 nanocomposite to be tuned. Thus these Au: VO_2 nanocomposites are unique probes of strong-correlation physics because, during the phase transition, the electron-electron interactions in VO_2 that drive the SMT are coupled with the plasmonic excitation of the Au nanostructure.

We fabricated arrays of Au nanoparticles (NPs), 180 nm in diameter and 20 nm high on indium-tin-oxide coated glass by electron-beam lithography. Subsequently, the nanoparticle arrays were coated with a 60 nm VO_2 film by pulsed laser ablation of vanadium metal targets in 10 mTorr oxygen (O_2) background gas, then annealed for 45 minutes at $450^\circ C$ in 250 mTorr of O_2 . Using a Peltier heater and thermocouple mounted on a copper sample holder, temperature-dependent extinction of the array was measured using plain VO_2 film as a reference to determine the LSPR wavelength and linewidth during the SMT.

The LSPR wavelength of the NPs was 1000 nm in the semiconducting state and approximately 840 nm in the metallic state, thus overlapping the VO_2 electronic transitions from the occupied vanadium $3d_{||}$ band to the empty $3d_{\perp}$ band centered at approximately 885 nm. As the film undergoes the SMT, the split $3d_{||}$ bands merge and, with the $3d_{\perp}$ band, form the metallic VO_2 conduction band. Since the Au NPs are sensitive to changes in both the real and imaginary parts of the VO_2 local dielectric function, they serve as a direct probe of the SMT. The results show a 30% decrease in plasmon dephasing time during the transition due to an increase in carrier-carrier scattering in the VO_2 . Both Maxwell-Garnett and Bruggeman effective-medium theories predict the decrease in dephasing time during the SMT; however, a linear theory is a more accurate model for the hysteresis in the LSPR wavelength.

2:20pm **NS-MoA2 Metamaterial Nanosensors based on the Metal-Insulator transition in VO_2** , *K. Appavoo, R.F. Haglund Jr.*, Vanderbilt University

The use of solid-solid phase transitions to modulate the plasmonic response of metal nanostructures is a promising approach to nanophotonic technologies, including sensors based on signal modulation in confined nanoscale volumes [1]. Consideration of phase-transforming materials has typically focused on composition, whereas relatively little attention has been paid to the question of size dependence in determining stable phases. However, size effects play a crucial role in determining the coupling with mechanical, optical, chemical or thermal input required to effect the phase transformation [2]. With rapid progress in nanofabrication techniques, size-dependent properties become relevant and systematic studies to assess both the role of nucleation in forming a new state and of the nanoscale dynamical effects are needed.

Here, we describe an example that shows how, by systematically varying the gap between the arms of split-ring plasmonic resonators, the in-arm coupling resonance in a split-ring metamaterial can be used to monitor the metal-insulator transition in discrete volumes of the strongly correlated VO_2 . Moreover, this “plasmonic hysteresis” technique also provides a means to correlate the electronic phase-transition with its structural counterpart which was previously measured using SERS technique [3]. If the number of intrinsic nucleation sites is directly proportional to the interrogated volume (a reasonable assumption) [4], we have effectively shown that well-crafted plasmonic structures with well-understood modes can be a helpful tool to probe size-dependent effect [5]. Full field 3D finite-difference time-domain simulations show that the physical origins of these non-isotropic electron oscillations leads to concentration of the electromagnetic energy for focused interrogation and high sensitivity.

As an additional example, we briefly describe an investigation into the use of similar nanostructures as chemical sensors based on coupling of autocatalytic reactions at the gold- VO_2 interface and molecular recognition moieties. In this case, the detection method involves the change in optical transition of a metamaterial array incorporating VO_2 when the heat of decomposition is sufficient to initiate the metal insulator transition.

2:40pm **NS-MoA3 Enhanced Photoluminescence from $Gd_2O_3:Eu^{3+}$ Based Core/Multi-shell Nanoparticles**, *J. Choi, M.R. Davidson, P.H. Holloway*, University of Florida

Core/shell and core/multi-shell nanoparticles with luminescent $Gd_2O_3:Eu^{3+}$ were successfully synthesized by a high boiling-point alcohol (polyol) and solution precipitation methods, respectively. The hetero-structured nanoparticles with Eu doped Gd_2O_3 exhibited intense ${}^5D_0-{}^7F_2$ photoluminescence (PL) from Eu^{3+} after calcination at $600^\circ C$ for 2h in air. Photoluminescence excitation (PLE) data showed that while a small fraction of the emission resulted from direct excitation of Eu^{3+} , most of the excitation resulted from adsorption in the Oxygen to Europium charge-transfer band (CTB) between 225 and 275 nm. $Gd_2O_3:Eu^{3+}/Y_2O_3$ core/shell nanoparticles exhibited PL intensities up to 40% larger than from bare $Gd_2O_3:Eu^{3+}$ nanoparticles and $SiO_2/Gd_2O_3:Eu^{3+}/Y_2O_3$ core/multi-shell samples showed quantum yield (QY) up to 72% larger than that of $SiO_2/Gd_2O_3:Eu^{3+}$ core/single-shell nanoparticles. The increased PL and QY were attributed to reduced non-radiative recombination based on longer luminescence decay time. Potential applications of the nanoparticles as scintillation radiation detectors will be discussed.

3:00pm **NS-MoA4 Au[SiO₂]Yb:Er:Y₂O₃ Core|Shell Optical Nanoantenna: Experiment & Simulation, V. Jankovic, J.P. Chang, University of California Los Angeles**

The conversion of electromagnetic (EM) energy from free propagating radiation to localized energy and vice versa in the radio frequency (RF) and microwave domains is accomplished with the use of antennas. Optical antennas are analogous to their RF and microwave counterparts, but there are crucial differences in their physical properties and scaling behavior because metal is a highly dispersive material with finite conductivity at optical frequencies. Optical antennas are not driven by galvanic transmission lines like RF antennas, instead, localized oscillators such as atomic emitters are brought close to the feed point of the antennas, and electronic oscillations are driven capacitatively.

In this work, Au nanoparticles of different shapes (spheres, rods and stars) were used as antenna elements, Er³⁺ ions in an Y₂O₃ host matrix were used as atomic emitter antenna driving elements while the capacitive gap between the antenna element and the atomic emitter was controlled by deposition of an ultra-thin SiO₂ inner shell between the Au nanoparticle and the Yb:Er:Y₂O₃ outer shell. A 4-5nm silica spacer layer was deposited through a controlled TEOS hydrolyzation reaction and was shown to be effective in preventing quenching yet enabling energy coupling between the Au nanorod and the RE-ion doped oxides. Spatially and compositionally controlled Yb:Er:Y₂O₃ outer shells were deposited using both wet chemistry methods and radical enhanced atomic layer deposition (RE-ALD).

Upconversion (UC) spectral, power dependence and radiative lifetime measurements with 532nm, 750nm 980 nm and 1064nm laser excitation were used to assess the coupling of the Au optical antenna to the emitter ions as a function of antenna shape, spacer layer thickness and spectral and spatial mode overlap efficiency. Preliminary optical characterization showed a 2X earlier onset of upconversion with 980nm excitation for Yb:Er:Y₂O₃ coupled to an Au nanorod antenna compared to pure (uncoupled) Yb:Er:Y₂O₃ nanoparticles. Power dependence measurements with 980nm excitation showed a >5 slope indicating a multi-photon absorption induced luminescence process for the Au-coupled erbium and a <2 slope for the uncoupled erbium, indicating a two photon absorption (expected for erbium with 980nm excitation). These optical antenna core|shell particles have potential application in bio-imaging and light trapping for solar and sensor applications.

3:40pm **NS-MoA6 Gap-Mode Plasmonic Cavities: Engineering Light-Matter Interactions in Metallic Structures, E.L. Hu, K.J. Russell, T.-L. Liu, S. Cui, K. Yeung, Harvard University** **INVITED**

Optical cavities can tightly confine light in the vicinity of optical emitters, enhancing the interaction of light and matter. The modes or optical states of the cavity can be precisely designed and engineered, and in recent years there has been remarkable progress in demonstrations of 'cavity quantum electrodynamics (cQED)' in solid state platforms. Such progress has been primarily for cavities fabricated in dielectric materials, with a steady improvement in cavity quality, with quality factors, Q, in excess of 10⁴ – 10⁶ realized for cavities with coupled emitters [1],[2]. These high Q-coupled emitter systems have demonstrated heralded single photon emission [3], ultra-low threshold lasing [4] and strong light-matter coupling [5],[6].

Metal-based optical cavities would have inherently lower Q's (and greater loss) than dielectrics; however, metal cavities utilizing surface plasmon polaritons (SPPs) can have sufficiently small mode volume to produce a substantial Q/V, the quantity relevant for high Purcell factors, a measure of the light-matter interaction. This talk will focus on such *plasmonic cavities*, with optical modes formed within the gap of the two metal layers which defined the cavity [7]. Initial structures comprised silver (Ag) nanowires (NW), 70 nm in diameter and 1 - 3 μm in length, placed into close proximity to a Ag thin film substrate, with the NW axis parallel to the substrate surface. Optically active material was interposed between the nanowire and the Ag substrate: this comprised one to two monolayers of PbS colloidal quantum dots, clad on top and bottom by thin dielectric layers of varying composition and thickness. The fluorescence spectrum of PbS quantum dots within the gap was strongly modified by the cavity mode, with peak position in quantitative agreement with numerical calculations, and demonstrating Q values of ~ 60.

Such plasmonic cavities allow the easy incorporation of a variety of light-emitting active areas, and we have also explored the incorporation of various organic, dye-containing layers within the gap-mode plasmonic cavities. In addition these structures lend themselves to relatively simple modifications of geometry, allowing effective *tuning* of cavity modes, and also control of modes through the use of photonic crystal geometries, fabricated into metal.

The high Q/V possible for these cavities, and the range of organic and nanocrystalline emitters they can accommodate make these important building blocks for the exploration of light-matter interaction in the solid state.

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4:20pm **NS-MoA8 Direct Characterization of Surface Plasmon Enhanced Electromagnetic Fields on Single Ag Nanostructure, W.D. Wei, J. Wang, Y. Wang, University of Florida, G. Xiong, S. Peppernick, A. Joly, K. Beck, W.P. Hess, Pacific Northwest National Laboratory**

Using two-photon photoemission electron microscopy (2P-PEEM) we have directly explored the optical fields on a single Ag nanostructure and quantitatively measured the field enhancement factor (FEF). The 2PPE intensity from the Ag nanostructure is enhanced by 2 orders of magnitude with respect to the 2PPE intensity from a smooth and homogeneous Ag thin film. This enhancement is attributed to a localized surface plasmon excitation and resonance of the local field, and the FEF is determined to be around 4. The capability of directly correlating the field enhancement with nanostructures makes 2P-PEEM a promising tool to investigate the fundamental optical properties of nanomaterials.

4:40pm **NS-MoA9 Comparisons of Optical and Magneto-Optical Properties between Core-Shell Fe-Ag and Co-Ag Nanoparticles based on Localized Surface Plasmon Resonance, L. Wang, C. Clavero, K. Yang, A. Nelson, College of William and Mary, K. Carroll, Z. Huba, E. Carpenter, Virginia Commonwealth University, D. Gu, Applied Research Center, R.A. Lukaszew, College of William and Mary**

Magnetic transition nanoparticles (NPs) have been developed and studied by many researchers for bio-imaging and bio-sensing applications [1,2] due to their special optical and magneto-optical (MO) properties. Nevertheless, it is possible to enhance the MO effects of the magnetic NPs by combining them with other materials such as noble metals which exhibit intense localized surface plasmon resonance (LSPR) under certain conditions[3,4]. Here, we present our investigations on LSPR enhanced MO effect in magnetic metal core-noble metal shell NPs, such as core-shell Fe-Ag and Co-Ag NPs. These systems present strong Faraday rotation due to LSPR, nevertheless differences are found among them due to their different optical properties. A blue-shift is experimentally observed in the optical and MO spectra peaks from Fe-Ag to Co-Ag NPs with similar Ag shell concentrations and constant NPs sizes. Also, the absorption and Faraday rotation spectra of Fe-Ag NPs are broader than those of Co-Ag NPs. We explain such differences by means of theoretical studies based on an adaptation of the Maxwell-Garnet model to core shell nanoparticles yielding an excellent agreement with the experimental results. The possibility to understand and tune the properties of core-shell nanoparticles reported here will have significant impact in photonic and plasmonic applications.

This work was financed by DARPA under a grant for the development of novel sensors for bio-defense.

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5:00pm **NS-MoA10 Plasmon Induced Current in Metal/Organic Hybrid Nanostructures, D. Conklin, S. Nanayakkara, T. Park, University of Pennsylvania, J. Stetcher, M. Therien, Duke University, D.A. Bonnell, University of Pennsylvania**

Recently we demonstrated a new mechanism of plasmon-induced electronic transport in hybrid metal nanoparticle-molecular devices. The mechanism realizes enhancements of up to a factor of 200. The hybrid structures consist of arrays of gold nanoparticles linked by (porphinato)zinc(II) oligomers. Here we examine the role of metal particle size, spacing, and molecular length on the transport mechanisms. Understanding the charge transport through the structures allows the relative roles of nano antennae field

focusing and hot electron distribution to the current enhancement to be compared. This phenomenon offers a pathway to wide ranging control of the opto electronic transport properties which enables concepts of energy harvesting, energy transduction and optoelectronic circuits.

5:20pm **NS-MoA11 Direct-bandgap Infrared Light Emission from Tensilely Strained Germanium Nanomembranes.** *J.R. Sanchez-Perez*, University of Wisconsin Madison, *C. Boztug*, Boston University, *F. Chen*, University of Wisconsin Madison, *F. Sudradjat*, Boston University, *D.M. Paskiewicz*, *R.B. Jacobson*, University of Wisconsin Madison, *R. Paiella*, Boston University, *M.G. Lagally*, University of Wisconsin Madison

Silicon, germanium, and related alloys, which provide the leading materials platform of electronics, are extremely inefficient light emitters because of their indirect fundamental energy bandgap. This basic materials property has so far hindered the development of group-IV photonic active devices, including diode lasers, thereby significantly limiting our ability to integrate electronic and photonic functionalities at the chip level. Here we show that Ge nanomembranes can be used to overcome this materials limitation. Theoretical studies have predicted that tensile strain in Ge lowers the direct energy bandgap relative to the indirect one. We demonstrate [1] that mechanically stressed nanomembranes allow for the introduction of sufficient biaxial tensile strain to transform Ge into a direct-bandgap, efficient light-emitting material that can support population inversion and therefore provide optical gain. [1] F. Chen, C. Boztug, J. R. Sanchez-Perez, F. Sudradjat, D. M. Paskiewicz, R. B. Jacobson, M. G. Lagally, and R. Paiella, *Direct-bandgap germanium pumped above optical transparency in tensilely strained nanomembranes*, submitted. Research supported in part by NSF and DOE

Tuesday Morning, November 1, 2011

Energy Frontiers Focus Topic

Room: 103 - Session EN+NS-TuM

Ultrafast Charge and Energy Transfer in Nanomaterials

Moderator: J.B. Baxter, Drexel University

8:00am EN+NS-TuM1 **Controlled Deposition of Nanocrystal Quantum Dots on Silicon Surfaces: Demonstration and Application of Forster Resonant Energy Transfer**, *O. Seitz, H.M. Nguyen, Y.N. Gartstein, A.V. Malko*, University of Texas at Dallas, *Y.J. Chabal*, The University of Texas at Dallas

Studying Forster resonant energy transfer (FRET) at semiconductor surfaces has been a challenge because of difficulties in grafting reliably nanocrystal quantum dots (NQDs) onto electronically passivated substrates. Poor control has often resulted in formation of aggregates (3D growth), inhomogeneity, and poor adhesion. In this study, combining IR absorption spectroscopy (IRAS) and X-ray photoelectron spectroscopy (XPS), photoluminescence, atomic force microscopy (AFM) and electrical measurements, we have grafted self-assembled monolayers (SAMs) on both oxidized and oxide-free silicon surfaces with appropriate functionality to obtain dense monolayer of NQDs and to study FRET. SAMs that are directly attached to the silicon via Si-C bonds display a high interface quality with a low density of interface states. This makes it possible to prepare systems with tunable thicknesses necessary for FRET investigation. The time evolution of the fluorescence intensity is in good agreement with the predicted thickness dependence. We are currently developing 3D structures to enhance energy collection for a given surface area. Such hybrid colloidal NQD/Silicon optoelectronic structures could potentially be attractive for both photovoltaic as well as light emitting applications.

8:20am EN+NS-TuM2 **Orbital-dependent Charge Transfer Dynamics in Potential Molecular Wires**, *H. Hamoudi*, Universität Heidelberg, Germany, *S. Nepl*, Technische Universität München, Germany, *P. Kao*, Penn State University, *B. Schüpbach*, Universität Frankfurt, Germany, *P. Feulner*, Technische Universität München, Germany, *A. Terfort*, Universität Frankfurt, Germany, *D.L. Allara*, Penn State University, *M. Zharnikov*, Universität Heidelberg, Germany

Continued progress in technologically important fields such as molecular and organic electronics as well as organic photovoltaics depends on reliable information about the charge transport (CT) through individual molecular groups, above all so-called molecular wires, since these represent important building blocks of a variety of devices. In this context, femtosecond CT dynamics in a series of self-assembled monolayers with oligo(phenyleneethynylene) and oligo(phenyl) backbone, which are prototypes of potential molecule wires, was addressed by resonant Auger spectroscopy using the core hole clock method. The length of the molecular backbone was varied to monitor the respective dependence of the CT time. The CT pathway was unambiguously defined by resonant excitation of the nitrile tailgroup attached to the backbone. Due to the conjugation of the electronic systems of this group and the adjacent terminal phenyl ring of the backbone, a splitting of the degenerated unoccupied molecular orbital (MO) of nitrile occurred, resulting in two different MOs which could be selectively addressed by X-rays and used as the starting points for CT. The characteristic CT times were found to depend strongly on the character of the MO which mediates the CT process. This demonstrates that the efficiency and rate of CT in molecular wires can be controlled by resonant injection of the charge carriers into specific MOs.

8:40am EN+NS-TuM3 **Photophysics of Semiconductor Nanostructures in Relation to Problems of Solar Energy Conversion**, *V.I. Klimov*, Los Alamos National Laboratory

INVITED

This presentation provides a brief overview of research activities in the Center for Advanced Solar Photophysics with focus on spectroscopic properties of semiconductor nanocrystals studied from the prospective of solar energy conversion. One process, which can be used for boosting a photocurrent of solar cells, is carrier multiplication (CM) or multiexciton generation. Our recent activities in this area include the development of reliable methods for efficient screening of CM performance using photon counting with superconducting nanowire detectors, the studies of the impact of "extraneous" processes on CM measurements, and the evaluation of the effects of the nanocrystal composition, dimensions, and shape on CM yields. As part of our effort on controlling excited-state dynamics, we study hot-electron transfer in nanocrystals. We find that the efficiency of this process can approach 10% even with incidental impurity-like acceptors, suggesting that even higher probabilities are possible with engineered

acceptors designed for testing the ideas of hot-electron extraction. We also apply spectroscopic tools for probing the physics of charge transport in nanocrystal assemblies using exploratory devices such as optical field-effect transistors (OFETs). The OFET studies help to understand the nature of conducting states in dark and under illumination and to rationalize many previously unexplained observations including a weak sensitivity of conductance to particles' polydispersity and a significant difference in a photovoltage compared to a nominal band-gap energy. These studies illustrate how key insights into the performance of nanoscale materials are gained through close integration of spectroscopic, materials and device efforts across the Center.

9:20am EN+NS-TuM5 **Hot Electron Transfer from Semiconductor Nanocrystals**, *W.A. Tisdale*, Massachusetts Institute of Technology

INVITED

In conventional semiconductor solar cells, absorption of photons with energies greater than the semiconductor band gap generate "hot" charge carriers that quickly "cool" before all of their energy can be captured – a process that limits device efficiency. Semiconductor nanocrystals (or quantum dots) have been touted as promising materials for photovoltaics because discretization of their electronic energy levels can slow down this cooling process, which might enable the extraction of photogenerated charge carriers before their excess energy is converted to heat.

In this talk, I will demonstrate hot electron transfer from PbSe nanocrystals to delocalized conduction band states of TiO₂ and the concomitant excitation of coherent surface vibrational modes associated with this ultrafast process. In order to make these measurements, we developed the use of optical second harmonic generation (SHG) for femtosecond time-resolved studies of interfacial charge separation. I will discuss the information we obtain from this technique as well as the effect of temperature, nanocrystal size, and surface chemistry, and how these observations inform our understanding of electronic coupling at interfaces between confined states and bulk materials.

10:40am EN+NS-TuM9 **Single Molecule Study of Charge Transfer in 6T-TBRPP-Co Molecular Complex**, *Y. Zhang, U.G.E. Perera, S.-W. Hla*, Ohio University

When two molecules having tendency to donate or accept electronic charge are put together, charge transfer between the molecules can take place. By a suitable selection of donor and acceptor molecules, it is possible to engineer an entire class of materials having metallic, semiconducting, insulating, or even superconducting properties [1, 2]. Here, we present a low temperature scanning tunneling microscopy and spectroscopy study of single molecule level charge transfer process between α -sexithiophene(6T) and TBRPP-Co molecules on a Cu(111) surface. We form molecular clusters composed of both molecular species on Cu(111). The charge transfer between the molecules is directly evident in the tunneling spectroscopy data, which reveals the shift of 6T HOMO towards the surface Fermi level indicating donation of charge from 6T to TBRPP-Co. This work is supported by the US-DOE-DE-FG02-02ER46012 grant.

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11:00am EN+NS-TuM10 **NEGF Quantum Simulation of Nanotip Thermionic Emitters for Direct Energy Conversion**, *T.D. Musho, D.G. Walker*, Vanderbilt University

Wide band-gap diamond nanotip field emission devices have been experimentally shown to have superior performance and lifetime. However, theoretical studies of the electronic emission from these devices using standard Fowler-Nordheim (FN) theory does not fully capture the physics as a result of the fitting parameters inherent to the FN approximation. The following research computationally models wide band-gap nanotip field emission devices from a quantum point of view, using a novel non-equilibrium Green's function (NEGF) approach previously applied to modeling the transport in solid-state electronic devices. In this research the IV characteristics of a single square tip diamond emitter are investigated under several bias conditions. Those bias conditions include both field emission in response to a potential bias and thermionic emission in response to a temperature bias. The NEGF model calculates the ballistic transport using a self-consistent Schrödinger-Poisson solver, calculating the transmission at discrete energy levels which is then used by the Landauer

formalism to determine the total current. Ultimately, this model allows the inherent quantum mechanical transport to be captured without any fitting parameters. Findings from this research have confirmed non-linearities in the FN curve and have demonstrated the experimental transport trends. Additionally, thermionic emission trends suggest that select geometric parameters are target for enhanced emission.

11:20am **EN+NS-TuM11 Mechanisms of Heterogeneous Charge Transfer at the Quantum Dot-Organic Interface**, *A. Morris-Cohen, M. Frederick, L. Cass, E.A. Weiss*, Northwestern University **INVITED**

We examine the rates and mechanisms of electron transfer between colloidal semiconductor quantum dots (QDs) and viologen derivatives using ultrafast transient absorption spectroscopy. Viologens accept electrons from photoexcited QDs on the femtosecond-to-single picosecond timescale. Modifications of the chemistry by which the ligands link to the QD surface, and the density of ligands on the QDs, facilitates control of charge separation and recombination rates, and determination of the operative mechanisms of charge transfer.

Electron Transport in Low Dimensional Materials Focus Topic

Room: 209 - Session ET+EM+NS+GR-TuM

Electron Behaviors in Nanoelectronics, Interconnect, and Carbon-based Materials

Moderator: J. Wendelken, Oak Ridge National Laboratory, A. Swan, Boston University

8:00am **ET+EM+NS+GR-TuM1 Electron Transport Study of Graphene on SiC Using Scanning Tunneling Potentiometry**, *K. Clark, S. Qin*, Oak Ridge National Laboratory, *G. He*, Carnegie Mellon University, *G. Gu*, The University of Tennessee, *R.M. Feenstra*, Carnegie Mellon University, *A.-P. Li*, Oak Ridge National Laboratory

The unique electronic and transport properties of graphene have helped this material emerge as a perspective graphene based electronic system. Single layers of graphene formed on SiC look to be a promising system for the realization of graphene electronics. To utilize the full potential of graphene on SiC a complete understanding of the physical and electronic properties of this system is needed. This study uses Scanning Tunneling Microscope (STM) images along with scanning tunneling spectroscopy to characterize the sample surface. STM images clearly show the distinction between 1 monolayer (ML) and 2ML regions. The 1ML to 2ML transition is further confirmed by point spectroscopy measurements and spectroscopic mapping across the boundary. Defects, grain boundaries, step edges and other potential scattering centers are thought to play a major role in the electronic properties, especially in transport, along the graphene sheets. Using a low temperature four-probe scanning tunneling microscope, potentiometry measurements are performed on epitaxial graphene grown on 4H-SiC. Potentiometry maps spanning the transition from 1ML to 2ML graphene layers show a contrast change indicating a potential change at this interface. Preliminary results of the transport along this potentially revolutionary new electronic system will be presented. This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Office of Basic Energy Sciences, U.S. Department of Energy.

8:20am **ET+EM+NS+GR-TuM2 Engineering the Electronic States of CVD Grown Few Layer Graphene by Twisting and Lattice Distortion**, *M.H. Pan*, Oak Ridge National Laboratory, *X.T. Jia*, *S. Bhaviripudi*, Massachusetts Institute of Technology, *V. Meunier*, Rensselaer Polytechnic Institute, *M.S. Dresselhaus*, *J. Kong*, Massachusetts Institute of Technology
Few layer graphene (FLG) can have advantages over single layer graphene because it has a larger current-carrying capacity and the electronic properties are sensitive to more engineerable system parameters. In particular, Hass et al. have demonstrated that orientational disorder is normally present in carbon-face SiC epitaxial FLG samples. [1] Recently both theoretical and experimental studies suggest that strain can be used to engineer graphene electronic states through the creation of a pseudo-magnetic field. [2] Here we present both scanning tunneling microscopic/spectroscopic (STM/S) studies of chemical vapor deposition grown few layer graphene samples. There indeed exists a twisting between the stacked graphene layers, confirmed by both high-resolution STM images and low temperature spectroscopic measurements. Our results show that, by stretching graphene along three symmetry directions, a strain-induced pseudo magnetic field can lead to the formation of different Charge Density Wave (CDW) states at the top layer of graphene.

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8:40am **ET+EM+NS+GR-TuM3 Unique One- and Two-Dimensional Phenomena Observed in Carbon Nanotubes and Graphene**, *S. Cronin*, University of Southern California **INVITED**

Our ability to fabricate nearly defect-free, suspended carbon nanotubes

(CNTs) has enabled us to observe several phenomena never seen before in CNTs, including breakdown of the Born-Oppenheimer approximation[1], mode selective electron-phonon coupling[2], leading to negative differential resistance (NDR) and non-equilibrium phonon populations, and a Mott insulator transition[3]. In this work, Raman spectroscopy is used to measure individual, suspended CNTs under applied gate and bias potentials. Raman spectroscopy of periodic ripple formation in suspended graphene will also be reported. As will be shown, preparing clean, defect-free devices is an essential prerequisite for studying the rich low-dimensional physics of CNTs and graphene.

1. Bushmaker, A.W., Deshpande, V.V., Hsieh, S., Bockrath, M.W., and Cronin, S.B., "Direct Observation of Born-Oppenheimer Approximation Breakdown in Carbon Nanotubes." *Nano Letters*, 9, 607 (2009).

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3. Bushmaker, A.W., Deshpande, V.V., Hsieh, S., Bockrath, M.W., and Cronin, S.B., "Large Modulations in the Intensity of Raman-Scattered Light from Pristine Carbon Nanotubes." *Physical Review Letters*, 103, 067401 (2009).

9:20am **ET+EM+NS+GR-TuM5 Probing Surface Band Conduction through Back-Gated Conductance Measurements on Si Nanomembranes**, *W.N. Peng**, *J. Endres*, *S. Scott*, *Z. Aksamija*, *D.E. Savage*, *I. Knezevic*, *M.G. Lagally*, *M. Eriksson*, University of Wisconsin Madison

Silicon-on-insulator substrates provide large-area Si nanomembranes (SiNMs) mechanically supported by bulk handle wafers. Because of the intervening oxides, SiNMs are also electrically isolated from the substrates. The typical membrane thickness is less than a few hundred nanometers. Because they are so thin, SiNMs display interesting transport phenomena influenced by surface effects. Here, we demonstrate a novel method to probe surface transport via conductance measurements on SiNMs. When contacts are placed on the front surface, a current flows between the source and the drain via the membrane body as well as its surface. By utilizing an underlying back gate (the Si handle substrate), the conductance through the membrane can be continuously tuned and made smaller than the surface contribution, enabling experimental determination of the surface conductance. We measure the membrane conductance as a function of both the membrane thickness and the backgate voltage in ultra-high vacuum. In contrast to H-terminated Si surfaces, clean reconstructed Si(001)(2x1) surfaces show a constant-conductance regime when the backgate voltage is varied, and the conductance in this regime does not depend on membranes thickness. We demonstrate that the constant conductance (on the order of 10^{-9} Siemens) stems from an additional conduction channel through the dimer-reconstructed surface π^* band. By comparing the experimental results to numerical simulations, the surface band mobility is determined to be in the range 10-50 cm^2/Vs .

Research supported by NSF [UW MRSEC, award DMR-0520527, as well as awards 0937060 (subaward CIF-146) and ECCS-0547415] and DOE

9:40am **ET+EM+NS+GR-TuM6 Ferroelectric Field-Effect Transistor Behavior in CdS Nanotetrapods**, *S. Qin*, Oak Ridge National Laboratory, *W. Fu*, *L. Liu*, Chinese Academy of Sciences, *T.H. Kim*, Oak Ridge National Laboratory, *S.L. Hellstrom*, Stanford University, *W. Wang*, *W. Liang*, *X. Bai*, *E. Wang*, Chinese Academy of Sciences, *A.-P. Li*, Oak Ridge National Laboratory

Complex nanostructures such as branched semiconductor nanotetrapods are promising building blocks for next-generation nanoelectronics. Here we report on the electrical transport properties of individual CdS tetrapods in a field-effect transistor (FET) configuration with a ferroelectric $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ film as high- κ , switchable gate dielectric. A cryogenic four-probe scanning tunneling microscopy is used to probe the electrical transport through individual nanotetrapods at different temperatures. A p -type field effect is

* NSTD Student Award Finalist

observed at room temperature, owing to the enhanced gate capacitance coupling. And the reversible remnant polarization of the ferroelectric gate dielectric leads to a well-defined nonvolatile memory effect. The field effect is shown to originate from the channel tuning in the arm/core/arm junctions of nanotrapods. At low temperature (8.5 K), the nanotrapod devices exhibit a ferroelectric-modulated single-electron transistor behavior. The results illustrate how the characteristics of a ferroelectric such as switchable polarization and high dielectric constant can be exploited to control the functionality of individual 3-dimensional nano-architectures. *Acknowledgement:* The research at the Center for Nanophase Materials Sciences is sponsored at Oak Ridge National Laboratory by the Office of Basic Energy Sciences, U.S. Department of Energy. The research in Beijing is supported by MOST and CAS of China.

10:40am **ET+EM+NS+GR-TuM9 Probing Electron-Electron Correlations in Quantum Dots Using Transport: Quantum Monte Carlo Studies, H.U. Baranger, Duke University INVITED**

Strong electron-electron correlations occur in nanoscale systems in a variety of contexts – when electrons form a crystal at low density, for example, or in correlations between quantum dots. Nanoscale systems introduce in addition an unprecedented level of control over the physical parameters determining such correlations. As electron transport is one of the primary probes of nanosystems, the effect of e-e correlations on transport is a key issue. I shall discuss an example in which we used quantum Monte Carlo (QMC) techniques to calculate the conductance:

Consider a system of four quantum dots designed to study the competition between three types of interactions: Heisenberg, Kondo, and Ising. We find that the competition produces a rich phase diagram containing two sharp features: a quantum phase transition (QPT) between charge-ordered and charge-liquid phases, and a dramatic resonance in the charge liquid visible in the conductance. The conductance is calculated using a world-line QMC method: extrapolation of the imaginary time QMC data to zero frequency yields the linear conductance, which is then compared to numerical renormalization group results in order to assess its accuracy. The QPT is of the Kosterlitz-Thouless type with a discontinuous jump in the conductance at the transition. We connect the sharp resonance phenomenon with the degeneracy of three levels in the isolated quadruple dot and argue that this leads to an emergent symmetry. I shall end by discussing the sensitivity to parameter variation and possible experimental realizations in laterally gated quantum dots as well as carbon nanotubes.

This work was done in collaboration with Dong E. Liu and Shailesh Chandrasekharan (Duke University).

11:20am **ET+EM+NS+GR-TuM11 Resistivity Increase due to Electron Scattering at Surfaces and Grain Boundaries in Metal Thin Films and Nanowires, J.S. Chawla, D. Gall, Rensselaer Polytechnic Institute**

The effect of surface and grain boundary scattering on the resistivity of Cu thin films and nanowires is quantified using (i) *in situ* transport measurements on single-crystal, atomically smooth Cu(001) layers, (ii) textured Cu(111) layers and patterned Cu wires with independently varying grain size, thickness and line width, and (iii) *in situ* grown interfaces including Cu-Ta, Cu-MgO, Cu-SiO₂ and Cu-oxygen. In addition, the electron surface scattering is also measured *in situ* for single-crystal Ag(001) and TiN(001) layers. These findings are important for the development of future generation narrow low-resistivity Cu interconnects and TiN metal gates.

Cu(001), Ag(001), and TiN(001) layers with a minimum continuous thickness of 4, 5 and 1.8 nm, respectively, are grown by ultra-high vacuum magnetron sputter deposition on MgO(001) substrates and are found to be atomically smooth single crystals by a combination of x-ray diffraction θ - 2θ scans, ω -rocking curves, pole figures, reciprocal space mapping, Rutherford backscattering, x-ray reflectometry, transmission electron microscopy, and *in-situ* scanning tunneling microscopy. Polycrystalline Cu layers with a 111-texture are deposited on thermally grown SiO₂, with and without Ta barrier layer. Subsequent *in-situ* annealing at 350°C followed by sputter etching in Ar plasma yields Cu layers with independently variable thickness and grain size. Cu nanowires, 50 to 150 nm long, 70 to 350 nm wide, and 45 nm thick, are patterned using electron beam lithography and sputter etching.

In-situ electron transport measurements at room temperature in vacuum and at 77 K in liquid nitrogen for single-crystal Cu and Ag layers is consistent with the Fuchs-Sondheimer (FS) model and indicates specular scattering at the metal-vacuum boundary with an average specular parameter $p = 0.6$ and 0.4, respectively. In contrast, layers measured *ex-situ* show completely diffuse surface scattering due to sub-monolayer oxidation. Electron transport measurements for polycrystalline Cu/Ta layers and wires show a

~10% and ~11% decrease in resistivity, respectively, when increasing the average lateral grain size by factor 2. *In-situ* deposition of 0.3 to 8 nm thick Ta barrier layers on Cu(001) leads to a resistance increase that indicates a transition from $p = 0.8$ to $p = 0$, independent of the Ta thickness. *In-situ* exposure of Cu(001) layers to O₂ between 10⁻³ and 10⁵ Pa-s results in a sequential increase, decrease and increase of electrical resistance which is attributed to specular surface scattering for clean Cu(001) and for surfaces with a complete adsorbed monolayer, but diffuse scattering at partial coverage and after chemical oxidation.

11:40am **ET+EM+NS+GR-TuM12 Control of Contact Formation via Electrodeposition on GaAs Nanowires, C. Liu, O. Einabad, S. Watkins, K.L. Kavanagh, Simon Fraser University, Canada**

Copper (Cu) electrical contacts to as-grown gallium arsenide (GaAs) nanowires have been fabricated via electrodeposition. The nanowires are zincblende (111) oriented grown epitaxially on n-type Si-doped GaAs(111)B

substrates by gold-catalyzed Vapor Liquid Solid (VLS) growth in a metal organic vapour phase epitaxy (MOVPE) reactor. The epitaxial electrodeposition process, based on previous work with bulk GaAs substrates, consists of a substrate oxide pre-etch in dilute ammonium hydroxide carried out prior to galvanostatic electrodeposition in a pure Cu or Fe sulphate aqueous electrolyte at 20C. The conductivity of wires was controlled via the addition of carbon tetrabromide (CBr₄) during growth. For nominally undoped GaAs nanowires, we find that Cu or Fe has a preference for growth on the gold catalyst avoiding the sidewalls. After etching the gold, both metals still preferred to grow only on the tops of the nanowire, consistent with the location of the largest electric field. Core-shell GaAs nanowires with highly conductive carbon-doped shells were fabricated via changing the Ga precursors from trimethylgallium to trimethylgallium for radial growth. Increasing the conductivity of the nanowires in this way, not surprisingly; meant that Cu nucleation and growth began to occur on the sidewalls as well as on the gold catalyst. Finite element simulations will be compared to our electrodeposition results towards the calibration of nanowire conductivity.

**Nanometer-scale Science and Technology Division
Room: 203 - Session NS-TuM**

Nanowires and Nanoparticles II: Characterization and Synthesis

Moderator: U.D. Schwarz, Yale University

8:00am **NS-TuM1 Formation of Metallic Glass Nanofiber, K.S. Nakayama, Y. Yokoyama, T. Wada, N. Chen, Tohoku University, Japan**

Metallic glasses have been receiving significant attention because their superior mechanical properties are attractive to structural materials. However, far less attention paid to metallic glass nanostructures though they have exciting potential for catalysis applications due to the expanding of metallic surface area. Progress has been hindered by the lack of bottom-up methodologies to produce self-assembly nanostructures. Recently, we show that the instantaneous fracture process of a bulk metallic glass produces amorphous nanostructures [Nakayama et al., Nano Lett. **8**, 516 (2008)] and the simple tensile draw under viscous deformation leads to the formation of individual amorphous nanowires [Nakayama et al., Adv. Mater. **22**, 872 (2010)]. However, these approaches are unsuitable for massive production because the amount of nanowires is limited. In this talk, we first report an approach to the synthesis of metallic glass nanofibers that exploits a conventional gas atomization which is a central technique in powder metallurgy. We found that the nanofiber forming ability is closely related to the super liquid cooling region of the alloys and the atomizing gas pressure.

8:20am **NS-TuM2 Plasma-assisted Dissociation of Organometallic Vapors for Continuous, Gas-Phase Preparation of Multimetallic Nanoparticles, R.M. Sankaran, P. Lin, Case Western Reserve University**

Metal nanoparticles (NPs) are desired for novel optical, magnetic, electric, and catalytic applications. Recently, there has been growing interest in multimetallic NPs, a special class of metal NPs composed of two or more distinct metal elements with alloyed, core-shell, or other architectures. Despite the development of numerous synthetic routes for metal NP synthesis, the preparation of multimetallic NPs with controlled size, composition, morphology, and purity remains a significant challenge.

Here, we present a single-step, continuous, gas-phase process that is capable of producing a wide range of size- and compositionally-tuned multimetallic NPs [12]. Our approach is based on plasma-assisted dissociation of metal-organic vapors which is a well-established technique for chemical vapor

deposition (CVD) of thin films of metals. In our case, these same precursors are dissociated in a continuous-flow, atmospheric-pressure microplasma to homogeneously nucleate metal NPs. To synthesize multimetallic NPs, more than one precursor is mixed in the microplasma reactor. The size of the multimetallic NPs is controlled by the total vapor concentration of the precursors while the atomic-scale composition is controlled by the relative ratio of the different metal precursors. Bimetallic and trimetallic NPs of various metals including Ni, Fe, Cu, and Pt, have been produced by this approach. In this talk, we will discuss our experimental method in detail, as well as the structural properties of the NPs as determined by *in situ* aerosol measurements, high-resolution transmission electron microscopy (HRTEM), energy-dispersive spectroscopy (EDS), and X-ray diffraction (XRD).

References

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2. P. A. Lin and R. M. Sankaran, submitted.

8:40am NS-TuM3 Electrical Characterization of III-V Semiconductor Freestanding Nanowires with Scanning Tunneling Microscopy, O. Persson, D. Suyatin, J. Wallentin, L. Samuelson, A. Mikkelsen, R. Timm, Lund University, Sweden

Semiconductor nanowires show great characteristics for implementations in a broad range of applications, e.g. optoelectronic devices [1]. The increased possibilities of using different materials to realize tailored *p-n*-junctions or bandgaps and the inherent property of low density of defects make the nanowire the perfect candidate to realize new electronic devices.

Vast arrays of freestanding nanowires are used in many applications such as LEDs and solar cells. The electronic properties of such wires are essential to investigate for understanding and further developing the devices. The prevalent method used to make electronic measurements on nanowires is complex and challenging. It consists of several processing steps where the nanowire has to be deposited onto a substrate, localized, and then contacts need to be defined and deposited [2]. The range of nanowire material systems and doping levels for which this method can provide good Ohmic contacts is strongly limited.

Here we show a novel technique for investigating the electronic properties of freestanding nanowires by utilizing a scanning tunneling microscope (STM). We can exactly obtain the position of individual freestanding nanowires by scanning them from the top [3]. By contacting the Au-seed particle on the top of the nanowire with the STM tip in a controlled manner, a well-defined point contact is established. The sample substrate will act as a back contact establishing a well-defined system in an ultra-high vacuum.

We have previously performed a variety of successful STM measurements on III-V nanowires [3,4]. Here we show that *I-V* measurements on single as-grown wires can be done reproducibly and consistently. GaAs wires with a doping concentration of 10^{18} cm^{-3} and a diameter of 80 nm are analyzed with this method and they consistently show a resistivity of approx. 700 Ω . Measurements on InP and InAs wires confirm the reliability of this new technique by revealing nanowire conductivities which agree well to the corresponding doping level. We will also present first results on individual nanowire *p-n*-junctions and Schottky diodes.

The main advantages of our method are that we get a well-defined contact, the measurements are done on as-grown nanowires, and we have a good control of the wire surfaces due to UHV conditions. To determine the chemical surface composition of these wires, the *I-V* studies are complemented by high intensity X-ray photoemission spectroscopy at the MAX-II synchrotron in Lund.

- [1] Li *et al.*, Mater. Today **9** (10), 18 (2006)
- [2] Suyatin *et al.*, Nanotechnology **18**, 105307 (2007)
- [3] A. Fian *et al.*, Nano Lett. **10**, 3893 (2010)
- [4] E. Hilner *et al.*, Nano Lett. **8**, 3978 (2008)

9:00am NS-TuM4 Semiconductor Nanowires: From Materials Physics to Devices, L. Samuelson, Lund University, Sweden **INVITED**

The field of self-assembled growth of semiconductor nanowires has emerged as a powerful way to form advanced materials and devices on the 10nm-scale. In this talk I will review the state of the art of the field, exemplified by our recent progress in growing ideal and defect-free III-V and III-nitride nanowires, on either III-V or silicon as substrates. I will discuss the hot materials physics aspects of structural control and the influence of zincblende vs wurtzite crystal structures on materials properties. I will then review recent progress in realizing various electronic as well as opto-electronic devices, such as nanowire field-effect transistors, tunnel devices, solar-cells as well as light-emitting diodes.

9:40am NS-TuM6 Self-Catalyzed Growth of InP_{1-x}Sb_x Nanowires on InP(111)B, C. Ngo, M. Pozuelo, M. Mecklenburg, H. Zhou, B.C. Regan, R.F. Hicks, S. Kodambaka, University of California Los Angeles

Group III-V semiconductors possess high carrier mobilities and small band gaps, making them applicable to nanoelectronics and optoelectronics.[1] Properties of these materials can in principle be controllably tuned by the fabrication of low-dimensional structures, such as nanowires. Nanowires are most commonly grown via the vapor-liquid-solid (VLS) process using Au as the catalyst. A variant of this approach is the self-catalyzed VLS process, where one of the elements of the growing material promotes the one-dimensional growth can also yield nanowires. Recent studies show that InP and InP_{1-x}Sb_x nanostructures can be grown via metalorganic chemical vapor deposition (MOCVD) using indium and indium-antimonide droplets as catalysts.[2] In this talk, we present results from studies focused on understanding the influence of metalorganic precursor flow rates on the compositional and structural evolution of InP_{1-x}Sb_x alloy nanowires.

All of our samples are grown via MOCVD using trimethylindium (TMIn), tertiarybutylphosphine (TBP), and trimethylantimonide (TMSb) as precursors, with liquid indium droplets as the catalysts and InP(111)B as substrates. The as-grown structures are characterized using scanning and transmission electron microscopies, selected area electron diffraction, energy dispersive x-ray spectroscopy, and scanning TEM to determine their morphology, crystallinity, and composition.

We demonstrate the successful growth of InP_{1-x}Sb_x alloy nanostructures of desired Sb content that is tunable with substrate temperature and TMSb flow rate. Interestingly, doubling the precursor flow rates, at a given temperature, leads to crystallization of pure wurtzite-structured InSb at the catalyst-wire interface. We attribute this phenomenon to the precipitation of excess Sb present in the indium droplets during InP_{1-x}Sb_x alloy growth. By taking advantage of the differences in growth kinetics of InP and InSb, we demonstrate the formation of compositionally-abrupt interfaces in InP/InSb axial nanowire heterostructures.

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10:40am NS-TuM9 The Surface Hydrogen-Controlled Crystal Structure of Group IV Nanowires, N. Shin, M.A. Filler, Georgia Institute of Technology

Semiconductor nanowires offer exciting opportunities to fabricate high performance devices for energy conversion, photonics, and quantum computation. The precise control of crystal structure and geometry is required to achieve a desired behavior, especially in highly confined nanoscale systems. Unfortunately, a fundamental understanding of the surface chemistry that controls surface energetics is currently lacking, despite its critical importance for robust synthesis. Although hydrogen is prevalent during the hydride-based vapor-liquid-solid growth of semiconductor nanowires, its role is largely unknown. To this end, we systematically studied the effect of hydrogen during the growth of Si nanowires and confirmed its influence on crystal growth direction, catalyst ripening, and sidewall faceting for the first time. *In-situ* transmission infrared (IR) spectroscopy was used to identify the presence and bonding of hydrogen on Si nanowires as a function of growth conditions. Si nanowires were grown via a two-step process: (1) brief nucleation at high temperature (550°C) and low pressure (5×10^{-5} Torr) followed by (2) elongation under different conditions (400 – 500°C, 5×10^{-5} – 5×10^{-3} Torr). Vertically-oriented epitaxial Si nanowires with uniform densities, diameters, and lengths were obtained with this method. *In-situ* IR data recorded in real-time reveals the evolution of surface Si-H stretching modes near 2090 cm^{-1} and 2075 cm^{-1} . Our data indicates that surface-bound hydrogen is responsible for changes in crystal orientation even for relatively large diameter nanowires. More specifically, the surface energy of the nuclei-vapor interface near the triple-phase-boundary is dramatically reduced by hydrogen adsorption and drives a transition from <111> to <112> oriented growth. We propose a simple nucleation model that explains this observation. This knowledge is then applied to rationally fabricate nanowire superstructures through the judicious incorporation of small quantities of Ge during growth. This work demonstrates the important role that surface chemistry plays in the growth of semiconductor nanowires, and the extensive use of hydride chemistries for most group IV and III-V semiconductor nanowire syntheses suggests significant implications for many materials systems.

11:00am **NS-TuM10 Inhomogeneous Longitudinal and Radial Dopant Distribution Measurements in Si Nanowires Using Scanning Auger**, *J.S. Hammond, D.F. Paul*, Physical Electronics, *U. Given*, Northwestern University

The incorporation of electrically active dopants into nanowires (NW) is essential to the development of semiconductor NWs based electronic devices. The ability to engineer the electrical properties of nanowires grown by the vapor liquid solid (VLS) process is currently limited by our incomplete understanding of the doping mechanism. Recently, several studies have shown evidence of inhomogeneous radial dopant distributions in Si NWs and the resulting effects on their electrical properties [1-2]. However, the longitudinal dopant profile has not been addressed to the same extent. Studies employing both indirect and direct measurement techniques (such as scanning photocurrent microscopy, Kelvin probe force microscopy and atom probe tomography) have addressed variations in longitudinal dopant profiles in Si NWs and related them to radial dopant variations induced by the growth process [3-4]. There have not yet been direct measurements of dopant concentrations along VLS grown nanowires. We have measured the longitudinal and radial doping profiles of phosphorus doped, untapered Si NWs using scanning Auger. We have found order of magnitude enhancements in the dopant concentration toward the NW's base as expected from previous indirect measurements. Importantly, the physical dopant profile is not identical to the active dopant profile, as shown by comparison with scanning photocurrent microscopy and Kelvin probe force microscopy measurements. The resolution and sensitivity of scanning Auger as an analytical tool for dopant concentration measurements will be compared to the other available techniques to indicate unique capabilities that can advance our understanding of nanowire doping.

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11:20am **NS-TuM11 Crystal Structure Engineering of Ge Nanowires**, *I.R. Musin, M.A. Filler*, Georgia Institute of Technology

Semiconductor nanowire engineering provides a promising route to achieve next generation energy conversion, photonic, and electronic materials. In order to enable the appropriate function for a particular application, control of nanowire crystal structure (e.g. lattice, orientation, faceting) is critical. Unfortunately, this remains a challenging task with bottom-up nanostructure syntheses. To this end, we rationally control Ge nanowire crystal structure for the first time via the addition of bifunctional alkylgermanes, which adjust the interface energetics near the three-phase line. More specifically, Ge nanowires are grown using the vapor-liquid-solid (VLS) technique with germane combined with methyl-, ethyl- or tertbutyl-germane. Scanning electron microscopy (SEM) and high resolution transmission electron microscopy (TEM) reveal that nanowires transition to a new growth direction upon addition of an alkylgermane, but remain single crystalline throughout. For the case of methyl-germane, nanowires transition from the $\langle 111 \rangle$ to $\langle 110 \rangle$ crystal growth direction. A significant reduction in tapering is also observed in all cases. Infrared spectroscopy (IR) shows that nanowire sidewalls are alkyl terminated and X-ray photoelectron spectroscopy (XPS) indicates this termination reduces the rate of oxidation. The impact of alkylgermane identity and surface coverage on crystal growth direction will be discussed in detail. The control of interface chemistry demonstrated by this work provides an important new handle for controlling nanowire structure and properties. Furthermore, the ability to effectively passivate nanowire sidewalls during growth is expected to enable more robust doping profiles by only permitting precursor incorporation through the catalyst tip.

11:40am **NS-TuM12 Towards an Understanding of Ligand Selectivity in Nanocluster Synthesis**, *S. Hong, G. Shafai*, University of Central Florida, *M. Bertino*, Virginia Commonwealth University, *T.S. Rahman*, University of Central Florida

Gold nanoclusters have been known to have a high catalytic reactivity. However, the difficulty in the synthesis of monodisperse nanoclusters (typically consisting of fewer than 100 atoms) in large amounts has been a considerable hurdle to catalytic research. Recently, bidentate ligands of the general formula $P(Ph)_2-(CH_2)_M-P(Ph)_2$ {labeled LM}, where Ph = phosphine and M is the length of the aliphatic chain separating the P atoms, is found to remarkably have the size selecting capacity for gold nanoclusters depending on M. To investigate the origins of size selectivity of the diphosphine ligands towards small-sized Au clusters, we performed scalar

relativistic density functional theory (DFT) calculations using the projector augmented wave scheme (PAW). We find that a diphosphine with long spacer such as L5 can relieve a strain induced by the spacer more easily than can one with short spacer such as L3. Hence, while L5 can interact effectively with a broad range of gold clusters of various sizes, L3 can interact only with a narrow range of gold clusters demonstrating its size-selecting power towards small gold clusters such as Au₁₁₊₃. Based on these results, we propose a two-body ligand system for an ideal, highly-selective ligand, in which one part of the ideal ligand provides a high reactivity towards the broad range of gold clusters and the other part of the ideal ligand provides the control over the reactivity, which could be the form of a short length of spacer, as in diphosphine, but not necessarily limited to, or any type of controllable, reactivity-poisoning component. The controllable competition between the two components of an ideal, highly-selective ligand system will produce a desirable selectivity for the generation of monodisperse nanoclusters of interest through tailoring process.

This work is supported in part by US-DOE under Grant No.DE-FG02-07ER46354.

Tuesday Afternoon, November 1, 2011

Energy Frontiers Focus Topic

Room: 103 - Session EN+NS-TuA

Nanostructured Materials for Thermophotovoltaics, Thermoelectrics & Plasmonics

Moderator: P. Nagpal, Los Alamos National Laboratory

2:00pm EN+NS-TuA1 Thermal Plasmonics as a Route to Photovoltaics?, *D.J. Norris*, ETH Zurich, Switzerland INVITED

Patterned metallic films allow the generation and manipulation of special electromagnetic waves known as surface plasmons that propagate along a metal interface. Because these waves allow the concentration of light in nanometer-scale volumes, they have implications for fundamental phenomena as well as applications such as imaging, sensing, and solar cells. Thus, the field of plasmonics has arisen to study and utilize surface plasmons. While light is typically used to create these waves, in some cases it would be more convenient to have a non-optical source for surface plasmons. One route is thermal excitation (*i.e.*, heat). Here, we will explore hot plasmonic structures for obtaining new optical behavior. For example, we will examine metallic films patterned with a series of circular concentric grooves (a bull's eye pattern). We show that, when heated, these films can emit light that is amazingly narrow, both in terms of its spectrum and its angular divergence. Thus, a simple metallic foil can generate a highly directional beam of monochromatic light by a thermal process. This effect has implications for creating efficient thermophotovoltaic devices, which convert heat into electricity. During these studies, we also developed a simple, high-throughput method for obtaining ultrasoft patterned metal films. Previously, roughness in such films has hindered the field of plasmonics. Therefore, our approach solves a critical problem and allows many high-quality plasmonic structures to be available for the first time.

2:40pm EN+NS-TuA3 Nanocrystal Assemblies: A Modular Approach to Materials Design, *D.V. Talapin*, University of Chicago INVITED

Colloidal nanocrystals can combine the advantages of crystalline inorganic semiconductors with the size-tunable electronic structure and inexpensive solution-based device fabrication. Single- and multicomponent nanocrystal assemblies, also known as superlattices, provide a powerful general platform for designing two- and three-dimensional solids with tailored electronic, magnetic, and optical properties. Unlike atomic and molecular crystals where atoms, lattice geometry, and interatomic distances are fixed entities, the nanocrystal arrays represent ensembles of "designer atoms" with potential for tuning their electronic structure and transport properties. Generally speaking, nanocrystal assemblies can be considered as a novel type of condensed matter, whose behavior depends both on the properties of the individual building blocks and on the interparticle exchange interactions.

The ability to assemble precisely engineered nanoscale building blocks into complex structures is opening the door to materials where components and functionalities can be added, tuned or combined in a predictable manner. I will show how self-assembly of nanocrystals can lead to a palette of unprecedented phases including superlattices isostructural with the Archimedean tilings and dodecahedral quasicrystals.

Efficient charge transport is crucial for performance of nanocrystal-based electronic and optoelectronic devices. The insulating nature of surface ligands traditionally used for nanocrystal synthesis results in the poor electronic coupling between individual nanocrystals. To facilitate charge transport in nanocrystal solids, we introduced the concept of inorganic ligands for colloidal nanocrystals. These ligands, namely metal chalcogenide complexes, can be applied to a broad range of inorganic nanomaterials. I will demonstrate the power of this approach on several examples of prospective electronic, thermoelectric and photovoltaic materials.

4:00pm EN+NS-TuA7 Photonic and Plasmonic Crystals for Thermophotonics and Energy Conversion, *R. Biswas*, Iowa State University & Ames Laboratory - US DOE INVITED

Photonic and plasmonic crystals that have various energy-related applications will be discussed. Metallic plasmonic crystals consisting of an array of nano-holes or nano-pillars on common substrates, with pitch at infrared length scales, have very sharp absorption properties at infrared wavelengths. Such arrays have diverse applications to sensors and thermophotonic applications. The absorption, thermal emission, and angular characteristics from these plasmonic arrays will be described with rigorous scattering matrix simulations and compared to measurements. I will also

survey the rich physics underlying plasmonic nano-arrays at optical length scales, and a few energy related applications.

4:40pm EN+NS-TuA9 Molecular and Hybrid Solution Processible Thermoelectrics, *R.A. Segalman*, *S. Yee*, University of California, Berkeley, *N. Coates*, *J. Urban*, Lawrence Berkeley National Laboratory INVITED

Thermoelectric materials for energy generation have several advantages over conventional power cycles including lack of moving parts, silent operation, miniaturizability, and CO₂ free conversion of heat to electricity. Excellent thermoelectric efficiency requires a combination of high thermopower (S , V/K), high electrical conductivity (σ , S/cm), and low thermal conductivity (κ , W/mK). To date the best materials available have been inorganic compounds with relatively low earth abundance and highly complex, vacuum processing routes (and hence greater expense), such as Bi₂Te₃. Molecular materials and hybrid organic-inorganics bring the promise of inexpensive, solution processible, mechanically durable devices. While highly conductive polymers are now common place, they generally demonstrate low thermopower. Our work on molecular scale junctions suggests that nanostructuring of organics allows them to act as thermionic filters between inorganic junctions which can lead to enhanced thermoelectric properties. We have taken inspiration from this fundamental understanding to design material systems in which we combine a high electrical conductivity, low thermal conductivity polymer with a nanoparticle that contributes high thermopower. Additionally, the work functions of the two materials are well-aligned which introduces the possibility of thermionic filtering at the interface and an additional boost to the power factor. The combination of these effects results in a new hybrid, solution processible material with a thermoelectric figure of merit approaching those of Bi₂Te₃. In this talk, I will discuss both the use of thermoelectric measurements to gain insight to molecular junctions and how this insight translates to design principles for polymer and hybrid thermoelectrics.

5:20pm EN+NS-TuA11 Semiconductor Nanowire Networks as Thermoelectric Platforms, *A.J. Lohm**, University of California Santa Cruz, *E. Coleman*, *G.S. Tompa*, Structured Materials Industries, Inc., *N.P. Kobayashi*, University of California Santa Cruz

Current energy production mechanisms for electrical power and transportation are plagued by inefficiencies which results in most of the energy source being lost as heat. In most cases that heat is found in the form of low-grade heat with temperatures below approximately 200 degrees C. Unfortunately, typical methods such as the Rankine cycle for converting heat to electricity suffer from poor efficiency for low-grade heat. Direct thermoelectric conversion is currently struggling to match the efficiency of the Rankine cycle at high temperatures but offers advantages in terms of reduced maintenance and form-factor which enable energy scavenging in places such as the exhaust line of a vehicle where larger systems could not be implemented.

Dominated by recent progress in nanostructured materials, the unitless thermoelectric figure of merit ZT has been increased to well beyond 1 such that efficiencies are reaching a range which makes them cost effective. Typically thermoelectric materials include elements such as lead or tellurium which are toxic and rare therefore alternative materials are being sought. Recent progress in silicon nanowire thermoelectric has shown a reduction in thermal conductivity, and therefore an increase in ZT of two orders of magnitude, making them viable candidates in the thermoelectric marketplace. Decreased cost and toxicity of silicon as compared to conventional thermoelectric materials make it an attractive candidate but to date nearly all studies on thermoelectricity of nanowires have focused on nanowires in isolation. Our platform based on interconnected 3-dimensional nanowire networks grown directly on metallic substrates provides large area thermoelectric modules capable of scavenging low-grade heat for low cost. The materials properties comprising ZT : thermal conductivity, electrical conductivity and Seebeck coefficient will be discussed for undoped, p-type and n-type silicon nanowire networks with particular emphasis on electrical conductivity and Seebeck coefficient within the temperature range of low-grade heat.

5:40pm EN+NS-TuA12 Diamond as an Electrode Material for the Direct Conversion of Thermal to Electrical Energy through Thermionic Emission, *W.F. Paxton*, *J.L. Davidson*, *W.P. Kang*, Vanderbilt University Introduction

* NSTD Student Award Finalist

Thermionic energy conversion is a candidate technology for the efficient conversion of thermal energy directly to electrical energy. In a thermionic converter, thermally excited electrons are emitted from the surface of a heated cathode into a vacuum gap. These electrons are then collected by a cooler anode and driven through an external load back to the cathode. The thermionic emission current density of a heated cathode can be described by the Richardson Equation (Eq. 1).

$$J = AT^2 e^{-\Phi/kT} \quad (1)$$

where: J: Thermionic emission current density (A/cm²); A: Richardson constant (A/cm² T²); T: Temperature (K); Φ : Material's work function (eV); and k: Boltzmann constant (eV/T)

It can be seen from Eq. 1 that a material with a lower work function, Φ , can achieve higher current densities at lower temperatures than a material with a higher work function, which implies lower work function values translate into better energy converters. Prior attempts to construct efficient thermionic converters were limited by available materials with work function values ranging from 3.5eV to 5eV requiring extreme cathode temperatures in order to achieve useable output power values. In this study, the thermionic emission properties of nitrogen-incorporated diamond films are examined as a potential electrode material to enhance the efficiency of such a device.

Experimental

Polycrystalline diamond films were synthesized on molybdenum substrate via Microwave Plasma-Enhanced Chemical Vapor Deposition (MPCVD). The source gases were H₂, CH₄, and N₂, microwave power was 1.5KW, and the nominal pressure was 50Torr. Scanning electron micrographs of the samples demonstrated uniform film coverage and a thickness of ~100 μ m.

Thermionic emission characterization was performed in a vacuum environment with a base pressure of 1×10^{-7} Torr. The diamond films were resistively heated and the temperature was constantly observed by a dual color pyrometer. Electron emission current was collected with an electrically isolated anode biased at a constant voltage of 100V positioned 0.5cm above the heated cathode.

Results and Discussion

Observation of the electron emission current above the noise level began at 600°C and increased exponentially with temperature up to 800°C. Analysis of this data demonstrated agreement with the Richardson equation with a correlation coefficient of 0.99. From this data, the nitrogen-incorporated diamond samples were determined to have a work function value less than 2eV which is considerably lower than previously mentioned materials. These results exhibit diamond's potential as an interesting cathode material for a thermionic energy converter.

Nanomanufacturing Science and Technology Focus

Topic

Room: 207 - Session NM+NS+MS-TuA

Manufacturable Nanoscale Devices and Processes

Moderator: R. Maboudian, University of California at Berkeley, R. Mu, Fisk University

2:00pm **NM+NS+MS-TuA1 Assessing Nanotechnologies for Volume Manufacturing.** *B.E. Goodlin, S. Butler, L. Colombo, R. Doering*, Texas Instruments Incorporated **INVITED**

Over the past several years, we have seen significant advances in nanotechnology. Much of the underlying purpose of "nanotechnology" research and development, at least as it applies to the electronics industry, is to revolutionize mainstream technology through the use of unique properties and capabilities of nanomaterials, like Si nanowires, graphene, CNTs, in an effort to provide advantages that could not be otherwise obtained thru evolutionary technology scaling. However, the ultimate goal of adopting such technologies into volume manufacturing will most certainly rely on the same tried and tested principles that govern adoption for mainstream manufacturing. Such principles include: performance (does the process hit the desired target?), cost (is it more/less costly as compared to alternatives?), capability (how reproducible is the process?), throughput (how many product can be produced and at what rate?), yield/defectivity, reliability, controllability/metrology (can the process be controlled and what measurements are needed?), maintainability (is equipment/process required easy to maintain?). Do these same governing manufacturing principles truly apply for nanotechnologies? If so, how do some of the current nanotechnologies fare? What gaps exist? Is sufficient focus being applied to address these gaps? Can we even provide adequate answers to these questions yet? Prior to addressing these questions, one must first step back

and clearly identify the important, unique requirements (process, materials, equipment) that exist for a given nanotechnology to enable delivery of the desired performance. Also, one must consider interactions and compatibility of the processes with upstream and downstream processes that are necessary for the final product. Have such requirements and interactions been thought out clearly for various nanotechnologies? If so what are the requirements? What are the interactions? This talk will seek to investigate answers to these questions in an effort to assess various emerging nanotechnologies and their capabilities for eventual adoption into volume manufacturing.

2:40pm **NM+NS+MS-TuA3 Material and Tool Design Challenges for Taking ALD to High-volume Production Beyond 30nm Node.** *B. Lu, Z. Karim, S. Ramanathan*, AIXTRON Inc. **INVITED**

Atomic Layer Deposition enables conformal coating of high-quality thin film on complex nano-scale structures. It has been the preferred choice of deposition technology for high-k and metal films in high-aspect ratio capacitor structure for memory applications. Maintaining 25 fF/cell in sub 30nm DRAM devices poses multiple challenges: (a) structural - very high aspect ratio (~100:1) capacitor cell structures and (b) material - the need for advanced Hi-k oxides beyond ZrO₂, which are typically multi-component oxides. Chemical precursors for a majority of the promising new high-k materials are typically low vapor-pressure liquids or even solids. Achieving excellent composition control inside these high aspect ratio structures using low vapour pressure precursors is a significant challenge. These challenges are pushing ALD technology to its limit and are testing its production-worthiness for high volume manufacturing of sub 30nm devices. Innovative technology in precursor delivery, reactor design, and platform architecture are required to overcome these challenges. This presentation will discuss the new developments in equipment design to meet the technology needs as well as practical manufacturing targets (such as throughput and cost of ownership) in order to provide a production-worthy ALD solution. Applications in new high-k oxide (La/Sr/Ba oxides), metals, and PCRAM materials (such as GST) will be discussed.

4:00pm **NM+NS+MS-TuA7 The Metal-Oxide-Metal Vacancy Drift Memristor - A CMOS Compatible, High Speed, Non-Volatile Switch for Universal Memory and Storage.** *R.S. Williams, J.P. Strachan*, Hewlett-Packard Labs **INVITED**

The existence of the fourth passive circuit element was proposed by Prof. Leon Chua of UC Berkeley in 1971 from fundamental symmetry arguments to augment the familiar resistance, inductance and capacitance equations. Although he showed that such a 'memristor' had many interesting and useful circuit properties, until 2008 no one knew if such a circuit element existed or not. In fact, researchers had been making and studying memristors for decades without knowing it - examples are resistive RAM devices, STTRAM devices and phase change memory devices. At HP, we have focused primarily on metal-oxide-metal bipolar resistive switches. Memristance arises naturally in these systems via coupling of electronic and ionic transport in thin semiconducting metal-oxide films under an external bias voltage. Simple analytical models show that memristance becomes much more important as the thickness of the active device region decreases, and thus memristors are mainly nanoscale structures. Memristor theory serves as the foundation for understanding a wide range of hysteretic current-voltage behavior, including both unipolar and bipolar switching, observed over the past 50 years. We have built nanoscale titanium dioxide and tantalum pentoxide memristors in our laboratory and have demonstrated both their fundamental electrical properties and several potential uses. They can be integrated into electronic circuits using conventional fabrication techniques and materials available in standard CMOS fabrication facilities. I will discuss recent results on such topics as device switching speed, endurance, measurements required to parameterize a physics-based SPICE model, and 3D stacking of memristive crossbars.

4:40pm **NM+NS+MS-TuA9 Large Scale Graphene: Progress and Challenges.** *R.S. Ruoff*, The University of Texas at Austin **INVITED**

Graphene-based materials hold promise due to their electronic and thermal transport properties, mechanical properties, high specific surface area, and that they can act as an atom thick layer, barrier, or membrane. Here, I focus on growth of large area graphene on metal substrates and the structure and thermal and mechanical properties of such graphene. A history of experimental work on graphene (from its discovery in 1969 until 2010) is provided at:

<http://bucky-central.me.utexas.edu/>.

Support of our work by The WM Keck Foundation, DARPA, ONR, SWAN NRI, NSF, ARO, AEC, and Graphene Energy, Inc., is appreciated.

5:20pm **NM+NS+MS-TuA11 Laser-Assisted Electron-Beam Induced Deposition and Etching**, N.A. Roberts, University of Tennessee and Omniprobe, Inc., J.D. Fowlkes, Oak Ridge National Laboratory, P.D. Rack, University of Tennessee and Oak Ridge National Laboratory, G.A. Magel, H.M. Marchman, C.D. Hartfield, T.M. Moore, Omniprobe, Inc.

Focused electron-beam induced deposition (EBID) and etching (EBIE) are direct-write nanofabrication techniques that allow localized deposition or etching of materials without the need for resists. These deposition and etching processes are controlled by electron-beam dissociation of a precursor gas. In both cases, by-product species are created, and if the unwanted byproduct is not desorbed from the surface it will be incorporated into the deposit or reduce the etch rate for deposition and etching, respectively. Substrate heating has been used in experiments to enhance desorption by reducing the residence time of the by-product. The substrate heating has the same impact on the residence time of the precursor gas and therefore reduces the growth or etch rate of the process. *Ex situ* treatments of deposits have also been investigated to remove impurities with some success, but these treatments result in void formation and shape changes. *In situ* laser processing at short pulse widths is ideal for electron-beam induced processing because desorption of the by-products can be achieved by local heating of the sample, but the narrow pulse width results in a short heating time and cooling time. Thus the by-products can be effectively desorbed and adequate recovery time for fresh reactant to re-adsorb.

Laser-assisted EBID and EBIE processes are made possible through the use of the OptoProbe™, which is an optical imaging and processing system that can be attached to an SEM and used in conjunction with an appropriate gas injection system. The design of this port-mounted optical accessory enables simultaneous optical imaging and delivery of laser irradiation to a sample within the SEM, without interfering with normal SEM/FIB imaging and processing modes. The optical system is mounted on a 3-dimensional nanomanipulator so that precision alignment and focusing is easily achieved. For this work, the OptoProbe™ has been optimized to deliver a high-irradiance near-infrared laser spot to provide localized time-dependent sample heating for enhancing focused electron-beam induced deposition and etching. In this presentation, we will discuss recent experimental results as well as modeling of laser-assisted EBID of Au and EBIE of SiO_x using XeF₂.

5:40pm **NM+NS+MS-TuA12 Channel SiGe Selective Epitaxy Process for DRAM High K Peripheral Transistors**, J. Yeo, H. Hwang, S. Lee, W. Yoo, S. Ahn, I. Jeon, B. Kim, S. Nam, S. Kim, K. Jung, J. Lee, S. Jang, T. Lee, K. Huh, S. Yamada, Samsung Electronics Co., Ltd, Republic of Korea
As the DRAM technology evolved towards the sub 2x era, the need for high performance transistor grows higher for the DRAM peripheral transistors. The novel technologies such as embedded SiGe, high K gate oxide, or 3-dimensional transistor technologies are indispensable in a near future. Especially, to scale the gate oxide further and to meet the gate oxide leakage constraint at the same time, high K gate dielectrics should be adapted. For a successful application of high K dielectrics to DRAMs, it is essential to realize the effective work-function (EWF) for both n, pMOSFETs, where this EWF should be maintained even after huge back-end thermal budget of DRAM process. Therefore, so called 'gate-first approach' has been examined, i.e. LaO, or MgO capping layers for NMOS [1,2], and AlO capping layer, F implantation, and ion implantation on metal for PMOS [2,3], respectively. A SiGe channel has been also examined by many research groups [4-7]. When SiGe epitaxial layer is introduced to the PMOS channel, interface trap density (D_{it}) has been increased by order of magnitudes, which consequently results in the degradation of transistor performance and reliability [4]. To control this interface degradation, Si capping layers often deposited on the SiGe channels, which reduces the V_t gain that can be gained by SiGe only. In this research, SiGe selective epitaxial growth (SEG) condition has been set-up first, Si capping condition has been optimized by tuning growth temperature, process pressure, and Cl/Si ratio in a LPCVD chamber. The process pressure was precisely controlled to grow Si capping layer 'selectively' as well as to avoid SiGe migration. When we increased the process pressure, surface atomic mobility can be decreased, which effectively reduced SiGe migration. However, when the pressure is increased too high, resulting in growth rate too high, selective growth condition fails. HCl/SiH₄ flow rates were also tuned to get a margin for selective growth condition. When introduced to DRAM peripheral transistors, a SiGe channel reduces PMOS V_{th} by 290 mV, and Si capped SiGe channel by 170 mV, respectively, which has good agreement with the expected value by Energy Band Simulation. This reduced V_t controllability could be recovered by increasing Ge content of SiGe channel. To conclude, the channel SiGe channel SEG process has been successfully applied for DRAM integration, and robust pMOSFET V_t tuner method was realized.

Nanometer-scale Science and Technology Division
Room: 203 - Session NS+AS-TuA

Frontiers in Nanoscale Imaging and Characterization
Moderator: E.I. Altman, Yale University

2:00pm **NS+AS-TuA1 Proximity, Phonon in Nanometer Size Superconducting Nb Islands : A STM Study**, S. Jeon, Seoul National University, Republic of Korea, H. Suh, Samsung Advanced Institute of Technology, Republic of Korea, Y. Oh, S. Kim, Y. Kuk, Seoul National University, Republic of Korea, M. Machida, Japan Atomic Energy Agency, Japan

Despite successful macroscopic picture on a conventional superconductor niobium(Nb), not much were reported on nanometer scale objects. One may have to consider quantum mechanical size effect, fluctuation, and quantum phase slip in a nanometer scale superconducting object. In this study, quantum size effect of superconducting niobium(Nb) nano-islands grown on a tungsten(W) surface was investigated with scanning tunneling microscopy(STM) and scanning tunneling spectroscopy(STS). Various size (30nm ~ 200nm) of niobium islands were formed on a W(110) surface after making several layers of wetting layer. STS measurement at 4.2K showed that the Nb island have a BCS-like superconducting gap of about 2meV around the Fermi level. The critical temperature is much lower than that of the bulk value. In addition, We found spatial dispersion of DOS (density of states) outside of the superconducting gap. Spatially-resolved scanning tunneling spectroscopy(SR-STs) data taken inside and outside of the niobium islands reveal unique dispersion. That can be understood by quantum size effect based on Bogoliubov - de Gennes equation.

2:20pm **NS+AS-TuA2 Spin Excitation Spectroscopy**, D. Eigler, IBM Almaden Research Center **INVITED**

The energies and relaxation times of spin excitations are traditionally measured using the classic spin resonance techniques, Nuclear Magnetic Resonance (NMR) or Electron Spin Resonance (ESR). The measurement of spatial variations of spin relaxation times is of profound practical importance as they are often used as the primary contrast mechanism in magnetic resonance imaging. It has been an outstanding challenge to extend the spatial resolution of these spectroscopies to the atomic scale. We have developed a new kind of spin spectroscopy, *Spin Excitation Spectroscopy*, that achieves this goal. Through a combination of inelastic tunneling spectroscopy and pump-probe techniques, we have extended the capability of the scanning tunneling microscope to interrogate both the energetics and dynamics of spin systems on the atomic scale. We anticipate that this will have application in a broad range of studies concerned with nanometer-scale magnetic systems, how they may be understood, and how they may be engineered to have a desired functionality.

Work done in collaboration with Cyrus Hirjibehedin, Andreas Heinrich, Christopher Lutz, Jay Gupta, Markus Ternes, Alexander Otte, Sebastian Loth and Bruce Melior

3:00pm **NS+AS-TuA4 Atom-Specific Interaction Quantification and Identification by Combined Scanning Tunneling and Atomic Force Microscopy**, M.Z. Baykara, H. Mönig, Yale University, T.C. Schwendemann, Southern Connecticut State University, M. Todorovic, R. Perez, Universidad Autónoma de Madrid, Spain, E.I. Altman, U.D. Schwarz, Yale University

On surfaces, forces extending into the vacuum direct the behavior of many scientifically and technologically important phenomena such as corrosion, adhesion, thin film growth, nanotribology, and surface catalysis. To advance our knowledge of the fundamentals governing these subjects, it would be desirable to simultaneously determine a surface's structure, map electron densities, quantify force interactions, and identify chemical species. For example, in the case of a catalytically active surface, this would allow study of the role and effectiveness of surface defects such as vacancies, steps, kinks, impurities, and domain boundaries as active sites.

In this talk, we will show the example of an oxygen/copper(100) surface phase that much of this information can be derived from combining the new method of three-dimensional atomic force microscopy (3D-AFM) [1,2], a variant of noncontact atomic force microscopy, with simultaneous scanning tunneling microscopy. The surface oxide layer of Cu(100) features domain boundaries and a distinct structure of the Cu and O sublattices that is ideally suited for such model investigations. By combining experimental results with theoretical simulations, we will show how 3D data sets enable the site-specific quantification of force interactions and tunneling currents, how different chemical species can be imaged using different tips, different tunneling conditions, and different interaction mechanisms, and how

structure-induced stress fields and their influence on the local chemical activity and topographical deformation can be studied.

- [1] B. J. Albers et al., *Nature Nanotechnology* **4**, 307 (2009).
[2] M. Z. Baykara et al., *Advanced Materials* **22**, 2838 (2010).

4:00pm NS+AS-TuA7 The Role of Surface States in Inelastic Electron Tunneling Into Metal Surfaces, P. Maksymovych, M.H. Pan, Q. Li, Oak Ridge National Laboratory

A small fraction of electrons tunneling across a vacuum junction will undergo inelastic scattering, exciting surface phonons, molecular vibrations, magnons and plasmons in the contact leads. Although the study of surface phonons is a most straightforward inelastic electron tunneling spectroscopy (IETS) experiment, relatively few systematic studies have been done to date. One of the most surprising observations was that of atomic resolution in the IETS of Au(111) [1], and an equally intriguing variation phonon energy from 20 meV to 9 meV depending on the vertical stacking across the $22 \times \sqrt{3}$ reconstructed surface.

To investigate the origin of these effects on Au(111), we have carried out systematic IETS measurements using a home-built scanning tunneling microscope operating in the temperature range from 20K to 77 K. Particular emphasis was put on understanding of the role of the surface state in the electron-phonon coupling, judged from the intensity of the IETS signal and the energy of the observed vibrational modes.

We have found that largely independent of the measurement temperature, IETS spectra feature a broad peak centered around 18 meV, representing a weighted average of the phonon density of states within the Brillouin zone. Lower lying surface phonon bands (with energies from 7 to 9 meV) were resolved, but the majority of spectra are dominated by the peak at 18 meV, corresponding to the bulk phonon modes at the zone boundary. Although the spectrum remained largely unchanged across the surface, in contrast to earlier observations, the IETS intensity markedly dropped at the step edges. Furthermore, the IETS intensity exhibited long-range oscillations, the wavelength of which coincided with the Friedel oscillations of the surface state in the vicinity of the defects. Combined, the observations attest to the important role of the surface state in electron-phonon coupling [2], likely emphasizing the critical enhancement in the lifetime of hot electrons that tunnel into surface states relative to bulk states. We will also discuss the important role of tip effects in the IETS measurement. Tip-sensitivity may produce significant variations in the IETS spectrum across the herringbone reconstruction because of selectivity toward a particular phonon mode due to the convolution of the tip-surface interactions and heterogeneity of the surface state across the surface.

Research was conducted at the Center for Nanophase Materials Sciences and sponsored by the Division of Scientific User Facilities, U.S. Department of Energy.

- [1] H. Gawronski, M. Mehlhorn, K. Morgenstern, *Science* **319** (2008) 930-933.
[2] Q. Li, P. Maksymovych, M. Pan et al, to be submitted (2011)

4:20pm NS+AS-TuA8 2011 AVS Medard Welch Award Lecture - Inelastic Electron Tunneling Spectroscopy and Imaging of Single Molecules, W. Ho*, University of California, Irvine INVITED

The transformation of matter invariably involves energy transfer and redistribution. By probing matter and its coupling to external perturbations at the atomic scale with the scanning tunneling microscope (STM), it is possible to gain a broad range of new knowledge that would be difficult to achieve by other techniques. Through high precision measurements of inelastic phenomena inside single molecules with the STM, chemical and physical properties of molecules are obtained by probing their response to electrons, photons, and an external magnetic field. The STM is used to measure the electronic and vibronic states, vibrational and spin excitations, and optical transitions in single molecules. New features emerge when measurements are carried out at increasingly extreme conditions of vacuum, temperature, magnetic field, and pulse duration of light while maintaining the atomic-scale spatial resolution. The inelastic processes can result in nuclear motions such as molecular rotation, diffusion, conformational change, bond dissociation, and bond formation. By studying a wide range of systems from atomic hydrogen to large molecules such as metal porphyrins and phthalocyanines on metal and thin oxide surfaces, the new knowledge obtained by the STM can be applied to the understanding and advancement of numerous technologies such as chemical catalysis, information storage, nanophotonics, alternative energies, and environmental remediation. Underlying these longer range applications is the immediate gain in the

fundamental scientific understanding of matter that can be derived from these studies.

5:00pm NS+AS-TuA10 Two-Color Ultrafast-Laser-Assisted STM, A. Dolocan, D. Acharya, P. Zahl, P. Sutter, N. Camillone, Brookhaven National Laboratory

Substrate-adsorbate charge transfer and carrier-mediated substrate-adsorbate energy transfer are central to photoinduced surface chemistry. To investigate fundamental links between surface electron dynamics and heterogeneous photocatalysis we are developing an ultrafast-laser-excited scanning tunneling microscopy approach to probing surface electron dynamics with simultaneous subnanometer spatial and subpicosecond temporal resolution. Historically, thermal effects associated with laser power variations have presented a major hurdle to progress. In particular, thermal load modulations due to optical interference have been a barrier to observing dynamics at timescales on the order of the temporal width of the laser pulses. In this talk we present results from a new two-color method that completely eliminates this interference. We will show results for two cases: (1) where the tip is retracted from the surface far enough to prohibit tunneling, and (2) where the tip is within tunneling range of the surface. A delay-modulation technique isolates the two-color photo-emission from concurrent one-color two-photon photoemission and the conventional tunneling current, and also enables subpicosecond time-resolved detection of the photoexcited surface electrons. Advantages of the two-color approach are highlighted by comparison with the one-color case where optical interference causes current modulations that are orders of magnitude larger than the desired signal. The two-color approach represents an important step toward the ultimate goal of simultaneous subnanometer and subpicosecond measurement of surface electron dynamics.

5:20pm NS+AS-TuA11 High Precision local electrical Probing: A New Low Temperature 4-Tip STM with Gemini UHV-SEM Navigation, B. Guenther, A. Bettac, M. Maier, M. Oertel, Omicron NanoTechnology, Germany, F. Matthes, C.M. Schneider, Forschungszentrum Juelich, Germany, A. Feltz, Omicron NanoTechnology, Germany

A major challenge in the development of novel devices in nano- and molecular electronics is their interconnection with larger scale electrical circuits required to control and characterize their functional properties. Local electrical probing by multiple probes with STM precision can significantly improve efficiency in analyzing individual nano-electronic devices without the need of a full electrical integration. Among a very few commercial approaches, the Omicron *UHV NANOPROBE* has been established as a suitable instrument for local electrical probing in UHV on nano-structures down to structure sizes in the 10 nm range. The mayor technical requirements for such sophisticated instrumentation are:

- Rapid and simultaneous SEM navigation of four local STM probes on small structures
- Localization of nanostructures by high resolution SEM (UHV Gemini)
- Individual probe fine positioning by atomic scale STM imaging
- STM based probe approach for "soft-landing" of sharp and fragile probes and controlled electrical contact for transport measurements
- Preparation techniques towards sharp and clean and STM tips
- Suitable low noise signal re-routing for transport measurements with third party electronics

Although the *UHV NANOPROBE* has been successfully used for various applications, today's scientific requirements motivated the development of the next generation probing system. We will present the newly developed *LT NANOPROBE* which takes experimental capabilities one step further and opens up new research opportunities in nano-electronics, spintronics, and molecular electronics. Besides SEM/STM probe fine navigation and imaging, the excellent STM performance level of the *LT NANOPROBE* expands applications to tunneling spectroscopy and even the creation or modification of nano-structures by an ultimately precise STM probe. The R&D project has been driven by the following major milestones:

- Operation at temperatures of $T < 5$ K for STM imaging and STM based probing
- SEM navigation at base temperature $T < 5$ K
- Simultaneous operation of STM and SEM at base temperature
- Thermal equilibrium of sample and probes for (i) extremely low thermal drift and electrode positioning accuracy in time and (ii) defined temperature of the local electrical contact and
- Performance and stability level of each individual STM Probe suitable for STM spectroscopy and atom manipulation

First evaluation measurements with the system installed at the Forschungszentrum Jülich will be presented: STM on Au(111) with pm

* Medard W. Welch Award Winner

stability, STS revealing the superconducting gap of a Nb tip with approx. 3meV gap size, and transport measurements on nanowires at T<5K.

5:40pm **NS+AS-TuA12 Spin-Polarized VLEED: Experimental Access to the Spin-Dependent Surface Barrier**, *K. Wulff, A.B. Schmidt*, Westfälische Wilhelms-Universität Münster, Germany, *J. Braun*, Ludwig-Maximilians-Universität München, Germany, *M. Donath*, Westfälische Wilhelms-Universität Münster, Germany

The spin-dependent reflectivity of very-low-energy electrons from ferromagnetic surfaces has recently been utilized in a new type of electron spin detector [1,2]. The underlying effect is a result of electron scattering from a spin-dependent substrate potential as well as from a spin-dependent surface-potential barrier.

We present the first spin-polarized very-low-energy electron-diffraction (SPVLEED) measurements on a ferromagnetic system. Our data on Co/Cu(001) reveal a significant spin dependence of the reflected intensities that varies strongly with electron energy, polar and azimuth angle of incidence.

In these intensity vs. energy spectra $I(V)$, additionally, fine structures appear [3], which are caused by the surface-potential barrier. Their particular intensities and energy positions are very sensitive to the shape of the surface-potential barrier. On the vacuum side far from the surface, the barrier resembles the well-known Coulomb potential, while, on the crystal side, it converges to the inner potential. In theoretical calculations, the transition region is usually described by a parameterized phenomenological model. Our experiment provides access to exactly this transition region.

We could determine the spin-dependent shape of the surface-potential barrier of Co/Cu(001) from the dispersion of the fine structure as a function of polar and azimuth angle.

[1] T. Okuda *et al.*, Rev. Sci. Instrum. **79** (2008) 123117 ; [2] A. Winkelmann *et al.*, Rev. Sci. Instrum. **79** (2008) 083303 ; [3] R.O. Jones, P.J. Jennings, Surf. Sci. Reports **9**, 165 (1988)

Vacuum Technology Division

Room: 111 - Session VT+MN+NS+SS+AS-TuA

Surface Science for Future Electronic Materials and Accelerator Applications

Moderator: M. Wüest, INFICON Ltd, Liechtenstein

2:00pm **VT+MN+NS+SS+AS-TuA1 New UHV Low Temperature Scanning Probe Microscopy Facility for the Study of Future Electronic Materials**, *J.A. Strosio*, National Institute of Standards and Technology
INVITED

Since the beginning of the last century new frontiers in physics have emerged when advances in instrumentation achieved lower experimental operating temperatures. Notable examples include the discovery of superconductivity and the integer and fractional quantum Hall effects. New experimental techniques are continually adapted in order to meet new experimental challenges. A case in point is scanning tunneling microscopy (STM) which has seen a wealth of new measurements emerge as cryogenic STM instruments have been developed in the last two decades. In this talk I describe the design, development and performance of a scanning probe microscopy facility operating at a base temperature of 10 mK in magnetic fields up to 15 T [1]. The STM system can be connected to, or disconnected from, a network of interconnected auxiliary UHV chambers used for sample and probe tip preparation. Results from current measurements on graphene and topological insulators will be described.

[1] *A 10 mK Scanning Probe Microscopy Facility*, Y. J. Song, A. F. Otte, V. Shvarts, Z. Zhao, Y. Kuk, S. R. Blankenship, A. Band, F. M. Hess, and J. A. Strosio, Rev. Sci. Instrum. **81**, 121101 (2010).

2:40pm **VT+MN+NS+SS+AS-TuA3 Contact Resistance of RF MEMS at a Randomly Rough Surface in the Presence and Absence of Adsorbed Organic Monolayers**, *D. Berman, J. Krim, M.J. Walker*, North Carolina State University

Understanding of current flowing through the asperities is interesting for many applications: in RFMEMS, Molecular electronics, Nanotube tunneling etc.

Previous results [2] suggest that the films are displaced from the contacts themselves, but remain present in nearby regions. The increase in resistance is associated with elimination of vacuum electrical tunneling currents in those regions. This raises the question of the relative proportions of contact resistance (R_c) and effective tunneling resistance (R_t).

Measurements on the gold on gold contacts adhered in the closed position, where the contamination film cannot possibly be placed inside the contacts are reported, to investigate vacuum tunneling current contributions to the total current at the contact. Electrical Contact Resistance measurements are reported for RF micro-electromechanical switches with Au/Au and Au/RuO₂ contacts, situated within an ultrahigh vacuum system equipped with *in situ* oxygen plasma cleaning capabilities. Fused Au/Au switch resistance increases by 3-5% (which corresponds to 20W tunneling resistance in parallel) after adding pentane to the switch environment. Moreover, the results are repeated with a different substrate (Ruthenium rather than Au), known for higher resistance, to change the resistance values with almost the same work function. If this is tunneling, the same effective tunneling resistance is expected, because tunneling depends on the work functions of the tip and substrate, which are close for gold and ruthenium oxide. In addition, the results are investigated for two different adsorbates, pentane and dodecane. Measurements have been recorded as the function of film coverage and the same tunneling resistance impact is observed. This is consistent with elimination of vacuum tunneling when adsorbed films are present.

Theoretical analysis of two possible mechanisms of the impact of molecular uptake is performed to interpret the experimental results: a) parallel connection of contact resistance and effective tunneling resistance before molecular adsorption, followed by molecules blocking the tunneling current; b) in series connection of contact resistance and pentane layer after adsorption. The data are more consistent with model a).

This work was supported by US National Science Foundation, AFOSR MURI and DARPA. We are grateful to C. Nordquist at Sandia National Lab and J. Hammond at RF Micro Devices for providing the experimental switches.

[1] D. Berman, M. Walker, C. Nordquist, J. Krim, *in preparation for Journal of Applied Physics*

[2] M. Walker, C. Nordquist, J. Krim, *in preparation for Tribology Letters...*

3:00pm **VT+MN+NS+SS+AS-TuA4 Surface Issues for Solid Niobium SRF Accelerator Cavities**, *M. Kelley*, College of William and Mary

The world-wide physics community looks forward to a slate of accelerator projects of unprecedented magnitude and diversity. Certainly its sheer size makes the International Linear Collider the most visible to the public eye, with 16,000 solid niobium cavities performing at historically high gradient, and built (and operated) for historically low unit cost. Net performance makes superconducting radiofrequency (SRF) technology the approach of choice.

Solid niobium is the material most widely used for construction of SRF cavities because it has the highest critical transition temperature ($T_c = 9.2$ K) of the pure metals, sufficiently high critical magnetic field ($H_c > 2$ k Oe) for SRF applications, and metallurgical properties adequate for fabrication and service load. Studies of the SRF performance of niobium cavities began to be reported more than 30 years ago and continue now with the application of improved experimental techniques. Niobium metal superconductivity is a nanoscale, near-surface phenomenon because of the shallow RF penetration. Considerable evidence indicates that cavity interior surface chemistry and topography strongly impact SRF accelerator performance, motivating investigation of how they are affected by post-fabrication treatments.

Current status and prospects are discussed with respect to accelerator needs and opportunities.

4:00pm **VT+MN+NS+SS+AS-TuA7 Examples of Surface Related R&D on Nb Samples and SRF Cavities for Particle Accelerators at JLab**, *A.T. Wu*, Thomas Jefferson National Accelerator Facility

This contribution will review some examples of surface related R&D on small and flat niobium (Nb) samples and single cell Nb superconducting radio frequency (SRF) cavities done at Jefferson Lab in the past few years. Most of the surface measurements were performed via the experimental systems available in the surface science lab that was set up¹ at JLab to study the various problems on the Nb surfaces in the SRF field.

The first topic is about a new Nb surface polished technique called buffered electropolishing (BEP) that was developed at JLab². This technique can produce the smoothest surface finish ever reported in the literature³. It was also demonstrated that under a suitable condition, a Nb removal rate higher than 10 $\mu\text{m}/\text{min}$ could be realized. Efforts have been made to try to understand the polishing mechanism through experiments with a well defined experimental geometry on small flat Nb samples. A unique versatile

vertical polishing system was constructed to perform BEP on Nb single cell cavities. Small flat samples, Nb dumbbells and Nb single cell cavities were also studied and treated at CEA Saclay in France and Peking University in China and the cavities were RF tested at JLab. Experimental results will be analyzed and summarized. It is shown that BEP is a very promising candidate for the next generation surface polishing technique for Nb SRF cavities.

A second topic will deal with a new Nb surface cleaning technique employed gas cluster ion beam (GCIB)⁴. This is a result of collaboration with Epion Corporation, Fermi Lab, and Argonne Lab. Beams of Ar, O₂, N₂, and NF₃ clusters with accelerating voltages up to 35 kV were employed in this technique to bombard Nb surfaces. The treated surfaces of Nb flat samples were examined by several surface experimental systems such as SEM, EDX, AFM, SIMS, and 3-D profilometer. The experiments revealed that GCIB technique could not only modify surface morphology of Nb, but also change the surface oxide layer structure of Nb and reduce the number of field emission sites on the surface dramatically. Computer simulation via atomistic molecular dynamics and a phenomenological surface dynamics was employed to help understand the experimental results. A system was set-up at Epion Corporation to do treatments on Nb single cell cavities and then RF-tested at JLab. The experimental results will be summarized and the perspective of this technique for real applications is discussed.

Finally, I will show two typical examples of surface studies of Nb using a high resolution transmission electron microscope⁵ and a home-made scanning field emission microscope⁶ respectively.

4:20pm VT+MN+NS+SS+AS-TuA8 Early Stages of Nb Growth on Cu for SRF Accelerator Applications. C. Clavero, The College of William and Mary, N.P. Guisinger, Argonne National Laboratory, R.A. Lukaszew, The College of William and Mary

Among the large range of possible applications for superconducting Nb thin films, coatings for superconducting radio-frequency (SRF) cavities in linear accelerators have greatly aroused the interest of researchers in the last years[1]. Superconducting thin films and multilayer coatings are expected to increase further the maximum field gradients that SRF cavities can withstand, pushing them above 100 MeV/m [2]. In this regard, Nb coated Cu cavities have been proposed as a prototypical system for this purpose since they combine the better thermal stability of Cu due to its much higher thermal conductivity and the superconducting properties of Nb thin films [3]. Nevertheless, it is well known that structural dislocations and localized surface resistive defects on the thin films have a dramatically negative influence on their superconducting properties and resonator quality. Indeed, the quality of the films is strongly conditioned by the growth mode below the single atomic layer coverage at the very early stages of growth, and thus special attention needs to be devoted to this range. Here we present a complete study on the early stages of growth of Nb on Cu(111). Different growth and annealing temperatures ranging from room temperature (RT) to 600 °C were used in order to investigate the characteristic growth mode of Nb in the sub-monoatomic coverage range. Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) were used to investigate morphology and chemical composition of the surfaces with atomic resolution. Growth of sub-monolayer coverages at RT leads to amorphous Nb islands with 1 and 2 AL heights. Annealing at 350 °C gives rise to crystallization of the islands pseudomorphically with the substrate, *i.e.* Nb(111). Further annealing at 600 °C promotes interdiffusion of Nb atoms into the Cu substrate and alloying of the islands. Growth of higher coverages above 1 AL at 350 °C reveals preferential Volmer-Weber growth mode.

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4:40pm VT+MN+NS+SS+AS-TuA9 Epitaxial Niobium Thin Films for Accelerator Cavities. W.M. Roach, D. Beringer, C. Clavero, College of William and Mary, C. Reece, Thomas Jefferson National Accelerator Facility, R.A. Lukaszew, College of William and Mary

The currently proven superconducting radio frequency (SRF) technology used in linear accelerators is based on bulk niobium cavities. Since this has a high cost and these cavities are approaching the maximum field gradients that they can withstand [1], development of a suitable, reliable, cost effective alternative to bulk niobium SRF cavities is needed. Attempts have been made to replace bulk niobium cavities with niobium-coated copper cavities since the thermal conductivity of a suitable base material such as copper is better than bulk niobium [2]. Coating niobium on SRF cavities is a promising but also challenging path, since there are several difficulties associated with various thin film deposition techniques and a lack of

systematic studies pertinent to niobium thin film nucleation and growth leading to surfaces of greatest benefit.

Our systematic studies show that the transport properties, in particular the residual resistance ratio (RRR), are improved when niobium is epitaxially grown on crystalline ceramic substrates such as MgO and Al₂O₃, compared to niobium grown on (001) copper templates. Since grain boundaries are typically one of the main obstacles to superconducting transport, we show how the increased number of crystallographic domains that can occur during epitaxial niobium growth onto copper surfaces leading to higher density of grain boundaries can explain our results. We will discuss a route to improved transport properties while maintaining thermal efficiency by using alternative seed-layers grown on copper templates that can limit increased grain boundary density. We will show our correlated studies of microstructure and surface morphology (RHEED and AFM) and the resulting transport/magnetic properties (four point probe and SQUID magnetometry) illustrating possible mechanisms to improve SRF cavity performance of such niobium films.

This work is funded by HDTRA1-10-1-0072 from the Defense Threat Reduction Agency as well as a subcontract from Thomas Jefferson National Accelerator Facility under contract DE-AC05-06OR23177 from the Department of Energy as supplemented by ARRA funds.

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5:00pm VT+MN+NS+SS+AS-TuA10 Development via Energetic Condensation of Niobium Thin Films Tailored for Superconducting RF Applications. A.-M. Valente-Feliciano, Jefferson Lab

For the past three decades, bulk niobium has been the material of choice for SRF cavities applications. In the recent years, RF cavities performances have approached the theoretical limit for bulk niobium. For further improvement of RF cavity performance for future accelerator projects, an interesting alternative has been recently proposed by Alex Gurevich with the Superconductor-Insulator-Superconductor multilayer approach, using the benefit of the higher critical field H_{c2} of higher-T_c superconductors without being limited with their lower H_{c1}.

JLab is pursuing this approach with the development of multilayer structures based on NbTiN via magnetron sputtering and High Power Impulse Magnetron Sputtering (HiPIMS). Insulators such as, AlN, Al₂O₃ and MgO are being investigated as candidates for the insulator layers.

This paper presents the characteristics of NbTiN and insulator layers produced and results on NbTiN-based multilayer structures on bulk Nb and thick Nb films.

5:20pm VT+MN+NS+SS+AS-TuA11 Evaluation of Secondary Electron Emission Yield Suppression Coatings at CEsrTA. Y. Li, X. Liu, J. Calvey, J. Conway, J.A. Crittenden, M.A. Palmer, J.P. Sikora, Cornell University, S.De. Santis, Lawrence Berkeley National Laboratory

The performance of particle accelerators may be significantly limited due to buildup of electron cloud (EC) in the vacuum chambers. The EC buildup intensity is strongly affected by secondary electron emission from interior surfaces of the chambers. Application of coatings with reduced secondary electron yield (SEY) onto vacuum chamber interior surfaces is one of the most economical EC suppression techniques. As a part of the International Linear Collider (ILC) R&D program, the Cornell Electron Storage Ring (CESR) has been successfully reconfigured as a Test Accelerator (CesrTA) to study EC buildup and suppression techniques. During the CesrTA program, various passive SEY-reduction coatings (TiN, amorphous-carbon and diamond-like carbon thin films) have been applied to diagnostic vacuum chambers in CESR in order to evaluate the efficacy of the EC suppression and the vacuum performance of these coatings in an accelerator environment. These chambers are equipped with both vacuum instrumentation (ion gauges and residual gas analyzers), as well as EC diagnostics (retarding field analyzers and RF-shielded pickups). In this paper, we present the results of studies of the vacuum conditioning and EC mitigation performance of these coatings.

5:40pm VT+MN+NS+SS+AS-TuA12 **Electron Cloud Mitigation for the Large Hadron Collider (LHC)**, *V. Baglin, G. Bregliozzi, P. Chiggiato, P. Costa Pinto, J.M. Jimenez, G. Lanza, M. Taborelli, C. Yin Vallgren*, CERN, Switzerland

One of the main issues for the vacuum system of the Large Hadron Collider (LHC) is the build-up of electron clouds generated by electron multipacting in presence of beams. The occurrence of spatially distributed negative charges can lead to beam instabilities and emittance blow-up, pressure rises with a consequent background growth in the experimental areas, and increased thermal load in the cryogenic sections. The development of electron clouds depends on beam intensity and structure, magnetic field, and, in particular, the secondary electron emission of the beam pipe walls. With respect to this latter point, electron clouds can be eradicated whenever the maximum secondary electron yield becomes lower than a critical threshold. In the LHC the problem has already been tackled at the design phase by introducing TiZrV non-evaporable getter thin film coatings as the baseline for most of the room temperature sectors of the ring. After activation by in situ heating, this material provides maximum secondary electron yield lower than 1.1. In addition, during operation, dedicated scrubbing runs are carried out by generating intentionally electron clouds and electron impingement onto the non-coated vacuum chambers, in a way to reduce their secondary electron yield. Recently magnetron sputtered carbon coatings have been also studied because they can reach exceptionally low secondary electron emission without any heating; their application in the LHC injectors and future LHC components is under investigation.

The effect of electron clouds in the pressure variations during the first months of LHC operation will be presented, together with the effects ascribed to the mitigation techniques.

Tuesday Afternoon Poster Sessions

Nanometer-scale Science and Technology Division

Room: East Exhibit Hall - Session NS-TuP

Nanometer-scale Science and Technology Division Poster Session

NS-TuP1 Electromigration Assisted Single Silver Nanowire Ammonia Sensing, *W. Xing, S. Kung, R. Penner*, University of California, Irvine

Due to small size, high sensitivity, and low power consumption, 1 dimensional nanowire sensors have attracted a lot of attention and may substitute for traditional thin film sensors in the future. To further improve the sensitivity, there is an obvious need to make sensors with a single nanowire and some seminal work has already been done using semiconductor nanowires in this direction. In this work, a single silver (Ag) nanowire was prepared on glass surface using Lithographically Patterned Nanowire Electrodeposition (LPNE) method. The produced Ag nanowire had a mean grain size of around 30nm and a height and width in the range from 20-80nm and 100-400nm, respectively. Chemiresistor type sensors were fabricated from these single electromigrated Ag nanowires with 4 probe contacts, and their resistances upon exposure to different concentrations of NH₃ gas were investigated at room temperature. Furthermore, electromigration was used to create a narrow junction inside the nanowire, which enhanced the sensing performance dramatically. The electromigrated sensors showed a resistance change, $\Delta R/R_0$, that was large (90% for 7% NH₃), fast (<30s) and reversible with a detection limit of approximately 200ppm. In addition, the characterization of these nanowires by AFM, TEM, and SEM will be presented.

NS-TuP2 Inhomogeneous Density Distribution of Silicon Dioxide Thin Film Thermally Grown at 1000 °C on Si (100) Surface, *K. Odaka, A. Kurokawa, Y. Azuma, L. Zhang, T. Fujimoto*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

We would report on the XRR (X-ray reflectivity) analysis to observe the density distribution of the SiO₂ thin film which is thermally grown on Si (100) at 1000 °C. The results show the non-uniform distribution in depth, and once the high density SiO₂ was formed during ramp-up it would remain under the following 1000 °C oxidation.

Experimental We measured XRR using an apparatus equipped with a shower of high purity N₂ to protect a specimen from contamination for a few hours of measurement. We analyzed the data with a fitting method [1], [2] which is well established to evaluate thicknesses, densities, and surface roughness of laminated layers of a specimen. We assumed a two-layer-fitting model consisting of a transition layer and an upper layer where each had uniform density in it. We oxidized a H-terminated Si (100) specimen of 15x15 mm² in dry O₂ flow at 1 atm. with a quartz tube furnace. The ramp rate was 33 Kmin⁻¹. We kept specimens at 1000 °C for 0 through 120 min to form SiO₂ films of 7.4 through 95.9 nm.

Results We measured XRR for the as grown samples. Then we etched the 95.9 nm sample with dilute HF solution and measured XRR at some thicknesses. The densities of the etched samples as a function of the thickness coincided with those of the as-grown samples. The transition layer was 1 nm thick and about 2.46 gcm⁻³ in density for all the samples. The upper layer density changed from 2.35 to 2.25 gcm⁻³ as the thickness increased. The upper layer density obtained above was an averaged value in its thickness according to our assumption. The density between the two-neighboring-measured points of the etched data might correspond to the real density distribution in depth. The results were as follows. The pre-formed layer of 7.4 nm including the transition layer which grew during the ramp-up process had density of 2.35 gcm⁻³ or more. The density of the main layer formed at 1000 °C decreased rapidly to 2.25 gcm⁻³ at 20 nm, however the non-uniformity occurred mainly within 10 nm. The pre-formed layer remained stable at 1000 °C in 1 atm. O₂ for 120 min. The thermal SiO₂ films had stoichiometric composition. [3] The non-uniformity might be caused by change in structure of SiO₂-network.

Conclusions The XRR analysis revealed the non-uniform density distribution of the thermally grown SiO₂ thin films which may originate from structural change in SiO₂-network near SiO₂/Si interface region.

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NS-TuP3 Growth and Characterization of Au-implanted MBE Grown CeO₂ Thin Films for Plasmonic Based Chemical Sensors, *N.A. Joy, University of Albany-SUNY, M.I. Nandasiri, Western Michigan University, T. Varga, V. Shutthanandan, W. Jiang, P. Nachimuthu, S.V.N.T. Kuchibhatla, S. Thevuthasan*, Pacific Northwest National Laboratory, *M.A. Carpenter*, University of Albany-SUNY

Au doped cerium oxide (CeO₂) material system has exhibited high activity, good selectivity and stability for low-temperature catalytic reactions. Recently, highly dispersed Au nanoparticles supported on metal oxides including CeO₂ have attracted a great deal of attention due to their high catalytic activity. Au nanoparticles are also promising candidates for plasmonic applications due to the sensitivity of their surface plasmon resonance (SPR) band to changes in the environment. In this study, we report the growth, characterization, and gas sensing properties of Au nanoparticles embedded in CeO₂ as optical beacons for the detection of H₂, CO and NO₂ in harsh environment.

CeO₂ thin films were grown on Al₂O₃(0001) by oxygen plasma-assisted molecular beam epitaxy (OPA-MBE). Following the MBE growth and in-situ characterization by reflection high energy electron diffraction (RHEED), as-grown CeO₂ thin films were irradiated by 2.0 MeV Au²⁺ ions generated in a tandem accelerator with high fluence of 1×10^{17} ions/cm² at 600°C. Subsequently, Au implanted ceria films were annealed at 600°C for 10 hours in air to form well defined Au nanoclusters. As-grown, irradiated, and annealed CeO₂ thin films were characterized by Rutherford backscattering spectrometry (RBS), x-ray photoelectron spectroscopy (XPS), and x-ray diffraction (XRD) techniques. The streaky RHEED patterns from the as-grown films indicate the epitaxial growth of the CeO₂ thin films. Glancing incidence XRD (GIXRD) pattern of the as-grown 300 nm thick ceria film indicates the presence of some polycrystalline material. Following the Au implantation at 600°C, GIXRD pattern shows the Au peaks and the reflections associated with ceria-alumina inter-mixing phase (CeAlO₃) in addition to CeO₂ peaks. It suggests the inter-diffusion of metal atoms at the ceria-alumina interface, which is possibly due to the bombardment of high energy Au²⁺ ions. RBS data of the Au-implanted CeO₂ sample also confirmed the inter-diffusion of the metal atoms at the film/substrate interface. Furthermore, the broader x-ray rocking curve of the CeO₂(111) reflection after Au implantation confirm the crystalline disorder of the CeO₂ film caused by irradiation. Despite the inter-diffusion and poor crystalline quality, both CeO₂ and Au crystallites are highly-oriented in (111) direction. After annealing and ex-situ characterization of Au/CeO₂ sample, SPR analysis and gas exposure experiments were performed in a high temperature optical transmission cell. The ppm level gas exposure experiments with the Au/CeO₂ sample has shown promising sensing characteristics towards the detection of H₂, NO₂ and CO in an air background at 500°C.

NS-TuP4 Facile Metal Oxide Nanosheet Synthesis using Atomic Layer Deposition, *K. Lee, G.N. Parsons*, North Carolina State University

Two dimensional nanosheets have attracted great interest due to their unique thermal and electrical properties. For example, graphene nanosheets which are exfoliated from graphite or synthesized using a chemical solution have shown the potential applications as an electrode, catalysts, and electrochemical sensors. In addition to graphene, various kinds of materials such as MoS₂, MnO₂, and MgO nanosheets have been studied extensively. This work demonstrates that atomic layer deposition (ALD) is a facile but effective technique for fabrication of metal oxide nanosheets precisely controlling thickness and chemical composition. We spin-coated a substrate with polymer such as PMMA, PVA, and PAA as a sacrificial layer, then coated the polymer with TiO₂ or ZnO ALD. We made small cuts through the metal oxide/polymer film, and then dissolved the polymer in solvent to release nanosheets from the substrate. We successfully attained two dimensional TiO₂ nanosheets with several hundred μm in lateral size and less than 10 nm in thickness. In addition to single material nanosheets, we can effectively form heterogeneous nanosheets with two metal oxides such as TiO₂/ZnO, where each layer thickness is individually controlled. We confirmed the thickness with AFM and compositions with EDX. We are exploring possible applications for these materials, and available results will be presented and discussed.

NS-TuP6 Nanoscale Surface Patterning for Controllable Metal Deposition, *G. Smith, C.L. Berrie*, University of Kansas

Nanoscale patterning techniques using an atomic force microscope on self-assembled monolayers (SAMs) are used to controllably form metal nanostructures on gold and silicon surfaces. Nanoetching and nanografting are done on methyl-terminated SAMs to pattern in molecules with carboxyl termination. Oxidative lithography is used to electrochemically oxidize

nanopatterns into methyl-terminated SAMs to achieve similar results. These nanopatterns are then treated with an electroless metal plating solution to form metal nanostructures selectively on the patterns. The patterns and features are characterized with atomic force microscopy. Controllable metal nanostructure formation has implications in nanoelectronics and nanodevice construction.

NS-TuP7 Probing the Size-Induced Electronic Structures of CdSe Quantum Dots, P. Nachimuthu, A.S. Karakoti, S.P. Sanghavi, P. Yang, V. Shutthanandan, L.J. Terminello, S. Thevuthasan, Pacific Northwest National Laboratory

The CdSe quantum dots have been studied for various applications ranging from biomedical imaging and sensing to hybrid solar cells. When the size of the nanocrystals reduces below the exciton Bohr's radius, the energy levels become discrete (quantized). Consequently, the band gap of quantum dots increases with decreasing the size of the dots. This is inherently reflected in the electronic structures of these quantum dots. In addition, these CdSe quantum dots are known to exhibit a phase transition from a stable hexagonal phase in larger dots to a metastable cubic phase at smaller dot sizes during their synthesis. As the size of quantum dot decreases, the number of surface atoms and the energy associated with the surface increase leading to creation of vacancies, which results in the non-stoichiometric CdSe. However, the mechanism is not clear at atomic level. Therefore, we took a systematic approach to study the size-induced structural and electronic properties of CdSe quantum dots in toluene and drop-casted on Si by various in-situ and ex-situ imaging, spectroscopy and diffraction techniques to obtain the correlation between the quantum confinement and the corresponding stoichiometry, crystalline phases and the effect of surface ligands. The CdSe quantum dots capped with trioctylphosphine oxide (TOPO) or hexadecylamine (HDA) in toluene exhibit predominantly wurtzite crystal structure, which undergoes a phase transformation to zinc blende crystal structure following drop casting on Si and this phase transition increases with decreasing the size of the CdSe quantum dots. A systematic increase in the core level binding energies of Cd 3d and Se 3d, the band gap and the Cd/Se ratio is found as the size of the quantum dots decreases from 6.6nm to 2.1nm. This is attributed to the quantum confinement of CdSe crystallites by the capping ligands in toluene which increases with decreasing the size of the quantum dots thereby increasing the Se vacancies. However, drop-casting of CdSe quantum dots on Si alters the arrangement of capping ligands on the quantum dots which facilitates significant phase transformation. To gain further insights in understanding these transitions we are seeking first principles investigation on model CdSe particles using density functional theory (DFT). The relative stability between the two phases as a function of particle sizes will be reported.

NS-TuP8 Plasmon-Enhanced Emission With GLAD-Functionalized ZnO Nanowires, D.C. Mayo, A.T. Mayo, A. Ueda, Z. Pan, R. Mu, Fisk University

ZnO has increasingly been the focus for optical emission studies due to both its wide band gap of 3.37 eV and high thermal stability. In this research, vertically oriented ZnO nanowires (NWs) are grown upon silicon substrates using a novel, modified vapor-solid method within a vertical furnace. Electron-beam evaporation is then used with glancing angle deposition (GLAD) to functionalize the sides of the ZnO NWs with both Ag and MgO:Ag. Comparative characterization is then performed using photoluminescence measurements at varying angles to examine both surface-plasmon-enhanced emissions and to study the underlying coupling mechanisms responsible for the enhancements. This research may serve as the foundation for applications which range from high-efficiency LEDs to optoelectronic plasmon waveguides.

NS-TuP9 Fabrication of High-Performance Carbon Nanotube Field-Effect Transistors with Semiconductors as the Source/Drain Contact Material, Z. Xiao, Alabama A&M University, F.E. Camino, Brookhaven National Laboratory

We report fabrication of high-performance single-walled carbon nanotube field-effect transistors (CNTFETs) using semiconductors as the source/drain contact material and defining submicron-meter gate within the source and drain, without overlapping the source and drain. Common problems in the fabrication of carbon nanotube field effect transistors (CNTFETs) include the positioning of tubes across electrodes and poor device electrical performance due to the presence of metallic nanotubes intermixed with semiconducting ones. To circumvent these problems, dielectrophoresis (DEP) will be used for tube alignment, while semiconducting electrodes such as Sb₂Te₃ and Bi₂Te_{3-x}Se_x instead of metal electrodes in CNTFETs will be employed to selectively turn off metallic nanotubes resulting in improved device electrical characteristics. The submicron-meter gates within the source and drain in the fabrication of CNTFETs will be fabricated using the ion beam assisted deposition capability of the dual

electron/ion beam system. The electrical measurements on the CNTFETs will be performed and the measurement results will be reported.

NS-TuP11 Preparation of Triethylamine Stabilized Silver Nanoparticles for Low-Temperature Sintering, S.L.C. Hsu, J.T. Wu, National Cheng-Kung University, Taiwan, R.O.C.

In this research, silver nanoparticles were synthesized by chemical reduction from silver nitrate using triethylamine as the protecting and reducing agents simultaneously. The average size of the silver nanoparticles was less than 5 nm, which allowed low-temperature sintering of the metal. X-ray diffraction (XRD), thermogravimetric analysis (TGA), and energy dispersive spectrometric (EDS) analysis results indicate that silver nitrate has been converted to silver nanoparticles completely. Using a 20 wt% silver nanoparticles suspension with thermal treatment at 150 °C, silver films with a resistivity of 8.09 x 10⁻⁵ W cm have been produced, which is close to the resistivity of bulk silver.

NS-TuP12 Selective Growth and Characterization of a SnO₂ Nano-Wire by Employing DNA-templated Gold Nanoparticle Chains, J.H. Heo, Korea Institute of Materials Science, South Korea, H.J. Kim, Sungkyunkwan University, South Korea

Recently, the Tin-oxide(SnO₂) has been widely used in the fabrication of various gas(O₂, CO, NO_x) detecting sensor. Basically, the SnO₂ is n-type semiconductor which has a wide band gap, about 3.99eV. Also, thin film of SnO₂ has been known as a transparent electrode and it is applicable for a various electronic parts. Nowadays, research on SnO₂ nano-wire characterization is very actively performed because it is able to realize a micro-sensor array with conventional Silicon processing. However, it isn't easy to align a single SnO₂ nano-wire on the specific site for the fabrication of integrated gas sensor device. To achieve a high-performance gas-sensor with SnO₂, we need to make integrated single SnO₂ nano-wire 2 electrode devices. In this study, we employed DNA-templated alignment using a combination of molecular combing and surface-patterning techniques to form a Au nanoparticle chain as a catalyst. It is possible to obtain parallel and latticed nanostructures consisting of DNA molecules and thus DNA-templated Au nano-wires aligned at 400nm intervals.[1,2] After that, a single SnO₂ nano-wire which had been synthesized on the Au nanoparticle by a thermal process.[3,4] By using the AFM probing technique, a Rh coated conducting cantilever can approach a single SnO₂ nano-wire in nano scale and get the I-V curves with sweeping applied voltage between Au electrode and cantilever with a controlled concentration of Oxygen in measuring chamber to change the ionosorption rate. From the results of such experiments, we selectively grow SnO₂ nano-wires and verified Oxygen detecting ability which would be necessary for the realization of micro-sensor array.

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Wednesday Morning, November 2, 2011

Applied Surface Science Division

Room: 102 - Session AS+BI+NS-WeM

Advances in Scanning Probe Microscopy

Moderator: S.A. Allen, The University of Nottingham, UK

8:00am AS+BI+NS-WeM1 High-Speed Atomic Force Microscopy for Filming Biomolecular Processes, T. Ando, Kanazawa University, Japan

INVITED

Vital phenomena are engendered through the dynamic activity of biological molecules. Therefore, observing the dynamic behavior of biological molecules in action at high spatiotemporal resolution is essential for elucidating the mechanism underlying the biological phenomena. The dynamic biomolecular processes are now widely studied using single-molecule fluorescence microscopy. However, the fluorescently labeled biological molecules themselves are invisible in the observations even using super-resolution fluorescence microscopy. The structure of biological molecules has been studied using x-ray crystallography, NMR, electron microscopy, and atomic force microscopy (AFM) but the obtained structures are essentially static. Thus, the simultaneous assessment of structure and dynamics is infeasible. To overcome this long-standing problem and make it possible to simultaneously record the structure and dynamics of biological molecules, we have been developing high-speed AFM for more than 15 years and at last it is now coming of age. Various AFM devices and control techniques were optimized or invented for high-speed scanning and low-invasive imaging. As a result, the imaging rate now reaches 10-30 frames/s for the scan range $250 \times 250 \text{ nm}^2$, 100 scan lines, and the spatial frequency of a sample surface corrugation 0.1/nm [Prog. Surf. Sci. **83**, 337-437 (2008)]. Remarkably, even delicate protein-protein interactions are not disturbed by the tip-sample contact. With this capacity of high-speed AFM, some biological processes are successfully captured on video, such as walking myosin V molecules along actin filaments [Nature **468**, 72-76 (2010)], photo-activated structural changes in bacteriorhodopsin [Nat. Nanotechnol. **5**, 208-212 (2010)], and cooperative GroEL-GroES interactions. The high-resolution movies not only provide corroborative 'visual evidence' for previously speculated or demonstrated molecular behaviors but also reveal more detailed behaviors of the molecules, leading to a comprehensive understanding of how they operate. Thus, the high-speed AFM imaging of functioning biological molecules has the potential to transform the fields of structural biology and single-molecule biology.

8:40am AS+BI+NS-WeM3 Integrated Imaging: Probing Molecular Interactions by Correlated Atomic Force Microscopy Approaches, C. Yip, University of Toronto, Canada

INVITED

The development of powerful single molecule functional imaging tools has been critical to our understanding of molecular dynamics and structure-function relationships in (bio)molecular systems. Our lab's focus on the design, implementation, and application of coupled imaging and spectroscopy is providing intriguing insights into the mechanisms of membrane disruption, receptor oligomerization, and protein-membrane interactions. We have devised several correlative approaches based on the integration of in situ atomic force microscopy with fluorescence and vibrational spectroscopies for extracting the orientation, conformation, and association dynamics of membrane-associated proteins in model membranes and in live cells. Some of the key challenges and opportunities afforded these new tools will be discussed.

9:20am AS+BI+NS-WeM5 Visible Light Emission from Fluorescent Proteins on Silver Substrate Induced by Tunneling Electrons, T. Yamada, RIKEN, Japan, T. Iwaya, S. Matsunaga, M. Kawai, The University of Tokyo, Japan

We detected the characteristic visible light emission from fluorescent protein molecules deposited on metallic silver (Ag) upon injection of tunneling electrons generated by a standard scanning tunneling microscope (STM) in ambient condition. A series of fluorescent proteins originating from jellyfish or coral, nowadays engineered to generate various colors of fluorescence by gene technology, is characterized with a β -barrel structure insulating the chromophore electronically from the surrounding. We purchased green, yellow, red and infrared fluorescent proteins (GFP, YFP, RFP, HcRed, molecular diameter $\approx 5 \text{ nm}$), deposited on a bare Ag surface, and used a Ag tip set on a STM setup to obtain images and to generate fluorescence. Light from the gap was collected by an optical fiber and introduced to a grating spectrometer with a liquid N₂-cooled CCD detector. On bare Ag surfaces, visible light was detected with the STM bias voltage within $\pm 1.8 \text{ V}$ in a modestly moisturized N₂ atmosphere. The spectra were

unstable in general, indicating light emission upon excitation of local plasmon [1], which depends on the changeable geometry of Ag tip. The wavelength onset of emitted light was equivalent to the STM bias voltage within $\pm 3.0 \text{ V}$, obeying the law of quantum energy conservation. The fluorescent proteins were dissolved in pure water, drop-cast on the Ag substrate and air-dried to form multilayers. STM images mostly showed flat terraces with steps composed of the protein molecules. Within a $200 \text{ nm} \times 200 \text{ nm}$ scanning area, the light emission spectra apparently involved the characteristic fluorescence peaks of proteins (GFP = 540 nm (2.30 eV), YFP = 550 nm (2.25 eV), RFP = 650 nm (1.91 eV), HcRed = 660 nm (1.88 eV)) over a background of weakened Ag plasmon spectrum. The same experiment with Au tips and Au(111) substrates was with almost no detection for the characteristic fluorescence of all the proteins. For clean Au(111), although visible light was detected, the above-mentioned plasmon energy conservation stood for the bias voltage only within $\pm 1.9 \text{ V}$. The maximum energy of local plasmon on Au(111) is too small to excite the fluorescent proteins electronically. The characteristic fluorescence from proteins is considered aided by the plasmon excitation of the Ag substrate. The protein β -barrel structure reserves the lifetime of excited state towards light emission, insulating electronically from the metallic substrate against the radiationless de-excitation process of the present surface-adsorbate system.

References:

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9:40am AS+BI+NS-WeM6 Characterization of Peptide Nanotubes by Atomic Force Microscopy, J.L. Remmert, M.C. Vasudev, Air Force Research Laboratory, L. Eliad, E. Gazit, Tel Aviv University, Israel, T.J. Bunning, R.R. Naik, A.A. Voevodin, Air Force Research Laboratory

This work investigates the properties of aromatic dipeptides, which are of interest due to their ability to self-assemble into nanotubes and nanowires. Peptide nanotubes have been used to template inorganic materials¹ and construct nanochannels in microfluidic devices². The mechanical, thermal, and electronic transport properties of these nano-structures are desired to evaluate their potential use for biomolecular electronics³ and other applications. Atomic Force Microscopy (AFM) offers multiple modes to interrogate the response of discrete nanotubes. For instance, AFM with dry sample heating has established the thermal stability of peptide nanotubes up to $100 \text{ }^\circ\text{C}$ ⁴ with a spring constant of 160 N/m at room temperature⁵. A separate study targeting a single nanowire bridging two electrodes revealed semiconductor characteristics under repeated bias cycling⁶. We have similarly sampled detached nanotubes among peptide bundles and vertically aligned 3D arrays. Peptide nanotubes were synthesized by either Plasma Enhanced Chemical Vapor Deposition (PECVD) or solvent phase growth in 1, 1, 1, 3, 3, 3 Hexafluoroisopropanol (HFP), using approaches similar to that described by Reches et al¹. The nanotubes were observed by SEM to vary between 85-100 nm in diameter and up to 50 μm in length. Sample density was controlled by suspension and dilution in various solvents, including HFP and water, prior to deposition on a variety of substrates. AFM studies have revealed details of the tubular outer shell with tapping and electrostatic force modes (EFM), while also probing the mechanical integrity and thermal response to localized tip-side heating.

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²N. Sopher, Z. Abrams, M. Reches, E. Gazit, Y. Hanein, "Integrating peptide nanotubes in micro-fabrication processes", *J Micromech Microeng* **17** 2360 (2007)

³V. Dinca, E. Kasotakis, J. Catherine, A. Mourka, A. Ranella, A. Ovsianikov, B. Chichkov, M. Farsari, A. Mitraki, C. Fotakis, "Directed Three-Dimensional Patterning of Self-Assembled Peptide Fibrils", *Nano Lett* **8** 538 (2008)

⁴V. Sedman, L. Adler-Abramovich, S. Allen, E. Gazit, S. Tendler, "Direct Observation of the Release of Phenylalanine from Diphenylalanine Nanotubes", *J Am Chem Soc* **128** 6903 (2006)

⁵N. Kol, L. Adler-Abramovich, D. Barlam, R. Shneck, E. Gazit, I. Rouso, "Self-Assembled Peptide Nanotubes Are Uniquely Rigid Bioinspired Supramolecular Structures", *Nano Lett* **5** 1343 (2005)

⁶J. Lee, I. Yoon, J. Kim, H. Ihee, B. Kim, C. Park, "Self-Assembly of Semiconducting Photoluminescent Peptide Nanowires in the Vapor Phase", *Angew Chem Int Edit* **50** 1164 (2011)

10:40am **AS+BI+NS-WeM9 Determination of Molecular Polarization at Protein-Electrode Interfaces with Combined Optical, Transport, and Dielectric Scanning Probe Microscopy.** *X. Chen, K. Kathan-Galipeau, B.M. Discher, D.A. Bonnell*, University of Pennsylvania

Bio-molecule integrated electronic devices are of great interest recently. For such systems to be designed and fabricated, the optoelectronic properties of protein molecules in ambient environment must be understood at a fundamental level. Here we demonstrate a new scanning probe based technique: torsional resonance nanoimpedance microscopy (TR-NIM), which simultaneously probes transport and dielectric properties in conjunction with optical excitation. To make a controlled interface, we start by designing a peptide molecule with ability to control protein/electrode interface interactions, as well as incorporation of several different optically active cofactors, and we successfully patterned peptides on HOPG substrates. Using TR-NIM electronic transport and the effect of optical absorption on dielectric polarizability in oriented peptide single or multiple molecular layers is determined. This approach enables quantitative comparisons of the change in polarization volume between the ground state and excited state in both single and multiple molecular layers.

11:00am **AS+BI+NS-WeM10 Scanning Local Capacitance Measurements with High Spatial and Dielectric Resolution.** *M.J. Brukman, S. Nanayakkara, D.A. Bonnell*, University of Pennsylvania

Spatial variation of dielectric properties often dictates the behavior of devices ranging

from field effect transistors to memory devices to organic electronics, yet dielectric

properties are rarely characterized locally. We present methods of analyzing 2nd

harmonic-based local capacitance measurements achieved through non-contact atomic

force microscopy. Unlike contact-based methods, this technique preserves tip

shape and allows the same probe to realize high-resolution topographic imaging and

scanning surface potential imaging. We present an improved analysis of the electrical

fields between tip and sample, yielding high sensitivity to the capacitance-induced

frequency shift.

The techniques are applied to thin-film strontium titanate and mixed-phase self-

assembled monolayers to illustrate application to high dielectric constant hard materials

and lower dielectric constant organic films. Conversion from frequency shift signal to

dielectric constant κ is demonstrated on both samples, with sub-5 nm spatial resolution

and dielectric constant resolution between 0.25 and 1.

11:20am **AS+BI+NS-WeM11 Parallel Momentum Conservation of Hot Electrons across a Metal Semiconductor Interface.** *J.J. Garramone, J. Abel, R. Balsano, V.P. LaBella*, College of Nanoscale Science and Engineering, the University at Albany-SUNY

Parallel momentum of electrons is a conserved quantity as the electron traverses a barrier between two materials which lead to refraction like effects in the electrons trajectories. Ballistic electron emission microscopy (BEEM) is a scanning tunneling microscopy (STM) based technique that injects hot electrons ($E > E_F$) into a metal-semiconductor Schottky diode[1]. A small fraction of these electrons will traverse the metal with little to no scattering and make it into the semiconductor and counted as BEEM current. This makes it an ideal technique to study parallel momentum conservation. However, direct observation of this effect has been rather elusive. To observe this effect the dependence of the attenuation length with hot electron energy of Ag on both the Si(001) and Si(111) substrates has been measured.

Samples consisted of nanometer thick Ag films that were deposited on HF cleaned Si(001) and Si(111) wafers and capped with 10 nm Au to prevent oxidation of the films. Attenuation lengths were extracted by measuring the BEEM current as a function of the metal overlayer thickness. The dependence of the attenuation length with tip bias (electron energy) displayed a sharp increase as the energy approached the Schottky barrier height for the Si(001) substrates and a slight decrease for the Si(111)

substrates. This contrast is a direct result of parallel momentum conservation and the lack of zero parallel momentum states at the Si(111) interface when compared to the Si(001) interface. Additional insight into the relative contribution of both elastic and inelastic scattering can be obtained by fitting the data to a Fermi liquid based model.

[1] L. D. Bell, et al., Phys. Rev. Lett. **61** 2368 (1988).

11:40am **AS+BI+NS-WeM12 High Resolution Scanning Probe Imaging of 2D-Supramolecular Networks on Au(111), Graphite and Molybdenite.** *V.V. Korolkov, S. Allen, C.J. Roberts, S.J.B. Tendler*, The University of Nottingham, UK

Chemical decoration of surfaces with various molecules and supramolecular structures has been a major strategy for introducing new properties to both organic and inorganic materials. Amongst these properties are wettability, biocompatibility, sensing properties, catalytic activity, optical properties and adhesion. Most of methods for surface modification include molecules binding to the surface via stable chemical bond. Recently methods have been developed to modify atomically flat surfaces with periodical porous molecular structures, termed 2D-supramolecular networks. The networks are commonly composed of two types of molecules serving different functions e.g. joints and ribbons. Such 2D-structures bring forward a unique surface property - a spatially controlled adsorption with almost single molecule precision.

Most networks reported in the literature have been studied using UHV STM on metal substrates and, to a lesser extent, on HOPG and non-conductive substrates. Here we present a study, utilizing both ambient STM and AFM, of 3,4,9,10-perylene-tetracarboxylic diimide (PTCDI) - melamine networks deposited on Au(111), HOPG and MoS₂ substrates. AFM imaging was performed using PeakForce Tapping AFM (Bruker Inc.) and Torsion Resonance (TR)-AFM. Both STM and AFM were able to resolve a clear periodical network structure for all substrates after exposure to a solution of PTCDI and melamine molecules in dimethylformamide at 373K. AFM images show that the network forms a monolayer on both HOPG and molybdenite substrates, and also that most of the HOPG surface is covered with network structure, with some minor defects. In contrast the Au(111) surface was mostly covered with network multilayers as suggested both by TR-AFM and STM. AFM also revealed that the network structure on HOPG and molybdenite remains intact for several hours in the ambient and can be stored in N₂-ambient for up to ~24h.

Energy Frontiers Focus Topic

Room: 103 - Session EN+EM+NS-WeM

Quantum Dot and Nanowire Solar Cells

Moderator: K. Leschkes, Applied Materials Inc.

8:00am **EN+EM+NS-WeM1 Hybrid Quantum-Dot/Organic Solar Cells Based on Silicon Nanocrystals.** *U. Kortshagen, C.Y. Liu, Z. Holman, J. Yang*, University of Minnesota

INVITED

Organic solar cells based on bulk heterojunctions between acceptor and donor semiconductors have attracted significant attention due to their low cost, compatibility with roll-to-roll processing, and relative lack of health and environmental concerns. However, the stability of organic semiconductors under solar irradiation remains to be a challenge. Producing bulk heterojunction solar cells based entirely on inorganic materials thus has become an attractive proposition.

In a first step into this direction, we have produced solar cells from silicon nanocrystals (Si NCs) and poly-3-hexylthiophene (P3HT). Silicon NCs 3–5 nm in diameter were synthesized by dissociating silane gas in a nonthermal radio frequency plasma, and collected on a mesh downstream of the plasma. The silicon-hydride terminated NCs were dispersed with P3HT in 1,2-dichlorobenzene. Films of this blend with thicknesses of 100–200nm were spin-cast onto an indium tin oxide (ITO) substrate pre-coated with 50 nm of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS). Metal electrodes (2mm wide, 100 nm thick) were then evaporated on top of the Si NC/P3HT film.

The Si NCs were found to be efficient electron acceptors. The optimal weight ratio of Si NC to P3HT was 50 wt%. The effects of annealing and different metal electrodes on Si NC/P3HT hybrid solar cells were studied. After annealing at 150 °C, Si NC/P3HT solar cells exhibited power conversion efficiencies as high as 1.47%. The hole mobility in the P3HT phase extracted from space-charge-limited current measurements of hole-only devices increased from 2.5×10^{-10} cm²/V-s to 1.1×10^{-9} cm²/V-s after annealing, resulting in better transport in the solar cells. A quenching of the open-circuit voltage and short-circuit current was observed when high work

function metals are deposited as the cathode on Si NC/P3HT hybrid devices.

Devices with silicon-hydride terminated Si NCs were plagued by poor film morphology. Hence we studied functionalizing Si NCs with organic ligands. Functionalization with 1-octene and 1-dodecene led to improved film morphology but the transport in the Si NC network became worse. However, excellent stability with respect to air exposure of these cells was observed. Efforts to improve the dispersability of Si NCs without inhibiting transport in the Si NC network are in progress.

This work was supported primarily by the MRSEC Program of the National Science Foundation under Award Number DMR-0819885 and by the DOE Energy Frontier Research Center for Advanced Solar Photophysics.

8:40am EN+EM+NS-WeM3 Precision Engineering of Semiconductor Nanowires for Advanced Photovoltaic Devices, N. Shin, I.R. Musin, S. Sivaram, M.A. Filler, Georgia Institute of Technology INVITED

Semiconductor nanowires offer exciting opportunities to engineer light absorption and carrier transport for ultrahigh efficiency photovoltaic devices. The precise control of crystal structure and geometry is required to achieve a desired behavior, especially in highly confined nanoscale systems. In the ideal situation, the combination of nanowire diameter, lattice structure (e.g. diamond cubic, wurtzite), crystal orientation (e.g. $\langle 111 \rangle$ vs. $\langle 110 \rangle$), and sidewall faceting that yields the most robust device performance would be known and could be rationally synthesized. Unfortunately, an inadequate understanding of nanowire chemistry-structure and structure-property relationships prevents the accomplishment of this task with bottom-up syntheses at the present time. This presentation will provide an overview of our recent efforts to bridge this knowledge gap. In our research, *in-situ* infrared spectroscopy is combined with an ultrahigh vacuum growth environment to fundamentally correlate nanowire chemistry with photophysics, while circumventing the sample degradation that can obscure the intrinsic properties of nanoscale structures. Group IV nanowires and their heterostructures are a model system and are fabricated with the vapor-liquid-solid (VLS) growth technique. The critical influence of surface-bound species near the three-phase boundary and their impact on nanowire crystal structure will be discussed in detail. This fundamental knowledge opens a generic and highly tunable route to engineer multiple classes (e.g. group IV and III-V, etc.) of semiconductor nanowires, heterostructures, and superstructures for advanced photovoltaic device applications.

9:20am EN+EM+NS-WeM5 Electrophoretic Deposition of CdSe Nanocrystals in Quantum Dot Sensitized Solar Cells, N.J. Smith, Middle Tennessee State University

Electrophoretic deposition (EPD) of nanocrystal thin films from the solution phase has received increasing attention due to its simplicity and ability to rapidly create controlled thickness films. In this presentation, we will discuss the impact of solvent choice, deposition time, and electrode voltage on the properties of CdSe nanocrystal films deposited by EPD for solar cell applications.

While hexanes are a commonly used solvent for depositing CdSe nanocrystals, resulting film formation by EPD is often not reproducible for different batches of nanocrystals. In this work, we report that adding acetone to solutions of nanocrystals in hexanes enables the consistent deposition of CdSe nanocrystal thin films of controllable thickness. These films form within a few seconds and require comparatively low electrode voltages for the deposition process. The addition of acetone appears to mitigate the effects of impurities in the precursor chemicals, the presence of solvents left over from nanocrystal synthesis, and variable environmental conditions that may otherwise compromise the quality of the resulting EPD nanocrystal films.

Quantum dot sensitized solar cells have been fabricated using the EPD process with CdSe nanocrystals solvated in hexanes with acetone. By modifying the EPD parameters, both the density and thickness of the nanocrystals films deposited on titanium dioxide coated ITO slides were affected. We will discuss the relationship between the EPD parameters and the resulting I-V characteristics and efficiency of the CdSe nanocrystal sensitized solar cells. Preliminary studies suggest that proper choice of EPD parameters can lead to more than one order of magnitude improvement in the solar cell performance metrics.

9:40am EN+EM+NS-WeM6 Selective and Highly Efficient Photo-Induced Activity Over Nano-Scale Sites in Porous Silicon: Potential Application for Hybrid Organic-Silicon PV, M. Asscher, The Hebrew University of Jerusalem, Israel, G. Toker, A. Nahor, O. Berger, S. Yitzchaik, A. Sa'ar, Hebrew University, Israel

Photo-induced processes over solid surfaces are of great basic and technological interest with applications in e.g. photolithography, sensing, catalysis and photovoltaics. Photo activity within porous silicon (PSi) following UV (193-266nm) irradiation has been studied. Unusually efficient, non-thermal, morphology and wavelength dependent photo-induced desorption (PID) of Xe was recorded. It is a selective process, revealing more than 3 orders of magnitude enhancement within pores, at the vicinity of nano-scale silicon tips, over atoms adsorbed on top of flat surfaces. Remarkably large cross sections up to $\sigma_{\text{PSi}} = 2 \cdot 10^{-15} \text{cm}^2$ were recorded, significantly larger than any previously published photo-induced events on solid surfaces at this wavelength range. Long lived, photo-induced positive charges (holes) located at inner surface nano-tips is proposed to stabilize transient negative Xe adsorbate ions as the precursor for this new photo-desorption process.

These results were utilized for the construction of hybrid conducting polymer-porous silicon photovoltaic cell. Proof of concept and preliminary results are discussed.

10:40am EN+EM+NS-WeM9 High-Performance, Low-Cost Nanopillar Array Photovoltaics, A. Javey, University of California Berkeley INVITED

Semiconductor nanowires (NWs) hold great promise for fabrication of high-performance, low-cost solar cells. These materials have been extensively studied, both computationally and experimentally. The key advantage of NW solar cells resides in the ability to grow single crystalline NWs non-epitaxially on support substrates. Additionally, by varying the NW geometry, the electrical, optical and mechanical properties of the solar cells can be controlled, providing opportunities unavailable to planar thin-film solar cells. Here we discuss our work on bottom-up CdS/CdTe nanopillar (NPL) solar cells, optical engineering of NPL arrays, and top-down fabrication of InP solar cells.

Bottom-up NPL solar cells were fabricated on anodized aluminum oxide (AAO) templates. Due to the 3-D geometry, the templated NPL architecture orthogonalizes the light absorption and carrier collection directions, enabling cells to be optimized even for poor quality materials. First-generation CdS/CdTe solar cells on low-cost Al foil exhibited 6% efficiency, 0.6 V open circuit voltage, V_{OC} , and 21 mA/cm² short circuit current, J_{SC} , despite significant (>30%) optical reflection from the top contact. Additionally, detailed electronic simulation was used to examine the design trade-offs involved with the NPL architecture. We found that even for a poor quality CdTe absorber layer, through proper design, moderate efficiencies of ~15% could be achieved. Additionally, all the processes used to fabricate the cell were roll-to-roll compatible. Thus, the combination of experiment and modeling show the promise of this method for fabrication of low-cost, high-performance solar cells.

The AAO templated growth enables a high degree of control over the geometry and dimensions of the NPL arrays. For single-diameter Ge NPL arrays embedded in AAO, increasing the Ge material filling ratio both increases the reflectance and decreases the transmittance. The absorbance of an array is shown to strongly increase for increased diameter NPL arrays. Thus, by fabricating arrays of dual-diameter Ge NPLs, ~99% of incident light was absorbed with a film only 2 μm thick. This behavior is caused by the smaller NPL diameter at the interface between the material and incident light, and the higher diameter base then absorbs the light.

Finally, radial p-n junction solar cells are fabricated from InP NPLs generated from a top-down etching procedure. The main challenge with radial p-n junctions is the ability to form ultra-shallow and conformal junctions along the radial axis. By utilizing a sulfur monolayer doping scheme, conformal junction depths of <10nm with high electrically active dopant concentrations ($\sim 10^{19} \text{cm}^{-3}$) are achieved. The fabricated solar cell exhibited a power conversion efficiency of 8.1%, a $V_{\text{OC}}=0.54 \text{V}$, and a $J_{\text{SC}}=25 \text{mA/cm}^2$.

In summary, we have presented both top-down and bottom-up approaches for fabricating NPL solar cells, from both crystalline starting materials as well as low-cost Al foil. The templated AAO growth method also enabled optical engineering of NPL arrays, allowing a single material to maximize absorption and minimize reflection. Finally, the utilization of a previously-developed conformal, ultra-shallow doping scheme was shown to enable radial InP solar cells.

11:20am EN+EM+NS-WeM11 **Extremely Thin Absorber Solar Cells Based on CdSe-Coated ZnO Nanowires**, *H. Majidi, T.P. Le, G.W. Gaglietta, J.B. Baxter*, Drexel University

Solar cells can provide an abundant, clean, and sustainable source of electricity, but high costs have limited their implementation. The use of sensitized nanostructured architectures may enable both low-cost processing and high efficiency by decoupling the functions of light harvesting and charge transport into different materials. Sensitized solar cells consist of a bicontinuous interpenetrating network of electron- and hole-transporting materials with an interfacial absorber layer. In this architecture, interfacial recombination is the dominant loss process, so controlling the interfacial chemistry during deposition is critical.

We report on the use of n-type ZnO nanowire arrays sensitized with thin CdSe coatings and covered with p-type CuSCN in extremely thin absorber (ETA) solar cells. Low temperature, solution deposition methods were used for each material, offering the potential for inexpensive and scalable nanomanufacturing. Nanowire arrays provide direct pathways for electron transport as well as sufficient surface area for sensitization. The electrodeposited CdSe coatings are nanocrystalline and conformal with well-controlled thickness. CuSCN is electrodeposited into the pore volume between nanowires. Morphology and microstructure of CdSe and CuSCN depend sensitively on bath chemistry and deposition potential. By controlling nucleation and growth rates, conformal and void-free materials can be deposited.

A combination of solar cell measurements and ex situ materials characterization for both planar thin film stacks and nanowire arrays have been used to direct the selection of optimal ETA cell architectures. For example, ultrafast transient absorption spectroscopy demonstrates that interfacial electron transfer from photoexcited CdSe to the ZnO is much faster than recombination (~3 ps vs ~50 ps) for thin coatings. Planar solar cells were used to identify the optimal coating thickness of ~70 nm for these materials. External quantum efficiency measurements show efficient sensitization throughout the visible region of the solar spectrum. However, interfacial recombination limits overall energy conversion efficiencies.

11:40am EN+EM+NS-WeM12 **Hybrid Photovoltaics Devices Based on Quantum Dot Functionalized ZnO Nanowire Arrays Embedded in a Polymer Matrix**, *N. Harris, L. Butler, G. Shen, N. Dawahre, S. Wilbert, W. Baughman, S. Balci, P. Kung, S. Kim*, University of Alabama

There is an increasing need to develop new low-cost materials and architectures for high efficiency solar cells in an attempt to provide a cost effective alternative to fossil fuels. Dyes, polymers and quantum dots have received tremendous amounts of attention due to their potential for solution processing and high absorption coefficients. Polymers and quantum dots are an attractive option for replacing dyes as the next generation low-cost absorber material due to their improved electronic properties and increased longevity. Bulk-heterojunction polymer based cells suffer from low carrier mobility and short carrier lifetimes which lead to high recombination rates. Quantum dots are promising sensitizing material because they potentially have improved stability over polymers and can potentially generate multiple excitons per photon. However, charge transport in solar cells based solely on quantum dots is generally accomplished through the hopping-mechanism and leads to increased recombination rates.

In this talk, we present a hybrid photovoltaic device structure based on quantum dot (QD)-functionalized single crystalline ZnO nanowire arrays embedded into a polymer matrix in order to achieve improved charge collection efficiencies from the QDs and transport through the cell. A number of issues need to be addressed, such as the enhancement of the coverage of the nanowires with quantum dots to increase photon absorption, as well as implementing a hole-transport medium that does not degrade the quantum dots and can potentially serve as a secondary absorber material that could potentially greatly improve device longevity, reproducibility and efficiency.

In this work, the specific photovoltaic device structure consisted of an InP/ZnS core-shell QD functionalized ZnO nanowire array that is embedded into a poly-3(hexylthiophene) (P3HT) hole transport matrix. The QD sensitized ZnO nanowires were characterized by optical absorption, confocal Raman and photoluminescence spectroscopy, as well as high resolution and scanning transmission electron microscopy. In addition, interface between QDs and ZnO NWs were studied by Atom Probe Tomography. QDs with different absorption bands were concurrently functionalized onto the same nanowire arrays in order to broaden the final device absorption bandwidth. The ZnO:P3HT matrix was then planarized using inductively coupled plasma etching. The performance of planarized, quantum dot functionalized devices was subsequently compared to as-deposited and non-functionalized devices and the effect of QDs on device efficiency is presented. These include the study of the charge transfer mechanism using terahertz time domain spectroscopy.

Energy Frontiers Focus Topic
Room: 209 - Session EN+NS-WeM

Organic Photovoltaics

Moderator: R.A. Quinlan, Naval Surface Warfare Center, Carderock Division

8:00am EN+NS-WeM1 **Sol-gel Prepared Ca Doped ZnO and Its Application in Polymer-Oxide Bilayer Hybrid Solar Cells**, *M. Wang, I. Hill*, Dalhousie University, Canada

Conjugated polymer/metal oxide hybrid photovoltaic devices have received considerable attention in recent years due to their potential for scalable, low-cost manufacturing. To improve device efficiency, most research has focused on increasing the fill factor and short circuit current. In this article, calcium doped zinc oxide ($Zn_xCa_{1-x}O$) is used as electron acceptor in the hybrid poly(3-hexylthiophene)/ $Zn_xCa_{1-x}O$ bilayer solar cells to modify the band offsets and increase the open circuit voltage. XRD results show the sol-gel prepared Ca doped ZnO films have a hexagonal wurtzite phase with no indication of calcium separation. Atomic force micrographs indicate the $Zn_xCa_{1-x}O$ surface becomes decorated with interconnected ridges approximately 100 nm in height. The rms surface roughness increases with increasing Ca. The band gap obtained from UV-vis absorption spectra widens from 3.20 to 3.60 eV as the Ca concentration increases from $x=0$ to $x=0.12$. The work function of the $Zn_xCa_{1-x}O$ films measured by Kelvin probe is seen to decrease with increasing Ca composition for values of x up to 0.12, which indicates a decrease in electron affinity. The open circuit voltage of hybrid P3HT/ $Zn_xCa_{1-x}O$ devices increases from 570 mV at $x = 0$ up to 800 mV for $x = 0.10$. Work is under way to incorporate Ca doped ZnO nanoparticles into bulk heterojunction solar cells to optimize device efficiency.

8:20am EN+NS-WeM2 **The Influence of ITO Surface Treatments on Spatially Localized Photocurrent Variation in Organic Photovoltaic Devices**, *B.J. Leever*, Air Force Research Laboratory, *I.P. Murray*, Northwestern University, *M.F. Durstock*, Air Force Research Laboratory, *T.J. Marks, M.C. Hersam*, Northwestern University

The fabrication process for bulk heterojunction (BHJ) organic photovoltaic (OPV) devices nearly always includes anode modification steps ranging from solvent cleaning to haloacid treatments to the deposition of interfacial layers such as polymer blends or transition metal oxides. The role of these treatments is not yet fully understood, but they are thought to modify the anode work function, contribute to electron-blocking, alter the anode surface energy, and prevent shunts among other functions. In separate work, conductive atomic force microscopy (AFM) and derivative techniques have been used to simultaneously probe both the morphological and electrical properties of BHJ photovoltaic layers. Previous work has demonstrated a correlation between BHJ nanostructure and properties such as photocurrent at the same scale (~20 nm) as the phase separation in these films. Photocurrent variability has also been observed at a length scale orders of magnitude larger the domains in the BHJ layer, and this variation has been speculated to have an origin in the anode or interfacial layers in the OPV architecture.

In this work, a correlation between indium tin oxide (ITO) surface treatment and spatially localized photocurrent variation has been found in OPV devices with a poly(3-hexylthiophene):[6,6]-phenyl-C-61-butyric acid methyl ester (P3HT:PCBM) BHJ layer. Atomic force photovoltaic microscopy (AFPM) was used to scan arrays of functioning 2 μ m solar cells with varied ITO surface treatments. The standard deviation of the average photocurrent was found to be 11.4% for devices fabricated on untreated ITO, 8.6% for devices with a poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) interlayer, and 6.7% for devices with a HCl-treated ITO surface. These results suggest that conductive non-uniformity in the ITO surface is transferred through the P3HT:PCBM film and that improving the anode conductive uniformity could be an important role of OPV interfacial layers or anode surface treatments.

8:40am EN+NS-WeM3 **Electronically Monodisperse Single-Walled Carbon Nanotube Thin Films as Transparent Conducting Anodes in Organic Photovoltaics**, *T.P. Tyler, R.E. Brock, H.J. Karmel, T.J. Marks, M.C. Hersam*, Northwestern University

Carbon nanomaterial thin films are being increasingly investigated for use as transparent electrodes in a variety of optoelectronic devices [1-3]. These flexible and solution-processible films are ideal candidates for organic electronics, including organic photovoltaics (OPVs), where low production costs and mechanical robustness are essential. While carbon nanotube networks have begun to be explored in such devices, the inherent

polydispersity of the samples—namely the mix of both semiconducting and metallic species—has prevented the realization of their full potential in these devices and convoluted a complete understanding of their implications on device operation. Herein we report the use of single-walled carbon nanotubes (SWNTs) sorted by electronic type via density gradient ultracentrifugation as the transparent anode in poly(3-hexylthiophene) (P3HT) [6,6]-phenyl-C₆₁ butyric acid methyl ester (PCBM) organic photovoltaic devices. Through a combination of dip coating and nitric acid treatment we achieve film roughnesses comparable to typical transparent oxides such as indium tin oxide. While carbon nanotube films are often electronically doped during processing, either intentionally or as a byproduct of roughness-reducing acid treatments, we find that the application of the quintessential electron-blocking interlayer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) removes sufficient adsorbed dopant groups to return the semiconducting nanotubes to their original state, vastly reducing their contribution toward current collection and transport. This is observed by both sheet resistance increases and UV-vis-NIR spectrophotometry. Further investigation using X-ray photoelectron spectroscopy reveals that the weakly-bound nitric oxide groups on the surface are almost entirely removed by PEDOT:PSS. By varying the semiconducting and metallic content in the electrodes, we find that metallic content greater than 70 percent yields devices with efficiencies 50 times greater than those comprised of almost entirely semiconducting SWNTs. This observation is counterintuitive considering that freshly acid-treated semiconducting SWNT films often possess a lower sheet resistance than their metallic counterparts [4]. This underscores the advantage of using metallic-enriched populations for transparent conductors, where unstable doping of semiconducting carbon nanotubes complicates processability and ultimately reduces device performance.

[1] T. M. Barnes; et al. *Appl. Phys. Lett.* **2010**, *96*, 243309.

[2] S. Kim; et al. *Adv. Funct. Mater.* **2010**, *20*, 2310.

[3] J. Li; et al. *Nano Lett.* **2006**, *6*, 2472.

[4] J. L. Blackburn; et al. *ACS Nano* **2008**, *2*, 1266.

9:00am **EN+NS-WeM4 In Situ Characterization of Lifetime and Morphology in Operating Bulk Heterojunction Organic Photovoltaic Devices by Impedance Spectroscopy**, *B.J. Leever, C.A. Bailey*, Air Force Research Laboratory, *T.J. Marks, M.C. Hersam*, Northwestern University, *M.F. Durstock*, Air Force Research Laboratory

Numerous reports have established that improving the performance of bulk heterojunction (BHJ) organic photovoltaic (OPV) devices requires not only the development of materials systems with improved spectral response and higher charge carrier mobility but also the ability to understand and tailor the morphology of these systems. Approaches for morphological characterization have included microscopic techniques such as scanning electron microscopy, transmission electron microscopy, and various atomic force microscopy techniques. Other methods have provided indirect information about active layer morphology by enabling the determination of charge carrier lifetimes. These approaches have included transient absorption spectroscopy, transient photovoltage, and time-of-flight techniques among others. While these methods have proven quite informative, the relationships between nanoscale morphology, device performance, and the underlying electrical characteristics of functioning devices are not yet fully understood.

Recently, impedance analysis has begun to be applied to BHJ OPV devices. These reports demonstrate that the impedance analysis framework established for dye-sensitized solar cells can, to some extent, be extended to bulk heterojunction devices in order to calculate average charge carrier lifetime, electron densities-of-states, and charge carrier concentrations. However, a detailed analysis of the impedance response of active devices, and its dependence on device processing history, morphology, and operating conditions is still needed. In this work we acquire and analyze the impedance behavior of operating P3HT:PCBM bulk heterojunction devices and its dependence on illumination and bias conditions, active layer composition, and annealing history. We also report a simplified equivalent circuit model that successfully describes bulk heterojunction devices over a range of illumination conditions and applied biases. We use this model to extract relevant device performance characteristics such as average electron lifetime and find, in agreement with other reports, that bimolecular recombination losses play a significant role in these devices. To this end, we demonstrate a correlation between device efficiency and lifetime, and describe how values extracted from the present equivalent circuit model can be used to optimize device performance with new materials systems.

9:20am **EN+NS-WeM5 Singlet Exciton Fission in Tetracene and Diphenyltetracene**, *P. Jadhav, A. Mohanty, J. Sussman, M. Baldo*, Massachusetts Institute of Technology

INVITED

Singlet exciton fission is a process by which a high energy singlet spontaneously decomposes into two low energy triplets. It is an example of

a multi-exciton generation process that could allow the efficiency of solar cells to reach beyond the Shockley-Queisser limit. In this talk we examine singlet exciton fission in solar cells based on tetracene and diphenyltetracene (DPT). Notably we find that the photocurrents in each cell have opposite dependencies on the application of a magnetic field, suggesting that fission increases the photocurrent in tetracene-based solar cells, but decreases the photocurrent in DPT-based solar cells.

We report an organic semiconductor solar cell using tetracene and CuPC (Copper Phthalocyanine) as donors, and C60 as the acceptor. Tetracene absorbs photons in the 450-550-nm region, generating high energy singlets which split into two lower energy triplets, potentially doubling the photocurrent in this part of the spectrum. CuPC extends the absorption of the solar cell to the red part of the spectrum. We also demonstrate bulk heterostructure tetracene-C60 devices and tested them for singlet exciton fission.

We observe that: (i) The addition of the CuPC layer does not affect the flow of excitons from tetracene to the CuPC – C60 junction significantly because of similarities in triplet energies of tetracene and CuPC, (ii) The application of a .5T magnetic field shows ~1.5% change in photocurrent, confirming singlet fission, (iii) Low temperature quantum efficiency measurements show a drop in the tetracene IQE (internal quantum efficiency), and a singlet fission yield of 72% at room temperature. The drop in performance at low temperature is expected since singlet exciton fission in tetracene is a thermally activated process. (iv) Singlet exciton fission has a very high yield even in bulk heterostructure devices and can be potentially used to improve the performance of polymer solar cells.

In comparison, we observe that solar cells consisting of DPT-C60 exhibit a large positive (+5%) effect of the magnetic field on the photocurrent, +5% at ~4T. We explain the anomalous magnetic field effect and demonstrate that it can be increased beyond 100% by biasing the device close to open circuit, potentially leading to applications as an anisotropic magnetic field detector.

10:40am **EN+NS-WeM9 Charge Separation and Relaxation in Phthalocyanine-C₆₀ Photovoltaic Systems**, *G.J. Dutton*, University of Maryland -College Park, *S.W. Robey*, National Institute of Standards and Technology

Organic photovoltaic (OPV) structures depend on charge transfer processes occurring within 10's of nanometers of donor-acceptor interfaces. Charge generation in these devices involves successive steps of (1) optical absorption to create excitons, (2) diffusion of the exciton population to the donor-acceptor interface, (3) exciton dissociation and charge transfer at the interface and (4) charge transport and collection at electrodes. The charge separation step depends critically on electronic level alignment between the donor and acceptor. Also, because exciton diffusion to the interface occurs on timescales of several to 10's of picoseconds (ps), relaxation processes occurring on sub-ps and ps timescales as the exciton diffuses can impact the energy available for charge separation at the interface. We have investigated the exciton relaxation and charge separation processes close to phthalocyanine (Pc)-C₆₀ interfaces by combining time-resolved two-photon photoemission (TR-2PPE) with organic MBE to form donor-acceptor interfaces layer-by-layer. Pc $\pi \rightarrow \pi^*$ transitions are excited by a pump pulse to generate singlet (S₁) excitons. The resulting population dynamics are then probed with a time-delayed UV pulse to follow the relaxation and charge separation as a function of energy. For CuPc /C₆₀ interfaces, we compared the decay dynamics as a function of CuPc thickness, and thus distance from the C₆₀ interface, to allow determination of the rate of charge transfer at the interface. We find a charge transfer rate of $\approx 8 \times 10^{12} \text{ sec}^{-1}$ for the initial exciton population formed immediately after pumping. For CuPc, the exciton population also undergoes vibrational relaxation and intersystem crossing (ISC) on a timescale of $\approx 1-2 \text{ ps}$, ultimately resulting in the production a triplet exciton population at significantly lower energy. By again comparing results for thin and thick Pc layers we estimate that the charge transfer rate of this lower energy triplet population is reduced by at least a factor of ≈ 1000 , giving charge transfer rates closer to $8 \times 10^9 \text{ sec}^{-1}$. We will also discuss measurements for the case of H₂Pc and C₆₀ where ISC of the Pc singlet excitons to triplet levels is negligible. Our results will be discussed within the context of the Marcus theory of charge transfer and connections will be made to calculated charge transfer rates for similar donor-acceptor interfaces.

11:00am **EN+NS-WeM10 Low Energy Ion-Assisted Modification of PbS Nanocrystal-Sexithiophene Composite Films**, *F.D. Pleticha*, University of Illinois at Chicago, *L. Donghwa*, University of Florida, *I.L. Bolotin*, University of Illinois at Chicago, *S.R. Phillipot*, *S.B. Sinnott*, University of Florida, *L. Hanley*, University of Illinois at Chicago

The properties of semiconductor nanocrystal-organic films are of interest for applications in photodetectors, light-emitting diodes and photovoltaics. The versatility of these films arises from the ability to tune the bandgaps by

adjusting the PbS nanocrystal size. Nanocrystalline photoelectric properties are also strongly affected by the chemical environment presented to them and by their bonding to the surrounding organic films. PbS nanocrystals are simultaneously deposited under vacuum into an organic matrix of evaporated α -sexithiophene while concomitantly modulating the film interface with 50 eV acetylene ions. Cluster beam deposition has been shown to allow the preparation of PbS nanocrystals that are surface terminated with either Pb or S [1]. Surface polymerization on ion assisted deposition (SPIAD) has shown an ability to increase the conjugation of oligothiophenes and otherwise lead to their chemical modification [2-4]. Cluster beam deposition and SPIAD are combined here to modulate the interface between the PbS and the organic matrix by introducing acetylene ions during the formation of the film. X-ray photoelectron spectroscopy analysis shows chemical shifts indicative of acetylene ion modulated interaction between the nanocrystals and sexithiophene. The deposition process was also simulated by a linearly scaled density functional theory method. These computer simulations indicate chemical bonding between the nanocrystals and sexithiophene, which is consistent with the chemical shifts observed by XPS.

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11:20am EN+NS-WeM11 Molecular Modulation of Solar Cells: Where Inorganic, Molecular and Organic Electronics Meet, D. Cahen, R. HarLavan, O. Yaffe, Weizmann Institute of Science, Israel

Organic materials present a promising direction for potentially cheaper solar cells. One way to use them and increase our understanding (e.g., define basic physical cell performance limits), is hybrid, organic / inorganic photovoltaics (PV). We explore 2 main directions to hybrid PV - with molecules as dipolar films, i.e., use electrostatics

- with molecular monolayers as electronic transport medium.

While we find that incomplete partial dipolar monomolecular films can control solar cell behavior for /single, poly- and nano-crystalline cells, for current to pass through the molecules, we need dense monolayers. Alkyl chain monolayers help form near-ideal Metal-Insulator-Semiconductor (MIS) diodes, with significant PV activity. Surprisingly, though we can actually make *MIS* cells without a separate *I*(nsulator) layer, suggesting that 'MIS' effects are at least partly more "chemical than is often thought.

In this way we demonstrate a near-ambient, simple, potentially low-cost approach to make and modify semiconductor solar cells, using a monolayer of molecules, as short as two carbons, that self-assembles onto the semiconductor (absorber) surface, passivating and buffering it. Good passivation is necessary to express the molecule-induced interface dipole, which can change the semiconductor electron affinity by up to 1 eV.

Good, stable interface passivation along with strong inversion allows minority carriers, generated by absorbed light, to move laterally within the semiconductor top layer, for collection by a minimal-area grid, deposited on the conducting polymer and also minimizes photo-current losses, due to sheet resistance. Thus, ≤ 1 nm thick organic molecules appear to convey a unique advantage over inorganic passivation or buffer layers.

11:40am EN+NS-WeM12 Correlation of Interfacial Electronic Structures and Open Circuit Voltages in Organic Solar Cells, M.H. Chen, National Dong Hwa University, Taiwan, Republic of China, W.H. Tseng, J.Y. Wang, C.T. Tseng, C.I. Wu, National Taiwan University

In this study, the interfacial electronic structures and energy band diagrams of polymer/fullerene bulk heterojunction (BHJ) solar cells are investigated. To study the device performance influenced by the interlayer, poly(3-hexylthiophene) (P3HT) mixed with 6,6-phenyl C61-butyric acid methylester (PCBM) are used as an active layer and bathocuproine (BCP) and calcium (Ca) are incorporated respectively with the cathodes. Since the mechanisms leading to the improvement of power conversion efficiency are more chemically and electronically complicated and have not been understood, the ultraviolet and x-ray photoemission spectroscopy (UPS and XPS) are used to investigate the properties of energy band, electronic structures and the interface chemistry at the interface. For the devices incorporated with BCP, highest occupied molecular orbital (HOMO) level of PCBM is pulled down about 0.3 eV with respect to the Fermi level after the deposition of BCP. It indicates that the BCP layer could modify the energy band by shifting the energy level of acceptors, causing the increase of built-in potential (V_{bi}). Thus, the open circuit voltage (V_{oc}) attributed to the increase of V_{bi} resulted from BCP could be enhanced. Moreover, AFM

image indicates that BCP molecules cannot form a uniform layer on the active layer surface, pointing out the band modulation is the key reason to the V_{oc} improvement. For the devices with Ca as cathodes, the UPS results with deposition of Ca illustrate a 0.8 eV-downward shift in energy levels of P3HT, but not in those of PCBM. Therefore, the energy difference between the HOMO of P3HT and the LUMO of PCBM is widened, resulting in the increase of V_{oc} and the enhancement of device efficiency. Moreover, from the XPS spectra, there is an extra new peak appear at the lower binding energy about 162 eV, which suggests that the addition of electrons around the reactive sulfur (S) atoms in P3HT molecules after Ca deposition. The combinations of S and Ca spectra imply that the formation of Ca-S bonding at the Ca/P3HT interface, which is in good agreement with the findings of UPS spectra.

Helium Ion Microscopy Focus Topic

Room: 106 - Session HI+AS+BI+NS-WeM

Nano- and Bio- Imaging with Helium Ion Microscopy

Moderator: A. Götzhäuser, University of Bielefeld, Germany, V.S. Smentkowski, GE-GRC

8:40am HI+AS+BI+NS-WeM3 Helium Ion Microscopy Techniques for Imaging and Characterization of nano-Device Materials and Structures, S. Ogawa, T. Iijima, National Institute of Advanced Industrial Science and Technology (AIST), Japan

INVITED

This paper presents several imaging modes for nano-devices fabrication that may make HIM a tool of particular value to soft materials such as low-k dielectrics (low-k) with less transformation and more materials contrast which reflects damaged areas, and copper interconnect buried in dielectrics, and shows luminescence induced by the focused helium ion beam using the HIM for the first time.

Imaging of -100 nm pitch patterned low-k is important for LSI Cu/low-k interconnect processes, while SEM imaging results in changes to the low-k line edge roughness and shape by damage during an electron beam irradiation. The HIM could provide low-k dielectric secondary electron (SE) image with nm order resolution, deeper focus depth, less transformation because of three order magnitude lower thermal energy transfer into a unit volume of the low-k than the SEM under an appropriate operation condition¹⁾.

During the imaging, even at very low helium ion current, surfaces of samples were atomically etched off, as in a graphene patterning, and then blistering or physical etch occurred with the increase of the helium ion current. This makes the interpretation of the HIM SE imaging difficult but helpful. Damaged areas at side walls of the low-k regions in a 140 nm pitch interconnect were successfully seen with a different contrast from non-damaged low-k regions at an "optimized" helium ion beam condition²⁾, which was similar to a TEM/Valence EELS result. On the other hand, using the SEM, the damaged areas contrast in the low-k regions could not be imaged.

A new imaging mode, through the inter-level dielectric, of the underlying copper, was explored. Cu interconnect was seen through a 130 nm thick low-k dielectrics. The incident helium ions might generate secondary electrons (SEs) at the buried Cu surface and the SEs of 1-2 eV energy passed through the dielectric of a few eV band gap without any energy transfer, and then the image was obtained. Helium ion channeling at the Cu surface area varied the secondary electron quantity, and it might generate a crystal orientation contrast of the buried Cu metal.

Luminescence induced by the focused helium ion beam was studied using the HIM³⁾. Helium ion beam of a few pA current was irradiated to a SiO₂ film, and peaks in a spectrum were observed at around 281, 447, and 672 nm; these positions were different from those by a conventional SEM cathode luminescence. The further study will be presented.

L.Stern, W.Thompson and J.Notte of Carl Zeiss are acknowledged for their discussions in the Cu / low-k works.

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9:20am HI+AS+BI+NS-WeM5 He Ions Image the Au (111) Herringbone Reconstruction, V. Veligura, G. Hlawacek, R. van Gastel, H. Zandvliet, B. Poelsema, MESA+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands

The herringbone reconstruction of the Au(111) surface was directly visualized using an Ultra High Vacuum Helium Ion Microscope. Ion channeling phenomena arise from the different atomic ordering in the outermost layer of the crystal. First, we investigated the channeling contrast

from the bulk Au fcc structure by imaging polycrystalline Au on glass films. The contrast that was observed as a function of crystal orientation was found to conform to what is calculated from a simple hard sphere model. Consequently, the herringbone reconstruction was investigated. It is a periodic zigzag structure of the three different types of crystal stacking (fcc, hcp and bridge sites connecting these regions) and, ideally, has a period of 6.3 nm. The different stacking of the atoms that constitute the surface reconstruction leads to lateral variations of the secondary electron yield that can be resolved in HIM imagery. The existence of the herringbone reconstruction on the sample was independently confirmed through STM measurements and the quantitative details from both techniques are similar, but seem to be affected by the differences in vacuum conditions. An influence of both the ion beam and vacuum environment on the visibility of the herringbone reconstruction is observed in our UHV-HIM system.

9:40am **HI+AS+BI+NS-WeM6 Imaging of Graphenoid Nanomembranes with Helium-Ion Microscopy**, *A. Beyer, A. Turchanin, A. Götzhäuser*, University of Bielefeld, Germany

Helium-ion microscopy is known for its high surface sensitivity. Here we present a study about imaging extremely thin nano-scale objects: graphenoid nanomembranes which consist exclusively of atoms near the surface. Such freestanding nanomembranes with a thickness of 1 nm are made from self-assembled monolayers (SAMs) by cross-linking and subsequent transfer to transmission electron microscopy (TEM) grids or other suitable substrates. We show that these nanomembranes exhibit a substantially higher contrast in helium-ion microscopes as compared to electron microscopes.

Cross-linking of SAMs is performed by large area exposures with electrons or photons which yield extended nanomembranes. On the other hand, patterned exposures allow the fabrication of nanosieves, i.e. perforated nanomembranes. Advantages in imaging such patterned cross-linked SAMs as well as freestanding nanosieves with the helium-ion microscope will be discussed.

10:40am **HI+AS+BI+NS-WeM9 Nanofabrication and Biological Imaging with the Helium Ion Microscope**, *D.S. Pickard*, National University of Singapore **INVITED**

The Helium Ion Microscope (HIM) is a new imaging technology based on a high brightness and stable Gas Field Ion Source (GFIS). The GFIS employed exhibits a low energy spread (<1 eV), small virtual source size (<0.3 nm) and a high brightness $> 4 \times 10^9$ A/cm².sr [1]. This, in conjunction with the shallow escape depth (<1 nm) of the secondary electrons generated by the incident 30 keV helium ions, contribute to the HIM's primary advantage in the imaging of solid samples: its high spatial resolution (0.25 nm) [2]. We have applied this novel technology across a broad spectrum of multidisciplinary applications (from basic materials science and semiconductor applications to the biological sciences) to assess its utility and possible advantages over alternative techniques.

One area where our investigations have gained significant traction is in the imaging of biological specimens. The utility of this instrument in addressing topics of the biological sciences is due in part to the HIM's high spatial resolution. However, in the context of biological specimens, it is the ability to image non-conductive samples without the application of a metal (or other conductive) overcoat and without the need of a background gas (both of which degrade resolution and surface details), which has proven to be a distinguishing attribute. This opens up a whole new range of biological problems that can be solved rapidly and with less risk of artifacts.

An equally compelling application is in the field of nano-structuring. The focused helium ions have the ability to directly modify the sample surface under a high ion flux (via surface sputtering). This enables the direct patterning of structures and promises great utility in the fabrication of sub-10 nm devices. It also provides a mechanism for high resolution patterning on nonconventional substrates (such as suspended graphene membranes), where resist-based lithographic techniques are not feasible. Our experiences in sub-10 nm pattern transfer for both graphene and plasmonics applications will be presented.

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11:20am **HI+AS+BI+NS-WeM11 Imaging and Characterizing Cellular Interaction of Nanoparticles using Helium Ion Microscopy**, *B.W. Arey, V. Shutthanandan, Y. Xie, A. Tolic, G. Orr*, Pacific Northwest National Laboratory

The helium ion microscope (HeIM) probes light elements (e.g. C, N, O, P) with high contrast due to the large variation in secondary electron yield,

which minimizes the necessity of specimen staining. A defining characteristic of HIM is its remarkable capability to neutralize charge by the implementation of an electron flood gun, which eliminates the need for coating non-conductive specimens for imaging at high resolution. In addition, the small convergence angle in HeIM offers a large depth of field ($\sim 5\times$ FE-SEM), enabling tall structures to be viewed in focus within a single image. Taking advantage of these capabilities, we investigate the interactions of engineered nanoparticles (NPs) at the surface of alveolar type II epithelial cells grown in culture. The increasing use of nanomaterials in a wide range of commercial applications has the potential to increase human exposure to these materials, but the impact of such exposure on human health is still unclear. One of the main routes of exposure is the respiratory tract, where alveolar epithelial cells present a vulnerable target. Since the cellular interactions of NPs govern the cellular response and ultimately determine the impact on human health, our studies will help delineating relationships between particle properties and cellular interactions and response to better evaluate NP toxicity or biocompatibility.

The Rutherford backscattered ion (RBI) is a helium ions imaging mode, which backscatters helium ions from every element except hydrogen, with a backscatter yield that depends on the atomic number of the target. Energy-sensitive backscatter analysis is being developed, which when combined with RBI image information, support elemental identification at helium ion submicron resolution. This capability will enable distinguishing NPs from cell surface structures with nanometer resolution.

11:40am **HI+AS+BI+NS-WeM12 Application of Helium Ion Microscope on Semiconductor Surface Imaging and Metrology**, *H.X. Guo*, National Institute for Materials Science, Japan, *H. Itoh*, National Institute of Advanced Industrial Science and Technology (AIST), Japan, *K. Onishi, T. Iwasaki, D. Fujita*, National Institute for Materials Science, Japan
Scanning electron microscope (SEM) has been used in the semiconductor surface imaging and metrology for more than 50 years. Now, a new tool, Helium ion microscope (HeIM), is developed and applied to this work. SEM and HeIM are the same in some fundamental characteristics. But, the latter has advantages in smaller probe size, higher resolution, and greater depth of field. These abilities enhance the performance of the HeIM in the semiconductor surface imaging and metrology, such as imaging of low- k materials [1] and measurement of critical dimension of the semiconductor devices [2].

A standard sample for scanning probe microscope tip characterization [3, 4] was measured by using HeIM and atomic force microscope (AFM) as shown in Fig. 1 and Fig. 2. Line profile of the HeIM image in Fig. 1 shows high accuracy in edge definition of the sample. The contrast of the image is related to morphology and materials of the sample [5], the probe size of the Helium ion beam, direction of the sample and beam, charge distribution, and so on. All the aspects will be analyzed in our presentation. The AFM image of the sample shown in Fig. 2 is a dilation of the real surface topography of the sample due to the finite-size AFM tip [6]. With an erosion algorithm, the surface of the sample was reconstructed to be compared with HeIM measurement.

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Nanometer-scale Science and Technology Division Room: 203 - Session NS-WeM

Carbon-Based Nanomaterials

Moderator: M.C. Hersam, Northwestern University

8:00am **NS-WeM1 Characterization of Large Area Graphene Crystallites Grown on Cu Foil Substrates**, *P. Tyagi, Z.R. Robinson, H. Geisler, C.A. Ventrice, Jr.*, University at Albany, *H. Yang, T. Valla*, Brookhaven National Laboratory, *Y. Hao, R.S. Ruoff*, University of Texas at Austin

Graphene growth on Cu foils by catalytic decomposition of methane forms predominately single layer graphene films due to the low solubility of carbon in Cu. One of the key issues for the use of CVD graphene in device

applications is the influence of defects on the transport properties of the graphene. In particular, the presence of grain boundaries within the graphene film will increase the probability for scattering of carriers, resulting in reduced mobilities. Therefore, an important goal is to develop techniques for growing graphene films with crystallites that have lateral dimensions of a few millimeters or larger. There are several factors that influence the size and orientation of the graphene crystallites such as the size and orientation of the grains within the metal foil, temperature gradients during growth, the hydrocarbon source pressure, and the growth temperature. By growing the graphene films using methane source pressures less than 50 millitorr, preanneal times of approximately an hour, growth temperatures of 1035 °C, and a tented Cu substrate geometry within a conventional tube furnace, graphene crystallites larger than a millimeter in size have been achieved.

Measurements of the graphene growth morphology and surface topography of the Cu substrate have been performed using scanning electron microscopy (SEM). The graphene crystallites show a dendrite pattern, and the Cu substrate typically shows a somewhat faceted structure at this growth temperature. Low energy electron diffraction (LEED) measurements show sharp diffraction spots but with multiple zero-order reflections, which results from the faceted structure of the Cu substrate after growth. Electron backscatter diffraction (EBSD) measurements have been performed on the Cu substrates to determine the crystallographic orientation and size of the substrate grains. Before growth, the average grain size is ~10 μm with a random orientation. After growth, the Cu substrate grain size is on the order of centimeters with a typical orientation towards the {100} surface termination. Synchrotron-based angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) measurements have also been performed to probe the electronic band structure of the graphene. A linear dispersion has been measured in the K direction with the Dirac point located near the Fermi level.

8:20am NS-WeM2 Gas Adsorption on Pt-Clusters Supported by Graphene. *J. Knudsen*, Lund University, Sweden, *T. Gerber*, University of Cologne, Germany, *E. Graanäs*, Lund University, Sweden, *P.J. Feibelman*, Sandia National Laboratories, *K. Schulte*, Lund University, Sweden, *P. Stratman*, *C. Busse*, *T. Michely*, University of Cologne, Germany, *J.N. Andersen*, Lund University, Sweden

Model systems of real catalysts consisting of nanoparticles deposited on substrates often have a broad size distribution, making it difficult to link the adsorption properties to the atomic scale structure of the nanoparticles using averaging techniques. Metal nanoparticles grown on a graphene/Ir(111) moiré film, however, show exceptionally well ordered arrays of nanoparticles with an extremely narrow size distribution [1, 2]. Further, it is possible to control the cluster size precisely by adjusting the amount of deposited material, since each moiré unit cell contains one cluster. The narrow size distribution and the easy control of cluster size make metal particles supported by graphene an ideal model system for adsorption studies with averaging techniques.

In this contribution we report on our studies on CO adsorption on such an ideal model system consisting of Pt-clusters grown on a graphene/Ir(111) moiré film using photoemission X-ray spectroscopy (XPS), scanning tunnelling microscopy (STM), and density functional theory (DFT) [3].

For Pt/graphene without CO we observe pinning of the graphene film, as a shoulder at the high binding energy side of the C 1s peak observed for pristine graphene. DFT calculations reveal that this shoulder should be assigned to carbon atoms positioned below and in the vicinity of the Pt clusters, which all are displaced towards the Ir(111) surface.

Upon CO adsorption we observe C 1s and the O 1s peak positions consistent with preferential adsorption in atop sites at the cluster step edges. We also observe that the pinning-induced shoulder in the C 1s spectrum diminish upon CO adsorption, and interpret this as unpinning of the graphene film when CO adsorbs on the clusters step edges. From real time STM movies taken during CO dosing we show that the unpinning of the graphene film leads to coalescences of the Pt clusters, when the clusters are smaller than approximately 10 atoms.

References:

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8:40am NS-WeM3 Seeding Atomic Layer Deposition of High-k Dielectrics on Epitaxial Graphene with Organic Self-Assembled Monolayers. *J.M.P. Alaboson**, *Q.H. Wang*, *J.D. Emery*, *A.L. Lipson*, *M.J. Bedzyk*, Northwestern University, *J.W. Elam*, *M.J. Pellin*, Argonne National Laboratory, *M.C. Hersam*, Northwestern University

The development of high-performance graphene-based nanoelectronics requires the integration of ultrathin and pinhole-free high-*k* dielectric films with graphene at the wafer scale. Here, we demonstrate that self-assembled monolayers of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) act as effective organic seeding layers for atomic layer deposition (ALD) of HfO₂ and Al₂O₃ on epitaxial graphene on SiC(0001). The PTCDA is deposited via sublimation in ultra-high vacuum and shown to be highly ordered with low defect density by molecular-resolution scanning tunneling microscopy. Whereas identical ALD conditions lead to incomplete and rough dielectric deposition on bare graphene, the chemical functionality provided by the PTCDA seeding layer yields highly uniform and conformal films. The morphology and chemistry of the dielectric films are characterized by atomic force microscopy, ellipsometry, cross-sectional scanning electron microscopy, and X-ray photoelectron spectroscopy, while high-resolution X-ray reflectivity measurements indicate that the underlying graphene remains intact following ALD. Using the PTCDA seeding layer, metal-oxide-graphene capacitors fabricated with a 3 nm Al₂O₃ and 10 nm HfO₂ dielectric stack show high capacitance values of ~700 nF/cm² and low leakage currents of ~5 × 10⁻⁹ A/cm² at 1 V applied bias. These results demonstrate the viability of sublimated organic self-assembled monolayers as seeding layers for high-*k* dielectric films in graphene-based nanoelectronics.

9:00am NS-WeM4 Graphene-based Electronics and Optoelectronics. *Ph. Avouris* †, IBM T.J. Watson Research Center **INVITED**

Graphene a two-dimensional, single atomic layer material with linear electron dispersion has rather unique electrical and properties¹. There is currently strong interest in taking advantage of these properties for technological applications². In my talk I will review some of the key properties of graphene, how these are affected by environmental interactions and how they can be utilized in electronics and optoelectronics.

Specifically, I will discuss high frequency (>100 GHz) graphene transistors^{3,4}, their fabrication and operation, as well as related device physics aspects, such as carrier transport mechanisms, electrical contacts, temperature effects, energy dissipation, etc. Simple integrated graphene circuits will also be presented. I will then discuss key optical properties of graphene and how they can be combined with its excellent electrical properties and used in optoelectronics applications. Specific examples involving ultrafast graphene photodetectors⁵ and their applications in the detection of optical data streams⁶ will be presented.

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9:40am NS-WeM6 Plasma-based Approach to Controlling the Properties of Graphene. *S.C. Hernández*, *M. Baraket*, *S.G. Walton*, *W.K. Lee*, *C.R. Tamanaha*, *P.E. Sheehan*, *J.T. Robinson*, *V.D. Wheeler*, *R.L. Myers-Ward*, *L.O. Nyakiti*, *Eddy*, *D.K. Gaskill*, Naval Research Laboratory (NRL)

Graphene has attracted a widespread of interest because of its unique structural and electronic properties however, manipulation of these properties is necessary before realizing its full potential as the next generation material in a broad range of electronic and sensing applications. Specifically, tailoring the surface chemistry of graphene by the addition of functional groups is an attractive way to simultaneously manage the conductivity and reactivity of this material. This work discusses the use of electron-beam generated plasmas to controllably functionalize graphene synthesized from different methods. Electron-beam generated plasmas, produced in a variety of background gases (e.g. N₂, O₂, SF₆, NH₃) were used to introduce functional groups in a range of atomic densities at the graphene surface, without damage to the underlying graphene structure. Plasma processing conditions and characteristics, as well as the resulting chemical,

* NSTD Student Award Finalist

† NSTD Recognition Award

structural, and electrical properties of the functionalized graphene were examined. This work is supported by the Office of Naval Research.

10:40am **NS-WeM9 Solution Plasma-Assisted Surface Functionalization of Chemically Converted Graphene Sheet toward an Enhancement of Solubility in Solution.** *N. Tsuda, T. Ueno, N. Zettsu, S. Cho, O. Takai, N. Saito*, Nagoya University, Japan

Graphene, a one-atom layer of graphite, possesses a unique two-dimensional structure and excellent mechanical, thermal, and electrical properties. Thus, it has been regarded as an important component for making various functional composite materials. Graphene can be prepared through micromechanical exfoliation, epitaxial growth, and chemical vapor deposition and electrochemical approaches. Different from these approaches, chemical synthesis of graphene using graphite, graphite oxide (GO) or other graphite derivatives as starting materials were tested to be effective for producing chemically converted graphene (CCG) from various precursors, such as graphite, carbon nanotubes, and polymers, in large scale and at low costs. Therefore, CCG is more suitable for synthesizing high-performance graphene based composites.

Graphene oxide can be chemically reduced to CCG. Hydrazine monohydrate was most widely used, mainly due to its strong reduction activity and the stability in aqueous media. Upon reduction with hydrazine, most oxygen-containing functional groups of graphene oxide are eliminated and the π -electron conjugation within the aromatic system of graphite is partially restored. As a result, the reduced graphene oxide (or CCG) is usually precipitated from the reaction medium because of the recovered graphite domains of CCG sheets increased their hydrophobic property and π -stacking interaction. The use of hydrazine as reducing agent also has several disadvantages. The trace residual may strongly decrease the performance of CCG in devices.

In this work, we demonstrate solution plasma-assisted surface functionalization of chemically converted graphene sheet in order to enhancement of solubility in both aqueous and organic solvent. Solution plasma (SPP) is a plasma discharge in solution, which is expected a higher reaction rate under low-temperature conditions, and the greater chemical reaction variability since the molecular density of liquid is much higher than that of gas phase.

A colloidal graphene oxide sheets was treated with SP in ammonium containing aqueous solution in order to make reduced CCG and functionalize CCG surface with primary amine group. A glow discharge was produced at bipolar-pulsed voltages with pulse width and frequency of 2 ms and 15 kHz, respectively. The all products were characterized by IR, Raman, spectroscopy, AFM, XRD, and TEM. Furthermore, we also demonstrate an introduction of organic and polymeric molecule as a second component onto the aminated CCG surface to insulate hydrophobic property and π -stacking interaction of neighboring CCG sheets in aqueous solution, and to be organic solvent solubilization.

11:00am **NS-WeM10 Horizontally Aligned Carbon Nanotubes on Quartz Substrate for Electrolyte-Gated Chemical and Biological Sensing.** *S. Okuda, Y. Ohno, K. Maehashi, K. Inoue, K. Matsumoto*, Osaka University, Japan

Electrolyte-gated carbon nanotube field-effect transistors (CNTFETs) based highly sensitive chemical and biological sensors were demonstrated. Dense, well-aligned CNTs grown on quartz substrates were utilized as channels of CNTFETs. Using the large number of CNTs is a simple strategy to realize excellent performance of CNTFETs. First, the pH dependence of CNTFETs was measured in buffer solution ranging from pH 4.0 to 8.3 by monitoring the drain current (I_D) in the CNTFET. Clearly and stepwise increases in I_D were observed against the change in pH in the solution. The detection limit for changes in pH was estimated to be 0.015, which is a superior characteristic to that of conventional CNTFETs. The result indicates that CNTFETs on quartz substrates can be used as highly sensitive pH sensors. Moreover, label-free biomolecule sensing was demonstrated. The target protein was a class of antibody, immunoglobulin E (IgE). To achieve the electric detection of IgE, we used aptamer-modified CNTFETs with multichannel. Then, binding event of target IgE onto the aptamers was detected. IgE-concentration dependence measurements revealed that we succeeded in detection of nM quantities of IgE. In conclusion, electrolyte-gated multichannel CNTFETs will be useful for highly sensitive chemical and biological sensors.

11:20am **NS-WeM11 Gas-phase Studies and Growth of Well-Defined Carbon Nanotubes.** *A. Kumar, P. Lin, R.M. Sankaran*, Case Western Reserve University

Carbon nanotubes (CNTs) have attracted interest for a wide-range of technological applications including nanoelectronic, energy storage, and energy conversion devices. In many of these applications, the nanotube structure must be sufficiently controlled at the growth stage; however,

current growth methods typically produce mixtures of tubes, including multi-walled, single-walled, and a range of different chiralities, that must be purified and separated to facilitate applications.

We are interested in controlling the properties of CNTs at the growth stage. We have recently developed a two-step process [1-3] to study and grow CNTs consisting of a microplasma reactor that controls the size- and composition of the nanoparticle catalysts and a flow furnace that nucleates and grows the nanotubes. In addition, the nanotubes are monitored *in situ* by aerosol measurements to provide real-time feedback and allow the reactor conditions to be rapidly optimized. By tuning the size of our catalyst, we have found that the fraction of single-walled CNTs in the as-grown product can be varied. Similarly, by tuning the composition of the catalyst, we have found that the chirality distribution of the as-grown nanotubes is changed. Here, we will present results for Ni-based bimetallic catalysts and the influence of the catalyst size and composition, as well as other growth parameters such as carbon feedstock and growth temperature, on nanotube growth. In addition to aerosol measurements, the nanotubes are collected and characterized by micro Raman spectroscopy and UV-Vis-NIR absorbance spectroscopy. The structure and properties of the nanotubes and their relationship to the catalyst and other growth parameters will be discussed in detail.

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11:40am **NS-WeM12 Visualizing Defect Distributions in Carbon Nanotubes using Linear Dichroism Signals in Scanning Transmission X-ray Microscopy (STXM) and TEM-EELS.** *E. Najafi, A.P. Hitchcock, D. Rossouw, G. Botton*, McMaster University, Canada

The X-ray Linear Dichroism (XLD) signal in spatially resolved X-ray absorption spectromicroscopy of individual carbon nanotubes (CNT) [1] has been shown to be sensitive to the local density of sp^2 defects along the nanotube. This dichroic signal is as strong for single-walled [2] as for multi-walled CNT, which is rather surprising given the much higher curvature in SWCNT than MWCNT. The link between the strength of the XLD of the C 1s $\rightarrow \pi^*$ peak at 285.2 eV and defect density within the sampled area has been verified by intentionally inducing sp^2 defects by ion bombardment [3]. This XLD signal is potentially useful for guiding optimization of CNT synthesis and preservation of the quality of nanotubes through various processing steps used to make functional devices where defect distribution and character play an important role. However STXM has limited spatial resolution; 10 nm, state-of-art while this work was performed at ~ 25 nm. Recently we have demonstrated that Electron Linear Dichroic (ELD) signals similar to XLD can be measured in q-dependent C 1s electron energy loss spectroscopy carried out in an aberration compensated, monochromated transmission electron microscope. The signals are detected by operating in STEM mode, carefully arranging the conditions such that the spectrometer accepts a narrow range of off-axis scattered electrons (with a specific location, identified in diffraction mode), and using a tilt stage to change the orientation of the CNT relative to the incident and outgoing electron directions. STEM-EELS maps measured with 2 nm sampling over a portion of a MWCNT, and over a range of tilt angles provide quantitative maps of the ELD signal. The experimental conditions will be described and the defect mapping capability of this method will be demonstrated.

STXM measurements were carried out at the SM beamline at the Canadian Light Source, which is supported by the Canada Foundation for Innovation (CFI), NSERC, Canadian Institutes of Health Research (CIHR), National Research Council (NRC) and the University of Saskatchewan. We thank Chithra Karunakaran, Jian Wang and Martin Obst for their expert support of the CLS STXM. TEM-EELS was performed with the Titan-1 system of the Canadian Centre for Electron Microscopy which is supported by CFI and NSERC.

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Wednesday Afternoon, November 2, 2011

Biomaterial Interfaces Division

Room: 108 - Session BI+AS+NS+SS-WeA

Functionalization and Characterization of Nanostructures

Moderator: A. Belu, Medtronic, Inc.

2:00pm BI+AS+NS+SS-WeA1 Characterization of Nano-objects by Cluster-SIMS, E.A. Schweikert, Texas A&M University INVITED

Secondary ion mass spectrometry, SIMS is a method of choice for the chemical analysis of nanodomains embedded in solids. We examine here a case which has received little attention, the analysis of individual, free-standing nano-objects. Our approach uses a variant of SIMS. The nano-objects are bombarded with a sequence of individual projectiles resolved in time and space, in the present case Au_{400}^{4+} of up to 520 keV impact energy. The successive projectiles impact stochastically the nano-objects dispersed on a solid support. Typically tens of secondary ions are ejected from each impact. They are identified with time-of-flight mass spectrometry and recorded individually. This approach reveals molecules co-located within the 10-20 nm diameter area of emission from one Au_{400}^{4+} impact. We demonstrate that the event-by-event bombardment-detection mode is sensitive to the chemical and/or physical nano-scale separation of molecular species. The performance is illustrated with the determination of the relative abundance of the oxide layer in the near surface of 50-100 nm nanoparticles; the nature and abundance of different nano-objects (5-20 nm in diameter) in mixtures of nano-sized solids; the composition of bio-objects such as a bacteriophage including the amino acids of the proteins surrounding the phage and the bases from the encapsulated DNA. The distinct feature of the nanoprobe technique presented here is in the detection of co-emitted ejecta from individual projectile impacts which allows to test chemical composition, in a nonimaging mode, yet at an exquisite level of spatial resolution. Moreover the co-emission of fragment and parent ions enhances the accuracy of molecular identification.

Work supported by NSF grant CHE-0750377

2:40pm BI+AS+NS+SS-WeA3 Strategies for Studying the Surface Chemistry of Engineered Nanoparticles with SIMS, C. Szakal, J. McCarthy, National Institute of Standards and Technology, K. Louis, R.J. Hamers, University of Wisconsin-Madison, R.D. Holbrook, National Institute of Standards and Technology

The environmental toxicity of engineered nanoparticles (ENPs) is of increasing importance as these materials become more widely used in manufacturing processes and consumer products. Nanoparticles have extremely high surface-to-volume ratios, which makes the surfaces more critical than their corresponding bulk materials in terms of reactivity, aggregation, and toxicity to various life forms. Therefore, it is critical that we develop methods to distinguish small chemical changes on nanoparticle surfaces in order to understand how these materials will interact outside of controlled laboratories. Conventional approaches of nanoparticle characterization have focused on high resolution morphological imaging (TEM, SEM) and physical property measurements such as surface charge. However, chemical information is generally only inferred from these materials with most current methods. If it is possible to obtain both elemental and molecular information from ENP surfaces, we may be able to determine the eventual fate of ENPs in the environment.

We have developed a comprehensive approach for studying the surface chemistry of ENPs, including 1) preparation of ENPs to controllably study desired variables, 2) development of methods such as time-of-flight secondary ion mass spectrometry (ToF-SIMS) and environmental scanning electron microscopy (ESEM) to probe small changes in ENP surface chemistry and/or aggregation, and 3) development of methods to improve the speed and reproducibility of ENP aggregation for batch studies. These approaches will be utilized as the basis of future toxicity studies of selected ecosystems.

3:00pm BI+AS+NS+SS-WeA4 Unusual Hydrogenation Isotherms for Pd Nanoring Model Systems Observed Via Nanoplasmonic Sensing, C.B. Langhammer, E.M.K. Larsson, I.L. Zoric, Chalmers University of Technology, Sweden, V.P. Zhdanov, Boreskov Institute of Catalysis, Russian Federation

Nanostructured materials have been proposed as a solution for the development of efficient hydrogen storage systems. As the size of the system gets reduced in the nanometer range enthalpies and entropies of hydrogen dissolution in the metal (α -phase) and hydride formation (β -

phase) as well as activation barriers for diffusion and desorption of hydrogen become size dependent thus influencing both thermodynamics (pressure-composition isotherms) and kinetics (loading/unloading kinetics). The pressure-composition isotherms for a H₂/M system show a well-known behavior typical for an α -phase in the low pressure-composition range followed by a plateau signaling the onset of a hydride formation (β -phase) via a first order phase transition and a coexistence of the two over a wide composition range. At higher pressure a pure β -phase exists characterized by a pressure-composition curve with a steep slope. The plateau pressure of the H₂/M system is determined by the requirement of equilibrium between the three phases in coexistence, thus primarily by the enthalpy and entropy of hydride formation. In case of more than one hydride type a coexistence region exhibits multiple plateaux determined by appropriate energetics as described above. In all known cases the same multiple plateaux features were observed both during the charging and discharging process, i.e. when hydrogen pressure was increased/decreased, accompanied of course by a perennial hysteresis.

In this work we report unusual pressure-composition isotherms for H₂/Pd nanosized rings where a double plateau isotherms are observed during the charging process and a single plateau one during the hydrogen discharging. The Pd nanorings were fabricated using colloidal lithography. Hydrogen isotherms were followed by monitoring the shift in the ring Localized Surface Plasmon Resonance, LSPR, upon exposing the system to increasing/decreasing hydrogen pressure steps (and equilibrating the sample at each pressure step). The shift of the LSPR resonance was calibrated by preparing the same ring structure on a quartz crystal microbalance and "weighing" directly absorbed hydrogen. A linear relation between the LSPR shift and QCM frequency shift (proportional to hydrogen concentration) was observed.

We present a simple model, based on the observed heterogeneity of the nanorings (as seen in TEM) and by taking into account the defect induced lattice strain, that accounts for the unusual behavior of the observed isotherms.

4:00pm BI+AS+NS+SS-WeA7 Surface Functionalization and Analysis of Functional "Soft" Nanostructures: From 2 to 3 Dimensions, H. Schönherr, University of Siegen, Germany INVITED

The local properties of soft matter, e.g. for the fabrication of functional biointerfaces or nanostructures, are of tremendous importance for ultimate functionality. In this presentation, the closely interrelated areas of surface chemical functionalization / engineering and analysis of properties will be discussed based on three key examples. These examples include: (i) synthesis and modification of polymer brushes with particular focus on the nanomechanical properties, (ii) ultra small diameter nanotubes obtained by the layer-by-layer assembly of polyelectrolytes inside a sacrificial porous template and (iii) block copolymer nanocapsules that are developed for advanced wound management. In all examples, confinement effects are expected to play a significant role in determining e.g. the mechanical properties, as assessed by atomic force microscopy (AFM) nanoindentation.

For thin polymer films (2D) the dependence of the mechanical properties on the film architecture was unraveled. Compared to spin-coated films, brushes synthesized on gold surface by surface initiated polymerization showed higher elastic moduli, which is attributed to entropy effects. Upon chemical crosslinking tunable elastic properties are obtained, which provides interesting pathways for the fabrication of defined cell - surface contacts.

Similarly important are defined nanoscale objects that can be obtained via the replication of small templates by the so-called layer by layer (LbL) deposition of polyelectrolytes (G. Decher Science 1997, 277, 1232). LbL deposition in porous Anodic Aluminum Oxide (AAO) was only very recently expanded to the 100 nm length scale due to an alleged entropic barrier caused by adsorbed polyelectrolytes close to the pore orifice [Y. Cho et al. Small 2010, 6, 23, 2683]. However, in contrast to this report, we show that the adsorption of polyelectrolytes on the top plane of the AAO and polymer sedimentation have been identified as main bottlenecks. Suppressing these processes enabled us to produce free standing polymer nanotubes with external diameters of < 55 nm.

Finally, first steps in the development of active nanocapsules filled with a reporter dye or an antimicrobial agent for applications in burn wound management will be presented. In particular the case of burn wounds and the devised biomimetic strategy of BacterioSafe will be introduced. Subsequently, the fabrication and characterization of a polystyrene-block-poly(acrylic acid) amphiphile-based model vesicle system, in particular the loading and release behavior and mechanical properties will be discussed.

4:40pm **BI+AS+NS+SS-WeA9 Large Area Fabrication of Biological Nanostructures**, *G. Tizazu, O. El-Zubir*, University of Sheffield, UK, *S. Brueck*, University of New Mexico, *D. Lidzey, G. Leggett*, University of Sheffield, UK, *G.P. Lopez*, Duke University

There has been enormous interest in the control of biological interactions at interfaces with nanometer spatial resolution, but important challenges still remain to be addressed. Of the established fabrication techniques, electron beam lithography is expensive, and requires exposure under vacuum, while scanning probe methods are slow and (with few exceptions) do not permit fabrication over large areas. In contrast, interferometric lithography (IL) is a simple approach that uses inexpensive apparatus to fabricate sub-wavelength structures over macroscopic areas. When two coherent laser beams interfere, they yield a sinusoidal pattern of intensity that may be used to modify photosensitive materials. Previously IL has been used extensively for semiconductor nanofabrication, but our recent data show that combined with self-assembled monolayer resists it provides a fast, simple method to create molecular nanostructures over macroscopic areas. Illustrations will be provided of bionanofabrication using interferometric modification of protein-resistant (oligo ethylene glycol) functionalised surfaces, where feature sizes as small as 30 nm ($\lambda/8$) have been achieved over square cm areas, and the controlled growth of protein-resistant brush structures from patterns of initiators for atom-transfer radical polymerisation. The fabrication of metallic nanostructures over macroscopic regions, including Ti structures as small as 35 nm, and gold nanostructures of controlled size and periodicity will also be demonstrated.

5:00pm **BI+AS+NS+SS-WeA10 Functionalization of Mesoporous Silicon Biosensors to Achieve Tunable DNA Bioreceptor Density**, *J. Lawrie, R.R. Harl, B.R. Rogers, P. Laibinis, S.M. Weiss*, Vanderbilt University

Porous silicon has become a widely studied material for sensing over the last decade based on its large surface to volume ratio and easily tunable morphology. With growing interest in the detection and analysis of genetic material, DNA oligos have become an increasingly important bio-recognition element in porous silicon and many other sensor platforms. As aptamers, nucleic acids serve as high affinity bioreceptors to a wide range of small molecules and biological materials, opening up a number of potential applications in environmental science, chemical and biological defense, and medical diagnostics. In this work, tuning of the porous silicon surface chemistry is described. Controlling surface silanization, bioreceptor density, and bioreceptor charge and secondary structure enables the fabrication of reusable, label-free optical sensors toward specific nucleic acid targets. Detection limits in the nanomolar range have been demonstrated.

We have previously shown that in situ DNA synthesis via the phosphoramidite method in porous silicon produces high bioreceptor coverage for label-free optical biosensing applications. Low hybridization efficiency, despite high sensitivity, for such sensors indicated that tuning the receptor surface density could further improve detection limits. To modify surface receptor density, two-component trichlorosilane monolayers were deposited from solution onto porous silicon. One monolayer component remained active to phosphoramidite chemistry while the second component was inert. This method enabled a range of surface probe densities to be achieved and controlled via silanization conditions. Monolayer composition and DNA receptor density were verified using XPS, contact angle, and UV-Vis spectrophotometry. For a 16mer DNA oligo bound within a porous silicon waveguide, detection of the complementary target nucleic acid was maximized when 25% of the internal pore surface area was active toward DNA synthesis. Tuning surface DNA density increases sensitivity by a factor of 2-3. Label-free, target-specific detection of oligos was observed at concentrations of 25nM.

We will present results from hybridization efficiency studies in which DNA bioreceptor surface density, length, and secondary structure are varied. These parameters are vital to nucleic acid aptamer sensing strategies in label-free optical biosensors. Predicting appropriate receptor surface density for aptamer sensors based upon oligo sequences will provide advantages in achieving fast and sensitive waveguide sensors for detection in complex media.

Acknowledgements: This work is supported in part by the Army Research Office (W911NF-08-1-0200).

5:20pm **BI+AS+NS+SS-WeA11 Composite Fluorocarbon Membranes by Surface-Initiated Polymerization**, *C.A. Escobar, A.R. Zulkifli, G.K. Jennings*, Vanderbilt University

This presentation describes the fabrication and characterization of a novel composite membrane that consists of two types of nanoporous materials, namely, nanoporous gold leaf (NPGL) and nanoporous alumina, and a selective poly(perfluorohexyl norbornene) (pNBF6) polymer. Integration of the three materials is achieved by means of silane and thiol chemistry, and

the use of surface-initiated ring-opening metathesis polymerization (SI-ROMP). The former two provide functionalization of the nanoporous substrates, and the latter promotes the generation of the polymer film within and atop of the alumina-NPGL membrane. The synthetic process is versatile in that simultaneous or selective growth of the polymer film in each nanoporous layer is straightforward. The use of SI-ROMP allows tailoring of the extent of polymerization of pNBF6 throughout the structure by varying polymerization time. Advancing contact angle measurements show that the surface of these composite membranes exhibits both hydrophobic and oleophobic behavior. Scanning electron microscopy (SEM) images indicate that the thin polymer films cover the porous substrates entirely. Results from electrochemical impedance spectroscopy (EIS) confirm that the membranes provide effective barriers to aqueous ions and that sulfonation of the polymer backbone substantially enhances ion transport through the composite membrane. Ion transport and selectivity of the membrane change by regulating the polymerization time. The fluorinated nature of the polymer thin film renders the membrane selective towards molecules with similar chemical characteristics.

Thursday Morning, November 3, 2011

Energy Frontiers Focus Topic

Room: 103 - Session EN+NS-ThM

Nanostructures for Energy Storage and Fuel Cells I

Moderator: J. Lewis, RTI International

8:00am EN+NS-ThM1 Exploring Intercalation Chemistry of Modified Graphene with Ionic Liquids for Energy Storage Applications, *M. Acik*, The University of Texas at Dallas, *D.R. Dreyer*, *C. Bielawski*, The University of Texas at Austin, *Y.J. Chabal*, The University of Texas at Dallas

One of a real-world application of Electrochemical Double Layer Capacitors (EDLCs) is their use in prototype electric vehicles. An EDLC simply consists of two non-reactive, porous electrodes and an electrolyte separated with a membrane. Activated charcoals are one of a commonly used electrode systems which has drawbacks such as limited energy storage due to their large ion size. Therefore, a replacement electrode system with a higher surface area is necessary for a superior EDLC performance. Modified graphene is one of a promising candidate with its high theoretical surface area (2630 m²/g). EDLC working principle also depends on how effectively it can polarize the electrolyte solution. In principle, ionic liquids are promising electrolyte systems with their high non-volatility, non-flammability, thermal stability and good solvating ability.

This study focuses on the intercalation studies of ionic liquids such as N-methyl-N,N,N-tris(2-hydroxyethyl)ammonium iodide, N-methyl-N,N,N-tris(2-hydroxyethyl)ammoniummethyl sulfate, 1-butyl-3-methylimidazoliummethylsulfate and N-octyl-N-methylpiperidinium methylsulfate. To achieve a high surface area material with modified graphene, it is essential to understand the interfacial interactions upon intercalation of ionic liquids.

We study powder X-Ray Diffraction Analysis to characterize the interlayer distance of modified graphene. For instance, its d-spacing increases by about 4-12 Å after intercalating as-synthesized graphite oxide (GO, ~9Å) with N-methyl-N,N,N-tris(2-hydroxyethyl)ammonium methylsulfate (IL) at room temperature. Annealing at 300-500°C, (002) orientation of GO disappears as a result of thermal exfoliation. In addition, *in-situ* Infrared Absorption Spectroscopy (IRAS) measurements were performed to explore the intercalation chemistry of modified graphene in the presence of ionic liquids. Therefore, we perform thermal reduction studies in vacuum coupled with IRAS measurements to characterize the chemical interactions during thermal exfoliation of reduced GO. After annealing GO intercalated with this IL, the loss of C-N and C-O containing species is identified at ~1000-1500 cm⁻¹ and 800-1200 cm⁻¹ with contribution from C-OH groups at 3000-3700 cm⁻¹. Complete removal of these species is observed after a ~500°C anneal resulting in a weak infrared absorbance intensity of sp²-hybridized C=C species at ~1580 cm⁻¹. The presence of new formation of sheet-to-sheet linking or bonding motifs was also studied with X-ray Photoelectron Spectroscopy (XPS).

*Research supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award DE-SC001951.

8:20am EN+NS-ThM2 Electronic Structure and Chemical Composition of Candidate Conversion Material Iron Oxyfluoride, *R. Thorpe*, *S. Rangan*, *R.A. Bartynski*, *O. Celik*, *N. Pereira*, *G. Amatucci*, Rutgers University

Transition metal fluorides have recently gained interest as possible electrode materials in lithium ion conversion batteries. Owing to their large band gaps, they operate at high voltages and enable high energy densities. However this large band gap inhibits charge conduction and thus impedes efficient charge and discharge. One path to overcome this limitation is the use of metal oxyfluorides, which are characterized by a slightly smaller energy gap and thus a higher electronic conductivity. Currently, little is known about the electronic structure of metal oxyfluorides, particularly the relation between chemical structure, composition, and energy gap. Hence, we have produced model oxyfluoride systems in order to characterize the conversion mechanism using surface science tools.

Of all metal fluorides, iron-based compounds are the most promising to maximize energy density. Ultra-thin FeF₂ films have been synthesized via the fluorination of clean Fe foil exposed to XeF₂, following a self-limited Mott-Cabrera mechanism. The FeF₂ films have then been sequentially exposed to a partial pressure of O₂ of 2x10⁻⁶ Torr at 285°C in order to produce iron oxyfluoride. Using x-ray and ultraviolet photoemission as well as inverse photoemission, we have probed the electronic structure of these

FeO_xF_y samples and characterized the occupied and unoccupied states near the band gap of the material.

It has been found that oxygen insertion into the FeF₂ matrix can be controlled until complete oxidation occurs. As expected for a Mott-Hubbard insulator, the valence band and conduction band of FeF₂ can be interpreted using a simple crystal field approach. In the case of Fe₂O₃, strong charge transfer effects need to be taken into account in order to interpret the band edges. To explore the conversion process, Li has been evaporated onto these iron oxyfluorides *in-situ*. Preliminary results addressing the reactivity of lithium at the surface of these materials will also be presented.

8:40am EN+NS-ThM3 Lithium Ion Batteries: Present and Future Technologies, *K. Amine*, *W. Wu*, *I. Belharouak*, *A. Abouimrane*, *Z. Zhang*, *J. Lu*, Argonne National Laboratory **INVITED**

In its goal of developing more fuel efficient vehicles, the US Department of Energy in collaboration with the US auto industries are focusing on high-power and high energy lithium-ion batteries to meet the energy storage requirements for HEV and PHEV applications. Under these auspices, Argonne National Laboratory is investigating several different lithium ion chemistries in order to address the calendar life, cost and safety of high power and high energy lithium ion batteries for transportation applications

To meet the high-energy requirement that can enable the 40-miles electric drive P-HEVs, It is necessary to develop very high energy cathode or anode that offers 5,000 charge-depleting cycles, 15 years calendar life as well as excellent abuse tolerance. These challenging requirements make it difficult for conventional cathode materials to be adopted in P-HEVs. In this paper, we report on several advanced battery chemistry that could be used to power Hybrid electric vehicles. We also discuss several future high energy battery technologies that can enable 40 miles Plug in Hybrid and long range electric vehicles.

9:20am EN+NS-ThM5 Templating of Porous Materials for Energy Storage and Generation, *A. Stein*, *J. Davidson*, *N. Petkovich*, *Y. Qian*, *S. Rudisill*, *L. Venstrom*, *A. Vu*, University of Minnesota **INVITED**

Materials containing pores in size ranges from micropores to macropores offer interesting features for a number applications involving energy storage and conversion, such as batteries, fuel cells, hydrogen storage, and sunlight-to-fuel conversion. Depending on the specific application, they can provide large surface areas for reaction, interfacial transport, or dispersion of active sites; they can provide nanostructured features which enhance reactivity, alter materials properties, or shorten diffusion paths; they can act as host materials to stabilize other active components; or, in the case of porous carbons, they can provide electrically conductive phases as well as intercalation sites. However, the higher reactivity brought about by nanostructured features can also lead to decreased stability, particularly in applications where phase changes may alter the structure of the material or where high temperatures are employed. This talk will focus on two redox systems (lithium-ion batteries and sunlight-to-fuel conversion) in which templated porous materials provide a platform for either electrical energy storage or light-to-chemical energy conversion. In the first system the role of pore architecture in carbon-based electrodes will be discussed. Improved rate capabilities for lithiation/delithiation are observed for hierarchically porous carbon electrodes. In composites with tin or tin oxide for anodes these structures maintain electrical contact between tin-based particles, even when those particles undergo significant volume changes during cycling, and hence the composite anode maintains good capacities over multiple cycles. Composites of hierarchically structured carbon with poorly conducting but otherwise desirable electrode materials (like sulfur or LiFePO₄) can be used to overcome limitations in electrical conductivity of those materials, increasing the choice of useful electrode materials. In the second system, we investigate the role of porosity in ceria-based materials of interest for solar thermal splitting of water or carbon dioxide to produce hydrogen or carbon monoxide fuels, respectively. Dopants for ceria are examined to stabilize the porous structures at the high reaction temperatures. The interplay between composition and morphology of these materials, thermal stability, and conversion efficiencies will be discussed.

11:00am EN+NS-ThM10 Exploration of the Effects of Si Nanowire Length and Doping on Li-ion Battery Anode Performance, *F. Rusli*, *V. Chakrapani*, *M.A. Filler*, *P.A. Kohl*, Georgia Institute of Technology
Silicon nanowires have recently garnered significant attention as a potential candidate to replace graphite as the negative electrode in a lithium-ion battery. Silicon's earth abundance, extensive knowledge base, and its theoretical capacity of 4200 mAh/g make it an attractive material for this purpose. While the high incorporation of lithium presents a problem as silicon undergoes a significant specific volume expansion upon

intercalation (up to 400%), nanowires permit facile radial strain relaxation and allow lithiation without pulverization. In this work, we report on the first systematic study of nanowire length and doping on the cycling performance of NW electrodes. Silicon nanowires were grown on stainless steel substrates via the vapor-liquid-solid technique in a cold-wall low pressure chemical vapor deposition reactor. Growth times ranging from 5-60 minutes and doping concentrations between 10^{18} – 10^{20} atoms cm^{-3} were studied. The half cells were cycled against lithium metal between (1) 0.01 and 2.0 V and (2) 0.07-0.7 V at a C/20 rate for 20 cycles. Cycling performance at different depths of discharge was also studied. Nanowires grown at short and long times both exhibit lower capacities than those grown at intermediate times. We attribute this effect to the loss of nanowire contact at the interface between the stainless steel and nanowire array for long nanowires, while the percolation network formed by short nanowires is not sufficiently robust to prevent loss of electrical connectivity upon wire breakage further from this interface. Nanowires at higher doping concentrations were not found to improve cycling performance drastically, which we attribute to the dopant effects on the growth mechanism of the nanowires and placement of dopant atoms in the silicon matrix that may have inhibited lithium atom insertion. We will present novel electrode fabrication routes that overcome these two challenges.

11:20am **EN+NS-ThM11 In Situ TEM Electrochemistry of Anode Materials in Lithium Ion Batteries, J.Y. Huang**, Sandia National Laboratories **INVITED**

We created the first nano-battery inside a transmission electron microscope (TEM), allowing for real time atomic scale observations of battery charging and discharging processes. Two types of nano battery cells [1], one ionic liquid based, and the other all solid based, were created. The former consists of a single nanowire anode, an ionic liquid (IL) electrolyte and a bulk LiCoO_2 cathode; the latter uses Li_2O as a solid electrolyte and metal Li as anode. Four case studies will be presented: 1) Upon charging of SnO_2 nanowires in an IL cell, a reaction front propagates progressively along the nanowire, causing the nanowire to swell, elongate, and spiral. The reaction front contains high density of dislocations, which are continuously nucleated at the moving front and absorbed from behind. This dislocation cloud indicates large in-plane misfit stresses and is a structural precursor to electrochemically-driven solid-state amorphization. 2) In charging Si nanowires, the nanowires swell rather than elongate. We found the highly anisotropic volume expansion in lithiated Si nanowires, resulting in a dumbbell-shaped cross-section which developed due to plastic flow and necking instability. Driven by progressive charging, the stress concentration at the neck region led to cracking, eventually splitting the single nanowire into sub-wires. 3) Carbon coating not only increases rate performance but also alters the lithiation induced strain of SnO_2 nanowires. The SnO_2 nanowires coated with carbon were charged 10 times faster than the non-coated ones. Intriguingly, the radial expansion of the coated nanowires was completely suppressed, resulting in reduced tensile stress at the reaction front, as evidenced by the lack of formation of dislocations. 4) The lithiation process of individual Si nanoparticles was observed in real time in a TEM. A strong size dependent fracture behavior was discovered, *i.e.*, there exists a critical size with a diameter of ~ 150 nm, below which the particles neither cracked nor fractured upon lithiation, above which the particles first formed cracks and then fractured due to lithiation induced huge volume expansion. For very large particles with size over 900 nm, electrochemical lithiation induced explosion of Si particles was observed. This strong size-dependent fracture behavior is attributed to the competition between the elastic energy and the surface energy of the nanoparticles. These results highlight the importance of in-situ studies in understanding the fundamental sciences of lithium ion batteries.

1. J.Y. Huang *et al.*, *Science* 330, 1515-1520 (2010); *Nano Lett.* (revised); *ACS Nano* (in press).

Graphene and Related Materials Focus Topic
Room: 208 - Session GR+NS+PS+SS-ThM

Graphene: Surface Chemistry, Functionalization, Plasma Processing and Sensor Applications

Moderator: G.G. Jernigan, U.S. Naval Research Laboratory

8:00am **GR+NS+PS+SS-ThM1 Tailoring Graphene's Properties through Chemistry, J.T. Robinson**, Naval Research Laboratory **INVITED**

Graphene's unique electron transport properties have motivated intensive research and development to mold it into the electronic material of the future. However, graphene can be much more than an electrical switch. Its high structural integrity and chemical flexibility enable extensive control of its optical, mechanical, and electronic properties. The most scalable and

inexpensive route to modify these properties is chemical functionalization. Consequently, chemically modified graphenes (CMGs) have emerged as a system of materials whose many attractive properties complement and extend those of unmodified graphene.

In this talk I will describe efforts at NRL to synthesize and characterize new CMGs as well as first steps towards applications such as sensors and nanomechanical resonators. To begin, I will discuss the interaction of small molecules (CCl_4 , CS_2 , H_2O and acetone) with single-layer graphene under steady-state conditions using infrared multiple-internal-reflection. Adsorption-induced changes in the IR spectra suggest the formation of in-plane strain, where we observe important differences arising between species that form liquid-like layers under steady-state conditions and those that do not. Second, I will discuss graphene oxide, a well known derivative of graphene that has a rich ensemble of oxygen-based functional groups and related defects. These defects are readily tunable through chemical or thermal treatments and facilitate the formation of vapor and bio-sensors with parts-per-billion and nanomolar sensitivities, respectively. Third, I will discuss the stoichiometric addition of fluorine atoms to graphene and describe their resulting properties. Experiments indicate fluorinated graphene derivatives become highly resistive and optically transparent, while DFT calculations show band gaps open depending on the fluorine coverage and ordering. Finally, through combining these two material systems, I will discuss the fabrication and performance of CMG-based nanomechanical resonators. Through chemical modification, the frequency of CMG-based resonators is tunable over 500% and their quality factors can exceed 20,000 at room temperature.

8:40am **GR+NS+PS+SS-ThM3 Water Splits Epitaxial Graphene on Ru(0001) from Domain Boundaries, X. Feng, S. Maier, M. Salmeron**, Lawrence Berkeley National Laboratory

Epitaxial growth of graphene on metal substrates has recently been demonstrated as a rational synthesis route for producing macroscopic graphene domains and may hold the key to realizing the potential of large-scale applications. However, the epitaxial graphene is generally polycrystalline, with domain boundaries that may severely affect its structure and properties. Here we report that water adsorption splits epitaxial graphene on Ru(0001) and results in nanoscale graphene flakes at temperatures as low as 90K. Scanning tunneling microscopy studies indicated that the splitting starts primarily from domain boundaries followed by water intercalation underneath graphene. The mechanism proposed is that Ru-induced water dissociation provides hydroxyl species that break the graphene starting at the dangling and stretched bonds at the boundaries.

9:00am **GR+NS+PS+SS-ThM4 Novel Strategies for the Chemical Functionalization of Graphene: Towards Graphene/Molecular Nanosheet Heterostructures, A. Turchanin, C.T. Nottbohm, Z. Zheng, M. Schmietz, A. Beyer**, University of Bielefeld, Germany, M. Heilemann, M. Sauer, Julius-Maximilians-University Würzburg, Germany, A. Götzhäuser, University of Bielefeld, Germany

Chemical functionalization of graphene is essential for implementations of the 2D carbon sheets in various functional devices (e.g. chemical and biochemical sensors, nanoelectromechanical components, etc.) and for tuning their electrical properties. However, the functionalization is difficult to achieve due to the chemical inertness of graphene sheets with high structural quality. On the other hand, ultrathin (~ 1 nm) molecular nanosheets made from self-assembled monolayers (SAMs) possess well-defined chemical groups intrinsically. Moreover, due to the directionality of the constituting molecules both faces of the free-standing nanosheets -*Janus nanomembranes*- can be independently and specifically functionalized. Simple mechanical stacking of the nanosheets allows fabricating ultrathin layered structures with tunable physical and chemical properties. Upon annealing these stacks are converted into graphene sheets with adjusted thickness. The engineering of graphene/nanosheet heterostructures opens up novel routes towards chemically functionalized graphene sheets for functional applications. A potential of this approach will be discussed.

Z. Zheng, C.T. Nottbohm, A. Turchanin, H. Muzik, A. Beyer, M. Heilemann, M. Sauer, A. Götzhäuser, "Janus nanomembranes: A generic platform for chemistry in two dimensions", *Angew. Chem. Int. Ed.* 49 (2010) 8493-8497

C.T. Nottbohm, A. Turchanin, A. Beyer, R. Stosch, A. Götzhäuser, "Mechanically stacked 1 nm thick carbon nanosheets: 2D layered materials with tunable optical, chemical, structural and electrical properties", *Small* 7 (2011) 874-883

A. Turchanin, D. Weber, M. Bünenfeld, C. Kisielowski, M. Fistul, K. Efetov, R. Stosch, T. Weimann, J. Mayer, A. Götzhäuser, "Conversion of self-assembled monolayers into nanocrystalline graphene: structure and electric transport", *ACS Nano* 5 (2011) DOI: 10.1021/nm200297n

9:20am **GR+NS+PS+SS-ThM5 Biosensors Based on Chemically Modified Graphene**, *R. Stine, J.T. Robinson, P.E. Sheehan, C.R. Tamanaha*, U.S. Naval Research Laboratory

The sensitive and specific detection of biomolecules without using a label is a long-standing goal of the biosensors community. Several promising advances of the past several years formed biological field effect transistors (bioFETs) that have as the gate nanoscale materials such as nanowires and carbon nanotubes. The nanoscale dimensions of these materials allow the small charges associated with biomolecules to significantly change conduction through the gate. These conduction changes can be correlated with solution concentration to give precise readouts. While bioFETs are a promising way forward, there are many processing difficulties associated with these 1-D materials that inhibit large scale, reproducible fabrication of devices. Here, we will discuss our efforts to develop biosensors based on 2-D chemically modified graphene. These devices impart the sensitivity gains seen from other nanoscale materials, but offer a configuration that is amenable to processing techniques that are common in the semiconductor industry. We will focus primarily on chemically modifying graphene for attachment of biomolecular probes. Devices utilizing both graphene and graphene oxide will be covered, and surface spectroscopic studies of the material modification will be discussed. Successful results for the detection of specific DNA hybridization will also be presented, with detection limits that compare favorably with the best results reported from nanowire bioFETs.

Acknowledgements: R.S. is an employee of Nova Research Inc., Alexandria, VA, USA. This project received support from the Defense Threat Reduction Agency-Joint Science and Technology Office for Chemical and Biological Defense.

9:40am **GR+NS+PS+SS-ThM6 Controllable Defect Healing and N-doping of Graphene by CO and NO Molecules**, *B. Wang*, Vanderbilt University, *S.T. Pantelides*, Vanderbilt University and ORNL

Point defects alter strongly the physical and chemical properties of graphene, e.g. they degrade electrical transport and enhance chemical reactivity. Defects could also be used to achieve graphene functionalization, e.g. N atoms, as n-type dopant, can be introduced to obtain n-type graphene. Thus, controllable defect healing and N-doping in graphene would be very valuable for potential device applications. Here we report first-principles molecular dynamic simulations that suggest a procedure for defect healing and N-doping with fast dynamics and low thermal budget. Vacancies in graphene can be healed by sequential exposure to CO and NO molecules. A CO molecule gets adsorbed at a vacancy site and a NO molecule subsequently removes the extra O by forming NO₂, which desorbs quickly resulting in a defect-free graphene sheet. Controllable N-doping can be achieved by sequential vacancy creation (e.g. by electron or ion beam) and subsequent exposure to NO molecules at room temperature. NO molecules are trapped at vacancies and other NO molecules remove the extra O atoms simultaneously, leaving N atoms incorporated in graphene. Both reactions (healing and doping) are exothermic. We suggest that a combination of CO and NO molecules can potentially provide simultaneous healing and doping. Adjusting the ratio could fine-tune the N-doping level. The proposed strategy introduces no extra defects and is promising for graphene-based electronic materials in radiation environments. Finally, we propose that NH₃, which is normally used in experiments to introduce N atoms, may not be a good choice for N-doping since the dissociated H atoms can be trapped at vacancies and act as impurities that increase the resistivity of graphene.

This work was supported by DTRA Grant No. HDTRA1-10-1-0016 and the William A. and Nancy F. McMinn Endowment at Vanderbilt University. The calculations were performed at ORNL's Center for Computational Sciences.

10:40am **GR+NS+PS+SS-ThM9 Aptamer Modified Graphene Bio Sensor**, *K. Maehashi, Y. Ohno, K. Matsumoto*, Osaka University, Japan

Since graphene has high mobility and a large surface area, it is suitable for the application of the high sensitive sensor. In the present paper, we have first succeeded in the selective detection of the bio molecule such as IgE using the aptamer modified graphene FET.

The graphene was formed using the conventional mechanical exfoliation method on the SiO₂/Si substrate. The source and drain electrode were formed by the electron beam lithography and Ti/Au evaporation. The silicon rubber pool was formed on the fabricated graphene FET, and phosphoric buffer solution was poured into the silicon rubber pool. The Ag/AgCl reference electrode was introduced into the phosphoric buffer solution, which works as a top gate electrode for the graphene FET.

As a first step of the biosensor, three bio molecule such as Immunoglobulin E(IgE), Streptavidin(SA), and Bovine serum albumin(BSA) were introduced into the phosphoric buffer solution of pH of 6.8, and the change of the drain current of the graphene FET was detected. In this case, the IgE

and SA shows the decrease of the drain current, while the BSA the increase of the drain current. Because, in the phosphoric buffer solution of pH of 6.8, IgE and SA are positively charged, while BSA negatively charged. Therefore, the hole current of the graphene FET change the drain current following the charge of the bio molecule. As a result, bare graphene FET can detect the bio molecule following the charge of the molecule, but it does not have the selectivity

As a second step, in order to get the selective sensing of the bio molecule, the surface of the graphene was modified by the IgE aptamer, which was connected to graphene using the linker(1-pyrenebutanoic acid succinimidyl ester). IgE aptamer was known to selectively couple to IgE. When the BSA and SA were introduced into the phosphoric buffer solution on the aptamer modified graphene FET, there occurred no change in the drain current, while the IgE was introduced in the solution, the drastic decrease of the drain current was observed. This means the BSA and SA do not couple to IgE aptamer, and only IgE couple to the IgE aptamer on the graphene FET. Therefore, the selective sensing of the IgE was successfully carried out.

We have first succeeded in the selective sensing of IgE using the modified graphene FET.

11:00am **GR+NS+PS+SS-ThM10 A Molecular Dynamics Study of Chemical Modification of Graphene Oxide Sheets**, *T. Liang, B. Devine, S.R. Phillpot, S.B. Sinnott*, University of Florida

Graphene, the single-layered graphite, has attracted tremendous attention owing to its fascinating physical properties. One of the main obstacles in this field is to find an efficient and consistent approach to produce graphene sheets in large quantities. In addition to the mechanical exfoliation method, many chemical approaches have been developed to synthesize graphene on a large scale. The key intermediate product in these chemical approaches is the graphene oxide sheets, which are often heavily oxygenated with hydroxyl or epoxide functional groups on the surface and carbonyl or carboxyl groups at the edge. However the energetic and kinetics associated with graphene oxide sheets have not been elucidated in detail due to the inherent chemical complexity of the system. Here, a new dynamic charge empirical potential is presented that is used in classical molecular dynamics simulations to elucidate the dynamics of graphene oxidation and the resulting influence on their mechanical and structural properties. In addition, the oxygenating and hydrogenating processes of defective graphene sheets at room temperature in addition to elevated temperatures are presented. The findings are compared to the results of first principles density functional theory findings and to experimental data.

11:20am **GR+NS+PS+SS-ThM11 Enhancing and Controlling the Chemical Reactivity of Epitaxial Graphene via Growth Induced Strain**, *J.E. Johns*, Northwestern University, *Md.Z. Hossain*, Gunma University, Japan, *M.C. Hersam*, Northwestern University

The high electrical and thermal conductivity of graphene, as well as its two dimensional nature, has led to its rapid incorporation into any practical applications including high frequency analog transistors and transparent conductors. However, many other potential applications, such as excitonic switches, pseudospin devices, or digital logic circuits, require covalent chemical modification of graphene. Due to the chemical inertness of its pi bonded network, previous methods for covalently modifying graphene have required extreme, irreversible conditions including acidic treatments, high energy radical polymerization, and ion beam implantation. Here we present an alternative method for increasing the chemical reactivity of graphene by systematically altering the compressive strain of epitaxial graphene (EG) on SiC(0001). Depending on its annealing history, EG has been shown to have a compressive strain of 0% to 1% due to a mismatch of thermal expansion coefficients with the underlying buffer layer and silicon carbide substrate. Using differing thermal treatments, we show that the amount of strain in EG can be tailored, as verified by characteristic peak shifts of the 2D Raman band. The resulting chemical reactivity of the strained EG is studied at the atomic-scale using ultra-high vacuum scanning tunneling microscopy following reversible gas phase reactions of EG with oxygen and fluorine. These results suggest a new method for controlling the electronic properties of graphene, and provide fundamental insight into the nature of chemical bonding on EG.

11:40am **GR+NS+PS+SS-ThM12 Plasma-based Functionalization of Graphene with Primary Amines for Biomaterials Applications**, *S.G. Walton, M. Baraket, S.C. Hernandez, R. Stine, W.K. Lee, C.R. Tamanaha, P.E. Sheehan, J.T. Robinson, C.E. Junkermeier, T.L. Reinecke*, Naval Research Laboratory (NRL)

Graphene, a sp²-structured monolayer of carbon atoms, has attracted much interest for its fundamental science and its potential in many device applications. By tailoring its surface chemistry, material properties can be regulated and thus broaden the number of potential applications. In this work, we demonstrate that by chemically functionalizing graphene the

electrical properties and its interaction with adsorbates may be controlled. Electron beam generated plasmas produced in ammonia-containing gas, is used to controllably introduce nitrogen and primary amines. A study of the chemical, electrical and structural properties of the chemically-modified graphene at different functional group concentrations is discussed. In addition, the use of amine-functionalized graphene as a bio-sensing platform for DNA detection using a field-effect-transistor-based sensor is demonstrated. This work is supported by the Office of the Naval Research.

Nanometer-scale Science and Technology Division

Room: 203 - Session NS-ThM

Molecular Assembly and Devices

Moderator: W. Gao, Brigham and Women's Hospital and Harvard Medical School

8:20am **NS-ThM2 Chemical Modification and Patterning of Self Assembled Monolayers using Scanning Electron and Ion-Beam Lithography**, *M.J. Perez Roldan, C. Pascual Garcia, G. Marchesini, D. Gilliland, G. Ceccone, P. Colpo, F.J. Rossi*, European Commission, JRC Institute for Health And Consumer Protection, Italy

We present chemical modification of self assembled monolayers (SAMs) using electron and ion-beam lithographies. We used thiolated polyethylene oxide (PEO) SAMs on gold to fabricate chemically contrasting patterns at the nanoscale. Patterned surfaces were characterized by X-ray photoelectron spectroscopy (XPS), time of flight-secondary ion mass spectrometry (ToF-SIMS). Results showed a chemical modification of surfaces patterned by means of electron beam (e-beam) lithography and a removal of PEO SAMs on the areas treated with the ion beam. The chemical modification of PEO SAMs converted the non-fouling surfaces on fouling surfaces.

8:40am **NS-ThM3 Interlocking Pinwheel Chains Formed by Self Assembly of Aromatic Cyanides**, *M. Luo, W. Lu, E. Chu, D. Kim, Z. Cheng, D. Sun, K. Cohen, Y. Zhu, J. Wyrick*, University of California, Riverside, *T.L. Einstein*, University of Maryland, College Park, *L. Bartels*, University of California, Riverside

As part of a bottom-up strategy, molecular self assembly can be a promising technique to create surface patterns with ultimately small feature sizes in an economic efficient fashion. Understanding of the factors which guide molecules into different patterns thus become an important goal for prediction and control of molecular patterns structures.

Here we present the formation of interlocked arrays ('gear chains') of pinwheels through self-assembly of 3-phenyl-propynenitrile (PPN) molecules on a Cu(111) surface. Variable temperature scanning tunneling microscopy (STM) reveals upon molecular deposition a pattern of small hexagonal features, which coalesce into sequences of larger, interlocking pinwheel-shaped structures. The pinwheels have an outer diameter as large as ~4nm. The driving force of this entropically disfavored pinwheel formation is discussed.

9:00am **NS-ThM4 Electronics and Mechanics of Single Molecule Circuits**, *L. Venkataraman*, Columbia University

INVITED

Understanding and controlling electron transfer across metal/organic interfaces is of critical importance to the field of organic electronics and photovoltaics. Single molecule devices offer an ideal test bed for probing charge transfer details at these interfaces. Results from these single-molecule measurements can be directly related directly theoretical models, unlike measurements at the ensemble level. The ability to fabricate single molecule devices and probe electron transfer reliably and reproducibly has enabled us to study and model transport through them.

In this talk, I will review the scanning tunneling microscope break-junction technique we use to measure electronic transport through single molecule junctions. I will discuss our measurements using novel metal-molecule link chemistries, including amines, phosphines[1] and results from recent work using tri-methyl tin linkers, which yield direct Au-C coupled single molecule junctions[2]. I will show how the intrinsic molecular properties influence measured single molecule conductance and bond rupture forces[3]. Finally, I will show how a mechanically controlled binary single molecule switch can be created using bipyridine molecules[4].

[1] Y. S. Park et al., *J. Am. Chem. Soc.* 129, 15768 (2007).

[2] Z.-L. Cheng et al., *Nat. Nano.* In Press (2011).

[3] M. Frei et al., *Nano Lett.* 11, 1518 (2011).

[4] S. Y. Quek et al., *Nat. Nano.* 4, 230 (2009).

9:40am **NS-ThM6 Complex Rotation Mechanisms of a Molecular Machine Probed by STM**, *H. Kersell, U.G.E. Perera, Y. Zhang*, Ohio University, *C. Joachim, G. Rapenne, G. Vives, X. Bouju*, CNRS, Cemes, France, *S.-W. Hla*, Ohio University

The complex rotation of a ruthenium based double-decker molecular rotor is resolved via ultrahigh vacuum low temperature scanning tunneling microscopy. The study was performed at temperatures of 4.2 K and 77 K on a Au(111) substrate. Inelastic electron tunneling (IET) was utilized to induce stepwise rotation of the molecule with respect to the surface. Subsequent rates of molecular switching, induced via tunneling currents, display sets of discrete energy minima with respect to the molecular stator and to the surface. The molecular rotator is composed of a set of semi-rigid arms whose non-rigid components, upon IET induced rotation, are observed to change conformation to the particular energy minima of the rotor. The resulting STM images were compared to calculated images of the same molecule. Additionally, the rotator was dissociated, revealing an intact stator adsorbed on the Au(111) surface. We acknowledge the financial support of US-DOE; DE-FG02-02ER46012, and NSF-PIRE; OISE 0730257 grants.

10:40am **NS-ThM9 Self-Assembled Double Strand DNA Monolayers as Spin Filters**, *Z. Xie, S.R. Cohen, T.Z. Markus, R. Naaman*, Weizmann Institute of Science, Rehovot Israel

Spin control provides new and interesting opportunities for control and study of the factors governing electron transport. Recent work by Naaman and co-workers has shown that self-assembled monolayers of double stranded DNA (ds-DNA) can act as a spin filter for electrons photoemitted from a gold substrate.[1,2] This phenomenon depends on the helicity of the ds-DNA, which leads to spin polarization and consequent capture of filtered electrons that tunnel back to the substrate. In this work, this effect is investigated for electron flow between two electrodes, a bottom Ni electrode to which one strand of the DNA is bound, and a top gold nanoparticle electrode which serves to identify the ds-DNA and provide good electrical contact through binding to the complementary strand. The current characteristics are measured by conductive scanning probe microscopy, as applied in a previous study of electron transport in DNA monolayers.[3] A magnetic field of approximately 0.3 T at the surface is provided by a permanent magnet placed below the sample. The results are consistent with the photoemission work, namely marked differences in the current flow depending on magnetic field alignment. Furthermore, the effect depends on length of DNA chain, with longer chains providing a more significant effect relative to shorter ones. These experimental findings, together with a physical model will be presented.

[1] Goehler, et al, *Science* 331, p. 894 (2011).

[2] Ray, et al, *Phys. Rev. Lett.*, 96, 03101 (2006).

[3] Noguez et al, *J. Phys. Chem. B* 110, 8910 (2006).

11:00am **NS-ThM10 Controllable Phase Transition Using a Probing Tip**, *Q. Li*, Oak Ridge National Laboratory

Molecular Self-assembled monolayers have applications in many different fields, such as sensing, lubrication and molecular electronics. In our study, a movie containing more than 50 STM images is acquired to investigate the dynamic behavior of the phenyl-acetylene molecular assembly process on Au(111) surface at LN2 temperature. Besides that, we found the phenyl-acetylene molecules are very sensitive to the polarity of the bias voltage. Therefore, phase transition between molecular ordered and disordered structure can be controllably achieved by applying positive or negative bias voltage. Systematically study of the phase transition process turned out it may be related to the charging effect of the molecules.

11:20am **NS-ThM11 How Size, Shape, and Bond Strain Affect Electronic Structure in sp^3 Carbon-Cage Molecules**, *T.M. Willey, J.R.I. Lee*, Lawrence Livermore National Lab, *L. Landt, D. Wolter*, Technische Univ. Berlin, Germany, *M. Bagge-Hansen*, Lawrence Livermore National Lab, *P.R. Schreiner, A.A. Fokin, B.A. Tkachenko, N.A. Fokina*, Justus-Liebig Univ. Giessen, Germany, *T. van Buuren*, Lawrence Livermore National Lab, *D. Brehmer*, Stanford Synchrotron Light Source

Novel nanocarbons such as fullerenes, nanotubes, graphene, and nanodiamond reside at the cutting edge of nanoscience and technology. This paper presents a fundamental study of how size, shape, chemical functionalization, and bond strain affect electronic structure in several benchmark series of chemically pure, novel carbon-cage compounds ranging from diamondoids (a fully sp^3 form of nanodiamond) to cubane. Size and shape are studied with the diamondoid series from adamantane to hexamantane, where the observed gap changes are primarily due to evolution in occupied states, as measured with photoelectron spectroscopy (XPS & UPS). Bond strain is studied with dodecahedrane, octahedrane, and cubane, where increasing bond strain leads to two major changes in the near-edge x-ray absorption fine structure (NEXAFS) spectra. First, a broad

C-C σ^* resonance in the absorption splits into two more narrow and intense resonances with increasing strain. Second, the first manifold of states previously associated with tertiary C-H σ^* in the diamondoid series appears to broaden and shift to lower energy. This feature is more than twice as intense in cubane as octadecane, even though these two molecules have similar stoichiometries ($C_{12}H_{12}$ vs. C_8H_8). We attribute the additional intensity to π^* states, indicating a high degree of p interaction between parallel C-C bonds in the cubane.

11:40am **NS-ThM12 Effect of Acetylene Concentration and Thermal Ramp Rate on the Growth of Spin-capable Carbon Nanotube Forests.**
K.H. Lee, D. Burk, L.J. Overzet, G.S. Lee, The University of Texas at Dallas

Spin-capable multi-walled carbon nanotube (MWCNT) forests that can form webs, sheets, and yarns provide a promising means for advancing various technologies [1-4]. The important factors enabling the growth of the spin-capable forests are still not well understood. Growing spin-capable CNT forests depends on several growth factors such as the catalyst film thickness, the growth temperature, and the carrier and reactant gases [5-9]. Other factors still remain to be investigated more thoroughly. These include the flow rate (or ratio) of the reactant gas, the reactant gas species, and the pressure.

Herein we show how both the spinning capability and morphology of MWCNT forests are changed significantly by controlling the acetylene (C_2H_2) concentration and the thermal ramp rate. The acetylene gas flow is varied in the range of 0.25 ~ 7.5 % in volume. The MWCNTs grown at C_2H_2 concentrations between 1.5 ~ 3.5 % are well-aligned and are spin-capable. The well-aligned forests have higher areal density and shorter distances between the CNTs caused by strong Van der Waals interactions. CNTs grown at C_2H_2 concentrations under 1.5 % or over 3.5 % are curled and have random orientation. The resulting forests have reduced areal density and have poor spinnability. The thermal ramp rate is varied from 30 °C/min to 70 °C/min. Only the CNT forests grown with 50 °C/min condition are well-aligned and spinnable due to high areal density and closer spacing between adjacent CNTs. This condition alone results in Fe nanoparticles which have the proper size and density to produce spin-capable CNT forests.

Figure 1 shows SEM images and picture of spin-capable CNTs grown at 1.5 vol.% of acetylene and 50 °C/min on 70k Ω /sq Fe film at 780°C for 5min with mixture of He, H₂, and C₂H₂. The spinnable CNTs of 330 μ m have good alignment which is dependent on the ability to form ribbons. From a 1 \times 1 cm substrate, the CNTs can form a 4 m length sheet.

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- [2] X. Zhang et al., *Adv. Mater.* **18**, 1505 (2006).
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- [4] A. E. Aliev et al., *Science* **323**, 1575 (2009).
- [5] M. Zhang et al., *Science*, **306**, 1358 (2004).
- [6] X. Zhang et al., *Adv. Mater.*, **18**, 1505 (2006).
- [7] X. Zhang et al., *Small*, **3**, 244 (2007).
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Thursday Afternoon, November 3, 2011

Energy Frontiers Focus Topic

Room: 103 - Session EN+NS-ThA

Nanostructures for Energy Storage and Fuel Cells II

Moderator: J. Lewis, RTI International

2:00pm EN+NS-ThA1 **Charge-Storage Processes in Model MnO₂-Li-HOPG Systems: UHV-STM Investigations.** S.C. Bharath, W. Song, J.E. Reutt-Robey, University of Maryland, College Park, K.R. Zavadil, Sandia National Laboratories

Nanostructured materials have the potential to substantially improve the speed, efficiency, and cyclic lifetime of energy storage systems such as the lithium-ion battery (LIB). Nanometer-scale oxide cathode elements allow for greater extent of lithium incorporation due to improved strain accommodation relative to conventional cathode structures. Exposed surface facets in structures with high surface/volume ratio will act as gateways to lithium insertion, playing an important kinetic role in charge storage. However, detailed mechanisms of lithium insertion and their dependence on oxide facet orientation and grain size and shape are largely unknown. As a platform for fundamental investigations of charge-transfer processes in nanocrystalline materials, we have developed a MnO₂-Li-HOPG model system. This system consists of low-dimensional β -MnO₂ and cubic spinel Li_{1+x}Mn_{2-x}O₄ nanocrystallites, synthesized by the reactive co-deposition of elemental Mn and molecular oxygen on native and modified graphite (C(0001)) supports under ultrahigh vacuum conditions. Nanocrystallite phase and composition has been confirmed using single particle electron diffraction, as well as TOF-SIMS and scanning AES. Morphology of individual nanocrystallites, and their registration to the C(0001) support, have been determined with ambient AFM and UHV STM methods. The morphological response of β -MnO₂ nanocrystallites to Li⁺ insertion has been preliminarily explored under solid-state conditions with UHV-STM. The sensitivity of these methods are currently limited by low β -MnO₂ - C(0001) electrical conductivity, and efforts to overcome this limitation will be described. Additionally, alkali seeded growth of MnO₂ nanocrystals will be presented as a means to guide the formation of alternative MnO₂ polymorphs.

Supported by the Science of Precision Multifunctional Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES) under award DESC0001160.

2:20pm EN+NS-ThA2 **The Influence of Surface Chemistry as a Function of Salt Composition on the Rate Capability of LiNi_{0.5}Mn_{0.5}O₂ Composite Electrodes for Li-ion Rechargeable Batteries as Investigated using XPS.** R.A. Quinlan, Naval Surface Warfare Center, Carderock Division, Y.C. Lu, Massachusetts Institute of Technology, A.N. Mansour, Naval Surface Warfare Center, Carderock Division, Y. Shao-Horn, Massachusetts Institute of Technology

LiCoO₂ is currently the most commonly used cathode material in commercial Li-ion battery technology because of its high working voltage, structural stability and long cycle life. However, cobalt is expensive and there are safety and toxicity concerns. Therefore, there has been a considerable amount of work on developing cheaper alternatives for the positive electrode of large-scale lithium ion batteries. LiNi_{0.5}Mn_{0.5}O₂ (LNMO) has emerged as one of the best options due to its high specific capacity, thermal stability and low material costs. Previous studies have illustrated that decreasing the interlayer mixing can increase the rate capability and that increasing the heat-treatment temperature can also increase the rate capability. Recently, the influence that surface chemistry has on the rate capability of LNMO composite electrodes was investigated and it was shown that an additional annealing treatment after quenching the material during synthesis increased the device performance from 50 mAh/g to 180 mAh/g at 55°C and 8C. Via an inspection using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), it was shown that the annealing treatment did not result in significant changes in the lattice parameters or in the cation distributions of the layered structure. However, the annealing treatment was shown to be responsible for removing surface impurity phases such as lithium carbonate species and Mn³⁺-containing species, which was associated with the observed increase in performance.

In this study, we further investigate the role that surface chemistry, as developed during the operation of the cell, has on the device performance. LNMO electrodes were constructed using quenched and annealed LNMO starting material. Both the quenched and annealed electrodes were cycled in the range of 2.0 V - 4.6 V in 1M LiPF₆/EC:DMC (1:1) or 1M LiClO₄/EC:DMC (1:1). The composite electrodes (in the discharged state)

were disassembled in an Ar environment glove box and transported to the XPS analysis chamber without exposure to ambient. Cycling performance shows enhanced capacity retention and device performance for annealed electrodes cycled in LiPF₆, with the little to no enhancement observed for annealed electrodes when cycled in LiClO₄. Our initial analysis indicates the formation of both Ni and Mn fluorides/oxyfluoride species on the surface of electrodes cycled in LiPF₆. Additional changes in the surface chemistry and the influence on the rate capability will be discussed.

2:40pm EN+NS-ThA3 **Hydrogen Storage in Metal Organic Frameworks (MOFs).** N. Nijem, University of Texas at Dallas, L. Kong, H. Wu, Y. Zhao, J. Li, D.C. Langreth, Rutgers University, Y.J. Chabal, University of Texas at Dallas

Hydrogen storage is one of the most challenging problems in hydrogen-based energy technologies. One of the goals of hydrogen storage is the ability to store a high volumetric density of hydrogen at room temperature. As a result, studies exploring molecular hydrogen interaction in storage materials are important to facilitate further development of materials. Metal-organic Frameworks (MOFs) are promising candidates for hydrogen storage because their high surface area and porosity facilitate high hydrogen physisorption on specific sites of the structures and because many options are possible to enhance the interaction of molecular hydrogen with the host.

This work explores the incorporation of hydrogen into MOFs using infrared (IR) absorption spectroscopy to characterize its interaction. IR spectroscopy can distinguish possible H₂ binding sites based on the perturbation of the internal H₂ stretch mode. IR measurements are performed on saturated metal center MOFs varying the ligand and/or the metal center and on unsaturated metal center MOF-74-M (M=Zn, Mg and Ni). We combine room temperature, high pressure with low temperature (20-100K) measurements and theoretical van der Waals density functional (vdW-DF) calculations to derive quantitative information from IR shifts and dipole moment strengths.

Our results show that, in contrast to the current understanding, IR shifts are independent of binding energies and depend instead on the chemical environment of the molecule, including effects such as H₂-H₂ interactions. For example, we see little difference in IR shifts between saturated MOFs with low binding energy (~4kJ/mol), and unsaturated MOFs with higher binding energy (~10kJ/mol) sites at room temperature. Furthermore, we show that dipole moments of adsorbed H₂ depends greatly on parameters such as geometry of adsorption site and H₂-H₂ interactions. Measurements performed at low temperatures on MOF-74 show that IR shifts of H₂ is greatly red shifted (an additional ~30 cm⁻¹) due to H₂-H₂ interactions on close proximity adsorption sites, and that dipole moments of adsorbed H₂ can appreciably vary with loading.

Our analysis indicate that the intensity of H₂ IR band cannot always be a measure of the amount of adsorbed H₂, therefore methods such as variable temperature IR (VTIR) used to deduce binding energies cannot always be implemented.

3:00pm EN+NS-ThA4 **Nanostructure Engineering and Modeling of 3D Electrostatic Nanocapacitors.** L.C. Haspert, G.W. Rubloff, S.B. Lee, University of Maryland, College Park

Increasing energy demands require innovative nanofabrication techniques for efficiently storing and supplying available energy. This talk discusses how anodic aluminum oxide (AAO) and atomic layer deposition (ALD) technologies are implemented and designed for creating high performance nanoelectrostatic metal-insulator-metal (MIM) capacitors. The densely porous (~10¹⁰ pores/cm²) self-aligned, self-assembled AAO nanostructure serves as a complex nanostructured template in which the self-limiting and conformal ALD process can uniformly coat this complex 3D structure. Thus, combining these two technologies results in a nano-capacitor with high power density and increased energy density, comparable to electrochemical batteries.

AAO template fabrication is a two-step anodization process, in which pores self-order in the first anodization. Then, the oxide is removed, leaving in a pre-patterned scalloped Al surface. Peak asperities are rounded with a barrier anodic alumina (BAA) and the rounded structures are retained during the subsequent anodization. Mild anodization (MA) chemistries provide interpore spacings, D_{int} (in nm), equal to 2.5x the anodization voltage, V_{anod} (in V), whereas hard anodization chemistries provide D_{int} ~ 2xV_{anod}. In this work, oxalic acid MA results in pores spaced 100nm apart and 40nm in diameter. A final step etches pore sidewalls, increasing pore diameters up to 85nm. MIM layers are deposited by sequentially depositing 10nm of Al-doped ZnO (AZO), 8nm of Al₂O₃ and ~100nm AZO.

The porous structure increases the available surface area on which charge is stored, thus increasing the energy density since $E = \frac{1}{2}CV^2$. The capacitance increases with increasing depth, where planar, 1 μ m, 1.5 μ m and 2 μ m pore depth have capacitance of ~1, 11, 19 and 26 μ F/cm², respectively. Introducing the BAA reduces leakage currents to $\sim 10^{-10}$ A/cm² and breakdown fields are increased to 9.3MV/cm. A model simulates performance of the 3D nanogeometry, distributed resistances and dielectric capacitances, and internal non-linear resistance of the capacitor as a function of voltage. Additionally, trade-offs between pore size vs. layer thickness, AAO template interpore spacings vs. capacitance, pore depth vs. electrode series resistance are considered.

The ability to create scalable nano-structured devices is highly desirable for integrating with energy harvesting technologies. The fully self-aligned, self-assembled and self-limiting MIM nanocapacitors fabricated with ALD deposition in AAO templates demonstrate excellent electrical performance. Simulating device performance will aid in further increasing device performance and energy densities.

3:40pm **EN+NS-ThA6 Atomic Scale Engineering for Energy Conversion Efficiency**, *F. Prinz, N.P. Dasgupta, C.-C. Chao*, Stanford University **INVITED**

The benefits of utilizing nanoscale materials include high surface to volume ratios, short transport lengths, tunable optical and electronic properties, and the ability to take advantage of quantum mechanical effects in low-dimensional structures. Simple scaling laws indicate how nano scale structures may help improving energy conversion efficiency.

Our group has been focusing on two primary application areas of ALD for energy conversion: fuel cells and photovoltaics. In the area of fuel cells, ALD presents several opportunities for reducing efficiency losses. By fabricating oxide-ion conducting electrolyte materials with thicknesses below 100nm which are pinhole free, we have been able to minimize ohmic losses due to ionic transport, allowing for a reduction in the operating temperature of solid oxide fuel cells (SOFCs)[1]. Furthermore, by fabricating 3-D fuel cell architectures[2] and modifying the surface of the electrolyte with a thin ALD layer[3], we have been able to reduce activation overpotentials in these cells and increase power density.

In the field of solar cells, we have been applying ALD to build quantum confinement structures for bandgap engineering. ALD of PbS thin films was performed, and measurements of the localized density of states (DOS) show the ability to tune the bandgap simply by controlling the number of ALD cycles[4]. We have demonstrated a new technique to directly fabricate quantum dots (QDs) during the initial nucleation cycles of ALD PbS[5]. These QDs were deposited directly on nanowire surfaces, suggesting the ability to combine light trapping in nanostructured templates with quantum confinement effects.

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- [1] J. H. Shim, C.-C. Chao, H. Huang and F. B. Prinz, *Chem. Mater.* **19**, 3850 (2007).
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 [3] C.-C. Chao, Y. B. Kim and F. B. Prinz, *Nano Lett.* **9**, 3626 (2009).
 [4] N. P. Dasgupta, W. Lee and F. B. Prinz, *Chem. Mater.* **21**, 3973 (2009).
 [5] N. P. Dasgupta, H. J. Jung, O. Trejo, M. T. McDowell, A. Hryciw, M. Brongersma, R. Sinclair and F. B. Prinz, *Nano Lett.* **11**, 934 (2011).

4:20pm **EN+NS-ThA8 Nanoscale Characterization of Water Distributions in PEM Fuel Cell Membrane Electrode Assemblies Measured by Scanning Transmission Soft X-ray Microscopy**, *A.P. Hitchcock, V. Berejnov*, McMaster University, Canada, *D. Susac, J. Stumper*, Automotive Fuel Cell Cooperation Co, Canada

Successful water management in proton exchange membrane (PEM) fuel cells requires a delicate balance of fuel, oxidant and water transport through a variety of length scales from ~ 1 mm in fuel channels, through ~10-100 nm in the gas diffusion media, to 1-10 nm in the catalyst layer. The combination of a high degree of porosity in the reaction zone, complex composition, heterogeneous wetting properties, and the presence of water in two phases (gas, liquid) makes optimization of the performance of PEM fuel cell challenging. We are studying water distributions *in situ* in thin sections of membrane electrode assemblies (MEA) equilibrated with water vapor under feed-back controlled relative humidity conditions using scanning transmission X-ray microscopy (STXM). The intrinsic soft X-ray absorbance properties of the constituent materials allows direct *in-situ* visualization of water uptake into MEAs and the differentiation and mapping of the gaseous and liquid/sorbed water. The method provides maps of liquid and gaseous water distributed over the catalyst layer, with coincident maps of the ionomer and carbon support in the catalyst layer, as

well as the polymer electrolyte membrane. Condensation at specific sites is observed when the relative humidity at the MEA is higher than ~80%.

Research funded by AFCC and NSERC. Measurements were also made at the Canadian Light Source (supported by NSERC, NRC, CIHR, and the University of Saskatchewan) and at the Advanced Light Source (supported by the Division of Basic Energy Sciences of U.S. DoE.)

4:40pm **EN+NS-ThA9 Optimization of the Delta Phase in Bismuth Oxide Thin Films**, *P. Silva-Bermudez, O. Garcia-Zarco*, Universidad Nacional Autónoma de México, *E. Camps, L. Escobar-Alarcón*, Instituto Nacional de Investigaciones Nucleares, México, *S.E. Rodil*, Universidad Nacional Autónoma de México

Bismuth oxide Bi₂O₃ has interesting technological applications, which have not been largely used due to the particular polymorphism of the material. Bismuth Oxide has five polymorphic forms: α , β , γ , δ and ω -Bi₂O₃. Among them, the low-temperature α and the high-temperature δ phases are stable and the others are metastable phases, as has been established by bulk solid-state studies. Each polymorph possesses different crystalline structures and various electrical, optical and mechanical properties. The face-centered cubic δ -Bi₂O₃ is stable over a narrow temperature range 729–825 °C (melting point) and it has the peculiarity of being among the few materials presenting high ionic conductivity at moderate temperatures (600–700°C). In this research, we aim to obtain δ -Bi₂O₃ thin films as possible ionic conductors for the development of micro solid state fuel cells. However, the first challenge is to find the deposition conditions of the magnetron sputtering system to ensure the formation of the desired δ -Bi₂O₃, which is only thermodynamically stable at high temperatures. Based on previous results of Fan et al. (Fan 2006), we choose as the deposition variables the substrate temperature (room temperature to 300 °C) and the power (100-200 W). Our target was pure Bi₂O₃, but the first results indicated that it was necessary to compensate oxygen losses; therefore the atmosphere was a mixture of Argon and Oxygen, where the Oxygen flow was 20% of the total. The results from the different characterization techniques suggested that substrate temperatures between 150 and 200°C are appropriate to obtain the δ -Bi₂O₃ phase at a high deposition rate, between 1.5 to 2 nm/s. X-ray diffraction (XRD) as a single technique to identify the film crystalline structure demonstrated to be rather difficult, since there is a large overlapping between the diffraction peaks corresponding to the α , β , γ and δ phases. However, we showed that by combining XRD and Raman spectroscopy, it was possible to clearly prove the presence of the δ -phase. The explanation for the stabilization of the high temperature phase might be related to the 2-dimensional confinement and/or then effect of the small crystalline size. The physical properties of the δ -Bi₂O₃ thin films were further investigated; optical properties by transmission spectroscopy and ellipsometric spectroscopy in the ultraviolet-visible range, surface resistivity by the four-points method, composition by X-ray photoelectron spectroscopy and X-ray energy dispersion.

Fan H. T, et al. *Thin Solid Films* 513 (2006) 142.

5:00pm **EN+NS-ThA10 Probing Physical and Interfacial Confinement Effects on Multilayered Piezoelectric Polymeric Films using Second Harmonic Generation Laser Spectroscopy**, *J. Jones*, Fisk University, *H. Park*, Vanderbilt University, *L. Zhu*, Case Western Reserve University, *N.H. Tolk*, Vanderbilt University, *R. Mu*, Fisk University

Piezoelectric materials may arguably be the most functional, versatile and widely used materials with a wide range of applications including mechanical sensors, actuators, energy storage and energy harvesting devices. The well established applications are largely based on inorganic piezoelectric materials. The successful employment of polymeric piezoelectric materials, such as polyvinylidene fluoride (PVDF) and its related co-polymers, although light weight, flexible, optically transparent and cost effective, are limited by relatively low piezoelectric coefficients, thermal stability, and durability. The focus of the group is to develop a multilayered piezoelectric PVDF system for improved energy harvesting and energy storage efficiency. These systems are fabricated using enabling technology in co-extrusion which allows more cost effective and large area device production as opposed to more conventional layer-by-layer techniques. Many efforts have been made by the team to fabricate these micro- and nano-layered systems resulting in much improved device performance. A three-time improvement of capacitive electrical energy density has been demonstrated. The focus of this research is to understand the physics of why these multilayered systems perform better than a single layer by developing a characterization technique using both confocal second harmonic generation (SHG) and electric field induced second harmonic (EFISH) laser spectroscopy. Our results have shown that SHG is a very sensitive, non-destructive and versatile technique that can be used to study the piezoelectric and structural properties of layered systems. When combined with EFISH this technique allows the interrogation of electrical properties within the individual layers and at the interfaces between the layers. Further, the proposed techniques can be readily employed *in-situ*

which can provide information in real time during sample processing with static and time-resolved spectroscopic measurements.

5:20pm EN+NS-ThA11 Electrical Transport in Ultrathin Ruthenium Films formed by Atomic Layer Deposition, K.E. Gregorczyk, P. Banerjee, G.W. Rubloff, University of Maryland, College Park

Next generation nanostructured devices require ultrathin layers of different materials (e.g. current collectors found in solar cells, batteries, and charge storage and memory devices, etc.). However, in the ultrathin regime, expectations from bulk resistivity can be misleading in designing such nanostructures. Here, we show the example of ultrathin (5-24nm) Ru films produced by atomic layer deposition (ALD), where resistivity is dramatically increased: at 5nm resistivity is ~7X higher (~135 $\mu\Omega$ cm) than at 24nm (~20 $\mu\Omega$ cm) and ~18X higher than bulk Ru (7.4 $\mu\Omega$ cm). The drastic differences seen here are explained through Mayadas-Shatzkes (MS) theory, which defines the increase in resistivity through geometrical constraints (e.g. film thickness and grain boundaries). Using MS theory the grain boundary reflection coefficients were calculated as ~0.32 for a 18nm thick film and ~0.66 for a 5nm film. Furthermore, the electrical transport properties of these films were studied as a function of both temperature (80-340K) and film thickness (5-24 nm). Finally, we show that the ALD Ru films are p-type, in agreement with the theory of compensated metals, and report both the temperature coefficient of resistivity and charge carrier mobility as a function of film thickness.

Graphene and Related Materials Focus Topic Room: 208 - Session GR+TF+NS-ThA

Graphene Nanoribbons and Related Structures

Moderator: Y.J. Chabal, University of Texas at Dallas

2:00pm GR+TF+NS-ThA1 Rationally Patterned Large-Area Semiconducting Graphene Materials from the Top-Down and the Bottom-Up, N. Safron, M. Kim, P. Gopalan, M. Arnold, University of Wisconsin-Madison

INVITED

We are experimentally investigating self-assembling lithography (e.g. block co-polymer and nanosphere lithography) to create nanostructured graphene materials with feature sizes below what is easily achieved using optical and electron-beam lithography (< 20 nm), with the motivation of opening up a technologically relevant band gap in graphene. We are particularly interested in a novel form of semiconducting graphene that we call nanoperforated graphene, which consists of graphene perforated by regular hexagonal arrays of nanoscale holes. Unlike nanoribbons, nanoperforated graphene advantageously retains a large-area two-dimensional form factor. In this talk, we will discuss the inter-relationship between the physical structure of nanoperforated graphene and its electronic properties, with specific emphasis on how its band gap experimentally varies with feature size and how charge transport is affected by structure (including the role of edge defects and the observation of single-electron charging effects). We will also report on efforts in our group to realize nanostructured graphene materials with well controlled edge structure and superior properties via scalable and rationally controlled bottom-up growth that avoids top-down etching without sacrificing arbitrary pattern forming ability.

2:40pm GR+TF+NS-ThA3 Quantum Pumping in Graphene Nanoribbons, T. Kaur, Ohio University, L. Arrachea, Universidad de Buenos Aires, Argentina, N. Sandler, Ohio University

The interest in the development of devices at the nanoscale has intensified the search for mechanisms that provide tailored control of transport properties while reducing effects of heat dissipation and contact resistance. For instance, *charge pumping* is one of the current generating methods that allows for minimizing the effects of contact resistance. *Charge pumping* is the mechanism used to generate DC currents in open-quantum systems by applying local de-phased time-dependent potentials.

We analyze the properties of non-equilibrium zero-bias current through nano-ribbons using tight-binding Hamiltonians and the *Keldysh formalism*. This theoretical treatment, based on non-equilibrium Green's function techniques, is the most appropriate one to address questions for systems in non-linear, out of equilibrium conditions. We develop a numerical implementation for the models described below in a wide range of non-equilibrium regimes.

After reviewing results for quantum pumping in a one-dimensional chain attached to two reservoirs, with two local single-harmonic potentials oscillating in time, we study finite-width ribbons of square and graphene lattices. The transmission function reveals the value of the *resonant frequency* and explains how the quantum charge pumping works. We

analyze the dependence of the *DC current* as a function of different parameters such as chemical potential, pumping amplitude, frequency, etc. In addition, the role of reservoirs is fully described. Pumped currents can also be generated by application of laser fields. We present the comparison between these two pumping methods. Possible extensions for disordered systems will be discussed.

3:00pm GR+TF+NS-ThA4 First-principles Study of Field Emission from Graphene Nanoribbons, J. Driscoll, K. Varga, Vanderbilt University

A real-space, real-time implementation of time-dependent density functional theory [1,2,3] is used to study electron field emission from graphene nanoribbons. The structures are shown to be good field emitters with spatial variation of the emission current influenced by the presence of passivating hydrogen. The nanoribbons are seen to produce slightly lower currents than nanotubes formed from the ribbons. Spin-polarized field emission from carbon nanotubes has been calculated with and without Fe adsorbates (atoms and clusters). It was observed that various adsorbates cause the separation of density into spin-polarized regions. The calculations predict that carbon nanotubes with various adsorbates can be used as spin-polarized current sources. The spin-polarized results for nanotubes will be compared to similar

calculations for graphene nanoribbons.

References

- [1] J.A. Driscoll and K.Varga, Phys. Rev. B 80, 245431 (2009).
- [2] J.A. Driscoll, S. Bubin, W. French, and K. Varga (submitted).
- [3] J.A. Driscoll, B. Cook, S. Bubin, and K. Varga (submitted).

Acknowledgments

This work is supported by NSF grant CMMI0927345.

3:40pm GR+TF+NS-ThA6 Quantum Transport Properties of Modified Graphene Nanoribbons with Boron Nitride Domains at the Nanoscale, A. Lopez-Bezanilla, Oak Ridge National Laboratory

Carbon-based systems are being widely investigated as potential candidates for nanoelectronic interconnects and transistors. The control of electric current is, therefore, an important challenge in nanostructures engineering. The possibility of creating hybrid one-atom thick layers containing C, B and N atoms have attracted much attention as they can provide an efficient way to create new materials with properties complementary to those of graphene and h-BN.

Here we present a theoretical methodology and study of charge transport through GNRs with BN domains randomly distributed along the ribbon surface. We resort to both first principles calculations, to obtain a suitable parametrization of the electronic structure, and a transport approach based on the ab initio results to explore conduction regimes through large and disordered systems. The quantum transport modeling is based on the Green's function formalism, combining an iterative scheme for the calculation of transmission coefficients with the Landauer's formula for the coherent conductance.

Our results describe how the conductance of the hybrid systems is altered as a function of incident electron energy and BN domain density. We explore the transport regimes comparing different degrees of BN doping and BN domain size for ribbons of various widths and lengths on the order of the micrometer. A comparison with other types of defects such as atoms in epoxy configuration and functional groups covalently attached to the ribbon surface will be also discussed.

4:00pm GR+TF+NS-ThA7 Simple and Scalable Route for the 'Bottom-Up' Synthesis of Few-Layer Graphene Platelets and Thin Films, K. Coleman, University of Durham, UK

Graphene has generated much interest owing to its exceptional electronic properties and high mechanical strength. This has enabled new types of electronic devices and composite materials to be envisaged. The main problem is the availability of the material and the difficulties associated with its synthesis. Here we present a simple, convenient and scalable chemical vapour deposition method involving metal alkoxides in ethanol to produce few-layer graphene platelets. The graphene platelets have been fully characterised using TEM, SEM, AFM, XPS and XRD. The methodology used has the added flexibility in that it can be used to grow conducting transparent thin films on inert substrates such as silicon wafer and quartz glass. Importantly, no heavy metal catalysts were required to produce the few-layer graphene platelets or graphene films and all non-carbon by-products are soluble in water.

4:20pm **GR+TF+NS-ThA8 Approaching the Intrinsic Bandgap in Suspended High-Mobility Graphene Nanoribbons**, *M.-W. Lin, C. Ling*, Wayne State University, *L.A. Agapito, N. Kioussis*, California State University Northridge, *Y. Zhang, M.-C. Cheng*, Wayne State University, *W.L. Wang, E. Kaxiras*, Harvard University, *Z.X. Zhou*, Wayne State University

We report the first variable-temperature electrical-transport study of suspended ultra-low-disorder GNRs with nearly atomically smooth edges. Suspension of the GNRs not only removes the substrate influence but also allows a thorough removal of impurities, including those trapped at the interface between the GNR and the substrate, leading to a substantial increase of the carrier mobility. We observe high mobility values over $3000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in GNRs that are $\sim 20 \text{ nm}$ wide, the highest reported to date on GNRs of similar dimensions. Furthermore, we demonstrate that the activation gap extracted from the simple activation behavior of the minimum conductance and residual carrier density at the charge neutrality point approaches the intrinsic bandgap in ultra-low-disorder GNRs. Comparison of the bandgap values of multiple samples shows that the bandgap in our ultra-low-disorder samples is approximately inversely proportional to the ribbon width, consistent with theoretical predictions. On the other hand, non-negligible disorder in GNRs obscures the observation of the intrinsic bandgap in transport measurements. In addition, the size of the bandgap derived from the transport measurements is in quantitative agreement with the results of our complementary tight-binding calculations for a wide range of chiral angles characterizing the GNR structure, suggesting that the underlying electronic origin of bandgap enhancement is the magnetism of the zigzag edges.

4:40pm **GR+TF+NS-ThA9 Fabrication of Polymer-Protected Graphene Nanoribbons by Thermal Dip-Pen Nanolithography (tDPN)**, *W.K. Lee, J.T. Robinson, R. Stine, A.R. Laracuente*, Naval Research Laboratory, *W.P. King*, University of Illinois at Urbana Champaign, *P.E. Sheehan*, Naval Research Laboratory

The lithographic patterning of graphene nanoribbons (GNRs) to engineer band gaps has gained much attention as one path to realizing graphene-based devices. We employed thermal dip-pen nanolithography (tDPN)¹ to pattern GNRs on CVD single-layer graphene (SLG) that had been transferred onto a SiO₂ substrate. In tDPN, a heatable AFM cantilever regulates the deposition of an ink through controlled melting, much like a nanoscale soldering iron. tDPN has been successful at depositing polymers ranging from semiconductors to insulators on a variety of surfaces. To create the nanoribbons, we deposited polystyrene (PS) ribbons via tDPN on a SLG film between the source and drain electrodes. The areas of the graphene not protected by the polymer were then modified to isolate thin graphene nanoribbons. We show that the PS protected ribbon was the only conductive pathway for active device. This method allows a wide range of nanoribbon widths to be created and avoids electron beams which can damage graphene. The impact of the polymer choice on conductivity as well as the choice of isolation will be discussed. For instance, we find that the PS ribbon can serve not only as an etch mask to pattern GNRs but also a stable dopant layer. The detailed fabrication and characterization of these structures will be presented.

1. WK Lee, et al. (2010) "Maskless Nanoscale Writing of Nanoparticle-Polymer Composites and Nanoparticle Assemblies using Thermal Nanoprobes", *Nano Letters*, 10, 129

5:00pm **GR+TF+NS-ThA10 Edge Termination of Modified Graphene Oxide during Thermal Exfoliation**, *M. Acik**, *Y.J. Chabal*, The University of Texas at Dallas

Nanopore formation in carbon materials (e.g. exfoliated nanostacks of graphite) has been widely studied through mechanical exfoliation, intercalation, electrochemical separation, chemical or thermal exfoliation of graphite oxide (GO) via expansion with partial oxygen removal. Amongst all these methods, exfoliation of modified graphene (GO), a solution-processable precursor compound where aromatic and heterocyclic rings with embedded oxygen functionalities exist, by thermal processing still remains elusive for the following reasons: (1) poor control of GO composition (initial oxygen content), (2) poor understanding of the chemical composition, (3) unknown role of oxygen, adjoining oxygen interactions, and edge termination with oxygen. Infrared absorption spectroscopy coupled with *in-situ* thermal annealing process [1] makes it possible to examine the chemical changes taking place during thermal reduction to identify and understand interacting molecular environment and the edge functionalization. To unravel the complex mechanisms leading the removal of oxygen in GO, we have performed *in-situ* transmission infrared absorption spectroscopy (IRAS) measurements of graphene/graphite oxide (GO) thin and bulk films upon thermal annealing (60-850°C) in vacuum

(10^{-3} - 10^{-4} Torr). Control of the edge geometry of finite-sized modified graphene flakes depends very much on the control of the processing methods. This edge reconstruction further determines electronic, electric, optical and mechanical properties of the exfoliated modified graphene flakes. Therefore, we not only perform studies deriving a thermal reduction mechanism, but also examine the edge reconfiguration with oxygen. We report here the observation of a surprisingly strong IR absorption band that occurs only upon thermal reduction of GO. After annealing at 850°C in vacuum, the strong enhancement of the new IR active absorbance band is observed at $\sim 800 \text{ cm}^{-1}$ [2]. The intensity of this band is 10-100 times larger than what is expected for the oxygen content of the reduced GO, namely between 5 and 8 at.%. This band is assigned to a specific oxidation state, involving oxygen located in the basal plane (forming C-O-C bonds) and *atomically straight* edges of reduced graphene. The large enhancement in IR absorption is attributed to the direct participation of electrons, induced by the asymmetric C-O-C stretch mode displacement. These findings open new possibilities in the field of nanoelectronics for all sensor and energy storage applications. [1] M. Acik, *et al.* J. Am. Chem. Soc. (2011), *in preparation*. [2] M. Acik, *et al.* Nat. Mater. 9, 840-845 (2010).

5:20pm **GR+TF+NS-ThA11 Study of Ridges on Epitaxial Graphene on 6H-SiC(0001)**, *Y.Y. Li, Y. Liu, L. Li*, University of Wisconsin-Milwaukee

The graphitization of hexagonal SiC surfaces provides a viable alternative for the synthesis of wafer-sized graphene for mass device production. During the later stages of growth, ridges are often observed on the graphene layers as a result of bending and buckling to relieve the compressive strain between the graphene and SiC substrate, which also introduce ripples in the otherwise atomically flat graphene sheet. In this work, we show, by atomic resolution STM imaging, that ridges are in fact bulged regions of the graphene layer, forming one-dimensional (nanowire) and zero-dimensional (quantum dot) nanostructures. We further demonstrate that their structures can be manipulated and even new ones created by the pressure exerted by the STM tip during imaging. These results and their impact on the electronic properties of epitaxial graphene on SiC(0001) will be presented at the meeting.

Nanometer-scale Science and Technology Division Room: 203 - Session NS-ThA

Biological Nanomaterials

Moderator: N.A. Burnham, Worcester Polytechnic Institute

2:20pm **NS-ThA2 Biologically-Inspired Reversible Adhesives: Where Are We Now?**, *S. Gorb*, Zoological Institute at the University of Kiel, Germany **INVITED**

Biological hairy attachment systems demonstrate their excellent adhesion and high reliability of contact. The structural background of various functional effects of such systems is discussed in the present paper. Additionally, it is demonstrated here, how comparative experimental biological approach can aid in development of novel adhesives. Experimental studies show that the effective elastic moduli of fiber arrays and spatula-like terminal elements are low, and this is of fundamental importance for adhesion enhancement on rough substrata and for an increased tolerance to defects at the level of individual contacts. Based on the broad structural and experimental studies of biological attachment devices, the first industrial bioinspired reversible adhesive foil was developed, which adhesive properties were characterised using variety of measurement techniques and compared with the flat surface made of the same polymer. The microstructured foil demonstrates considerably higher pull off force per unit contact area. The foil is less sensitive to contamination by dust particles, and after washing with water, its adhesive properties can be completely recovered. This glue-free, reversible adhesive is applicable in dynamic pick-and-drop processes, climbing robots, and other systems even under vacuum conditions. The foil represents therefore a considerable step towards development of industrial dry adhesives based on the combination of several principles previously found in biological attachment devices.

3:00pm **NS-ThA4 Ultrastable Superparamagnetic Nanoparticle Design for Membrane Assembly and Triggered Release**, *E. Amstad, M. Textor*, ETH Zurich, Switzerland, *E. Reimhult*, University of Natural Resources and Life Sciences Vienna, Austria

Application of superparamagnetic iron oxide nanoparticles as biomedical imaging contrast agents and as actuators in smart materials, e.g. for drug delivery and release, require them to retain high stability even in extremely dilute suspensions, high salt and at elevated temperatures. These requirements can only be met by steric repulsive stabilization through

* Morton S. Traum Award Finalist

irreversibly binding, low molecular weight dispersants of e.g. poly(ethylene glycol) or a similarly irreversibly bound organic shell which stabilizes the nanoparticle into another matrix material.

We have recently demonstrated that we can stabilize magnetite nanoparticles which fulfill these stability criteria using self-assembling dispersants with nitrocatechol anchors (1-2). This allows us free control over the dispersant type by simple co-adsorption of dispersants to as-synthesized core Fe₃O₄ particles. Combined with independent control over the Fe₃O₄ core size in the range 3-15 nm a versatile toolbox for assembly of various smart materials and for biomedical applications has been created.

This presentation is focussed on recent results demonstrating and characterizing assembly of such nanoparticles into membranes of stealth liposomes (3). We show that there are strict requirements for the size of particles that can be assembled into lipid bilayer membranes and that a requirement for efficient assembly and actuation as well as liposome stability is to ensure stability of the hydrophobic shell surrounding the nanoparticle within the membrane. Encapsulated molecules were released multiple times by application of short bursts of alternating magnetic fields through a localized phase change in the membrane without heating of the surrounding aqueous environment. This allowed control of both timing and dose of release. The highest efficiency of release and encapsulation was obtained for irreversibly stabilized superparamagnetic iron oxide nanoparticles with diameters <6 nm inserted into the lipid membrane.

1. E. Amstad et al., Nano Lett, 9:4042 (2009)
2. E. Amstad et al., J Phys Chem C 115:683-691 (2011)
3. E. Amstad et al., Nano Lett, 11:1664-1670 (2011)

3:40pm NS-ThA6 Nanoscale Electrical Interaction between Carbon Nanotubes and DNA, Y. Cao, Y. Xu, Vanderbilt University

Carbon nanotube-biomolecule hybrids have emerged as one of the most promising materials for biological and biomedical applications, such as biosensors, drug delivery, and imaging. Recently, Carbon nanotubes (CNTs) have shown the ability to protect bound DNA cargos from enzymatic cleavage both during and after delivery into cells. This ability may result from the interaction between CNTs and DNA, which makes DNA unrecognizable to enzyme binding pockets. Therefore, it is important to study the interaction between CNTs and DNA. In this work, we have developed a nanoscale optoelectronic probing system by combining highly-sensitive CNT transistors with advanced dual-trap optical tweezers to investigate the interaction between CNTs and DNA at the single-molecule level. We tightly bonded both ends of a DNA molecule with microbeads, which could be held and manipulated by optical tweezers. When the DNA molecule was moved close to a suspended CNT transistor, the negative charge from the DNA molecule would change the local electrostatic environment around the CNT. Through scanning photocurrent measurements, the electrical coupling between individual DNA molecules and CNTs could be investigated.

4:00pm NS-ThA7 Surface Functionalization of Nanomaterials: From Heterogeneous Catalysis to Nanoparticle Drug Delivery, W. Gao, Brigham and Women's Hospital and Harvard Medical School INVITED

The advent of nanotechnology has vastly advanced our fundamental understandings on nanomaterials, in particular their surface properties. It has also revolutionized the way we functionalize these materials to exploit novel properties and applications. For example, metallic nanoclusters can be processed into different morphologies on support surfaces and subsequently allow desired reaction pathways to occur. In addition, a great number of metal oxides have been grown into single crystal surfaces with precisely controlled atomic arrangements. They have aided researchers to unlock principles governing the extraordinary chemical and electronic properties of oxides. Furthermore, various functionalities can be introduced to polymers and have resulted in multifunctional nanoparticles with superb surface properties. These nanoparticles can therefore overcome biological barriers and effectively deliver therapeutic agents to the disease sites. Using examples from my research in surface functionalization of metals, oxides, and polymeric nanoparticles, I would like to show how the surface functionalization of diverse materials can be guided by a common principle of understanding material structure-property relationship. The continuing effort in studying surface functionalization of nanomaterials will lead them to a brighter future in the fields of biomedicine, energy, and environment.

4:40pm NS-ThA9 Perfluoropentane Filled Boron Doped Hollow Silica Microspheres for Ultrasound Guided Surgery, A. Liberman, H.P. Martinez, Z. Wu, S.L. Blair, Y. Kono, R.F. Mattrey, A.C. Kummel, W. Trogler, University of California, San Diego

The reported positive margin rate from wire localized excisions of breast cancers is approximately 20-50%; however, using radioactive seeds and a radiation detector the excision rate is halved because the surgeon can

constantly reorient the dissection to place the seed in the center of the specimen. Unfortunately, radioactive seed localization has several safety challenges, only single foci can be localized, and incisions are required to implant the seeds, so it is rarely employed. As a safe alternative, gas-filled hollow boron-doped silica particles have been developed, which can be used for ultrasound-guided surgery for multiple foci. The function of the boron doping is to increase the mechanical strength of the silica shell. The particles are synthesized through a sol-gel method on a polystyrene template, and subsequently calcined to create hollow, rigid microspheres. The boron doped silica shell is derived from tetramethoxy orthosilicate (TMOS) and trimethyl borate (TMB), which forms a rigid, mesoporous shell upon calcination. The microspheres are filled with perfluoropentane vapor. The perfluorocarbon vapor is contained within the porous shell due to its extremely low solubility in water. In addition, the high surface tension of water may serve to seal the fluorine phase within the pores of the shell wall as water enters the outer surface of the porous shell by capillary action. Considerable testing of particle functionality, signal persistence and acoustical properties have been performed in various phantoms including ultrasound gel, chicken breast, and excised human mastectomy tissue. Furthermore, preliminary particle injection longevity studies have been performed in a rabbit animal model. *In vitro* studies have shown that continuous particle imaging time is up to approximately 45 minutes. *In vivo* studies have shown consistent signal presence even 48 hours post injection in rabbits with an injection volume of 50 μ l carrying only 100 μ g of particles. As a result these particles may provide a significant improvement over current methods in terms of patient comfort in having a small injection 1-2 days prior to surgery. On going studies are currently aimed at improving the understanding of the mechanism by which these microspheres are capable of producing such robust signal under color doppler ultrasound.

Transparent Conductors and Printable Electronics

Focus Topic

Room: 106 - Session TC+EM+NS-ThA

Transparent / Printable Electronics Part 2

Moderator: S. Durbin, University at Buffalo

2:00pm TC+EM+NS-ThA1 ZnO-based Schottky Diodes and Their Utilization in Transparent Electronics, H. von Wenckstern, Universität Leipzig, Germany INVITED

Transparent conducting oxides (TCO) have found application as electrode in emerging markets like that of thin films solar cells or flat panel displays. For this passive functionality the TCO material must combine high transparency preferentially over a wide spectral range and high conductivity. In the last years active transparent devices like photodetectors, transistors or a complete transparent circuitry are envisioned and rely on semiconducting properties of the material. Besides a precise control of the doping level in the active part of devices the creation of space charge regions by rectifying contacts is a prerequisite for active devices. In the emerging field of transparent electronics, only metal-insulator-semiconductor field-effect transistors (MISFETs) were considered so far. In this contribution transparent, high-performance MESFETs, inverters etc. based on ZnO and related ternaries are presented. We discuss design prospects as well as limitations regarding device performance, reliability and stability.

The influence of the contact metal and dielectric passivation layers on the properties of ZnO Schottky diode, used as gate electrode within the MESFETs, as well as sources of non-idealities will be highlighted.

2:40pm TC+EM+NS-ThA3 Photoresponse of Amorphous In-Ga-Zn-O / Pt Schottky Junction, D.H. Lee, K. Nomura, T. Kamiya, H. Hosono, Tokyo Institute of Technology, Japan

Amorphous oxide semiconductors (AOSs) are expected as an alternative to amorphous/poly-Si for thin-film transistors (TFTs) in next-generation flat-panel displays (FPDs) because AOS TFTs have many advantages such as large field-effect mobilities (>10 cm²(Vs)⁻¹) and low-temperature process [1]. For more advancing AOS optoelectronic technology, it is important to develop more various devices other than TFTs, and to study some remaining issues such as operation characteristics of AOS devices under light illumination.

In this study, we fabricated good and stable metal-AOS Schottky contacts made of amorphous In-Ga-Zn-O (a-IGZO) and bottom Pt electrodes at temperatures below 200°C even though it is generally difficult to make high performance oxide Schottky junctions [2]. It was found that the a-IGZO/Pt Schottky contacts have an ideality factor $n \sim 1.1$ and a Schottky barrier height $\phi_b \sim 0.9$ eV, which were evaluated from their J-V curves using the

thermionic emission model. From C-V results, the Schottky junctions operate at the full-depletion condition, whose C corresponds to the geometrical capacitance of the a-IGZO layer, and relative permittivity ϵ_s of a-IGZO was obtained approximately 13. However, the results of temperature dependences of J-V characteristics were unexplained if we take a simple uniform Schottky barrier model; we found that the barrier potential fluctuations model [3] explained them well, and the mean barrier height ϕ_b , m of 1.2 eV and the net electron affinity χ_s of a-IGZO of 4.2 eV were obtained. On the other hand, the Schottky contacts showed very small open circuit voltages (V_{oc} 's) < 0.1 V under 100 mW/cm² AM1.5 light illumination, which are far smaller than the built-in potential ($V_{bi} \sim 0.4$ eV) estimated from the C-V measurements in dark. We also observed that V_{oc} decays with time after starting the light illumination. We will discuss the mechanism of the small V_{oc} based on these results.

[1] T. Kamiya et al. *Sci. Technol. Adv. Mater.* **11** 044305 (2010).

[2] K. Ip et al., *J. Cryst. Growth* **287**, 149 (2006).

[3] J. H. Werner and H. H. Güttler, *J. Appl. Phys.* **69**, 1522 (1991).

3:00pm TC+EM+NS-ThA4 Novel Metal-organic Precursors for Printed Electronics - Synthesis, Implementation, and Properties. *J.A. Belot, R.A. Potash, R.D. McCullough, K.A. Singh, L. Porter*, Carnegie Mellon University

Printed electronics is a rapidly growing industry and within this emerging field there are three required material categories critical to fabricating active and passive circuitry – insulators (dielectrics), semiconductors (polymers), and conductors (metals). The increased interest in printable electronics as alternatives to silicon-based technologies is fueled by the promise of large-area, flexible, and ultra-low-cost devices. To enable the growing demands of printing processes this work develops metal-containing inks for the deposition of the coinage metals - copper, silver, and gold. These metals are chip components ranging from interconnects to source and drain contacts in organic field effect transistors. The liquid ink approach is based on fundamental advances in coordination chemistry to fabricate discrete metal complexes that can be heated or irradiated to yield metallic films. Ultimately inkjet printing technologies were employed to deposit these metal inks in specific, predetermined patterns that were directly transformed into active and passive devices. The versatility of this approach holds the possibility of printing any metallic design and pattern on virtually any type of substrate.

3:40pm TC+EM+NS-ThA6 A New Application for a-IGZO TFTs: An Addressable Microfluidic Electrowetting Channel Device. *J. Noh, J.H. Noh*, University of Tennessee, *E. Kreit, J. Heikenfeld*, University of Cincinnati, *P.D. Rack*, University of Tennessee

An electrowetting (EW) microfluidic platform designed for control and transport of aqueous and polar species has been fabricated on passive electrodes as well as an active matrix thin film transistor (TFT) array. To drive the EW devices we integrated the micro fluidic platform on a base-plane of transparent TFTs. Specifically, we have used an InGaZnO (IGZO) active layer for the TFT device which has superior performance and offers the benefit of transparent devices for biological and display applications. The TFTs are fabricated with a bottom-gate staggered structure with Cr gate and SiO₂ gate dielectrics deposited via plasma enhanced chemical vapor deposition (PECVD). The a-IGZO semiconducting active layers are deposited using rf magnetron sputtering in a reactive Ar-O₂ atmosphere. Finally, source and drain electrodes are formed by e-beam evaporating Ti/Au. Finally the device is annealed in an N₂ ambient for electrical activation. For the EW device integration, Al electrodes are have been deposited various passivation layers. Subsequently a top dielectric and a hydrophobic Fluoropel layer are applied. In this presentation we will review the process flow and will discuss the materials integration issues of EW device and its effect on the TFT performance. We will illustrate the EW characteristics based on standard planar electrowetting on dielectric (EWOD) platforms and compare them to a new concept we have termed the “Laplace Barrier” which includes post arrays and enhances electrowetting characteristics.

4:00pm TC+EM+NS-ThA7 Amorphous Oxide Semiconductor Thin-Film Transistors. *J.F. Wager, K. Hoshino*, Oregon State University, *B. Yeh, R.L. Hoffman*, Hewlett-Packard Company **INVITED**

Amorphous oxide semiconductor (AOS) thin-film transistors (TFTs) are transitioning towards commercialization for active-matrix liquid crystal display flat-panel display backplane applications. They also appear to be well-positioned to meet the more demanding challenges associated with active-matrix organic light-emitting device backplanes. Additionally, AOS TFTs offer an attractive approach to printed electronics. The primary focus of this talk will be to discuss our novel approach to top-side passivation of bottom-gate indium gallium zinc oxide (IGZO) and zinc tin oxide (ZTO) AOS TFTs. Device performance between passivated and unpassivated AOS

TFTs will be compared. Passivation mechanisms will be considered in the context of induced-gap state and device physics electrostatic modeling.

4:40pm TC+EM+NS-ThA9 Why Optimum Oxygen Pressure Range Exists for Fabricating Amorphous In-Ga-Zn-O Thin-Film Transistor and How it Should be Optimized. *K. Ide, K. Nomura, T. Kamiya, H. Hosono*, Tokyo Institute of Technology, Japan

Amorphous oxide semiconductors (AOSs) represented by amorphous In-Ga-Zn-O (a-IGZO) are expected for large-area high-performance flexible electronic devices, because AOSs have large electron mobilities greater than 10 cm²(Vs)⁻¹ even if fabricated at room temperature (RT). In particular, a-IGZO has good controllabilities of carrier concentration, and their thin-film transistors (TFTs) exhibit superior properties including long-term stability.

In this study, we investigated effects of oxidation on operation characteristics of a-IGZO TFTs. Bottom gate, top-contact a-IGZO TFTs were fabricated on SiO₂/c-Si substrates by RF magnetron sputtering. Sputtering conditions were the RF power of 70 W and the total pressure of 0.55Pa. Two oxidation treatments were examined; (i) ozone annealing and (ii) varying a mixing gas ratio of Ar : O₂ from 18 : 2 to 19.8 : 0.2 in standard cc per minute (sccm) during the channel deposition.

For the ozone annealed TFTs, annealing at $\leq 250^\circ\text{C}$ produced good TFTs, while those annealed at 300°C caused large hysteresis and S slope. After applying a high V_{GS} larger than 40 V, the transfer characteristics showed the large V_{th} of 40V and the small hysteresis. Trap state around Fermi level of the large S state and the large V_{th} state were $\sim 4 \times 10^{17}$ and $\sim 1 \times 10^{17}$ cm⁻³eV⁻¹, which were estimated by C-V analysis. The large V_{th} state is very stable in the dark, but the TFT recovers to the initial large S state by light illumination. The photoresponse measurements revealed that deep trap states were formed at 2.3 eV below the conduction band minimum by applying a high V_{GS} . Thermal desorption spectra showed that weakly-bonded excess oxygens were incorporated in the a-IGZO layer. From these results, we built a subgap DOS model of the trap states of the excess oxygens. We also confirmed similar behaviors in a-IGZO TFTs fabricated in high oxygen pressure conditions.

This study reveals that the control of oxygen stoichiometry is important for obtaining good performance and stability of AOS TFTs.

5:00pm TC+EM+NS-ThA10 Effects of Low-Temperature Annealing and Deep Traps in Operation Characteristics of Amorphous In-Ga-Zn-O Thin-Film Transistors. *T. Kamiya, Y. Kikuchi, K. Ide, K. Nomura, H. Hosono*, Tokyo Institute of Technology, Japan

Amorphous oxide semiconductors (AOSs) represented by a-In-Ga-Zn-O (a-IGZO) are expected for channel materials in thin-film transistors (TFTs) for next-generation flat-panel displays such as jumbo-size / fast / ultrahigh-resolution liquid-crystal displays and organic light-emitting diode displays. These are also expected for flexible electronics devices because they may be fabricated on unheated substrates, and thus produce flexible displays and circuits on inexpensive plastic substrates such as PET. On the other hand, it is known that, although room-temperature fabrication is possible for AOS TFTs, post-deposition thermal annealing at $\geq 300^\circ\text{C}$ is better employed to obtain good stability. To employ this technology to the flexible electronics, the annealing temperature should be lowered to 200°C or far below. We reported that wet O₂ annealing produces the best performance TFTs when annealed at $\geq 300^\circ\text{C}$, while it caused serious negative threshold voltage (V_{th}) shift at $\leq 200^\circ\text{C}$. In this paper, we report the origin of the negative V_{th} shift by employing photoresponse spectroscopy of TFT characteristics. It revealed that the near-valence band maximum (VBM) states are reduced significantly even by the low-temperature 200°C annealing, and implied that the negative V_{th} shift originates from free electrons released by annihilation of the near-VBM states.

5:20pm TC+EM+NS-ThA11 β -alumina (SBA): A Promising High Dielectric Constant Gate Material for Solution Processed, Transparent and Low Voltage Transistor Devices. *B. Zhang, Y. Liu, H. Katz*, Johns Hopkins University

β -alumina (SBA) has been discovered as a promising high dielectric constant gate material for solution processed, transparent and low voltage transistor devices. Some experimental evidence indicates that the mobile Na ion within two spinel blocks made by Al and O is responsible for the high dielectric constant. Transistors (W/L ratio 10) using SBA as gate layer and zinc tin oxide (ZTO) as active layer only need 2V to obtain 0.7mA output current. SBA material is compatible with organic semiconductors such as PQT12 and pentacene as well. Some key issues regarding using SBA for real applications, such as device stability in the ambient atmosphere, response under high frequency, and threshold voltage shift under gate bias have also been studied. It is found that encapsulating the device with CYTOP fluorinated polymer is an effective way to increase the operational stability of the devices in the ambient environment.

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Davis, R.F.: EM1-MoA2, 4
Dawahre, N.: EN+EM+NS-WeM12, 27
Devine, B.: GR+NS+PS+SS-ThM10, 37

Dezelah, C.: NM+MS+NS+TF-MoM6, 1
Dickey, E.: NM+MS+NS+TF-MoM10, 2
Dietz, N.: EM1-MoA4, 4
Discher, B.M.: AS+BI+NS-WeM9, 25
Doering, R.: NM+NS+MS-TuA1, 16
Dolocan, A.: NS+AS-TuA10, 18
Donath, M.: NS+AS-TuA12, 19
Donghwa, L.: EN+NS-WeM10, 28
Dresselhaus, M.S.: ET+EM+NS+GR-TuM2, 11
Dreyer, D.R.: EN+NS-ThM1, 35
Driscoll, J.: GR+TF+NS-ThA4, 42
Durstock, M.F.: EN+NS-WeM2, 27; EN+NS-WeM4, 28
Dutton, G.J.: EN+NS-WeM9, 28

— E —

Eddy: NS-WeM6, 31
Eigler, D.: NS+AS-TuA2, 17
Einabad, O.: ET+EM+NS+GR-TuM12, 12
Einstein, T.L.: NS-ThM3, 38
Elam, J.W.: NS-WeM3, 31
Eliad, L.: AS+BI+NS-WeM6, 24
El-Zubir, O.: BI+AS+NS+SS-WeA9, 34
Emery, J.D.: NS-WeM3, 31
Endres, J.: ET+EM+NS+GR-TuM5, 11
Eriksson, M.: ET+EM+NS+GR-TuM5, 11
Escobar, C.A.: BI+AS+NS+SS-WeA11, 34
Escobar-Alarcón, L.: EN+NS-ThA9, 41
Esposito, M.: NS+EM-MoM6, 3
Evans, K.R.: EM1-MoA2, 4

— F —

Feenstra, R.M.: ET+EM+NS+GR-TuM1, 11
Feibelman, P.J.: NS-WeM2, 31
Feltz, A.: NS+AS-TuA11, 18
Feng, X.: GR+NS+PS+SS-ThM3, 36
Ferguson, J.D.: EM1-MoA3, 4
Ferrara, D.W.: NS-MoA1, 7
Feulner, P.: EN+NS-TuM2, 10
Filler, M.A.: EN+EM+NS-MoA7, 6; EN+EM+NS-WeM3, 26; EN+NS-ThM10, 35; NS-TuM11, 14; NS-TuM9, 13
Fokin, A.A.: NS-ThM11, 38
Fokina, N.A.: NS-ThM11, 38
Fowlkes, J.D.: NM+NS+MS-TuA11, 17; NS+EM-MoM10, 3
Frederick, M.: EN+NS-TuM11, 11
Fu, W.: ET+EM+NS+GR-TuM6, 11
Fujimoto, T.: NS-TuP2, 22
Fujita, D.: HI+AS+BI+NS-WeM12, 30

— G —

Gall, D.: ET+EM+NS+GR-TuM11, 12
Gamage, S.: EM1-MoA4, 4
Gao, W.: NS-ThA7, 44
Garcia-Zarco, O.: EN+NS-ThA9, 41
Garramone, J.J.: AS+BI+NS-WeM11, 25
Gartstein, Y.N.: EN+NS-TuM1, 10
Gaskill, D.K.: NS-WeM6, 31
Gazit, E.: AS+BI+NS-WeM6, 24
Geisler, H.: NS-WeM1, 30
George, S.M.: NM+MS+NS+TF-MoM8, 1
Gerber, T.: NS-WeM2, 31
Gilliland, D.: NS-ThM2, 38
Given, U.: NS-TuM10, 14
Göhlhäuser, A.: GR+NS+PS+SS-ThM4, 36; HI+AS+BI+NS-WeM6, 30
Goodlin, B.E.: NM+NS+MS-TuA1, 16
Gopalan, P.: GR+TF+NS-ThA1, 42
Gorb, S.: NS-ThA2, 43
Graanäs, E.: NS-WeM2, 31
Gregorczyk, K.E.: EN+NS-ThA11, 42
Gregory, C.: EM1-MoA11, 5; EN+EM+NS-MoA3, 6
Gu, D.: NS-MoA9, 8
Gu, G.: ET+EM+NS+GR-TuM1, 11
Guenther, B.: NS+AS-TuA11, 18

Guglietta, G.W.: EN+EM+NS-WeM11, 27
 Guisinger, N.P.: VT+MN+NS+SS+AS-TuA8, 20
 Guo, H.X.: HI+AS+BI+NS-WeM12, 30

— **H** —

Ha, R.: NS+EM-MoM1, 2
 Haglund Jr., R.F.: NS-MoA2, 7
 Haglund, R.F.: NS-MoA1, 7
 Hamers, R.J.: BI+AS+NS+SS-WeA3, 33
 Hammond, J.S.: NS-TuM10, 14
 Hamoudi, H.: EN+NS-TuM2, 10
 Hanley, L.: EN+NS-WeM10, 28
 Hao, Y.: NS-WeM1, 30
 Harl, R.R.: BI+AS+NS+SS-WeA10, 34
 HarLavan, R.: EN+NS-WeM11, 29
 Harris, N.: EN+EM+NS-WeM12, 27
 Hartfield, C.D.: NM+NS+MS-TuA11, 17
 Haspert, L.C.: EN+NS-ThA4, 40
 He, G.: ET+EM+NS+GR-TuM1, 11
 Heikenfeld, J.: TC+EM+NS-ThA6, 45
 Heilemann, M.: GR+NS+PS+SS-ThM4, 36
 Hellstrom, S.L.: ET+EM+NS+GR-TuM6, 11
 Heo, J.H.: NS-TuP12, 23
 Hernandez, S.C.: GR+NS+PS+SS-ThM12, 37
 Hernández, S.C.: NS-WeM6, 31
 Hersam, M.C.: EN+NS-WeM2, 27; EN+NS-WeM3, 27; EN+NS-WeM4, 28; GR+NS+PS+SS-ThM11, 37; NS-WeM3, 31
 Hess, W.P.: NS-MoA8, 8
 Hicks, R.F.: NS-TuM6, 13
 Hill, I.: EN+NS-WeM1, 27
 Hitchcock, A.P.: EN+NS-ThA8, 41; NS-WeM12, 32
 Hla, S.-W.: EN+NS-TuM9, 10; NS-ThM6, 38
 Hlawacek, G.: HI+AS+BI+NS-WeM5, 29
 Ho, W.: NS+AS-TuA8, 18
 Hoffman, R.L.: TC+EM+NS-ThA7, 45
 Holbrook, R.D.: BI+AS+NS+SS-WeA3, 33
 Holloway, P.H.: EN+EM+NS-MoA8, 7; NS-MoA3, 7
 Holman, Z.: EN+EM+NS-WeM1, 25
 Hong, S.: NS-TuM12, 14
 Hoshino, K.: TC+EM+NS-ThA7, 45
 Hosono, H.: TC+EM+NS-ThA10, 45; TC+EM+NS-ThA3, 44; TC+EM+NS-ThA9, 45
 Hossain, Md.Z.: GR+NS+PS+SS-ThM11, 37
 Hsu, S.L.C.: NS-TuP11, 23
 Hu, E.L.: NS-MoA6, 8
 Huang, C.-H.: EN+EM+NS-MoA1, 6
 Huang, J.Y.: EN+NS-ThM11, 36
 Huang, L.: EM1-MoA2, 4
 Huba, Z.: NS-MoA9, 8
 Huh, K.: NM+NS+MS-TuA12, 17
 Hwang, H.: NM+NS+MS-TuA12, 17
 Hwang, J.: EN+EM+NS-MoA9, 7

— **I** —

Iagarashi, M.: EN+EM+NS-MoA1, 6
 Ide, K.: TC+EM+NS-ThA10, 45; TC+EM+NS-ThA9, 45
 Iijima, T.: HI+AS+BI+NS-WeM3, 29
 Im, S.I.: NS+EM-MoM1, 2
 Inoue, K.: NS-WeM10, 32
 Itoh, H.: HI+AS+BI+NS-WeM12, 30
 Iwai, H.: NM+MS+NS+TF-MoM5, 1
 Iwasaki, T.: HI+AS+BI+NS-WeM12, 30
 Iwaya, T.: AS+BI+NS-WeM5, 24

— **J** —

Jacobson, R.B.: NS-MoA11, 9
 Jadhav, P.: EN+NS-WeM5, 28
 Jang, S.: NM+NS+MS-TuA12, 17
 Jankovic, V.: NS-MoA4, 8
 Javey, A.: EN+EM+NS-WeM9, 26
 Jennings, G.K.: BI+AS+NS+SS-WeA11, 34
 Jeon, I.: NM+NS+MS-TuA12, 17
 Jeon, S.: NS+AS-TuA1, 17
 Jia, X.T.: ET+EM+NS+GR-TuM2, 11
 Jiang, W.: NS-TuP3, 22
 Jimenez, J.M.: VT+MN+NS+SS+AS-TuA12, 21

Joachim, C.: NS-ThM6, 38
 Johns, J.E.: GR+NS+PS+SS-ThM11, 37
 Joly, A.: NS-MoA8, 8
 Jones, J.: EN+NS-ThA10, 41
 Joy, N.A.: NS-TuP3, 22
 Juang, B.: EN+EM+NS-MoA9, 7
 Jung, K.: NM+NS+MS-TuA12, 17
 Junkermeier, C.E.: GR+NS+PS+SS-ThM12, 37
 Jur, J.S.: EM1-MoA9, 5

— **K** —

Kakushima, K.: NM+MS+NS+TF-MoM5, 1
 Kamiya, T.: TC+EM+NS-ThA10, 45; TC+EM+NS-ThA3, 44; TC+EM+NS-ThA9, 45
 Kang, W.P.: EN+NS-TuA12, 15
 Kao, P.: EN+NS-TuM2, 10
 Karakoti, A.S.: NS-TuP7, 23
 Karim, Z.: NM+NS+MS-TuA3, 16
 Karmel, H.J.: EN+NS-WeM3, 27
 Kathan-Galipeau, K.: AS+BI+NS-WeM9, 25
 Katz, H.: TC+EM+NS-ThA11, 45
 Kaur, T.: GR+TF+NS-ThA3, 42
 Kavanagh, K.L.: ET+EM+NS+GR-TuM12, 12
 Kawai, M.: AS+BI+NS-WeM5, 24
 Kaxiras, E.: GR+TF+NS-ThA8, 43
 Keating, C.D.: NS+EM-MoM8, 3
 Kelber, J.: EM1-MoA8, 5
 Keller, S.: NS+EM-MoM6, 3
 Kelley, M.: VT+MN+NS+SS+AS-TuA4, 19
 Kent, T.F.: NS+EM-MoM2, 2
 Kersell, H.: NS-ThM6, 38
 Kikuchi, Y.: TC+EM+NS-ThA10, 45
 Kim, B.: NM+NS+MS-TuA12, 17
 Kim, D.: NS-ThM3, 38
 Kim, H.: EM1-MoA1, 4
 Kim, H.J.: NS-TuP12, 23
 Kim, J.: NS+EM-MoM8, 3
 Kim, J.K.: NS+EM-MoM1, 2
 Kim, M.: GR+TF+NS-ThA1, 42
 Kim, S.: EN+EM+NS-MoA9, 7; EN+EM+NS-WeM12, 27; NM+NS+MS-TuA12, 17; NS+AS-TuA1, 17
 Kim, T.H.: ET+EM+NS+GR-TuM6, 11
 King, W.P.: GR+TF+NS-ThA9, 43
 Kioussis, N.: GR+TF+NS-ThA8, 43
 Klem, E.J.D.: EM1-MoA11, 5; EN+EM+NS-MoA3, 6
 Klimov, V.I.: EN+NS-TuM3, 10
 Knezevic, I.: ET+EM+NS+GR-TuM5, 11
 Knudsen, J.: NS-WeM2, 31
 Kobayashi, N.P.: EN+NS-TuA11, 15
 Kodambaka, S.: NS-TuM6, 13
 Kohl, P.A.: EN+NS-ThM10, 35
 Kong, J.: ET+EM+NS+GR-TuM2, 11
 Kong, L.: EN+NS-ThA3, 40
 Kono, Y.: NS-ThA9, 44
 Korolkov, V.V.: AS+BI+NS-WeM12, 25
 Kortshagen, U.: EN+EM+NS-WeM1, 25
 Kostamo, J.: NM+MS+NS+TF-MoM6, 1
 Kouda, M.: NM+MS+NS+TF-MoM5, 1
 Kreit, E.: TC+EM+NS-ThA6, 45
 Krim, J.: VT+MN+NS+SS+AS-TuA3, 19
 Kuchibhatla, S.V.N.T.: EM1-MoA2, 4; NS-TuP3, 22
 Kuk, Y.: NS+AS-TuA1, 17; NS+EM-MoM5, 2
 Kumar, A.: NS-WeM11, 32
 Kummel, A.C.: NS-ThA9, 44
 Kung, P.: EN+EM+NS-WeM12, 27
 Kung, S.: NS-TuP1, 22
 Kurokawa, A.: NS-TuP2, 22
 Kwon, J.: NS+EM-MoM5, 2

— **L** —

LaBella, V.P.: AS+BI+NS-WeM11, 25
 Lagally, M.G.: ET+EM+NS+GR-TuM5, 11; NS-MoA11, 9
 Laibinis, P.: BI+AS+NS+SS-WeA10, 34
 Landt, L.: NS-ThM1, 38
 Langhammer, C.B.: BI+AS+NS+SS-WeA4, 33

Langreth, D.C.: EN+NS-ThA3, 40
 Lanza, G.: VT+MN+NS+SS+AS-TuA12, 21
 Laracunte, A.R.: GR+TF+NS-ThA9, 43
 Larsson, E.M.K.: BI+AS+NS+SS-WeA4, 33
 Lawrie, J.: BI+AS+NS+SS-WeA10, 34
 Le, T.P.: EN+EM+NS-WeM11, 27
 Lecordier, L.: NM+MS+NS+TF-MoM3, 1
 Lee, D.H.: TC+EM+NS-ThA3, 44
 Lee, G.S.: NS-ThM12, 39
 Lee, J.: NM+NS+MS-TuA12, 17
 Lee, J.R.I.: NS-ThM11, 38
 Lee, K.: NS-TuP4, 22
 Lee, K.H.: NS-ThM12, 39
 Lee, S.: NM+NS+MS-TuA12, 17
 Lee, S.B.: EN+NS-ThA4, 40
 Lee, T.: NM+NS+MS-TuA12, 17
 Lee, W.K.: GR+NS+PS+SS-ThM12, 37; GR+TF+NS-ThA9, 43; NS-WeM6, 31
 Lee, Y.T.: NS+EM-MoM1, 2
 Leever, B.J.: EN+NS-WeM2, 27; EN+NS-WeM4, 28
 Leggett, G.: BI+AS+NS+SS-WeA9, 34
 Lehto, T.: NM+MS+NS+TF-MoM6, 1
 Lewis, J.: EM1-MoA11, 5; EN+EM+NS-MoA3, 6
 Li, A.-P.: ET+EM+NS+GR-TuM1, 11; ET+EM+NS+GR-TuM6, 11
 Li, J.: EN+NS-ThA3, 40
 Li, L.: GR+TF+NS-ThA11, 43
 Li, M.: NS+EM-MoM8, 3
 Li, Q.: NS+AS-TuA7, 18; NS-ThM10, 38
 Li, Y.: VT+MN+NS+SS+AS-TuA11, 20
 Li, Y.Y.: GR+TF+NS-ThA11, 43
 Liang, T.: GR+NS+PS+SS-ThM10, 37
 Liang, W.: ET+EM+NS+GR-TuM6, 11
 Liberman, A.: NS-ThA9, 44
 Liddell, K.: NS+EM-MoM8, 3
 Lidzey, D.: BI+AS+NS+SS-WeA9, 34
 Lim, S.J.: NS+EM-MoM5, 2
 Lin, M.-W.: GR+TF+NS-ThA8, 43
 Lin, P.: NS-TuM2, 12; NS-WeM11, 32
 Lin, S.-H.: EN+EM+NS-MoA1, 6
 Ling, C.: GR+TF+NS-ThA8, 43
 Lipson, A.L.: NS-WeM3, 31
 Liu, C.: ET+EM+NS+GR-TuM12, 12
 Liu, C.Y.: EN+EM+NS-WeM1, 25
 Liu, F.: EM1-MoA2, 4
 Liu, G.: NM+MS+NS+TF-MoM3, 1
 Liu, L.: ET+EM+NS+GR-TuM6, 11
 Liu, T.-L.: NS-MoA6, 8
 Liu, X.: VT+MN+NS+SS+AS-TuA11, 20
 Liu, Y.: GR+TF+NS-ThA11, 43; TC+EM+NS-ThA11, 45
 Lohn, A.J.: EN+NS-TuA11, 15
 Lopez, G.P.: BI+AS+NS+SS-WeA9, 34
 Lopez-Bezanilla, A.: GR+TF+NS-ThA6, 42
 Louis, K.: BI+AS+NS+SS-WeA3, 33
 Lu, B.: NM+NS+MS-TuA3, 16
 Lu, J.: EN+NS-ThM3, 35
 Lu, W.: EM1-MoA1, 4; NS-ThM3, 38
 Lu, Y.C.: EN+NS-ThA2, 40
 Lukaszew, R.A.: NS-MoA9, 8; VT+MN+NS+SS+AS-TuA8, 20; VT+MN+NS+SS+AS-TuA9, 20
 Luo, M.: NS-ThM3, 38

— **M** —

Machida, M.: NS+AS-TuA1, 17
 MacQuarrie, E.R.: NS-MoA1, 7
 Maehashi, K.: GR+NS+PS+SS-ThM9, 37; NS-WeM10, 32
 Magel, G.A.: NM+NS+MS-TuA11, 17
 Maier, M.: NS+AS-TuA11, 18
 Maier, S.: GR+NS+PS+SS-ThM3, 36
 Majidi, H.: EN+EM+NS-WeM11, 27
 Maksymovych, P.: NS+AS-TuA7, 18
 Malinen, T.: NM+MS+NS+TF-MoM6, 1
 Malko, A.V.: EN+NS-TuM1, 10
 Mansour, A.N.: EN+NS-ThA2, 40
 Marchesini, G.: NS-ThM2, 38
 Marchman, H.M.: NM+NS+MS-TuA11, 17

Marks, T.J.: EN+NS-WeM2, 27; EN+NS-WeM3, 27; EN+NS-WeM4, 28
 Markus, T.Z.: NS-ThM9, 38
 Martinez, H.P.: NS-ThA9, 44
 Matsumoto, K.: GR+NS+PS+SS-ThM9, 37; NS-WeM10, 32
 Matsunaga, S.: AS+BI+NS-WeM5, 24
 Matthes, F.: NS+AS-TuA11, 18
 Mattrey, R.F.: NS-ThA9, 44
 Mayer, J.S.: NS+EM-MoM8, 3
 Mayer, T.S.: NS+EM-MoM8, 3
 Mayo, A.T.: NS-TuP8, 23
 Mayo, D.C.: NS-TuP8, 23
 McCarthy, J.: BI+AS+NS+SS-WeA3, 33
 McCullough, R.D.: TC+EM+NS-ThA4, 45
 Mecklenburg, M.: NS-TuM6, 13
 Melechko, A.V.: NS+EM-MoM10, 3
 Meunier, V.: ET+EM+NS+GR-TuM2, 11
 Michely, T.: NS-WeM2, 31
 Mikkelsen, A.: NS-TuM3, 13
 Miller, S.: EM1-MoA10, 5
 Mills, M.J.: NS+EM-MoM2, 2
 Mishra, U.K.: NS+EM-MoM6, 3
 Mohanty, A.: EN+NS-WeM5, 28
 Mönig, H.: NS+AS-TuA4, 17
 Moore, T.M.: NM+NS+MS-TuA11, 17
 Morris-Cohen, A.: EN+NS-TuM11, 11
 Morrow, T.: NS+EM-MoM8, 3
 Mu, R.: EN+NS-ThA10, 41; NS-TuP8, 23
 Murayama, A.: EN+EM+NS-MoA1, 6
 Murray, I.P.: EN+NS-WeM2, 27
 Muscat, A.J.: EM1-MoA10, 5
 Musho, T.D.: EN+NS-TuM10, 10
 Musin, I.R.: EN+EM+NS-WeM3, 26; NS-TuM11, 14
 Myers, R.C.: NS+EM-MoM2, 2
 Myers-Ward, R.L.: NS-WeM6, 31

— N —

Naaman, R.: NS-ThM9, 38
 Nachimuthu, P.: NS-TuP3, 22; NS-TuP7, 23
 Nag, J.: NS-MoA1, 7
 Nagpal, P.: EN+EM+NS-MoA6, 6
 Nahor, A.: EN+EM+NS-WeM6, 26
 Naik, R.R.: AS+BI+NS-WeM6, 24
 Najafi, E.: NS-WeM12, 32
 Nakayama, K.S.: NS-TuM1, 12
 Nam, S.: NM+NS+MS-TuA12, 17
 Nanayakkara, S.: AS+BI+NS-WeM10, 25; NS-MoA10, 8
 Nandasiri, M.L.: NS-TuP3, 22
 Nath, D.N.: NS+EM-MoM6, 3
 Nelson, A.: NS-MoA9, 8
 Neppel, S.: EN+NS-TuM2, 10
 Ngo, C.: NS-TuM6, 13
 Nguyen, H.M.: EN+NS-TuM1, 10
 Nijem, N.: EN+NS-ThA3, 40
 Noh, J.: TC+EM+NS-ThA6, 45
 Noh, J.H.: TC+EM+NS-ThA6, 45
 Nomura, K.: TC+EM+NS-ThA10, 45; TC+EM+NS-ThA3, 44; TC+EM+NS-ThA9, 45
 Norris, D.J.: EN+NS-TuA1, 15
 Nottbohm, C.T.: GR+NS+PS+SS-ThM4, 36
 Nyakiti, L.O.: NS-WeM6, 31

— O —

Odaka, K.: NS-TuP2, 22
 Oertel, M.: NS+AS-TuA11, 18
 Ogawa, S.: HI+AS+BI+NS-WeM3, 29
 Oh, Y.: NS+AS-TuA1, 17; NS+EM-MoM5, 2
 Ohno, Y.: EN+EM+NS-MoA1, 6; GR+NS+PS+SS-ThM9, 37; NS-WeM10, 32
 Okuda, S.: NS-WeM10, 32
 Oldham, C.J.: EM1-MoA9, 5
 Onishi, K.: HI+AS+BI+NS-WeM12, 30
 Orr, G.: HI+AS+BI+NS-WeM11, 30
 Overzet, L.J.: NS-ThM12, 39

— P —

P. Ryan Fitzpatrick, P.R.: NM+MS+NS+TF-MoM8, 1
 Paiella, R.: NS-MoA11, 9
 Palmer, M.A.: VT+MN+NS+SS+AS-TuA11, 20
 Pan, M.H.: ET+EM+NS+GR-TuM2, 11; NS+AS-TuA7, 18
 Pan, X.: EN+EM+NS-MoA9, 7
 Pan, Z.: NS-TuP8, 23
 Pantelides, S.T.: GR+NS+PS+SS-ThM6, 37
 Park, H.: EN+NS-ThA10, 41
 Park, P.S.: NS+EM-MoM6, 3
 Park, T.: NS-MoA10, 8
 Parsons, G.N.: EM1-MoA9, 5; NS-TuP4, 22
 Pascual Garcia, C.: NS-ThM2, 38
 Paskiewicz, D.M.: NS-MoA11, 9
 Paskova, T.: EM1-MoA2, 4
 Pasquale, F.: EM1-MoA8, 5
 Paul, D.F.: NS-TuM10, 14
 Paxton, W.F.: EN+NS-TuA12, 15
 Pellin, M.J.: NS-WeM3, 31
 Peng, W.N.: ET+EM+NS+GR-TuM5, 11
 Penner, R.: NS-TuP1, 22
 Peppermick, S.: NS-MoA8, 8
 Pereira, N.: EN+NS-ThM2, 35
 Perera, A.G.U.: EM1-MoA4, 4
 Perera, U.G.E.: EN+NS-TuM9, 10; NS-ThM6, 38
 Perez Roldan, M.J.: NS-ThM2, 38
 Perez, R.: NS+AS-TuA4, 17
 Persson, O.: NS-TuM3, 13
 Petkovich, N.: EN+NS-ThM5, 35
 Phillips, J.: EN+EM+NS-MoA9, 7
 Phillips, P.J.: NS+EM-MoM2, 2
 Phillipot, S.R.: GR+NS+PS+SS-ThM10, 37
 Phillipot, S.R.: EN+NS-WeM10, 28
 Pickard, D.S.: HI+AS+BI+NS-WeM9, 30
 Pilvi, T.: NM+MS+NS+TF-MoM6, 1
 Plaisant, M.: EN+EM+NS-MoA8, 7
 Pleticha, F.D.: EN+NS-WeM10, 28
 Poelsema, B.: HI+AS+BI+NS-WeM5, 29
 Porter, L.: EM1-MoA2, 4; TC+EM+NS-ThA4, 45
 Potash, R.A.: TC+EM+NS-ThA4, 45
 Pozuelo, M.: NS-TuM6, 13
 Preble, E.A.: EM1-MoA2, 4
 Prinz, F.: EN+NS-ThA6, 41

— Q —

Qian, Y.: EN+NS-ThM5, 35
 Qin, S.: ET+EM+NS+GR-TuM1, 11; ET+EM+NS+GR-TuM6, 11
 Quinlan, R.A.: EN+NS-ThA2, 40

— R —

Rack, P.D.: NM+NS+MS-TuA11, 17; NS+EM-MoM10, 3; TC+EM+NS-ThA6, 45
 Rahman, T.S.: NS-TuM12, 14
 Rajan, S.: NS+EM-MoM6, 3
 Ramanathan, S.: NM+NS+MS-TuA3, 16
 Rangan, S.: EN+NS-ThM2, 35
 Rapenne, G.: NS-ThM6, 38
 Reece, C.: VT+MN+NS+SS+AS-TuA9, 20
 Regan, B.C.: NS-TuM6, 13
 Reimhult, E.: NS-ThA4, 43
 Reinecke, T.L.: GR+NS+PS+SS-ThM12, 37
 Remmert, J.L.: AS+BI+NS-WeM6, 24
 Reshchikov, M.A.: EM1-MoA3, 4
 Reutt-Robey, J.E.: EN+NS-ThA1, 40
 Roach, W.M.: VT+MN+NS+SS+AS-TuA9, 20
 Roberts, C.J.: AS+BI+NS-WeM12, 25
 Roberts, N.A.: NM+NS+MS-TuA11, 17
 Robey, S.W.: EN+NS-WeM9, 28
 Robinson, J.T.: GR+NS+PS+SS-ThM1, 36; GR+NS+PS+SS-ThM2, 37; GR+NS+PS+SS-ThM5, 37; GR+TF+NS-ThA9, 43; NS-WeM6, 31
 Robinson, Z.R.: NS-WeM1, 30
 Rodil, S.E.: EN+NS-ThA9, 41
 Rogers, B.R.: BI+AS+NS+SS-WeA10, 34
 Rossi, F.J.: NS-ThM2, 38
 Rossouw, D.: NS-WeM12, 32

Rubloff, G.W.: EN+NS-ThA11, 42; EN+NS-ThA4, 40
 Rudisill, S.: EN+NS-ThM5, 35
 Ruoff, R.S.: NM+NS+MS-TuA9, 16; NS-WeM1, 30
 Rusli, F.: EN+NS-ThM10, 35
 Russell, K.J.: NS-MoA6, 8

— S —

Sa'ar, A.: EN+EM+NS-WeM6, 26
 Safron, N.: GR+TF+NS-ThA1, 42
 Saito, N.: NS-WeM9, 32
 Salmeron, M.: GR+NS+PS+SS-ThM3, 36
 Samatova, N.: NS+EM-MoM10, 3
 Samuelson, L.: NS-TuM3, 13; NS-TuM4, 13
 Samukawa, S.: EN+EM+NS-MoA1, 6
 Sanchez-Perez, J.R.: NS-MoA11, 9
 Sandler, N.: GR+TF+NS-ThA3, 42
 Sanghavi, S.P.: NS-TuP7, 23
 Sankaran, R.M.: NS-TuM2, 12; NS-WeM11, 32
 Santis, S.De.: VT+MN+NS+SS+AS-TuA11, 20
 Sauer, M.: GR+NS+PS+SS-ThM4, 36
 Savage, D.E.: ET+EM+NS+GR-TuM5, 11
 Schmidt, A.B.: NS+AS-TuA12, 19
 Schneider, C.M.: NS+AS-TuA11, 18
 Schnietz, M.: GR+NS+PS+SS-ThM4, 36
 Schönherr, H.: BI+AS+NS+SS-WeA7, 33
 Schreiber, D.K.: EM1-MoA2, 4
 Schreiner, P.R.: NS-ThM11, 38
 Schuette, M.: EM1-MoA1, 4
 Schulte, K.: NS-WeM2, 31
 Schüpbach, B.: EN+NS-TuM2, 10
 Schwarz, U.D.: NS+AS-TuA4, 17
 Schweikert, E.A.: BI+AS+NS+SS-WeA1, 33
 Schwendemann, T.C.: NS+AS-TuA4, 17
 Scott, S.: ET+EM+NS+GR-TuM5, 11
 Segalman, R.A.: EN+NS-TuA9, 15
 Seitz, O.: EN+NS-TuM1, 10
 Senevirathna, I.: EM1-MoA4, 4
 Sershen, M.: NM+MS+NS+TF-MoM3, 1
 Shafai, G.: NS-TuM12, 14
 Shao-Horn, Y.: EN+NS-ThA2, 40
 Sheehan, P.E.: GR+NS+PS+SS-ThM12, 37; GR+NS+PS+SS-ThM5, 37; GR+TF+NS-ThA9, 43; NS-WeM6, 31
 Shen, G.: EN+EM+NS-WeM12, 27
 Shin, N.: EN+EM+NS-WeM3, 26; NS-TuM9, 13
 Shutthanandan, V.: HI+AS+BI+NS-WeM11, 30; NS-TuP3, 22; NS-TuP7, 23
 Sikora, J.P.: VT+MN+NS+SS+AS-TuA11, 20
 Silva-Bermudez, P.: EN+NS-ThA9, 41
 Singh, K.A.: TC+EM+NS-ThA4, 45
 Sinnott, S.B.: EN+NS-WeM10, 28; GR+NS+PS+SS-ThM10, 37
 Sivaram, S.: EN+EM+NS-MoA7, 6; EN+EM+NS-WeM3, 26
 Smith, G.: NS-TuP6, 22
 Smith, N.J.: EN+EM+NS-WeM5, 26
 Song, W.: EN+NS-ThA1, 40
 Sowa, M.: NM+MS+NS+TF-MoM3, 1
 Stein, A.: EN+NS-ThM5, 35
 Stetcher, J.: NS-MoA10, 8
 Stine, R.: GR+NS+PS+SS-ThM12, 37; GR+NS+PS+SS-ThM5, 37; GR+TF+NS-ThA9, 43
 Strachan, J.P.: NM+NS+MS-TuA7, 16
 Stratman, P.: NS-WeM2, 31
 Strocio, J.A.: VT+MN+NS+SS+AS-TuA1, 19
 Stumper, J.: EN+NS-ThA8, 41
 Sudradjat, F.: NS-MoA11, 9
 Suh, H.: NS+AS-TuA1, 17
 Sun, D.: NS-ThM3, 38
 Sun, K.: NS+EM-MoM8, 3
 Sundaram, G.M.: NM+MS+NS+TF-MoM3, 1
 Susac, D.: EN+NS-ThA8, 41
 Sussman, J.: EN+NS-WeM5, 28
 Sutter, P.: NS+AS-TuA10, 18
 Suyatin, D.: NS-TuM3, 13
 Suzuki, T.: NM+MS+NS+TF-MoM5, 1
 Sweet, W.: EM1-MoA9, 5

Szakal, C.: BI+AS+NS+SS-WeA3, **33**

— **T** —

Taborelli, M.: VT+MN+NS+SS+AS-TuA12, 21
Takai, O.: NS-WeM9, 32
Talapin, D.V.: EN+NS-TuA3, **15**
Tamanaha, C.R.: GR+NS+PS+SS-ThM12, 37;
GR+NS+PS+SS-ThM5, 37; NS-WeM6, 31
Temple, D.: EM1-MoA11, 5; EN+EM+NS-MoA3,
6
Tendler, S.J.B.: AS+BI+NS-WeM12, 25
Terfort, A.: EN+NS-TuM2, 10
Terminello, L.J.: NS-TuP7, 23
Textor, M.: NS-ThA4, 43
Therien, M.: NS-MoA10, 8
Thevuthasan, S.: NS-TuP3, 22; NS-TuP7, 23
Thorpe, R.: EN+NS-ThM2, **35**
Timm, R.: NS-TuM3, 13
Tisdale, W.A.: EN+NS-TuM5, **10**
Tizazu, G.: BI+AS+NS+SS-WeA9, 34
Tkachenko, B.A.: NS-ThM11, 38
Todorovic, M.: NS+AS-TuA4, 17
Toivola, M.: NM+MS+NS+TF-MoM6, 1
Toker, G.: EN+EM+NS-WeM6, 26
Tolic, A.: HI+AS+BI+NS-WeM11, 30
Tolk, N.H.: EN+NS-ThA10, 41
Tomp, G.S.: EN+NS-TuA11, 15
Trogler, W.: NS-ThA9, 44
Tseng, C.T.: EN+NS-WeM12, 29
Tseng, W.H.: EN+NS-WeM12, 29
Tsuda, N.: NS-WeM9, **32**
Turchanin, A.: GR+NS+PS+SS-ThM4, **36**;
HI+AS+BI+NS-WeM6, 30
Tweedie, J.S.: EM1-MoA4, 4
Tyagi, P.: NS-WeM1, **30**
Tyler, T.P.: EN+NS-WeM3, 27

— **U** —

Ueda, A.: NS-TuP8, 23
Ueno, T.: NS-WeM9, 32
Urban, J.: EN+NS-TuA9, 15

— **V** —

Valente-Feliciano, A.-M.: VT+MN+NS+SS+AS-
TuA10, **20**
Valla, T.: NS-WeM1, 30
van Buuren, T.: NS-ThM11, 38
van Gastel, R.: HI+AS+BI+NS-WeM5, 29
Varga, K.: GR+TF+NS-ThA4, 42
Varga, T.: NS-TuP3, 22
Vasudev, M.C.: AS+BI+NS-WeM6, 24
Veligura, V.: HI+AS+BI+NS-WeM5, **29**

Venkataraman, L.: NS-ThM4, **38**

Venstrom, L.: EN+NS-ThM5, 35
Ventrice, Jr., C.A.: NS-WeM1, 30
Vives, G.: NS-ThM6, 38
Voevodin, A.A.: AS+BI+NS-WeM6, 24
von Wenckstern, H.: TC+EM+NS-ThA1, **44**
Vu, A.: EN+NS-ThM5, 35

— **W** —

Wada, T.: NS-TuM1, 12
Wager, J.F.: TC+EM+NS-ThA7, **45**
Walker, D.G.: EN+NS-TuM10, 10
Walker, M.J.: VT+MN+NS+SS+AS-TuA3, 19
Wallentin, J.: NS-TuM3, 13
Walton, S.G.: GR+NS+PS+SS-ThM12, **37**; NS-
WeM6, 31
Wang, B.: GR+NS+PS+SS-ThM6, **37**
Wang, E.: ET+EM+NS+GR-TuM6, 11
Wang, J.: NS-MoA8, 8
Wang, J.Y.: EN+NS-WeM12, 29
Wang, L.: NS-MoA9, 8
Wang, M.: EN+NS-WeM1, **27**
Wang, Q.H.: NS-WeM3, 31
Wang, W.: ET+EM+NS+GR-TuM6, 11
Wang, W.L.: GR+TF+NS-ThA8, 43
Wang, X.-Y.: EN+EM+NS-MoA1, 6
Wang, Y.: NS-MoA8, 8
Watkins, S.: ET+EM+NS+GR-TuM12, 12
Wei, W.D.: NS-MoA8, **8**
Weiss, E.A.: EN+NS-TuM11, **11**
Weiss, S.M.: BI+AS+NS+SS-WeA10, 34
Wernersson, L.-E.: NS+EM-MoM3, **2**
Wheeler, V.D.: NS-WeM6, 31
Wilbert, S.: EN+EM+NS-WeM12, 27
Willey, T.M.: NS-ThM11, **38**
Williams, R.S.: NM+NS+MS-TuA7, 16
Wolter, D.: NS-ThM11, 38
Won, B.: NS+EM-MoM8, 3
Wu, A.T.: VT+MN+NS+SS+AS-TuA7, **19**
Wu, C.I.: EN+NS-WeM12, 29
Wu, H.: EN+NS-ThA3, 40
Wu, J.T.: NS-TuP11, 23
Wu, W.: EN+NS-ThM3, 35
Wu, Z.: NS-ThA9, 44
Wulff, K.: NS+AS-TuA12, **19**
Wyrick, J.: NS-ThM3, 38

— **X** —

Xiao, K.: EM1-MoA6, 5
Xiao, Z.: NS-TuP9, **23**
Xie, Y.: HI+AS+BI+NS-WeM11, 30

Xie, Z.: NS-ThM9, 38

Xing, W.: NS-TuP1, **22**
Xiong, G.: NS-MoA8, 8
Xu, Y.: NS-ThA6, 44

— **Y** —

Yaffe, O.: EN+NS-WeM11, **29**
Yamada, S.: NM+NS+MS-TuA12, 17
Yamada, T.: AS+BI+NS-WeM5, **24**
Yang, H.: NS-WeM1, 30
Yang, J.: EN+EM+NS-WeM1, 25; NS+EM-
MoM2, 2
Yang, K.: NS-MoA9, 8
Yang, P.: NS-TuP7, 23
Yasuda, T.: NM+MS+NS+TF-MoM5, 1
Yee, S.: EN+NS-TuA9, 15
Yeh, B.: TC+EM+NS-ThA7, 45
Yeo, J.: NM+NS+MS-TuA12, **17**
Yeung, K.: NS-MoA6, 8
Yin Vallgren, C.: VT+MN+NS+SS+AS-TuA12,
21
Yin, W.: EM1-MoA6, 5
Yip, C.: AS+BI+NS-WeM3, **24**
Yitzchaik, S.: EN+EM+NS-WeM6, 26
Yokoyama, Y.: NS-TuM1, 12
Yoo, W.: NM+NS+MS-TuA12, 17

— **Z** —

Zahl, P.: NS+AS-TuA10, 18
Zandvliet, H.: HI+AS+BI+NS-WeM5, 29
Zavadii, K.R.: EN+NS-ThA1, 40
Zettsu, N.: NS-WeM9, 32
Zhang, B.: TC+EM+NS-ThA11, **45**
Zhang, L.: NS-TuP2, 22
Zhang, M.: EM1-MoA2, 4
Zhang, Y.: EN+NS-TuM9, **10**; GR+TF+NS-ThA8,
43; NS-ThM6, 38
Zhang, Z.: EN+NS-ThM3, 35
Zhao, Y.: EN+NS-ThA3, 40
Zharnikov, M.: EN+NS-TuM2, **10**
Zhdanov, V.P.: BI+AS+NS+SS-WeA4, 33
Zheng, Z.: GR+NS+PS+SS-ThM4, 36
Zhong, X.: NS+EM-MoM8, 3
Zhou, H.: NS-TuM6, 13
Zhou, Z.X.: GR+TF+NS-ThA8, **43**
Zhu, L.: EN+NS-ThA10, 41
Zhu, Y.: NS-ThM3, 38
Zoric, I.L.: BI+AS+NS+SS-WeA4, **33**
Zulkifli, A.R.: BI+AS+NS+SS-WeA11, 34