

Monday Morning, October 18, 2010

Nanometer-scale Science and Technology

Room: La Cienega - Session NS-MoM

Oxide Based Nanoelectronics

Moderator: C. Nakakura, Sandia National Laboratories

8:40am **NS-MoM2 Oxidation Kinetics of Electron Beam Evaporated Nano Copper Thin Films by Kelvin Probe Measurements**, A. *Subrahmanyam*, IIT Madras, India

Copper is a very good interconnect in microelectronics because it has a high thermal and electrical conductivities and low electromigration resistance. However, the formation of an oxide layer on Cu (even at room temperature) induces trap states at the Cu/Cu oxide interface that can ultimately cause a decrease in its thermal and electrical conductivities, as well as a significant degradation in its interconnection capabilities. These effects become more and more critical when the copper is in nano form for use in ULSI. The partial oxides of copper can also be a very good candidate for plasmonic structures.

Copper exhibits two valences. The size effects and partial oxidation of copper bring significant changes in the electrical resistivity. Thus the surface oxidation kinetics of nano copper are important. In the present communication, pure copper thin films have been prepared by electron beam evaporation technique on cleaned glass substrates at 500 K. The thickness is varied in the range : 20 nm to 300 nm. The electrical resistivity of these films ranges from $5.201 \times 10^6 \Omega \text{ cm}$ to $9.206 \times 10^6 \Omega \text{ cm}$. The carrier concentration and electron mobility have been evaluated by Hall measurements. In order to follow the surface oxidation kinetics of copper thin films with varying grain sizes exposed to the ambient at 300K, the contact potential (cpd) / work function measurements by Kelvin probe technique have been performed. The increase in the contact potential difference (cpd) indicates the oxidation kinetics of these films.

9:00am **NS-MoM3 Hot-wire Chemical Vapor Deposition of Tungsten Oxide Nanoparticles for Use in Energy Applications**, C.-P. *Li*, C.A. *Wolden*, Colorado School of Mines, R. *Tenent*, A.C. *Dillon*, National Renewable Energy Laboratory

Crystalline tungsten oxide nanoparticles were synthesized by hot-wire chemical vapor deposition (HWCVD). These materials are being examined for use in numerous energy related applications including electrochromic windows and fuel cells. It is possible to tune the particle morphology by changing key synthesis parameters including filament temperature, substrate temperature, and oxygen partial pressure. The resulting nanostructures are characterized by a number of techniques including transmission electron microscopy, X-ray diffraction, and Raman spectroscopy. The dependence of nanoparticle size and morphology will be described both as a function of HWCVD synthesis conditions as well as post-deposition annealing treatments. The resulting nanoparticles are suspended in solution and used to form thin films on transparent conducting oxide coated glass substrates using an ultrasonic spray deposition process. Ultrasonic spray coating is a cost effective, scalable deposition process that offers an excellent route to achieve large-scale implementation of electrochromic films. Important ultrasonic spray variables include substrate temperature, precursor concentration, carrier solvent and other parameters related to solution atomization. The electrochromic properties of these films were characterized by performing cyclic voltammetry in registry with *in situ* measurements of optical transmission. Particular attention is paid to optimizing performance metrics such as coloration efficiency and cycling stability. Using the measurements described above, we will evaluate the important process-structure-performance relationships in these systems.

9:20am **NS-MoM4 Monitoring Charge Storage Processes in Nanoscale Oxides using Electrochemical Scanning Probe Microscopy**, K.R. *Zavadil*, J. *Huang*, P. *Lu*, Sandia National Laboratories

Advances in electrochemical energy storage science require the development of new or the refinement of existing *in situ* probes that can be used to establish structure – activity relationships for technologically relevant materials. The drive to develop reversible, high capacity electrodes from nanoscale building blocks creates an additional requirement for high spatial resolution probes to yield information of local structural, compositional, and electronic property changes as a function of the storage state of a material. In this paper, we describe a method for deconstructing a lithium ion battery positive electrode into its basic constituents of ion insertion host particles and a carbon current collector. This model system is then probed in an electrochemical environment using a combination of atomic force microscopy and tunneling spectroscopy to correlate local

activity with morphological and electronic configurational changes. Cubic spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ nanoparticles are grown on graphite surfaces using vacuum deposition methods. The structure and composition of these particles are determined using transmission electron microscopy and Auger microprobe analysis. The response of these particles to initial de-lithiation, along with subsequent electrochemical cycling, is tracked using scanning probe microscopy techniques in polar aprotic electrolytes (lithium hexafluorophosphate in ethylene carbonate:diethylcarbonate). The relationship between nanoparticle size and reversible ion insertion activity will be a specific focus of this paper.

This work is funded within the Nanostructures for Electrical Energy Storage, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DESC0001160. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for US DOE's NNSA under contract DE-AC04-94AL85000.

9:40am **NS-MoM5 Tuning Superconductivity at the $\text{LaAlO}_3/\text{SrTiO}_3$ Interface**, A.D. *Caviglia*, S. *Gariglio*, N. *Reyren*, C. *Cancellieri*, A. *Fête*, University of Geneva, Switzerland, M. *Gabay*, University of Paris-Sud, France, J.-M. *Triscone*, University of Geneva, Switzerland **INVITED**

Electronic states with unusual properties can be promoted at interfaces between complex oxides [1]. A striking example is the interface between the band insulators LaAlO_3 and SrTiO_3 , which displays conductivity with high mobility and 2D superconductivity [2,3]. We will discuss recent experiments that revealed the sensitivity of the normal and superconducting state to external electric fields. Using the electrostatic field effect, the phase diagram of the system has been mapped out, revealing a quantum phase transition between a superconducting state and an insulating state [4]. We will also lay out an example of an electronic property arising from the interfacial breaking of inversion symmetry, namely a large spin-orbit interaction, whose magnitude can be modulated by the application of an external electric field [5].

[1] E. Dagotto, *Science* **318**, 1076 (2007)

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10:40am **NS-MoM8 Fabrication and Characterization of Ferroelectric BiFeO_3 Nanocapacitors for Next Generation FeRAMS**, L.E. *Ocola*, S. *Hong*, R. *Nath Premnath*, W. *Li*, Argonne National Laboratory, S. *Jackson*, Illinois Mathematics and Science Academy, R. *Kattiyar*, University of Puerto Rico, O.H. *Auciello*, Argonne National Laboratory

11:00am **NS-MoM9 Polarization-Dependent Electron Transport in Thin Films of Uni- and Multiaxial Ferroelectrics**, P. *Maksymovych*, Oak Ridge National Laboratory, J. *Seidel*, University of California, Berkeley, S. *Jesse*, Oak Ridge National Laboratory, P. *Yu*, Y.-H. *Chu*, University of California, Berkeley, A.P. *Baddorf*, Oak Ridge National Laboratory, R. *Ramesh*, University of California, Berkeley, S.V. *Kalinin*, Oak Ridge National Laboratory

The intrinsic coupling of soft-phonon order parameters and electron transport in ferroic materials can usher a wide range of novel physical phenomena with potential for new applications in information technology, energy harvesting and quantum computing. In this talk we will present local conductivity and piezoresponsive measurements on the surfaces of uniaxial ($\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$) and multiaxial (BiFeO_3) perovskite ferroelectrics, with film thicknesses ranging from 30 nm to 100 nm. Conductive atomic force microscopy revealed that most of these films possesses highly non-linear, and often hysteretic current-voltage characteristics, and in many cases the hystereses could be correlated to local polarization switching induced by the electric field of the AFM tip. In lead zirconate titanate, the large spontaneous polarization produced up to 500-fold enhancement of local conductivity, and the film remained sufficiently conducting in the bias-region significantly smaller than the switching voltage. As a result, this effect can be used for a non-destructive and resistive read-out of the polarization state on length-scales down to 10 nm, implementing a prototypical memory function. Extending the I-V measurements to low-temperatures revealed a strong exponential dependence of the conductivity.

We developed a novel analysis scheme, which enabled identifying trap-assisted Fowler-Nordheim tunneling and Poole-Frenkel hopping as two dominant mechanisms behind non-linear I-V curves. Curiously, we have been able to separate the contributions due to interface- and bulk-limited conduction, as well as to visualize spatially-resolved variations due to each transport regime.

We will further discuss the peculiarities of local electron transport through BiFeO₃, and in particular the mechanism behind local conductivity of 10⁹ ferroelastic domain walls. Based on a statistical analysis of I-V curves and simultaneous measurements of local transport and piezoresponse, we suggest that the domain wall is not a static conducting object under a biased tip, but instead that a transient, local and microscopically reversible topological distortion of polarization structure at the wall contributes to enhanced electron transport. In particular, it produces a seminal example of ferroic memristive functionality.

The measurements were conducted at the Center for Nanophase Materials Sciences sponsored at Oak Ridge National Laboratory by the Division of Scientific User Facilities, U.S. DOE.

[1] P. Maksymovych, S. Jesse, P. Yu, R. Ramesh, A. P. Baddorf, S. V. Kalinin,

Science 324 (2009) 1421.

[2] P. Maksymovych, J. Seidel et. al, submitted (2010)

11:20am **NS-MoM10 Observation of Unintentionally Incorporated Nitrogen Complexes in Vapor-Liquid-Solid Grown ZnO and GaN Nanowires**, *A. Souidi, Y. Gu*, Washington State University

Semiconductor nanowires have been intensively explored as building blocks for the next-generation electronic and opto-electronic devices. Further advances towards real-world applications require a reliable and precise control of material properties, which, to a large extent, are determined by impurities. Controlled incorporation of functional impurities enables an impurity-engineering approach, whereby novel material properties can be engineered based on the interactions between impurities and the one-dimensional material host. On the other hand, unintentional impurity incorporation can be significant in determining nanowire electronic properties. Therefore, efforts towards identifying impurity species, especially those incorporated unintentionally, as well as understanding their microscopic structures and effects on material properties, are critical to advancing nanowire-based device technologies.

To this end, Raman scattering spectroscopy provides an effective approach to probing impurity incorporation in various materials. When complemented by mass spectrometry studies, this technique can enable unambiguous identifications of impurity species by their vibrational frequencies (i.e. impurity vibrational modes). As impurity vibrational characteristics are sensitive to the surrounding environment, the lattice locations of these impurity atoms can also be determined. Furthermore, the nanoscale spatial resolution of Raman scattering spectroscopy can provide insightful information on the possible routes of impurity incorporation, shedding light on the relationship between nanowire synthesis conditions and material properties.

In this work, using Raman scattering spectroscopy complemented by mass-selected time-of-flight particle emission techniques, we show the presence of unintentionally incorporated nitrogen complexes (most likely interstitial nitrogen molecules) in ZnO and GaN nanowires grown via the vapor-liquid-solid (VLS) process. Spatially resolved Raman scattering spectra obtained at various locations on single nanowires suggest a possible route of nitrogen incorporations via metal nanocatalysts during the growth. As nitrogen impurities have profound effects on electronic properties of ZnO and GaN, these results have significant implications for current efforts on realizing high-performance opto-electronic device applications based on these nanomaterials. In addition, with the VLS process as one of the most common growth modes for synthesizing semiconductor nanowires, these experimental findings might be relevant for many nanowire systems, signifying the necessity of more studies on unintentional impurity incorporation in these nanomaterials.

Monday Afternoon, October 18, 2010

Graphene Focus Topic

Room: Brazos - Session GR+NS-MoA

Graphene: Chemical Reactions

Moderator: T. Seyller, Universität Erlangen, Germany

2:00pm **GR+NS-MoA1 Chemical Interactions during Thermal Reduction of Multilayered Graphene Oxide**, *M. Acik*, University of Texas at Dallas, *C. Mattevi*, Imperial College London, *C. Gong*, *G. Lee*, *K.J. Cho*, University of Texas at Dallas, *M. Chhowalla*, Imperial College London, *Y.J. Chabal*, University of Texas at Dallas

Graphene/graphite oxide (GO), with its non-stoichiometric chemical structure and highly hygroscopic functionalized graphene backbone, has been of interest for chemical energy storage applications such as supercapacitors and ultracapacitors as well as its reduced form for bioelectronic applications such as sensor networks and for printed electronics. For all these applications, it is important to characterize and control the chemical nature of GO at various stages of thermal reduction. In particular, the formation and evolution of defect structures within GO can greatly impact the resulting properties. Similarly, the properties of species intercalated between individual planes can alter the reduction chemistry. The interplay between intercalated species and defect sites can lead to interesting new chemistry.

To understand these chemical interactions, we have studied the deoxygenation process of both single- and multi-layer(s) of GO and focused on comparing the removal of oxygen upon heating both from the basal plane and the edges, by bringing to bear a number of methods. In particular, we have carried out a series of experiments using *in-situ* IR absorption spectroscopy (FTIR), x-ray diffraction technique (XRD), *ex-situ* raman scattering, thermogravimetric analysis (TGA), transmission electron microscopy (TEM), and x-ray photoelectron spectroscopy (XPS), together with density functional (DFT) calculations and molecular dynamic (MD) simulations of various oxygen structures and resulting electronic states. The IR absorption spectra reveal the formation of ketones, ethers and sp^2 -hybridized C=C as well as a loss of hydroxyls, carboxyls and epoxides upon gradual annealing. They also confirm that defect formation is a direct result of CO_2 and CO formation, and highlight the role of intercalated species, such as water. At higher temperatures ($\sim 850^\circ C$), oxygen is found to remain at the edges of defective sites in a very stable configuration, involving the alignment of edge ether. Overall, the structure of GO upon annealing exhibits interesting, and in some cases unexpected features, which could have a crucial role and applicability to various systems such as vibration-powered energy scavenging, night vision tracking systems and optoelectronics.

*The authors acknowledge funding from the SWAN/NRI program and Texas Instruments.

2:20pm **GR+NS-MoA2 Non-bonding State formed Around Defects on HOPG**, *J. Nakamura*, *T. Kondo*, *J. Oh*, *D. Guo*, *Y. Honma*, *T. Machida*, University of Tsukuba, Japan

Understanding the interface interaction between metal nano-clusters and carbon supports composed of graphite materials is one of the most important needs in the development of carbon related-catalysts. We have studied the carbon support effects on the electrocatalysts for fuel cell as well as the interface interaction using model catalysts of Pt-deposited highly oriented pyrolytic graphite (HOPG) by IETS-STSTM, TPD, and molecular/atomic beam technique. Here, we report the formation of non-bonding state in the vicinity of defects on the HOPG surface. We have measured STS spectra at many different points in the vicinity of the point defect. STS spectra were very different depending on the point of the measurement. In the directions perpendicular to short zigzag edges at the point defect, STS peaks appear near the Fermi level, suggesting the edge state or non-bonding state. The non-bonding state propagates 3-4 nanometers away from the defect with three-fold symmetry. No such a STS peak was observed near the point defect in the other directions. We thus constructed a STS map showing the distribution of the non-bonding state. We also observed spatial "oscillations" in the dI/dV peak position and the intensity. The oscillations have been explained as electron-electron interaction or electron-hole interaction. We currently consider that the non-bonding state is responsible for the chemical reactivity such as adsorption of atom, molecules, and clusters.

References

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2. T. Kondo, J. Nakamura, et al., Phys. Rev. B 80 (2009) 233408.

3. J. Oh, T. Kondo, J. Nakamura, et al., J. Phys. Chem. Lett. 1 (2010) 463.

4. T. Kondo, J. Nakamura, et al., J. Phys. Chem. C 112 (2008) 15607.

2:40pm **GR+NS-MoA3 Opto-electronic Properties of Solution Processable Chemically Derived Graphene Oxide**, *M. Chhowalla*, Rutgers University **INVITED**

A solution based method that allows uniform and controllable deposition of reduced graphene oxide thin films with thicknesses ranging from a single monolayer up to several layers over large areas will be described. Transport of carriers in reduced GO is limited by the structural disorder. However, conductivity of 10^5 S/m and mobilities of ~ 10 $cm^2/V\cdot s$ are sufficiently large for applications where inexpensive and moderate performance electronics are required. The oxidation treatment during synthesis of GO creates sp^3 C-O sites where oxygen atoms are bonded in the form of various functional groups. GO is therefore a two dimensional network of sp^2 and sp^3 bonded atoms, in contrast to an ideal graphene sheet which consists of 100% sp^2 carbon atoms. This unique atomic and electronic structure of GO, consisting of variable sp^2/sp^3 fraction, opens up possibilities for new functionalities. The most notable difference between GO and mechanically exfoliated graphene is the opto-electronic properties arising from the presence of finite band gap. In particular, the photoluminescence can be tuned from blue to green emission. The atomic and electronic structure along with tunable photoluminescence of graphene oxide at various degrees of reduction will be described.

3:40pm **GR+NS-MoA6 Structural Evolution during the Reduction of Chemically Derived Graphene Oxide**, *V.B. Shenoy*, Brown University / Rhode Island Hospital

The excellent electrical, optical and mechanical properties of graphene have driven the search to find methods for its

large-scale production, but established procedures (such as mechanical exfoliation or chemical vapour deposition) are not

ideal for the manufacture of processable graphene sheets. An alternative method is the reduction of graphene oxide, a

material that shares the same atomically thin structural framework as graphene, but bears oxygen-containing functional

groups. Here we use molecular dynamics simulations to study the atomistic structure of progressively reduced graphene

oxide. The chemical changes of oxygen-containing functional groups on the annealing of graphene oxide are elucidated and

the simulations reveal the formation of highly stable carbonyl and ether groups that hinder its complete reduction to

graphene. The calculations are supported by infrared and X-ray photoelectron spectroscopy measurements. Finally, more

effective reduction treatments to improve the reduction of graphene oxide are proposed [1].

[1] Akbar Bagri, Cecilia Mattevi, Muge Acik, Yves J. Chabal, Manish Chhowalla and

Vivek B. Shenoy, Nature Chemistry (in press, 2010).

4:00pm **GR+NS-MoA7 Perfluorographane: Synthesis and Properties**, *J.S. Burgess*, National Research Council, *J.A. Robinson*, Naval Research Laboratory, *M. Zalalutdinov*, SFA, inc, *K. Perkins*, *P.M. Campbell*, *E. Snow*, *B.H. Houston*, *J.W. Baldwin*, Naval Research Laboratory

4:20pm **GR+NS-MoA8 Stability and Activity of Pt Nanoclusters Supported on Graphene Monolayers on Ru(0001)**, *O. Alves*, *C. Lorenz*, *H.E. Hoster*, *R.J. Behm*, Ulm University, Germany

Being an atomically thin half-metal and exhibiting moiré-type nm-scale superstructure, graphene monolayers supported on metal single crystals [1-3] can serve as a template for the growth of ordered arrays of nanosized metallic (electro-)catalyst particles. These particles, which are fabricated by simple metal vapour deposition in ultrahigh vacuum [4-6] and comprise monodispersed Pt clusters seeded on the graphene monolayer on Ru(0001), were found to nucleate preferentially at a unique region in the Moiré unit cell and displayed heights of 1-5 atomic layers and lateral diameters within the range 1-4 nm. The size selectivity of the Pt nanoclusters, jointly with their self-assembled array, assign them as interest and promising system for (electro-)catalytic model studies.

We will report on the activity and stability either of a single graphene monolayer or of the Pt clusters. The graphene layers and the cluster arrays are prepared in ultrahigh vacuum, whilst the potential-dependent reaction studies are measured in a wall-jet type flow cell sited in an electrochemical

pre-chamber attached to the main UHV system. Cluster arrays with different total Pt coverages and cluster size distributions were tested as electrodes for elementary reactions as hydrogen evolution/oxidation, CO oxidation, or O₂ reduction. According to STM analyses before and after the electrochemical tests, we discuss in how far the stabilities of clusters of various sizes can be rationalized in terms of reaction conditions and applied potentials. The general electrochemical behaviour of the Pt cluster arrays will be discussed in comparison to bulk Pt. As a main (electro-)catalytic result, we find a surprisingly high activity for hydrogen evolution.

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4:40pm GR+NS-MoA9 Writing Graphene Electronics Into Chemically Modified Graphene, P.E. Sheehan, Z. Wei, Naval Research Laboratory, D. Wang, Georgia Institute of Technology, W.-K. Lee, M.K. Yakes, Naval Research Laboratory, W.P. King, University of Illinois at Urbana-Champaign, E. Riedo, Georgia Institute of Technology, A.R. Laracuente, J.A. Robinson, S.G. Walton, Naval Research Laboratory

Graphene is the most likely carbon-based successor material for CMOS electronics. Recently, interest in chemically modified graphene (CMG) has risen for producing large-scale flexible conductors and for its potential to open an electronic gap in graphene structures. We have developed a means to tune the topographical and electrical properties of several CMGs with nanoscopic resolution by local thermal processing with an AFM tip. Heating converts the CMG back towards graphene with nanoscale resolution. Nanostructures of one CMG, graphene oxide, show an increase in conductivity up to four orders of magnitude as compared to pristine material. Variably conductive graphene nanoribbons have been produced in a single step that is clean, rapid and reliable. Critically, the "carbon skeleton" is continuous across the CMG/graphene boundary. Recent work suggests that ribbons formed this way may be superior to ribbons that were cut.

5:00pm GR+NS-MoA10 Oxygen Etching of Graphene on Ir and Ru, E. Starodub, N.C. Bartelt, K.F. McCarty, Sandia National Laboratories

We have used low-energy electron microscopy to investigate how graphene is removed from Ru(0001) and Ir(111) by reaction with oxygen. We find two mechanisms on Ru(0001). At short times, oxygen reacts with carbon monomers on the surrounding Ru surface, decreasing their concentration below the equilibrium value. This undersaturation causes a flux of carbon from graphene to the monomer gas. In this initial mechanism, graphene is etched at a rate that is given precisely by the same nonlinear dependence on carbon monomer concentration that governs growth. Thus, during both growth and etching, carbon attaches and detaches to graphene as clusters of several carbon atoms. At later times, etching accelerates. We present evidence that this process involves intercalated oxygen, which destabilizes graphene. On Ir, this mechanism creates observable holes. It also occurs most quickly near wrinkles in the graphene islands, depends on the orientation of the graphene with respect to the Ir substrate, and, in contrast to the first mechanism, can increase the density of carbon monomers. We also observe that both layers of bilayer graphene islands on Ir etch together, not sequentially. Work at Sandia was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U. S. Department of Energy under Contract No. DE-AC04-94AL85000.

Nanometer-scale Science and Technology

Room: La Cienega - Session NS-MoA

Nanomaterials in the Environment

Moderator: U.D. Schwarz, Yale University

3:40pm NS-MoA6 Nanotechnology in the Environment: Safety by Design, V. Colvin, Rice University **INVITED**

Nanotechnology-enabled systems offer much promise for solving difficult environmental problems ranging from water purification to waste remediation. These solutions must not only be cost-effective and sustainable, but they must also be safe for people and the environment. Our emerging understanding of the interface between nanomaterials and biological systems gives us the critical ability to approach the latter issue early in the development of nanotechnology. This talk will discuss in some detail how the chemical and physical properties of engineered

nanomaterials impact their biological effects in model systems. Three case studies, ranging from fullerenes to metal oxides, illustrate the vast diversity of nanomaterial features and biological response. The composition of a nanomaterial is the primary factor in describing acute biological effects, and among the different examples nanoparticle charge and surface coating can be of equal importance. Interestingly, the size of the inorganic material itself – such an important feature for applications development – in these three examples is secondary in defining the materials' acute biological effect. In all cases, the biological and environmental compartments experienced by nanomaterials lead to substantial modification of their hydrodynamic size and charge. The bio-modified material that results is the central element to understand and characterize in order to detect the underlying correlations between the inorganic nanomaterial phase, composition and size with biological outcomes. These correlations form the basis for guidelines that permit researchers creating new nanoparticles to focus their energy on materials that are 'safe by design'.

4:20pm NS-MoA8 Surface Functionalization of TiO₂ Nanoparticles: Photo-stability and Reactive Oxygen Species (ROS) Generation, K. Louis, O. Bar-Ilan, W. Heideman, M. Konrath, J. Pedersen, R. Peterson, S. Yang, R.J. Hamers, University of Wisconsin-Madison

Nanoparticles made from TiO₂ and other metal oxides are of increasing interest for applications including sunscreens, cosmetics, paints, biomedical imaging, and photovoltaic devices. While TiO₂ is generally considered to be non-toxic, TiO₂ and other metal oxides can generate highly toxic reactive oxygen species when exposed to water and sunlight. The ROS species can, in turn, modify the stability of the TiO₂ nanoparticles by altering the organic ligands that typically are present on the exterior of the nanoparticles. We are investigating the formation of ROS species by TiO₂ nanoparticles and the relationship between organic ligands, ROS generation, and nanoparticle stability. These factors all affect the bioavailability of TiO₂ nanoparticles and consequently are important factors in understanding the safety and health impacts of nanomaterials. As model systems, we have investigated TiO₂ nanoparticles functionalized with several ligands including citrate, 3,4-dihydroxybenzaldehyde, and rutin, a model of humic substances. Using fluorescent probes we are measuring the amount of ROS species produced from nanoparticles of different sizes and relating this to the chemical alteration/degradation of the ligands using XPS and FTIR, and examining the impact on stability of nanoparticles in aqueous media. Concurrent measurements are being made of the toxicity of the nanoparticles using zebrafish in the presence and absence of ultraviolet light in order to understand how surface chemistry of nanoparticles ultimately impacts bioavailability and environmental impact of engineered nanomaterials.

4:40pm NS-MoA9 Environmental Effects on Nanoparticle Properties and Chemical Reactivity, D.R. Baer, J.E. Amonette, A. Dohnalkova, M.H. Engelhard, Pacific Northwest National Laboratory, R.L. Penn, University of Minnesota, P. Nachimuthu, J. Liu, Pacific Northwest National Laboratory, J.T. Nurmi, P.G. Tratnyek, Oregon Health and Sciences University, C.M. Wang, Pacific Northwest National Laboratory

Nanoparticles of many types are increasingly used in a variety of applications. Parts of our work have focused on the reactions of Fe metal-core oxide-shell nanoparticles with water and solution contaminants that may be found in ground water. An important factor in understanding the ability of such particles to reduce environmental contaminants and the ultimate fate of such particles is knowledge of how the particles and their properties change with time in a variety of environments. Our work has demonstrated that these particles can change rapidly over periods of hours to days in water. Our research has focused attention on three aspects of these time dependent phenomena: 1) developing the ability to extract particles from solution, thereby stopping the reaction process and preserving, to the extent possible, the chemical and structural information; 2) how changes in the solution (adding buffers and organics) alter particle reactivity and aging in solution; and 3) using *in situ* methods to track particle changes and chemical properties. A variety of *ex situ* methods have been used to characterize the particles, including XPS, TEM, BET and XRD. Electrochemistry measurements have been used as an *in situ* real-time method. The method of sample extraction involves handling samples in a nitrogen atmosphere, a solvent rinse, and vacuum pumping to remove excess solvent. Even when particles appear dry, aggregates of particles may retain significant solvent. In addition to examining the influence of a variety of common buffers, we have examined the impact of natural organic material on the oxidation and chemical behavior of nanoparticles. Although natural organic matter (NOM) slows aging of the particles, the NOM coating helps the particles migrate relatively quickly through soil. Electrochemical measurements of various types including the open-circuit potential demonstrate the time dependence of particle changes and highlight the effects of varying environments on particle properties. Surface-potential measurements also highlight the impact of differing solutions on particle behavior.

5:00pm **NS-MoA10 Functionalized Ceria Nanoparticles – Influence of Coating Thickness and Density on Their Reactivity**, *A. Karakoti*, University of Central Florida, *S. Kuchibhatla, G. Orr, H. Wang, D.R. Baer*, Pacific Northwest National Laboratory, *S. Seal*, University of Central Florida, *S. Thevuthasan*, Pacific Northwest National Laboratory

Topical interest in the biomedical applications of cerium oxide nanoparticles (CNPs) has emerged from its radical scavenging, antioxidant like, behavior. The ability of CNPs to carry these single electron redox processes (radical scavenging) stems from the ability of cerium to switch between the Ce^{3+} and Ce^{4+} oxidation states. It is essential to test and increase the biocompatibility and solubility of CNPs to be able to use these in biomedical applications as it involves a direct interface of nanoparticles with the intracellular environment. The biocompatibility as well as solubility of CNPs can be increased by modifying the surface with biocompatible polymers as ligands. Such a composite system should be able to demonstrate the unaltered characteristics of the parent CNPs and biocompatibility as well as high solubility of the polymeric system. Thorough characterization of CNP-polymer system such as thickness of polymeric coating, surface coverage and number density of the polymer per nanoparticle is necessary to relate its properties with biocompatibility.

CNPs were synthesized using two different wet chemical methods and coated with different concentration of polymer (polyacrylic acid) using conventional precipitation and redispersion technique. The molecular weight of the polymer was varied between 2,000 and 250,000 g/mol and composite system was characterized for particle size, stability/solubility of dispersion, surface charge, surface density of the polymer and thickness of the polymeric coating. Dynamic light scattering measurements were used to characterize the size as well as surface charge of the coated nanoparticles. A combination of surface area and thermogravimetric analysis was used to ascertain the number density of the polymers per unit surface area of the nanoparticles. The extent of polymeric functionalization will be determined by estimating the number of carboxyl groups on the surface of nanoparticles by chemical probing. Non linear optical (NLO) measurements are becoming increasingly popular to quantify the surface of nanoparticles. NLO analyses such as Sum Frequency Generation Vibrational Spectroscopy (SFG-VS) will be used to quantitatively estimate the polymeric ligands on the surface of CNPs. The presentation will be concluded by some of the preliminary results from the biocompatibility tests carried out on the well analyzed composite/functional CNPs.

Nanometer-scale Science and Technology

Room: La Cienega - Session NS-TuM

Nanomanufacturing and Nanomachines

Moderator: M. Hersam, Northwestern University

8:00am NS-TuM1 Nanomanufacturing Processes using Mechanosynthesis Applications, *S.L. Sullivan*, NanoSource Inc.

Quality, production capacity and production cost have been identified as the current barriers to the implementation of carbon nanotubes and nanofibers within the industrial markets and military applications where such materials offer superior performance benefits. Significant use of nanotubes and nanofibers will require substantial increases in production volume coupled with decreases in production cost of $< \$ 15/\text{Kg}$. Based on low cost, high-volume, high yield, and the ability to highly control diameter, length and chirality, a Mechanosynthesis process was selected as the most viable approach for a scalable, top down mass manufacturing process of nanoscale structures such as nanoparticles, nanotubes and nanofibers that are continuous.

Index Terms- Mechanosynthesis, nanomanufacturing, nanoimprinting, nanofibers, material science.

8:20am NS-TuM2 Enabling Surface Patterning on Polyhedral and Curved Nanoparticles, *J.-H. Cho*, Los Alamos National Laboratory, *T. James, D. Gracias*, Johns Hopkins University

It is well known that surface patterning on three dimensional (3D) nanostructures can alter their physical and chemical properties. However, present day nanoparticles such as nanowires and nanopolyhedra have limited to no surface patterning. Lithographic processes enable precise patterning and are very well developed. There are several nanolithographic techniques such as electron beam (e-beam), imprint, and dip pen lithography that can enable patterning, but in an inherently two dimensional manner.

In this talk, we describe strategies to curve and rotate precisely patterned thin film templates to form 3D nanostructures such as cubes, pyramids, tubes, scrolls and talons. The highlight of the approach is that the process leverages already existing nanolithographic techniques and enables structures to be formed with any desired surface patterns in all three dimensions; a line width resolution of 10 nm was achieved.

We utilized multiple layers of electron beam lithography to pattern 2D templates. Patterns with homogeneous (pores in nickel panels) or dissimilar materials (e.g. gold lines on nickel or alumina) were defined. Curvature of hingeless templates and rotation of hinged panels was achieved by triggering grain coalescence in tin (Sn). Polyhedral particles ranging in size from 100-900 nm and surface patterning of 15 nm could be achieved. In addition, curved nanostructures with both homogeneous (rings, tubes) and variable (spirals, talons) radii of curvature could be formed.

Our demonstration of patterning of self-assembly of precisely patterned polyhedral and curved nanoparticles has material versatility and we believe that this strategy can be utilized to integrate optical, electronic and biological elements on the surfaces of nanoparticles with unprecedented precision and in all three dimensions for a range of applications.

8:40am NS-TuM3 Atomic Precision Fabrication Using Patterned Si Atomic Layer Epitaxy: Processing Capabilities, Throughput Limitations, and Applications, *J.N. Randall, J.B. Ballard, J.R. Von Ehr, J. Alexander, R. Saini, Zyvex Labs, J.W. Lyding*, Univ. of Illinois at Urbana-Champaign, *R.M. Wallace, Y.J. Chabal*, Univ. of Texas at Dallas, *R.M. Silver, J. Gorman*, National Inst. of Standards and Tech., *N. Sarkar*, Univ. of Waterloo, Canada, *T. Toth-Fejel*, General Dynamics **INVITED**

Atomically precise Si fabrication technology is being pursued via atomic-precision, H-depassivation lithography with a scanning tunneling microscope (STM) and silicon atomic layer epitaxy (ALE). The details of this process and progress towards its realization are published elsewhere. In this presentation we will cover the expected process capabilities, throughput limitations, applications that will be feasible in spite of these limitations, extensions of the processing capabilities, and paths to scaleup of the throughput. Initially the fabrication process will involve simply patterned homo-epitaxy of Si on Si surfaces, but will allow arbitrary three dimensional structures with some design rules imposed by the Si lattice. The limitations imposed by the physics of the H depassivation lithography and the need for repeated patterning is the principal process bottleneck and leads to estimations of a cost per unit volume of atomically precise fabricated

material that seems extremely high. However, the ability to create structures with atomic precision will enable very valuable applications and products that can be cost effectively manufactured in the relatively near term. This process, which can be conceived of as spatially controlled deprotection, appears to be general enough to adapt to the large number of materials that may be deposited with ALE or atomic layer deposition (ALD). Further, there are clear paths to scaling up the process via MEMS-based STM scanner arrays that would significantly widen the range of products and applications resulting from this Atomically Precise Manufacturing technology.

This material is based upon work supported by the Defense Advanced Research Project Agency (DARPA) and Space and Naval Warfare Center, San Diego (SPAWARSYSCEN-SD) under contract N66001-08-C-2040. It is also supported by a grant from the Emerging Technology Fund of the State of Texas to the Atomically Precise Manufacturing Consortium.

9:20am NS-TuM5 Axial Ge/Si Nanowire Heterostructures: Synthesis and Asymmetric Band-gap Engineered Tunnel FETs, *S.A. Dayeh*, Los Alamos National Laboratory, *J. Huang, A. Gin*, Sandia National Laboratories, *S.T. Picraux*, Los Alamos National Laboratory

While new materials and device concepts are being developed to extend CMOS device scaling beyond the 22 nm node, the potential of combining Si/Ge heterostructured materials with the dimensionality of semiconductor nanowires (NWs) remains to be explored. The vapor-liquid-solid (VLS) mechanism allows modulation of doping and alloy composition in the axial NW direction which is the transport direction for NW FETs. This provides an additional degree of freedom for energy band-edge engineering in the transport direction which is difficult to access in planar devices. Such unique aspect of semiconductor nanowires when added to Ge compatibility for integration with Si technology, makes Ge/Si axial NW heterostructures advantageous over other existing material and device possibilities, in particular for tunnel FETs.

This work reports on two significant advances in the area of heterostructure nanowires and tunnel FETs: (i) the realization of 100 % compositionally modulated Si/Ge axial heterostructure nanowires with lengths suitable for device fabrication and (ii) the design and implementation of Schottky barrier tunnel FETs on these nanowires for high-on currents and suppressed ambipolar behavior. A growth procedure was devised to eliminate Au diffusion on the NW sidewalls and minimize random kinking in the heterostructured NWs as deduced from detailed electron microscopy analysis. Our prototype devices resulted in a current drive in excess of 100 $\mu\text{A}/\mu\text{m}$ ($I/\pi D$) and $10^5 I_{\text{on}}/I_{\text{off}}$ ratios over a wide range of source-drain biases, thus exceeding earlier performance results in the literature of tunnel FET devices made of semiconductor nanowires and carbon nanotubes by ~ 2 -3 orders of magnitude. These results demonstrate the potential of such asymmetric heterostructures (both in the semiconductor channel and metal-semiconductor barrier heights) for low-power and high performance electronics.

9:40am NS-TuM6 Direct Writing of Polymers using a Heated Probe for Patterning Nanoparticles and Graphene, *W.-K. Lee, J.A. Robinson, A.R. Laracuate*, Naval Research Laboratory, *Z. Dai, W.P. King*, University of Illinois at Urbana-Champaign, *P.E. Sheehan*, Naval Research Laboratory

In thermal Dip Pen Nanolithography (tDPN), a heatable AFM cantilever regulates the deposition of an ink through controlled melting, much like a nanoscale soldering iron. Control over writing is exceptional—deposition may be turned on or off and the deposition rate easily changed without breaking surface contact. tDPN has been successful at depositing polymers ranging from semiconductors to insulators at speeds up to 200 $\mu\text{m}/\text{s}$. Recently, we developed the technique depositing polymer-nanoparticle composites. Nanoparticles and nanoparticles-polymer composites may offer many new capabilities that could greatly advance nanoelectronics, data storage, biosensors, and optical imaging applications. With tDPN, we could deposit with nanoscale precision a wide range of polymers (PMMA, P(VDF-TrFE), polyethylene) that contain nanoparticles or small molecules. An oxygen plasma can remove the polymer to reveal evenly dispersed nanoparticles or, for some combinations, precisely-placed 10 nm wide rows of nanoparticles.

Another substrate, a single layer of graphene on a SiO_2 , was also used to deposit polymers by tDPN. We used the deposited polymer on graphene as an etch mask to pattern graphene nanoribbons (GNRs). Background graphene was then either etched by oxygen plasma to expose SiO_2 or modified by graphene fluoride to form an insulating substrate. The electrical measurements of nanopatterned graphene structures will also be presented.

10:40am **NS-TuM9 Understanding and Controlling Rotation at the Single-Molecule Level: Turning Rotors into Motors**, *H.L. Tierney**, *A.D. Jewell, A.E. Baber, E.V. Iski, E.C.H. Sykes*, Tufts University

While molecular machines driven by chemical, light or thermal energies can be found throughout nature, little progress has been made toward creating synthetic counterparts. The gap between nature and nanotechnology remains due to the limited fundamental understanding of the transfer of energy to mechanical motion at the nanoscale. Understanding and actuating the rotation of individual molecules on surfaces is a crucial step towards the development of nanoscale devices such as fluid pumps, sensors, delay lines, and microwave signaling applications. Towards this end we have used a group of small molecules in order to understand the fundamental aspects of molecular rotation. Thioethers constitute a simple, robust system with which molecular rotation can be actuated thermally, mechanically and electrically, and can be studied using scanning tunneling microscopy (STM) as a function of molecular chemistry and proximity of neighboring molecules. Interestingly, the thermal onset to rotation was found to be nearly identical for studied thioether molecules with alkyl tails of two carbons or more. It is proposed that this plateau in thermal onset was due to an interplay between degrees of freedom in the alkyl tail vs. the S-metal bond length. While small amounts of thermal energy are capable of inducing rotation, thermodynamics dictates that thermal energy alone cannot be used to perform useful work in the absence of a temperature gradient. Therefore, for molecules to meet their full potential as components in molecular machines, methods for coupling them to external sources of energy that selectively excite the desired motions must be devised. To this end, we have studied using an electrical current to rotate individual dibutyl sulfide molecules on command. For these studies the source of energy is supplied via high energy electrons from the STM tip. By monitoring the rate of rotation as a function of tunneling electron energy (action spectroscopy) we have demonstrated that the rotors can be driven electrically via a mechanism that involves excitation of a C-H stretch. Finally, using theoretical methods the minimum energy adsorption site was determined and the mechanism of rotation was elucidated for the simplest thioether, dimethyl sulfide. These theoretical results indicate that the rotation of a small, simple molecule is actually rather complex; as the CH₃ groups of dimethyl sulfide rotate around the Au-S bond, the central S atom precesses around a surface Au atom.

11:00am **NS-TuM10 Atomic Layer Deposition on Self-Assembled Block Copolymer Films**, *Q. Peng, Y.-C. Tseng, S.B. Darling, J.W. Elam*, Argonne National Laboratory

We establish a new method for preparing ordered nanoscale patterns of various materials with tunable domain sizes by applying atomic layer deposition onto block copolymer thin films. The mechanism is based on the selective interaction of the ALD precursors with moieties in one of the polymer blocks. Well aligned, patterned Al₂O₃ and TiO₂ stripes with controllable dimensions were fabricated by applying ALD onto PS-*b*-PMMA block copolymer templates. Moreover, due to the self-limited cyclic deposition nature of ALD, a seed layer generated from Al₂O₃ ALD provides a secondary selective chemistry, which in turn enables a far broader suite of materials to be patterned into the PMMA domains. For example, ZnO and W nucleate easily on the PMMA-Al-OH domains formed from one cycle of Al₂O₃ ALD. By carefully designing block copolymers and selecting ALD parameters, patterned designer materials with controlled size, center-to-center space, and composition could be synthesized onto a broad range of substrates.

11:20am **NS-TuM11 In Control of Molecular Motion From Molecular Motors to Nano-Machines**, *B.L. Feringa*, The University of Groningen, the Netherlands **INVITED**

Inspired by Nature we design nano-scale systems in which the control of dynamic properties of molecules is coupled to specific functions. Molecular machines ultimately require control over structure, organization and function of multi-component molecular assemblies at different hierarchical levels. Major challenges are the integration of kinetic driven processes in multifunctional molecular systems and control over translational and rotary motion.

Molecular switches and motors offer ample opportunity to control functions in a dynamic way. Following the development of the first light-driven unidirectional molecular motor, the focus is now on the control of dynamic functions in more complex systems as well as autonomous motion. Synthetic approaches to various molecular switches and motors and the construction of integrated systems featuring trigger and motor elements are discussed.

Specific challenges that we address are the acceleration of molecular rotary motors and the construction of a nanoscale "windmill park" powered by

light. Recent advances in the design of new generation motors that allow the increase of the speed of rotation over a million fold are presented. Furthermore the design of molecular motors in which the rotary direction can be reversed, a molecular crankshaft and brake and molecular transmission phenomena are discussed. Besides rotary motion induced by light, we present unique molecular motors that run on a chemical fuel and discuss our attempts to achieve autonomous motion.

* Morton S. Traum Award Finalist

Tuesday Afternoon, October 19, 2010

Nanometer-scale Science and Technology

Room: La Cienega - Session NS-TuA

Carbon-Based Nanomaterials

Moderator: N.A. Burnham, Worcester Polytechnic Institute

2:00pm **NS-TuA1 Covalent Synthesis and Optical Characterization of Double-Walled Carbon Nanotube - Nanocrystal Heterostructures**, **X. Peng**, State University of New York at Stony Brook, *M.Y. Sfeir, J.A. Misewich*, Brookhaven National Laboratory, *S.S. Wong*, State University of New York at Stony Brook

Double-walled carbon nanotubes (DWNTs) have been a key focus material of research in recent years owing to their unique electronic structure and properties. However, the incorporation of DWNTs with quantum dots (QDs) into nanocomposites via a covalent chemical approach as well as the optical properties of the composites have rarely been explored. In particular, the investigation based on CNT-QD systems, one of well-studied nanomaterial heterostructures, provides insights into a fundamental understanding of efficient charge separation within heterostructures via charge transfer relative to other relaxation pathways such as exciton recombination. In this specific work, DWNT-CdSe heterostructures were obtained by covalently conjugating 2-aminoethanethiol (AET)-modified CdSe QDs with terminal amino groups onto the surfaces of oxidized DWNTs via the formation of amide bonds. For AET-CdSe, a characteristic emission in NIR was observed due to the trap states induced by the presence of AET capping ligands. Besides, the magnitude of the trap emission was found to be associated with the concentration of AET added into systems. Interestingly, the observed trap emission is effectively quenched upon conjugation with the DWNT as a result of the charge transfer from trap states of CdSe to DWNTs. More strikingly, the time-resolved photoluminescence studies showed the exciton decay of DWNT-CdSe composites was recovered from multi-exponential to nearly mono-exponential behavior, thereby suggesting that a unique exciton dynamic occurred in the DWNT-CdSe heterostructure. More careful kinetic studies are in progress.

2:20pm **NS-TuA2 Carbon Nanotube Nonvolatile Memory**, **K. Matsumoto**, Osaka University, Japan

Since single-walled carbon nanotubes (SWNTs) have small diameter of ~1 nm, high-electric field concentration is easily generated around SWNTs. Therefore, the carbon nanotube field-effect transistors (CNTFETs) using SWNTs as a channel are expected for low power consumption nonvolatile memory. The conventional CNTFETs, however, whose channels are exposed to the atmosphere, exhibit large hysteresis due to charge trapping by impurities, such as water molecules, around SWNT channels. In the present paper, we have fabricated nonvolatile memory based on top-gated CNTFETs with double gate insulator layers after removal of the impurities around SWNT channels.

A double layer thin SiN_x/SiO₂ films were deposited on SWNT channels using catalytic chemical vapor deposition. After the double layers deposition, a top gate electrode was fabricated. The interface between SiN_x and SiO₂ films in the device is expected as a charge storage node of nonvolatile memory. The transfer characteristics of the CNTFET as a function of back- and top-gated voltages at 300 K in vacuum were measured. The negligible hysteresis is observed for sweeping the back-gated voltage, indicating that impurities around the SWNT channel are completely removed. In contrast, hysteresis increases with increasing sweep range for top-gated voltage. The counterclockwise hysteresis loops are due to the charging and discharging processes of holes in the top-gated CNTFETs. These results mean that the charge was trapped at the interface of SiN_x/SiO₂ films by the applied top gate bias. Due to the small diameter of the CNT, the electric field concentration occurs, and only 2V application of the top gate bias produces the hysteresis. This gate bias is 10 times smaller value than that of the conventional planer type memory. The single-charge effects are observed using the CNT-based memory devices. When top-gated voltage was swept forth and backward for the ranging of ± 0.7 V, the abrupt peaks on the currents are observed for both directions. The abrupt drop or increase in drain currents corresponds to single-hole charging and discharging phenomena in CNT-based memory devices, respectively. The same measurements were carried out twenty times, and four discrete Id-Vg curves are clearly observed, which are attributed from the effect of single-holes traps.

We have fabricated the CNTFETs nonvolatile memory, which operate 10 times smaller bias owing to the electric field concentration effects. Single charge detection was also demonstrated in the CNT memory device.

2:40pm **NS-TuA3 Single Walled Nanotube (SWNT) Fiber Field Emission Cathodes**, **S.B. Fairchild**, **B. Maruyama**, **J.J. Boeckl**, **D.A. Shiffler**, **N.P. Lockwood**, Air Force Research Laboratory, **M. Pasquali**, Rice University

High power THz sources and amplifiers hold the potential to revolutionize the remote sensing and communication industries. Traveling wave tubes (TWT) are the most promising technology for compact high power amplifiers at THz frequencies. High frequency applications necessitate the need for small diameter beam tunnels and thus small diameter high current electron beams. Small diameter beams are typically achieved by emitting electrons from a thermionic cathode surface much larger than the THz TWT beam tunnel and focusing the beam using either electrostatic or magnetic field electron beam optics. To avoid using focusing optics, a micron sized high aspect ratio field emission (FE) cathode can be immersed in the confining magnetic field and used to generate an electron beam with a smaller diameter than the THz TWT beam tunnel. The key technical challenge with using a micron sized FE cathode is achieving the high current densities, long life time, and uniform current densities within the electron beam. The Air Force Research Laboratory (AFRL) began research on small diameter (<100 micron) single fiber DC cathodes for this application. Two types of fibers were tested, 1) those made from carbon with graphitized outer shells, and 2) fibers made solely from single walled carbon nanotubes (SWNT) that are densely packed and highly aligned along the axial direction of the fiber. Carbon fiber cathodes suffered serious degradation due to joule heating after only 25 hours of operation while only producing up to 200 microamps of current. A single SWNT fiber cathode has emitted approximately 3 milliamps of current for hundreds of hours while suffering minimal damage, as well as an 8x reduction in turn-on voltage over carbon fiber cathodes. Efforts are currently underway to optimize these SWNT fiber FE cathodes by tip shaping and applying low work function coatings.

3:00pm **NS-TuA4 Spectroscopic Identification of Bond Strain and P Interactions in a Series of Saturated Carbon-Cage Molecules: Adamantane, Twistane, Octahedrane, and Cubane**, **T.M. Willey**, **J.R.I. Lee**, Lawrence Livermore National Lab, **D. Brehmer**, SLAC National Accelerator Lab, **L. Landt**, 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

Novel nanocarbons such as fullerenes, nanotubes, graphene, and nanodiamond reside at the cutting edge of nanoscience and technology. Along with chemical functionalization, geometrical constraints (such as extreme curvature in nanotubes or graphene, or defects within or at the surfaces of nanodiamond crystallites) can modify the electronic states of the nanocarbon material. Understanding the effects of bond strain on electronic structure is critical to developing nanoelectronic applications based on these materials. This paper presents a fundamental study of how bond strain affects electronic structure in a benchmark series of novel saturated carbon cage compounds. Adamantane, C₁₀H₁₆, the smallest diamondoid, and arguably the smallest nanodiamond crystallite, has carbon atoms essentially commensurate with diamond lattice positions and possesses by far the least bond strain of the series. Twistane has the same stoichiometry (C₁₀H₁₆), but introduces some strain into the cage. Octahedrane (C₁₂H₁₂) and cubane (C₈H₈) contain increasing amounts of bond strain, culminating in cubane where carbon-carbon bonds lie either parallel, or orthogonal to one another. Using gas-phase near-edge x-ray absorption fine structure spectroscopy to probe the unoccupied electronic states, we observe two major progressions across this series. 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 octahedrane, even though these two molecules have similar stoichiometries (C_xH_x). We attribute the additional intensity to π* states, indicating a high degree of π interaction between parallel C-C bonds in the cubane.

4:00pm **NS-TuA7 Self-Assembly of Photo-reduced Graphene-Titanium Films**, **C.A. Chavez**, **T.N. Lambert**, **C.M. Washburn**, **N.S. Bell**, **B.B. McKenzie**, **M.T. Brumbach**, **D.R. Wheeler**, Sandia National Laboratories

In an aim to develop photo-responsive composites, the UV photo-reduction of aqueous titanium oxide nanoparticle-graphene oxide (TiO₂-GO) dispersions (Lambert et al. J Phys. Chem. 2010 113 (46), 19812-19823) was undertaken. Photo-reduction led to the formation of a black precipitate as well as a soluble portion, comprised of titanium oxide nanoparticle-reduced graphene oxide (TiO₂-RGO). When allowed to slowly evaporate, self assembled titanium oxide nanoparticle-graphene oxide (SA-TiO₂-RGO)

films formed at the air-liquid interface of the solution. The thickness of SA-RGO-TiO₂ films range from ~30-100 nm when deposited on substrates, and appear to be comprised of a mosaic assembly of graphene nanosheets and TiO₂, as observed by scanning electron microscopy. Raman spectroscopy and X-ray photoelectron spectroscopy indicate that the graphene oxide is only partially reduced in the SA-TiO₂-RGO material. These films were also deposited onto inter-digitated electrodes and their photo-responsive behavior was examined. UV-exposure lead to a ~ 200 kOhm decrease in resistance across the device, resulting in a cathodically biased film. The cathodic bias of the films was utilized for the subsequent reduction of Ag(NO₃) into silver (Ag) nanoparticles, forming a ternary Ag-(SA-RGO-TiO₂) composite. Various aspects of the self assembled films, their photoconductive properties as well as potential applications will be presented.

This work supported by the Department of Energy, Office of Basic Energy Sciences and the United States Department of Energy under contract number DE-AC04-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the United States Department of Energy.

4:20pm **NS-TuA8 Temperature Dependence of Carbon Nanofiber Resistance**, *S. Maeda, T. Yamada, H. Yabutani, T. Saito, C. Yang*, Santa Clara University

Carbon nanostructures such as nanotube (CNT) and nanofiber (CNF) are the most promising materials for applications in next-generation silicon integrated circuits. Knowledge of the temperature dependence of these materials is critically important as it relates directly to circuit performance. However, in practice, it is extremely difficult to measure and control the temperature of each test device and maintain thermal equilibrium because of its small thermal capacity. Therefore, one must determine the temperature of test devices by other means. Here we report results of such a study on vertical via and horizontal CNF test devices. CNF can potentially be a replacement for copper in on-chip via interconnects [1], as well as in through-silicon-vias (TSVs) in three-dimensional chips [2,3]. The horizontal CNF test device can be used as a prototype of interconnect lines between adjacent transistors in the same silicon layer. In the horizontal structure, the temperature of the CNF is extracted from current stress measurements using our heat transport model [4]. For the via test device, the CNF temperature is estimated from that of the temperature-controlled measurement system [1]. In both cases, the conductivity of CNF is determined from the measured current-voltage characteristics. We find that in either case, the conductivity increases with increasing temperature as expected. However, the measured resistance of the test device in each case contains a very different contact resistance component, due to the much higher contact resistance in the horizontal structure [5]. From the conductivity versus temperature behavior, we extract the activation energy, which turns out to be about 30 meV in each case. This finding suggests that the change in conductivity in CNF, regardless of device configuration, is due to electron trapping and detrapping at defect sites within the carbon nanostructure.

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4:40pm **NS-TuA9 New Concepts in Molecular and Energy Transport Within Carbon Nanotubes: Thermopower Waves and Stochastically Resonant Ion Channels**, *M. Strano*, Massachusetts Institute of Technology
INVITED

Our laboratory has been interested in how carbon nanotubes can be utilized to illustrate new concepts in molecular and energy transfer. In the first example, we predict and demonstrate the concept of thermopower waves for energy generation. Coupling an exothermic chemical reaction with a thermally conductive CNT creates a self-propagating reactive wave driven along its length. We realize such waves in MWNT and show that they produce concomitant electrical pulses of high specific power >7 kW/kg. Such waves of high power density may find uses as unique energy sources. In the second system, we fabricate and study SWNT ion channels for the first time and show that the longest, highest aspect ratio, and smallest diameter synthetic nanopore examined to date, a 500 μm SWNT, demonstrates oscillations in electro-osmotic current at specific ranges of

electric field, that are the signatures of coherence resonance, yielding self-generated rhythmic and frequency locked transport. The observed oscillations in the current occur due to a coupling between stochastic pore blocking and a diffusion limitation that develops at the pore mouth during proton transport.

5:20pm **NS-TuA11 All-Diamond Particles Prepared by Layer-by-Layer Deposition for High Performance Liquid Chromatography**, *M.R. Linford, L.A. Wiest, D.S. Jensen*, Brigham Young University, *A. Dadson, M.A. Vail*, U.S. Synthetic

All-diamond, core-shell particles for HPLC have been prepared by layer-by-layer deposition. The process begins with the amine functionalization of ca. 2 micron diamond particles by their immersion in an aqueous solution of a primary amine-containing polymer, polyallylamine (PAAm). The amine-functionalized microdiamond is then immersed in an aqueous suspension of nanodiamond, which leads to adsorption of the nanodiamond. Alternating immersions in the solutions of PAAm and the nanodiamond suspension are continued until the desired number of nanodiamond layers is formed around the core particle. Finally, the core-shell particles are functionalized with 1,2-epoxyoctadecane to create a C18 phase. Other surface modifications, including cross linking of the PAAm polymer have been demonstrated. Scanning electron microscopy and Brunauer Emmett Teller (BET) surface area and pore size measurements show formation of the expected particles. To date, we have made core-shell particles that can be used for an HPLC separation of a four-component mixture with more than 40,000 plates/m.

5:40pm **NS-TuA12 Fabrication of High-Performance Carbon Nanotube Field-Effect Transistors with Dense and Aligned Nanotubes**, *Z. Xiao*, Alabama A&M University

Multilayered dense single-walled carbon nanotubes (SWCNTs) were deposited and aligned for fabrication of carbon nanotube field-effect transistors (CNTFETs) using the alternating electric field-directed dielectrophoresis (DEP) method. Ultrapurified high-pressure carbon monoxide (HiPCO)-grown SWCNTs were ultrasonically dispersed in n-methyl pyrrolidone (NMP) for deposition and alignment. High-performance CNTFETs with high on/off drain-source current ratios and good saturation of drain-source current were fabricated using semiconductors as the source/drain contact materials. The current-voltage (IV) electrical property of the fabricated CNTFETs was measured. The processes for alignment of multilayered dense SWCNTs and fabrication of CNTFETs and the electrical property of the fabricated CNTFETs will be reported in the conference.

Tuesday Afternoon Poster Sessions

Nanometer-scale Science and Technology

Room: Southwest Exhibit Hall - Session NS-TuP

Nanometer-Scale Science and Technology Poster Session

NS-TuP1 Fabrication and Characterization of Piezoelectric Polymer Nanostructure. *D. Kim, Y.-Y. Choi, H.W. Choi, M. Han, M. Park, G. Ahn, K. No*, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

We show the microstructures and ferroelectric domains of 200nm diameter poly(vinylidene fluoride-trifluoroethylene), P(VDF-TrFE) with composition of 75/25 mol%, nanorods fabricated by a porous template technique. In order to characterize the piezoelectric properties of P(VDF-TrFE) nanorods, both nanoscale manipulation and polarization switching were studied using piezoresponse force microscopy (PFM). Ferroelectric domains and their properties were confirmed using X-ray diffraction and PFM analysis. The ferroelectric domains in the nanorods were homogeneously switchable below 5V. This offers our rationale for a promise in energy harvesting and switchability would be good for plastic electronics.

NS-TuP2 Uniform Printing of PEG Hydrogel Arrays by Dip-Pen Nanolithography[®]. *J.-W. Jang, P.L. Stiles, S.R. Nettikadan*, NanoInk Inc.

Dip Pen Nanolithography[®] (DPN[®]) is an established method of nanofabrication in which materials are deposited onto a surface via a sharp tip. DPN enables controlled deposition of a variety of materials with nanoscale registry onto various substrates. Recent advances in DPN technology has resulted in the ability to directly print larger, biologically relevant materials on to a variety of surfaces under ambient conditions.

A novel method for the construction of hydrogel patterns has been developed. Hydrogels are of great interest to tissue engineers and other biomedical researchers because of the versatility of PEG chemistry and excellent biocompatibility. Also the mechanical and swelling properties of PEG hydrogels can be easily tuned by controlling the degree of cross-linking and choosing the appropriate molecular weight. Patterning of hydrogels in submicron scale with defined mechanical properties is highly desirable as a scaffold for tissue engineering and *in vitro* cell culture studies.

We report a novel method for generation of hydrogel patterns at subcellular scales. Hydrogel precursors are directly deposited at defined location and then polymerized to form hydrogels. This method allows for rapid fabrication of high resolution patterns. We used a simple desktop nanolithography platform (NLP 2000[™], NanoInk, Inc.) for the deposition of the hydrogel precursors. The NLP 2000 consists of a stacked 3axis stage system with a travel range of 40 mm and a resolution of 25 nm. A high resolution optical microscope is available for monitoring the printing process. A custom fabricated array of cantilever based writing tools (M-Type, 12-pen, NanoInk, Inc.) were used to transport the hydrogel precursors on to the surface. Controlling the environmental conditions during the printing process allows for the transfer of defined volumes of hydrogel precursors. At 37°C, hydrogel domains of 6 μm were printed while at 25 °C 1.5 μm domains were printed. Patterning areas of 1 mm² with domains of less than 5 μm can be easily achieved in less than 30 min. AFM result confirmed the size and homogeneity of the printed hydrogel patterns.

NS-TuP3 Localized Surface Plasmons and Hot Spots from the Interstitial Sites in Linear Nano-Hole Array Structures of Gold Revealed by Near-Field Two-Photon Excitation. *S.I. Kim*, KAIST, Republic of Korea, *K. Imura*, Institute for Molecular Science, Japan, *S. Sehun Kim*, KAIST, Republic of Korea, *H. Okamoto*, Institute for Molecular Science, Japan

We analyzed spatial distribution of enhanced optical field at the gap between nano-holes in nano-hole array structures on gold thin film by near-field two-photon excitation imaging. We prepared linear chain-like array structures of circular nano-holes on gold thin film on a glass substrate, based on the method developed by Fischer [1]. A home-made scanning near field microscope [2] was used to observe two-photon excitation images for individual nano-hole array structures. We used a Ti:Sapphire laser (<100fs, 780 nm) to excite two-photon induced luminescence. Polarization dependences of the two-photon images were also measured. In the near-field two-photon excitation images of the nano-hole arrays, we found strong enhanced signal localized at interstitial sites between nano-holes, when the incident polarization is parallel to the chain axis of the array.

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NS-TuP4 Band and Dielectric Discontinuities of the Si_{1-x}Ge_x/Si_{1-y}C_y Superlattices. *T. Ohsugi, J. Nakamura*, The University of Electro-Communications (UEC-Tokyo), Japan

Si_{1-x}Ge_x and Si_{1-y}C_y alloys have attracted much attention from the perspective of the fabrication of novel devices, e.g., resonant tunneling diodes with strained alloys [1] and hetero bipolar transistors with double quantum wells [2]. It has been known that the lattice constants of these alloys are approximately proportional to their compositional ratios in accordance with Vegard's law [3]. Further, it has been reported that the band-gap of Si_{1-x}Ge_x, other than the lattice constant, changes with its composition [4]. In this study, we draw attention to the dependence of the dielectric constant on the composition of Si_{1-x}Ge_x and Si_{1-y}C_y as well as the dependence of other physical quantities such as lattice constants and band-gaps. We explore the band discontinuity and the spatial modulation of dielectric constants for the Si_{1-x}Ge_x/Si_{1-y}C_y superlattices as novel device structures, using first-principles ground-state calculations in external electric fields [5, 6].

We have adopted the cubic supercells containing 8 atoms for the Si_{1-x}Ge_x and Si_{1-y}C_y bulk models. It has been shown that the lattice constants of Si_{1-x}Ge_x and Si_{1-y}C_y alloys increase and decrease linearly with their compositions, respectively, obeying the Vegard's law. In contrast, the nonlinearity with the composition is found for the band gap and the dielectric constants. In our presentation we discuss the origin of the onset of the nonlinearity and report the band and dielectric discontinuities of the Si_{1-x}Ge_x/Si_{1-y}C_y superlattices from an atomic scale point of view.

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NS-TuP5 Single Domain Homogeneous Monolayer at the Water/Oil Interface and its Application for Surface Enhanced Raman Scattering. *S.I. Kim, P.S. Fabien, H. Song, S. Kim*, KAIST, Republic of Korea

We made mm-range closely packed monolayer by using the water/oil interface with Au nanoparticles whose nominal sizes are about 32 nm. We transfer this monolayer to the hydrophilic Si substrates by pulling up the sample softly and we measure the surface enhanced Raman scattering of Rhodamine 6G dye molecules. For this structure, we simulate the electromagnetic field enhancement when the laser light shines the sample whose unit cell is hexagonal structures ideally. We suggest that the strong field enhancement comes from the every interstitial gap among nanoparticles.

NS-TuP6 Synthesis of Ge Nanostructures by Reactive RF Sputtering. *A. Hernández-Hernández, F.J. De Moure-Flores, J.G. Quiñones-Galvan, K.E. Nieto-Zepeda, J. Santoyo-Salazar*, CINVESTAV-IPN, Mexico, *V.T. Rangel-Kuoppa, T. Plach*, Johannes Kepler Universitat, Austria, *M.A. Melendez-Lira*, CINVESTAV-IPN, Mexico

In this work we report the results of the synthesis and structural and optical characterization of heterostructures SiO_x/Ge/SiO_x by reactive RF sputtering. The characteristics of germanium along with its compatibility with silicon technology and the sensitivity of its band structure to confinement confer a high attractive to the synthesis of germanium nanostructures.

The samples were prepared on substrates of p-type Si monocrystalline (1 1 1) and commercial glass by reactive sputtering. The effect of the partial pressure of oxygen and Ge interlayer thickness on the electronic properties of the heterostructure is reported[1]. Structural characterization was carried out by grazing angle X-ray diffraction and atomic force microscopy. The electronic properties were studied by UV-Vis transmission, infrared and Raman spectroscopies. Surface roughness was quantified by atomic force microscopy. X-ray diffraction showed the amorphous characteristics of the heterostructures. UV-vis spectroscopy results do not presented relevant differences with respect to those from SiO₂ reference samples.

The Raman spectra shown modes associated to germanium indicating the formation of low dimensionality germanium particles embedded in an

amorphous phase. Ellipsometry and electronic transmission micrographs confirm the presence of Ge nanoparticles. Ohmic contacts were deposited in a van der Pauw geometry using AuSb. Temperature dependent Hall (T-Hall) measurements were done between 35K and 373K, using the van der Pauw method. The results indicate low resistivity values that could be explained due to the formation of a two dimensional electron gas or the presence of mini bands due to the quantum dots interaction.

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NS-TuP7 Spinel $M_xCo_{3-x}O_4$ Nanoparticles: Facile Low Temperature Solution Synthesis and Characterization. *D. Davis, M. Bencomo, T.N. Lambert, P. Lu, S. Limmer, W.G. Yelton*, Sandia National Laboratories

The synthesis and characterization of spinel $M_xCo_{3-x}O_4$ ($M = Mn, Fe, Ni, Cu$) nanoparticles was undertaken. Cobalt oxide-based nanoparticles doped with transition metals have a wide variety of potential applications, ranging from new material coatings for concentrating solar power applications to performing as cathode catalysts in fuel cells and metal-air batteries. We have recently demonstrated that $M_xCo_{3-x}O_4$ nanoparticles can be prepared using simple, low temperature solution precipitation methods, and that the final size and morphology of the nanoparticle depends on the extent of doping. These materials have been characterized by powder X-ray diffraction (P XRD), high-resolution transmission electron microscopy (HR-TEM), N_2 adsorption-desorption, and thermal gravimetric analysis/differential thermal analysis (TGA/DTA). The synthesis, characterization, as well as some potential applications of these materials, will be presented.

This work is supported by the Department of Energy, Office of Basic Energy Science and the United States Department of Energy under contract number DE-AC04-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the United States Department of Energy.

NS-TuP8 UV Induced Synthesis and XPS Characterization of Gold Nanoparticle-PMMA Composites. *E. Yilmaz, S. Suzer*, Bilkent University, Turkey

Polymer-nanoparticles are technologically important composite systems, gaining increasing interest from many different fields of science in the last decade. Many procedures were introduced for synthesis of gold and other metallic NPs in solution and their integration to polymer films afterwards. But a more efficient approach is to synthesize nanoparticles directly inside the polymer matrix. Irradiation of polymer-metal precursor mixtures with energetic light is a practical method for this purpose. In this study, we present in-situ synthesis of gold nanoparticles within poly(methylmethacrylate) (PMMA) films by UV irradiation.

An advantage of synthesizing gold NPs within polymer films is the opportunity of photo-patterning. Films having patterns made of regions with and without gold NPs can be produced, using masks designed to cut off the UV radiation at desired places. Such patterned films were investigated with secondary electron microscope (SEM) and dark regions between irradiated regions and masked regions were observed. These dark regions are speculated to be "ion free regions", where gold ions diffuse through irradiated regions during UV irradiation. These regions of about 10 μm width, suggests a very large distance for gold ions to diffuse through a rigid matrix like PMMA, which is very interesting. Supporting evidence for the existence and the properties of these regions was obtained from fluorescence studies with Rhodamine 6G molecule and x-ray electron spectroscopy (XPS). In XPS the gold content gradient shows, the border of the irradiated region contains more gold than the middle of the irradiated region which supports the diffusion of gold ions from masked regions through the irradiated regions.

Additionally, the electrical properties of PMMA with and without gold nanoparticles were investigated using XPS, while applying external bias to PMMA films with and without gold nanoparticles to probe the charging properties of the films. We observe an enhancement of conductivity of PMMA films containing gold nanoparticles.

NS-TuP9 Fabrication of Ordered Nanodot Arrays Utilizing Anodic Aluminum Oxide Template Formed on Si Substrate. *N.Y. Kwon, N.K. Kim, J.K. Yeon, G.Y. Yeom, I.S. Chung*, Sungkyunkwan University, Republic of Korea

We have fabricated anodic aluminum oxide (AAO) with two types of structures, namely, hexagonal and matrix arrays of pores. At first, Al thin

films with the thickness of 2 μm grown on Si (100) substrates were anodized in 0.3 M oxalic acid under conditions of 4 $^{\circ}C$ at 40 V. Then the hexagonal AAO templates with the thickness of 300 nm were obtained using two-step anodization. Alternatively, AAO template with a matrix pores was prepared utilizing focused ion beam milled indent. The size of pores was controlled between 30 nm and 60 nm by immersing in 5 % phosphoric acid at 20 $^{\circ}C$. In order to obtain smaller size of pores, the barrier layer was removed by neutral ion beam etching. Finally, we successfully fabricated hexagonal and matrix AAO templates with the pore sizes between 10 nm and 60 nm. The Si surfaces at the AAO pore bottoms were cleaned with dilute hydrofluoric acid after annealing at 900 $^{\circ}C$ in Ar gas. We then fabricated ordered Au and Ni nanodots arrays with controllable size between 10 nm and 60 nm. Scanning probe microscopy (SPM) and field emission secondary electron microscopy (FE-SEM) were used for characterization on shape of AAO and nanodots arrays.

NS-TuP10 On the Photoluminescence of Zn_2GeO_4 Nanorods Synthesized by a Simple Solution Route. *M.Y. Tsai*, National Applied Research Laboratories, Taiwan, Republic of China, *T.P. Perng*, National Tsing Hua University, Taiwan, Republic of China

NS-TuP11 Fabrication of Vertically Aligned Si Nanowires on Si (100) Substrates using AAO. *N.K. Kim, N.Y. Kwon, J.H. Lee, D.M. Whang, I.S. Chung*, Sungkyunkwan University, Republic of Korea

Vertically aligned Si nanowires were grown on using ordered AAO. At first anodic aluminum oxide (AAO) templates with both hexagonal pores and matrix pores were prepared. 2 μm Al thin film grown on Si (100) substrates were anodized in 0.3 M oxalic acid under conditions of 4 $^{\circ}C$ at 40 V. Then, the hexagonal AAO template with the thickness of 300 nm was obtained using a two-step anodization. On the other hand, AAO template with a matrix pores was obtained utilizing focused ion beam milled indent and anodization process. AAO template with pore sizes of 30 nm and that of 60 nm were obtained by immersing the AAO in 5 % phosphoric acid at 20 $^{\circ}C$ for 30 min and 60 min, respectively. The Si surfaces at the AAO pore bottoms were cleaned with dilute hydrofluoric acid after annealing at 900 $^{\circ}C$. Then, Si was deposited using LPCVD on AAO templates grown on Si substrate. The mixture gas with SiH_4 and HCl was used for Si deposition. Finally, we can obtain vertically aligned Si nanowires by removing AAO template using 1.8 wt% H_2CrO_4 and 7.4 wt% H_3PO_4 at 65 $^{\circ}C$ for 120 min.

NS-TuP12 Controlled Hybrid Bioactive Nanostructures by Integrating Gold Nanoparticles and Peroxidase to the ssDNA Nanotemplate. *M.-Y. Lin, F.H. Ho, Y.S. Yang*, National Applied Research Laboratories, Taiwan, Republic of China

Controlled positioning of metallic nanoparticles to assembly nanostructure has drawn interests in the field of nano-architecture, because of their electronic and optical properties. To achieve this, scientists have adopted various materials and methods for "bottom-up" and "top-down" fabrication of nanostructures. DNA nowadays is more than just a carrier for genetic codes, but it has also been used as novel materials for building nano-architectures. In this study, we aim to assemble the long, periodic single-stranded DNA nanotemplate (ssDNA) on the silicon-based substrate covalently and couple the supramolecules into a functional bioactive system. The preparation of ssDNA nanotemplates is based on the aptameric recognition of tumor marker: platelet-derived growth factors and rolling circle amplification (RCA) technology. Because of the periodic, repeated sequence with secondary structures on the ssDNA nanotemplate, the supramolecules, including gold nanoparticles and peroxidase enzyme will be incorporated on the specific sites of the ssDNA nanotemplate based on the Watson-Crick base-pairing strategy in a programmable way. The distance between the gold nanoparticles and peroxidase enzyme can be controlled by manipulated the sequence on each repeat. In addition, the distance can also be increased merely by thermal treatment (around 80 $^{\circ}C$) to open up the secondary structure on the ssDNA nanotemplate. Gold nanoparticles and peroxidase were periodically allocated precisely on each repeating sequence. The property of the peroxidase was affected by the gold nanoparticles and demonstrated by the luminescence measurement. In this study, we attempt to incorporate the gold nanoparticles on the ssDNA nanotemplate through hierarchical self-organization. The gold nanoparticle chains integrated with ssDNA nanotemplate were confirmed and visualized by the atomic force microscopy. We anticipate this study will pave a way for assembling novel bioactive materials with metallic nanoparticles for the development of modern electronic devices.

NS-TuP13 Magnetic Properties of Fe–O Nanonetworks, *C.V. Ramana, C.G. Franco, K.B. Karuppanan*, University of Texas at El Paso

NS-TuP14 Charge Transport across Phosphonate Molecular Wire-Indium Tin Oxide Junctions, *D.M. Rampulla, J.G. Kushmerick*, National Institute of Standards and Technology

Current-voltage analysis and transition voltage spectroscopy were used to measure the charge injection properties of monolayers of bithiophene phosphonate, quarterthiophene phosphonate, and decylphosphonate covalently bonded to an indium tin oxide surface. Hysteresis was observed for all three phosphonates, which is possibly explained by charge retention in the phosphonate. As compared to similar thiol/Au molecular junctions, there is no significant difference between the charge injection barriers of the three phosphonates, indicating that the phosphonate moiety dominates the observed charge injection properties.

NS-TuP16 Extreme Luminescent Signature of Coalesced Cd,Zn_{1-x}Se Quantum-Rod Alloys, *M. Plaisant, P.H. Holloway*, University of Florida

Common ion semiconductor alloys in quantum structures such as dots and rods have the added benefit of control of the electron affinity of the material in addition to the fundamental spectral control provided by quantum confinement. Such alloys could be useful in mixed-material devices such as organic/inorganic photovoltaic cells, since inorganic valence and conduction energy levels can be appropriately matched to the HOMO/LUMO levels of the compatible organic phase. In this research we have synthesized common anion II-VI alloys consisting of a large band-gap core/small band-gap shell. We have been able to achieve a spectral signature ranging up to 200nm over the visible spectrum by a one-pot synthesis of Cd_xZn_{1-x}Se alloys. The morphology of the alloy (supported by TEM, XRD and PL characterization) was a prolate rod-like quantum structure resulting from coalesced quantum dots consisting of three regions, each of which provides for a specific spectral signature. The 440nm PL peak was from ZnSe, while intermediate wavelengths were due to alloyed Cd_xZn_{1-x}Se, and a peak at 640nm was due to a CdSe rich shell. With the judicious control of time and temperature of reaction, it was possible to create a multi-region quantum structure that mimicked the spectral characteristics of a selected alloy composition, i.e. achieve emission over a much larger range of the electromagnetic spectrum.

NS-TuP17 Au-catalyzed Self Assembly of Ge-Sb-Te Nanowires by Metalorganic Chemical Vapour Deposition, *M.L. Longo, C. Wiemer, O. Salicio, R. Fallica*, CNR-IMM, Italy, *M. Fanciulli*, CNR-IMM and University of Milano Bicocca, Italy, *L. Lazzarini, L. Nasi, E. Rotunno*, CNR-IMEM, Italy

NS-TuP19 Folate Functionalized Hollow Silica Nanoshells: Synthesis, Characterization and Application as an Intracellular Delivery Container, *A. Liberman, S. Sandoval, J. Yang, S. Aschemeyer, J.G. Alfaro, D. Martin, M. Makale, A.C. Kummel, W.C. Trogler*, University of California, San Diego

An important area of biomedical nanotechnology is based on the interaction of living systems with inorganic and organic materials at the nanoscale. Silica nanospheres (NS) are attractive biomaterials because of their advantages as readily functionalized transport and imaging devices: the porous amorphous structure of silica colloid allows small molecule storage; the surface of silica can be modified easily with trimethoxysilyl reagents; silica has low biotoxicity and good biocompatibility. Silica nanospheres potentially have multiple biomedical applications as imaging agents, targeted drug delivery agents or gene transferring motherships. A simple method to fabricate hollow silica nanospheres with 100 nm or 200 nm diameters has been developed and tested. Amino polystyrene beads were used as templates and a 5-10 nm thick silica gel coating was formed by the sol-gel reaction. After removing template by calcinations, porous dehydrated silica gel nanoshells of uniform size were obtained. The porous structure of silica shell wall was characterized by transmission electron microscopy measurements, while particle size and zetapotentials of the particles suspended in aqueous solution were characterized by dynamic light scattering. The surfaces of the NS have been functionalized with folic acid in order to specifically target cancer cells. Folic acid, also known as vitamin B₉ or Folate, is essential for the synthesis of nucleotide bases and binds with high affinity to Folate receptors, which are frequently over-expressed in tumor cells and epithelial lined tumors such as ovarian carcinomas. With the use of confocal and two-photon microscopy, it was found that as the amount of folate on the surface of the NS was increased, a higher amount of NS endocytose into HeLa cancer cells, a cervical cancer cell line. Cytotoxicity studies will quantify the effectiveness of using folate coated silica shells for enhancing endocytosis of chemotherapy drugs in cell lines and in animal studies.

NS-TuP20 New Insights to Coarsening Phenomena and Nanoparticle-Mediated Surface Patterning: Pt/TiO₂(110), *F. Behafarid, A. Naitabdi, B. Roldan*, University of Central Florida

NS-TuP21 Some Effects of Iron Doping on Titanium Dioxide Nanoparticles, *D. González-Sánchez, J.L. González-Solis, G. Toriz, C.R. Michel-Urbe, G. Gómez-Rosas, A. Pérez-Centeno, M.A. Santana-Aranda*, Universidad de Guadalajara, Mexico

Iron doped titanium dioxide nanoparticles were synthesized using the sol-gel method. Solution was prepared in propanol, diluting Tween 80 surfactant (as pore directing agent), acetic acid and finally titanium tetrapropoxide (TTP); constantly stirred with a motor driven Teflon® palette. Doping iron was introduced by dissolving iron (III) chloride in propanol and adding to the solution; in the required amount to obtain 0.25; 0.5; 0.75; 1.0; 1.25 and 1.57 mol% iron with respect to titanium. Employed proportions of Tween80/PrOH/acetic acid/TTP were defined mostly following the values reported by Dionysiou's group on pure TiO₂ [1]. We obtained nanoparticles with sizes around 9 nm; being larger for lower iron content and smaller for higher iron content, as observed by electron microscopy and calculated from the full width at half maximum (FWHM) of X ray diffraction peaks, using Scherrer's formula. Raman spectroscopy and X ray diffraction measurements showed the presence of additional features, possibly related to a foreign phase into an almost pure anatase powder, increasing along with iron content.

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NS-TuP22 Study on High-Current-Density CNT Field Emitter: Current Enhancement with Titanium Micro-powders, *V. Chouhan*, The Graduate University for Advanced Studies, Japan, *T. Noguchi*, KEK-High Energy Accelerator Research Organization, Japan, *H.R. Liu*, Mie University, Japan, *S. Kato*, KEK-High Energy Accelerator Research Organization, Japan

CNT film field emitters (FFE) with a high current density up to a couple of 100 A/cm² and a high total current up to 100 mA are applicable to electron sources such as accelerators and high intensity X-ray sources for medical and security examinations. Based on our previous work of FFE, it turned out that one of the most crucial factors for high current and long time operation is to select appropriate CNT junction and substrate materials so as to maintain high thermal and electric conduction with high tensile strength. Our FFE was prepared by dispersing MWCNTs over a titanium film deposited on a metallic substrate by magnetron sputtering technique followed with rooting of MWCNTs into the titanium film at high temperature. In this study, use of titanium micropowders was attempted to sprinkle on the dispersed MWCNTs. This powder would allow to enhance reaction for better carbide formation. This paper describes the detailed procedures and the experiments to achieve the high emission current density from the FFE.

NS-TuP23 Role of the pH Obtaining Microstructures and Size-Controlled SnO₂ Nanocrystals by the Precipitation Method, *C.E. Marin-Pineda, M.A. Santana-Aranda, C.R. Michel-Urbe, G. Gómez-Rosas*, Universidad de Guadalajara, Mexico, *O.E. Contreras-López*, Universidad Nacional Autónoma de México, *A. Pérez-Centeno*, Universidad de Guadalajara, Mexico

In this work we present the results of the pH effect on the synthesis of SnO₂ by precipitation. This simple chemical route allowed us to obtain SnO₂ nanocrystals whose grain size depends linearly on the pH, ranging from 3 to 8nm, from basic to acid solutions, respectively. The most important, microstructures were also fabricated by this simple method, mainly whiskers and long fibers. The crystalline quality and the morphology were confirmed by X-ray diffraction and electron microscopy. The samples showed high-energy optical absorption as observed by UV-Vis measurements.

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NS-TuP25 Nanoscale Roughness Analysis through System Evaluation by Atomic Force Microscopy. C.Y. Su, Y.H. Lin, S.S. Pai, P.L. Chen, N.N. Chu, C.C. Yang, C.C. Chen, M.H. Shiao, Instrument Technology Research Center, NRL, Taiwan, Republic of China

Atomic Force Microscopy (AFM) has become an essential tool in various applications of nanotechnology. Although roughness inspection is one of the most important and most common measurement since scanning probe microscopes (SPMs) have been invented, there is lack of international comparison on this application and it is in the early stage of prototype testing up to now. By combining a high precise three-axis closed-loop feedback scanner stage with the AFM, the mapping capability of surface roughness distribution from the sample topography with the sub-angstrom resolution is achievable. In this study, a procedure has been designed to optimize AFM parameters such as inspection area size, target amplitude, drive frequency, set-point, scan rate, integral gain, proportional gain, look-ahead gain and so forth for optimized surface roughness inspection. System evaluation of the measurement uncertainty is compliant to ISO, Guide to the Expression of Uncertainty in Measurement and ISO 5436-2:2001/Cor 2:2008, Geometrical Product Specifications (GPS) - Surface texture: Profile method; Measurement standards - Part 1: Material measures. Key factors such as repeatability, non-linearity, straightness, noise, probe deformation error, numerical error, system long-term stability and sample uniformity have been included for evaluation. By carefully control of probe deformation error, measurement uncertainty can be suppressed effectively.

NS-TuP26 Absorption based Model of Porous Silicon Photoluminescence. C.G. Lowrie, S.B. Earles, Florida Institute of Technology

Irradiating porous silicon with a 532 nm laser produces a photo luminescent (PL)

peak at 722 nm. This peak corresponds to the (3,1,1) absorption level of a cubic silicon

nanocrystal 3.79 nm in length.

NS-TuP27 Comparative Study on the Properties of ZnO Nanowires and Nanocrystalline Thin Films. E. Broitman, Carnegie Mellon University, C. Bojorge, CINSO-CITEFA-CONICET, Argentina, F. Elhordoy, V. Kent, Universidad de la Republica, Uruguay, G. Zanini Gadioli, Carnegie Mellon University, R.E. Marotti, Universidad de la Republica, Uruguay, H. Canepa, CINSO-CITEFA-CONICET, Argentina, E.A. Dalchiele, Universidad de la Republica, Uruguay

Nanostructures made of wurtzite ZnO, such as dots, nanobelts, nanowires, and nanocrystals, have recently attracted attention due to their proposed applications in electronic and optoelectronic devices. Here we present a comparative study on the properties of ZnO thin films containing nanocrystals and nanowires.

ZnO nanocrystalline (NC) films, obtained by the sol-gel process, were deposited from a precursor solution using zinc acetate dehydrate in ethyl alcohol. After a four-layer spin-coating on crystalline substrates, the films were transformed into nanocrystalline films by a thermal treatment at 370 °C during 3 hours. ZnO nanowires (NW) were electrochemically grown onto a ZnO seed layer sol-gel spin-coated using a conventional three electrode cell, with the substrate as the cathode, a Zn sheet as the counter electrode and a saturated calomel electrode (SCE) as the reference one. The electrolyte was an aqueous solution of the Zn²⁺ precursor (1 mM zinc acetate) and a supporting electrolyte (0.1 M sodium acetate), saturated with bubbling oxygen. The electrodeposition was carried out at 70 °C under potentiostatic conditions at two different potential values (-0.900 and -1.000 V vs. SCE) and during 70 min. The initial pH was adjusted to 6.76. Both, NC and NW samples, were deposited onto crystalline quartz substrates covered by a Au or Ag electrode, and ready to use in a quartz crystal microbalance (QCM).

Samples microstructure was characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Optical Diffuse Reflectance Spectroscopy (DRS). XRD measurements show in both cases a typical diffraction pattern of ZnO wurtzite structure. SEM micrographs of NC films have a smooth surface, while the NW sample reveal the presence of nanowires with hexagonal section and diameters ranging from 40 to 100 nm. No specific structure was observed by the DRS measurements on the seed layer, probably due to the fact that these films were not thick enough as required by the technique. For the NW onto seed layer samples, the optical characterization reveals the presence of ZnO with bandgap energy between 3.22 eV (for the ones grown onto Au metallic contacts) and 3.29 eV (for the Ag metallic contacts).

A QCM placed in a vacuum chamber was used to measure the water adsorption of the samples. Water vapour was introduced through a leak valve while a capacitance manometer was used to measure the partial pressure of water in the range 10¹-10⁵ Pa. The mass of water adsorbed on

the surface of the quartz crystal was calculated using the Sauerbrey equation. The NW drastic increase of the surface area was revealed through a higher amount of water adsorption.

NS-TuP28 Effects of Surface-Sulfurization on Field Emission Characteristics of Al-doped ZnO Nanorods. T. Hirate, T. Kaneshiro, T. Satoh, Kanagawa University, Japan

ZnO is a promising material for ultraviolet (UV) and white light-emitting diode (LED) applications, because of its large exciton binding energy of 60 meV relative to the thermal energy of 25 meV, as well as its large band gap of 3.37 eV at room temperature. In the past several years, the fabrications and characterization of one-dimensional ZnO nanostructures have been extensively investigated for their applications, such as LEDs, gas sensors, field emission devices, nanolasers and photovoltaics. We have studied on application of vertically aligned ZnO nanorods grown by CVD to field emission devices. In this paper we report on surface-sulfurization of Al-doped ZnO nanorods and the effects on the field emission characteristics.

Al-doped ZnO nanorods are grown by low-pressure thermal CVD cooperated with 10Hz Nd-YAG pulsed laser ablation of Al₂O₃ target, which is developed by us. Precursors for CVD are Zn vapor and O₂. Substrates are n-Si(111) wafers. ZnO nanorods are grown in two stages. In first stage of growth no laser ablation is used to grow aligned ZnO nanorods and in second growth stage laser ablation is used to grow Al-doped ZnO layer on ZnO nanorods grown in 1st stage. Concentration of Al in ZnO nanorods is controlled by laser power. Finally surface-sulfurization is performed in H₂S atmosphere. It is revealed that the conditions of sulfurization have very complex effects on field emission characteristics. An example of the conditions are 39.6 Pa of H₂S partial pressure, 550 °C and 5 min. Field emission characteristics are measured in vacuum of 10⁻⁴ Pa using 12.7mm diameter metal ball as anode electrode with separation of 160 micron meter.

When laser power is high (2.0W), the low initial electric field of 4 V/micron meter for emission is obtained. In this case, however, ZnO nanorods with sharp tips are grown due to high laser power, thus the reason of improvement of field emission characteristics is not clear at present. We are studying on this point. We estimate that the surface-sulfurization of ZnO nanorods are effective to improve the field emission characteristics because the electronic affinity of ZnS is lower than ZnO.

Wednesday Morning, October 20, 2010

Energy Frontiers Topical Conference
Room: Mesilla - Session EN+NS-WeM

Organic Photovoltaics

Moderator: R.J. Holmes, University of Minnesota

8:00am **EN+NS-WeM1 Interface Properties between Organic Blend Films and Metallic Substrates for Solar Cell Applications.** *L. Lozzi, S. Santucci*, University of L'Aquila, Italy

In the last years a strong effort has been devoted to develop new solar cells based on organic compounds. These organic compounds can be mixed with other molecules, as, for example fullerene or its derivatives, forming a blend film to increase the charge separation efficiency. An important issue to evaluate the properties of these devices is to investigate the interface properties between these films and the metallic substrates generally used to realize the contacts.

In this work we have analysed, by using the photoemission spectroscopy (X-ray, Soft X-ray and Ultraviolet photons) the core levels and the valence band structures, in particular the HOMO states, of copper phthalocyanine (CuPc) and fullerene (C₆₀) blend films, composed by different CuPc:C₆₀ concentrations, deposited onto several metallic substrates (Au, oxidized Al and ITO), generally used as metallic contacts.

The molecular levels show, as a function of the blend film thickness and composition, a different behaviour depending on the substrate type. On Au the organic molecular level show, as the blend film thickness increases, a shift towards high binding energy. This shift depends on the organic composition. Depositing the blend film onto oxidized Al, a small shift in the opposite direction, i.e. towards lower binding energy, has been observed. Instead, when ITO substrate have been used, no shift have been observed.

The core levels generally show a different behaviour with respect to the molecular levels suggesting that no strong interaction with the substrates exist but a small redistribution of the molecular levels is present.

8:20am **EN+NS-WeM2 Energy Level Alignment at Conductive Polymer/Metal Interfaces.** *M.M. Beerbom, W. Wang, R. Schlaf*, University of South Florida

The energy level alignment between two prototypical conductive polymers, poly(3-hexylthiophene) (P3HT) and poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and metals was investigated with ultraviolet and x-ray photoemission spectroscopy (XPS, UPS) dependent on the metal substrate work function. In these experiments thin films of the polymer material were grown in several steps on in-vacuum cleaned metal substrates. In between deposition steps the surface was characterized with UPS and XPS without breaking the vacuum. This was enabled by electrospray polymer thin film deposition directly from solution, which allows the growth of clean macro-molecular films in vacuum. This enabled the measurement of the hole injection barriers and interface dipoles unaffected by environmental contamination artifacts. The presented results demonstrate a systematic dependence of the interface dipole on the substrate work function. This indicates that the charge neutrality level-based "induced density of interface states" (IDIS) model also holds for non-reactive conductive polymer/metal interfaces.

8:40am **EN+NS-WeM3 Electronic Structure of Key Interfaces in Organic Photovoltaic Cells.** *A. Kahn*, Princeton University **INVITED**

This talk reviews recent work on two types of interfaces that are important for organic photovoltaic cells. In the first part, we present the first direct determination via ultra-violet and inverse photoemission spectroscopy (UPS, IPES) of molecular level alignment between donor (D) and acceptor (A) in a bulk heterojunction.[1] We take the example of the interface between poly(3-hexyl thiophene) (P3HT) and [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM). The P3HT/PCBM blend is a standard, prototypical system for bulk heterojunction organic photovoltaic (OPV) cells. In question here is the relative position of the molecular levels of the donor (D) and acceptor (A) materials in the blend, given that LUMO(D) - LUMO(A) is linked to the charge separation process, and LUMO(A) - HOMO(D) is linked to the open circuit voltage (V_{oc}) of the OPV cell. A precise measurement of these molecular level offsets provides a firm basis for the accurate modeling of V_{oc} produced by these cells. The second part of the talk looks at the electronic structure of transition metal oxide films, such as MoO₃ or WO₃, and their role as hole-collecting electrode or central element of a charge recombination layer (CRL) in a tandem solar cell. Recent work has shown that these compounds exhibit exceptionally large electron affinity and work function.[2,3] N-doped by oxygen vacancies,

they can act as efficient high work function hole-extractor (via electron injection through their conduction band) on the anode side of the solar cell. Similarly, combined with a low work function interlayer electrode, they form the central element of a CRL in a tandem cell.

[1] Z. Guan, J. Kim, Y.-L. Loo, and A. Kahn, *Org. Electr.* (submitted)

[2] M. Kröger, S. Hamwi, J. Meyer, T. Riedl, W. Kowalsky, and A. Kahn, *Appl. Phys. Lett.* **95**, 123301 (2009)

[3] J. Meyer, M. Kröger, S. Hamwi, T. Riedl, W. Kowalsky and A. Kahn, *Appl. Phys. Lett.* (in press, 2010)

9:20am **EN+NS-WeM5 Photocarrier Generation and Transport Characteristics in Organic Heterojunction Solar Cells.** *J.D. Myers, W.T. Hammond, J.P. Mudrick, J. Xue*, University of Florida

There have been many recent advances in improving the efficiency of organic photovoltaics (OPVs) by using new organic active materials and/or employing improved device architectures. However, our understanding of fundamental OPV device operation principles is still incomplete. A new measurement technique for OPVs, synchronous photocurrent measurement, can give insight into the generation and transport characteristics of photogenerated charge carriers. In synchronous photocurrent measurements, a device is illuminated with chopped monochromatic light in addition to a constant white light bias with an intensity close to 1 sun. With the device biased at any given voltage, the current of the OPV is fed into a lock-in amplifier, which extracts the relevant photocurrent response to the monochromatic light with a varying wavelength.

With this technique, we have shown the bias dependence of the photocurrent for various small-molecule device structures. In planar (or bilayer) and planar-mixed organic heterojunctions (HJs), the photocurrent under forward bias is negative (flowing from the cathode to the anode, opposite to the direction of the dark current), up to high forward biases (~1 V), well in excess of the built-in potential. This reveals the surprisingly dominant nature of the diffusion photocurrent in these architectures. However, for mixed HJ cells, the photocurrent reverses direction at a certain forward bias with the reversal of directions for the electric field and the drift current inside the active layer. There exists a strong correlation between the zero-photocurrent voltage and charge generation profile in mixed HJ OPVs.

This technique can also determine the relative contributions of field-induced exciton dissociation and donor-acceptor interface exciton dissociation in planar HJ cells. Traditionally, exciton dissociation in planar HJ cells is assumed to occur almost exclusively at the donor-acceptor interface; field-induced dissociation is taken as a negligible contributor to the photocurrent in these devices. However, as the thickness of an active layer (either donor or acceptor) increases, field-induced dissociation becomes more important. The field-induced contribution increases as the average location of exciton generation moves greater than one exciton diffusion length away from the interface, as demonstrated by using optical field simulations.

We have further used photocurrent measurements as an instrument in analyzing the recombination behavior in planar organic HJs utilizing different materials. Synchronous photocurrent measurement is a useful technique in determining the photocarrier behavior in organic HJ solar cells.

9:40am **EN+NS-WeM6 Interface Engineering for Improved Organic Photovoltaic Performance.** *C.K. Chan, D.S. Germack, P. Haney, L.J. Richter, D.M. DeLongchamp, D.J. Gundlach*, National Institute of Standards and Technology

Organic photovoltaic (OPV) cells are attractive for flexible, low-cost, large-area, and lightweight solar conversion applications. Despite this demand, robust and efficient devices have been limited by the quality of organic semiconductor materials and by the poor understanding and control of their interfaces. Interface modification using self-assembled monolayers or conducting polymers can be leveraged to tune the composition and phase segregation in binary bulk heterojunction photovoltaic cells. In this work, the interface composition of a 1:1 mixture of poly(3-hexylthiophene):[6,6]-phenyl-C₆₁-butyric-acid-methyl-ester (P3HT:PCBM) was characterized using near-edge x-ray absorption fine structure (NEXAFS) spectroscopy as a function of surface energy. The substrates consisted of a low surface energy Nafion-based copolymer, 4-phenylbutyltrichlorosilane or octyltrichlorosilane self-assembled monolayers on SiO₂, or high surface energy native SiO₂. It was observed that while the free surface of the film was always P3HT-rich (7:3 P3HT:PCBM), the bottom interfacial composition varied from P3HT-rich (4:1 P3HT:PCBM) to PCBM-rich (1:4 P3HT:PCBM) as the surface energy of the substrate increased from 20 mN/m² to 80 mN/m². These observations were further supported by electrical characterization of bulk heterojunction films deposited on thin-film transistor structures where the surface energy of the gate dielectric was

modified with self-assembled monolayers. The transistor performance exhibited higher hole mobility at P3HT enriched organic-dielectric interfaces (low surface energy substrates), while ambipolar transport was observed in devices with a PCBM enriched interface (high surface energy substrates). These observations of surface energy dependant interfacial composition should have clear implications for optimizing photovoltaic cell design in regards to "conventional" and "inverted" device architectures. However, P3HT:PCBM bulk heterojunction solar cells constructed on low and high surface energy substrates in conventional and inverted device structures exhibit nominally identical performance. Early efforts at modelling the effect of compositional gradients on photovoltaic performance suggest that this is expected given that current densities increase in constricted percolation pathways to maintain constant overall current. Although this may have little impact on initial device performance, the effects of higher current densities in the constricted interfacial regions on device lifetime are currently being investigated.

10:40am **EN+NS-WeM9 Experimental and Theoretical Investigation of Excitonic Energy Transfer in Organic Photovoltaic Cells**, *W.A. Luhman, R.J. Holmes*, University of Minnesota

This work demonstrates a novel approach for measuring the Förster radius of energy transfer between electron donating and accepting materials commonly used in organic photovoltaic cells (OPVs). Typically an exciton must diffuse to an electron donor-acceptor interface in order to be dissociated and contribute to photocurrent. Alternatively, if an exciton in the donor layer is instead able to undergo long-range energy transfer to the acceptor layer, diffusion is no longer required, and dissociation occurs from the acceptor layer. While such processes are surprisingly common in OPVs, they are often incorrectly ignored in measurements of the exciton diffusion length and in models of device performance. In this work, the efficiency of energy transfer between an emissive donor and an absorptive acceptor is investigated using complementary experimental and theoretical techniques. This is accomplished by spatially separating the donor and acceptor materials using a wide energy gap spacer layer to suppress charge transfer, and tracking the donor photoluminescence as a function of spacer layer thickness. Fitting experimental data obtained for a variety of small molecule and polymer donor materials allows for the extraction of Förster radii that correlate very well with predicted values. The effect of energy transfer on device performance and on measurements of the exciton diffusion length is also investigated using the archetypical small molecule donor material boron subphthalocyanine chloride (SubPc). An exciton diffusion length of (7.5 ± 0.4) nm is extracted from photoluminescence quenching experiments that carefully account for the role of energy transfer. These results will ultimately provide insight into the fundamental processes of exciton diffusion and dissociation in OPVs.

11:00am **EN+NS-WeM10 Molecular Architecture and Charge Separation at Abrupt Donor-Acceptor Interfaces**, *G.J. Dutton*, NIST, *W. Jin*, University of California at San Diego, *D.B. Dougherty*, North Carolina State University, *W.G. Cullen*, University of Maryland, *S.W. Robey*, NIST, *J.E. Reutt-Robey*, University of Maryland

Photocurrent production in organic photovoltaic structures differs fundamentally from current generation in inorganic semiconductor solar cells. Dissociation of excitons formed by optical absorption in organic materials requires heterointerfaces between electron donor and acceptor components. The extent to which molecular architecture, particularly along the donor-acceptor interface, impacts electronic level alignment and charge separation is of fundamental interest. In this work, we prepare well-defined molecular interfaces by the physical vapor deposition of select donor (MPc, Pn) and acceptor (C_{60}) components under UHV conditions. We determine the detailed structure of the donor-acceptor interface with Scanning Tunneling Microscopy and establish a correlation with electron band alignment (PES) and exciton dynamics (2PPES).

For technologically relevant interfaces between C_{60} and donors such as pentacene (Pn) or phthalocyanines (Pc), distinct structures/molecular orientations can be selectively engineered by organic MBE through deposition sequence and flux. For the case of C_{60} and Pn, "co-facial" C_{60} -Pn interfaces are formed by C_{60} deposition on crystalline Pn bilayer films supported by Ag(111), whereas "edge-on" C_{60} -Pn interfaces result from Pn deposition on hexagonal close-packed C_{60} monolayers supported by Ag(111). Such "edge-on" interfaces expand into large dendritic islands, as per reported "thin-film" phases, and support C_{60} cluster formation under subsequent C_{60} deposition. We show how electronic level alignments critical to V_{oc} and charge separation efficiency are impacted by these structural changes, and extend this information to other small-molecule cases, ZnPc: C_{60} and perfluorinated ZnPc, as time permits.

Finally, for interfaces between CuPc and C_{60} , we will present the first studies of charge separation at well-characterized organic donor-acceptor interfaces using TR-2PPE. By pumping the CuPc Q-band at 1.65eV, a time-delayed UV pulse then probes the excited state population. We identify

dominant relaxation processes on timescales from 100fs to >100ps. By varying the CuPc film thickness, we observe significantly enhanced charge transfer of the singlet exciton at the interface with C_{60} . Following the population dynamics as a function of energy also provides evidence for recombination from charge transfer states back to the low-lying CuPc triplet.

This work has been supported in part by the NSF under the UMD MRSEC (DMR0520471) and the Surface & Analytical Chemistry Program (CHE0750203).

11:20am **EN+NS-WeM11 Hybrid Organic/Inorganic Solar Cells Based on Silicon Nanowires**, *M. Pietsch*, Max Planck Institute for the Science of Light, Germany, *V.A. Sivakov*, *B. Hoffmann*, *G. Broenstrup*, *F. Talkenberg*, Institute of Photonic Technology, Germany, *T. Seyller*, Friedrich-Alexander Universität Erlangen-Nürnberg, Germany, *T. Fritz*, *B. Schroeter*, Friedrich-Schiller University Jena, Germany, *S.H. Christiansen*, Max Planck Institute for the Science of Light, Germany

11:40am **EN+NS-WeM12 Influence of UV Radiation on Charge Injection Barriers in Dye-Sensitized Solar Cells**, *S. Gutmann*, *M.A. Wolak*, *M.M. Beerbom*, *R. Schlaf*, University of South Florida

The electronic structure of the interfaces in dye-sensitized solar cell structures was investigated using x-ray and ultraviolet photoemission spectroscopy (XPS, UPS). Electro spray thin film deposition in high vacuum was used to build the interfaces of interest directly in vacuum without exposure to the ambient. Electro spray enables the fabrication of clean, essentially uncontaminated thin films of organic molecules and nanoparticles directly in vacuum.

The experiments focused on the investigation of the indium tin oxide (ITO)/nanocrystalline TiO_2 interface, as well as the characterization of the $TiO_2/RuL_2(NCS)_2$ [cis-bis(4,4'-dicarboxy-2,2'-bipyridine)-bis(isothiocyanato)-ruthenium(II)] ("N3", a prototypical dye used in many currently pursued device structures)-dye interface. Both TiO_2 and N3 films were built up in several steps. After each step, characterization by XPS and UPS was performed. The resulting sequence of spectra allowed the determination of charge injection barriers and interface dipoles at the ITO/ TiO_2 and $TiO_2/N3$ interfaces. Our experiments revealed a strong influence of the UV radiation during UPS measurements on the band line-up at these interfaces. This was revealed though low intensity x-ray photoemission spectroscopy (LIXPS) measurements, which allow the measurement of the work function prior to UV exposure. These results suggest that even low-level UV radiation, such as encountered in an encapsulated solar cell, may lead to cell degradation over time due to a re-alignment of the electronic structure with detrimental effect on charge transport.

In Situ Microscopy and Spectroscopy Topical Conference

Room: Acoma - Session IS+AS+NS+MI-WeM

In Situ Microscopy/Spectroscopy – In Situ Nanoscale Processes

Moderator: A. Mkhoyan, University of Minnesota

8:00am **IS+AS+NS+MI-WeM1 Low-dimensional Superconductivity of Pb Nanostructures**, *J. Kim*, *H. Nam*, *G.A. Fiete*, *C.K. Shih*, The University of Texas at Austin

The influence of low-dimensional geometries on superconductivity is an important issue to study because in low dimensions it is key to understanding coherence and robustness of the superconducting state in quantum-mechanically confined geometries. The lateral size dependence of superconductivity on 2 dimensional Pb islands is studied by using *in-situ* low temperature Scanning Tunneling Microscopy/Spectroscopy (STM/S). The superconducting transition temperature (T_c) of each island is obtained by fitting the STS data with a BCS-like density of states. It is found that superconductivity shows a clear dependence on the Pb island lateral size even when it is larger than the bulk coherence length (~80nm), and it is also found that T_c drops very quickly below a certain lateral size. In addition, an intriguing lateral proximity effect is observed at the interface of different local superconducting regions of Pb islands. Current imaging tunneling spectroscopy (CITS) is used to visualize this proximity effect in real space.

8:20am **IS+AS+NS+MI-WeM2 Enabling the Measurement of In-Situ, Site-Specific Mineral Transformation Rates in Supercritical CO₂ through Development of a High Pressure AFM.** *S. Lea*, Pacific Northwest National Laboratory, *S.R. Higgins*, Wright State University, *K.G. Knauss*, Lawrence Berkeley National Laboratory, *K.M. Rosso*, Pacific Northwest National Laboratory

Capture and storage of carbon dioxide in deep geologic formations represents one promising scenario for minimizing the impacts of greenhouse gases on global warming. At issue is the ability to demonstrate that CO₂ will remain stored in the geological formation over the long-term and so knowledge of mineral-fluid transformation rates is critical for this determination. The majority of previous research on mineral-fluid interactions has focused primarily on the reactivity of minerals in aqueous solutions containing CO₂. However, caprock integrity would be dictated primarily by mineral interaction with supercritical CO₂ (scCO₂) as the buoyant phase slowly displaces or desiccates residual aqueous solution at these surfaces. Many of the mechanisms of mineral interfacial reactions with hydrated or water-saturated CO₂ are unknown and there are unique challenges to obtain kinetic and thermodynamic data for mineral transformation reactions in these fluids.

A high-pressure atomic force microscope (AFM) is currently under development that will enable *in-situ* site-specific measurements of metal carbonate nucleation and growth rates on mineral surfaces in contact with scCO₂ fluids. This apparatus is based on the hydrothermal AFM that was developed by Higgins et al., but includes some enhancements and is designed to handle pressures up to 1500 psi. The noise in our optically-based cantilever deflection detection scheme is subject to perturbations in the density (and therefore index of refraction) of the compressible supercritical fluid. Consequently, variations in temperature and pressure within the fluid cell can have a significant impact in our ability to discern atomic steps on mineral surfaces. We demonstrate with our test fluid cell that the equivalent rms noise in the deflection signal is similar to (and in some cases less than) the equivalent noise for an AFM in its 'standard configuration' under controlled pressures of ~80 bar and temperatures of 60-80 °C and therefore *in-situ* atomic scale imaging of mineral surfaces in scCO₂ should be possible. This talk will also focus on recent progress in the development of this instrumentation, which will enable a unique platform for elucidating the role of water in mineral transformations, providing a means for determining effective kinetic constants.

1. Higgins, S. R.; Eggleston, C. M.; Knauss, K. G.; Boro, C. O., A hydrothermal atomic force microscope for imaging in aqueous solution up to 150°C. *Review of Scientific Instruments* **1998**, *69* (8), 2994-2998.

8:40am **IS+AS+NS+MI-WeM3 Au on VLS-grown Si Nanowires: Spreading of the Liquid Metal Seed.** *E. Dailey*, *P. Madras*, *J. Drucker*, Arizona State University **INVITED**

In situ TEM shows that liquid AuSi spreads from the seed along the NW sidewalls to form a thin liquid sheath for some growth conditions. The thin liquid film phase separates to form small solid Au clusters when the NW is cooled below the solidus temperature. Quantitative composition maps show that the Au composition is highest near the NW tip. The thickness and length that the liquid film spreads from the seed is growth condition and NW diameter dependent and represents a steady state during growth. These observations can be related to the spreading thermodynamics of liquid droplets along cylinders. Growth conditions for which the liquid AuSi spreads from the seed stabilize 'vertical' growth along <111> by lowering the surface energy of the high-energy {112} bounding facets. In contrast, the NWs kink toward <112> when grown using conditions that favor growth with Au-free sidewalls since these NWs are bound by facets that are found on the Si equilibrium crystal shape.

9:20am **IS+AS+NS+MI-WeM5 Advanced Study of Nanoscale Mechanisms: Plans for In-Situ TEM Microreactor, Gas Cell, and Multi-Beam Irradiation Experiments.** *B.G. Clark*, *K. Hattar*, Sandia National Laboratories, *D. Nackashi*, *J. Damiano*, *S. Mick*, Protochips, Inc., *B.L. Doyle*, Sandia National Laboratories

Over the years, in-situ TEM experiments have allowed for observation of material mechanisms at high resolution and in real time; a feat often not possible with any other experimental technique. With increasing demand for understanding nanoscale material mechanisms, both with growth in the applications of nanomaterials and in the development of predictive materials models based on experimental observation, the realm of in-situ TEM experiments has continued to expand. Highlighted in this presentation will be the development of three, exciting new capabilities for in-situ TEM experiments at Sandia National Labs.

The first part of the talk will focus on the development of two new in-situ TEM stages. Expanding on the success of static and single inlet-outlet liquid cells, we are designing a new in-situ TEM microreactor liquid cell with the capability to mix fluids in controlled temperature regimes, to view

reactions as a function of time, and to capture and analyze reaction products. Research programs using this stage will pursue studies of self-assembly, directed assembly, and nanoparticle formation and growth. In addition, for observation of advanced degradation of materials in the presence of gases and/or vapor, a new in-situ TEM gas cell stage is being developed. This stage will have the capability to study a variety of gas-solid and vapor-solid interactions, such as corrosion, oxidation, and hydriding, with accurate control over temperature and pressure. Envisioned research will include understanding environmental degradation of materials during storage of spent nuclear fuels, an issue of critical importance for the future of nuclear energy.

The second part of the talk will highlight the development of a new, triple-ion-beam in-situ irradiation TEM. By combining expertise in in-situ TEM experiments with expertise in ion beam studies, planning is currently underway that would culminate in the construction of an instrument capable of studying the effects of bombardment by up to three ion beams simultaneously within the TEM. This unique, triple-ion-beam capability would enable advanced experiments such as real-time studies of neutron induced damage and transmutation in a fission/fusion reactor by combining Fe, He, and H ions.

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9:40am **IS+AS+NS+MI-WeM6 In Situ TEM Investigation into the Thermal Stability of Nanograined FCC Metals and Alloys.** *K. Hattar*, *B.G. Clark*, Sandia National Laboratories, *J. Kacher*, University of Illinois at Urbana-Champaign, *J.A. Knapp*, *D.M. Follstaedt*, *L.N. Brewer*, Sandia National Laboratories, *I.M. Robertson*, University of Illinois at Urbana-Champaign

10:40am **IS+AS+NS+MI-WeM9 In Situ TEM Studies of Nanomagnetism and Thermal Transport.** *J. Cumings*, University of Maryland **INVITED**

The transmission electron microscope is a powerful tool for many areas of nanoscience. The combination of high spatial resolution and high time resolution, giving video-rate imaging, makes it uniquely capable of many types of studies of phenomena in-situ during imaging. Here I will present two areas where we have made recent advances. In nanomagnetic structures, it is possible to image in real-time the reversal process of coupled systems called artificial spin ice. These systems exhibit frustration, leaving disorder in their lowest energy magnetic configurations. I will present studies showing the magnetic reversal processes for these structures, revealing that microscopically correlated events lead to avalanche phenomena. A second topic that I will present is electron thermal microscopy of carbon nanotubes. Here, a new technique will be introduced that allows thermal imaging with nanoscale spatial resolution. This technique has been used to study the thermal transport through carbon nanotubes, and I will present results showing that thermal contact resistance can limit the thermal transport in nanotubes. I will show that this contact resistance can be tuned by two orders of magnitude by appropriately controlling the fabrication of the contacts. Together these results serve to demonstrate the capabilities of studies utilizing in-situ transmission electron microscopy.

11:20am **IS+AS+NS+MI-WeM11 In-situ Infrared Transmission Analysis of Atomic Layer Deposition Reactions on Polymer Films and Fibers.** *G.N. Parsons*, *B. Gong*, *J.S. Jur*, *C. Oldham*, *K. Lee*, North Carolina State University

Many new product applications related to packaging, filtration, protection and others offer substantial opportunities and raise new demands for polymer/inorganic thin film integration and surface modification. In-situ transmission infrared spectroscopy can provide critical insight into reaction mechanisms that proceed during inorganic film deposition on organics. We are particularly interested in low-temperature atomic layer deposition (ALD) which ideally proceeds through a binary sequence of self-limiting surface reactions to form highly conformal and uniform films on high surface area structures. In-situ IR spectroscopy allows us to probe and identify specific polymer/precursor reaction mechanisms that occur during precursor and reactant exposure. Typical atomic layer deposition precursors and reactants include trimethylaluminum (TMA), diethyl zinc (DEZ) and water, and polymer materials studied to date include polypropylene, polyamide-6, polyesters (such as polybutylene terephthalate), cellulose, polyvinyl alcohol and others. We have investigated deposition reactions on planar polymer sheets as well as micro- and nano-scale polymer fibers.

In-situ IR transmission data demonstrates that typical non-reactive materials such as polypropylene will take up precursors with minimal precursor/polymer reaction, resulting in subsurface alumina nucleation. Polymers with more reactive backbone or side chain groups, such as cellulose, polyvinyl alcohol or polyamide-6 react readily with the precursor. For example, when polyamide-6 is exposed to TMA, N-H and C-O stretching modes decrease markedly, indicating that TMA attacks the electrophilic carbon atom in the carbonyl group leading to methyl insertion and formation of C-O-Al- and C-CH₃ bonds. Electron micrograph images of polyamide fibers after TMA exposure confirms significant extent of reaction. Deposition on cellulose cotton fibers, however, shows primarily surface adsorption, resulting in true ALD growth and highly conformal film coatings by TEM. We will show details of the in-situ transmission ALD reactor, and illustrate how the tool is especially amenable and adaptable to in-situ surface reaction analysis on polymer fiber networks.

Nanometer-scale Science and Technology

Room: La Cienega - Session NS+AS+MN-WeM

Characterization and Imaging at Nanoscale

Moderator: E.I. Altman, Yale University

8:20am **NS+AS+MN-WeM2 Surface Preparation of Supported Flat Gold Nanoparticles for use as Au(111) Single Crystal Substrates, D.H. Dahanayaka, L.A. Bumm, The University of Oklahoma**

8:40am **NS+AS+MN-WeM3 Determination of the Adsorption Site for Alkanethiol Monolayers on Au(111), Q. GUO, University of Birmingham, UK**

The bonding sites for Au-atom-octanethiolate within the ($\sqrt{3}\times\sqrt{3}$)R30° structure on Au(111) has been investigated with high-resolution scanning tunneling microscopy (STM) imaging. By establishing the relationship between the lateral positions of adsorbates on the top layer of gold and those inside an etch pit, we are able to determine the adsorption configuration with a high degree of accuracy for the illusive ($\sqrt{3}\times\sqrt{3}$)R30° molecular layer. Within any one particular domain, the Au-atom-octanethiolate species are found to occupy either the fcc hollow or the hcp hollow site.

9:00am **NS+AS+MN-WeM4 Atomic Co Wires: Room and Low Temperature STM/STS Measurements, N. Zaki, Columbia University, D. Acharya, Brookhaven National Laboratory, D.V. Potapenko, Columbia University, P. Johnson, P. Sutter, Brookhaven National Laboratory, R.M. Osgood, Columbia University**

We recently reported [1] on a new surface phase of the Co-vicinal-Cu(111) system which exhibits self-assembled uniform Co quantum wires that are stable at 300K. STM images show that the wires form along the leading edge of the step rise, differentiating it from previously theoretically predicted atomic-wire phases as well as experimentally observed step-island formation. Our observations allow us to comment on the formation kinetics of the atomic-wire phase and on the fit of our data to a recently developed lattice-gas model. Low-temperature STS measurements, taken on self-assembled Co chains, reveal a resonance at the Fermi energy. While it has been shown that single Co atoms and Co-Cu_n clusters [2] exhibit a Kondo effect, a Co chain at a Cu step may exhibit a different many-body effect that is the cause for our Fermi-energy resonance observation. Furthermore, we have observed different charge-density modulation that is dependent on tip bias. Since these charge-modulations are observed for tip-bias relatively far away from the Fermi level, we suspect that these modulations are not ground state charge-density-waves (CDW), but rather excited states of this 1-D system.

[1] N. Zaki et al, Phys. Rev. B 80, 155419 (2009)

[2] N. Néel et al, Phys. Rev. Lett. 101, 266803 (2008)

9:20am **NS+AS+MN-WeM5 Atomic-Resolution Spin Mapping by Exploiting Magnetic Exchange Forces, R. Wiesendanger*, University of Hamburg, Germany**

INVITED

While Spin-Polarized Scanning Tunneling Microscopy (SP-STM) [1] is nowadays well established for revealing atomic spin configurations at surfaces, its application is limited to electrically conducting samples such as magnetic metals or semiconductors. In order to map atomic spin structures at surfaces of insulators and to open up the exciting possibility of studying spin ordering effects with atomic resolution while going through a metal-

insulator transition, we have developed Magnetic Exchange Force Microscopy (MExFM) [2]. This technique is based on the detection of short-range spin-dependent exchange and correlation forces at very small tip-sample separations (a few Angstroms), in contrast to Magnetic Force Microscopy (MFM) where the magnetic dipole forces are probed with a ferromagnetic probe tip at a typical tip-to-surface distance of 10-20 nm [3]. MExFM has allowed a first direct real-space observation of spin structures at surfaces of antiferromagnetic bulk insulators [2] as well as ultrathin films [4]. Moreover, it provides a powerful new tool to investigate different types of spin-spin interactions based on direct-, super-, or RKKY-type exchange down to the atomic level. By combining MExFM with high-precision measurements of damping forces [5] localized or confined spin excitations in magnetic systems of reduced dimensions become experimentally accessible [1].

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[3] Y. Martin and K. Wickramasinghe, Appl. Phys. Lett. **50**, 1455 (1987); J. J. Saenz, N. Garcia, P. Grütter, E. Meyer, H. Heinzelmann, R. Wiesendanger, L. Rosenthaler, H. R. Hidber, and H.-J. Güntherodt, J. Appl. Phys. **62**, 4293 (1987)

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[5] M. Ashino, D. Obergfell, M. Haluska, S. Yang, A. N. Khlobystov, S. Roth,

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M. Ashino, R. Wiesendanger, A. N. Khlobystov, S. Berber, and D. Tomanek,

Phys. Rev. Lett. **102**, 195503 (2009)

10:40am **NS+AS+MN-WeM9 Chemical Imaging and Interaction Quantification on the Surface Oxide Layer of Cu(100) Using High-Resolution Atomic Force Microscopy, M.Z. Baykara, T.C. Schwendemann, H. Mönig, Yale University, M. Todorovic, R. Pérez, Universidad Autónoma de Madrid, Spain, E.I. Altman, U.D. Schwarz, Yale University**

Chemistry is governed by the interactions between atoms and molecules. On surfaces, chemical forces extending into the vacuum direct the behavior of many scientifically and technically important phenomena including surface catalysis. Therefore, it would be useful to map and quantify the interactions between a catalytically active surface and a probe with atomic resolution in order to study the role and effectiveness of various surface defects such as vacancies, impurities, steps, kinks, and domain boundaries as active sites. An ability to discriminate between different chemical species on the sample surface would offer further insight. In this talk, we will show with the example of an oxygen-reconstructed copper (100) surface that much of this information can be derived from combining the new method of three-dimensional atomic force microscopy (3D-AFM) [1], a variant of noncontact atomic force microscopy, with 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. While different tips show different chemical contrasts, 3D data sets enable site-specific quantification of force interactions and tunneling currents. In order to clarify the different contrast modes data, DFT total-energy calculations and Non-equilibrium Green's Function (NEGF) methods for electronic transport have been used to determine the interaction and the tunneling current [2-4] for a large set of tip models. These calculations provide insight into (1) the fundamentals of contrast formation in this experimental technique and (2) into the correlation between tip-sample forces and local chemical reactivity, factors that are essential for the further development and application of this novel approach to characterizing catalytic activity.

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[2] Y. Sugimoto et al., Nature **440**, 46 (2007)

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11:00am **NS+AS+MN-WeM10 Comparison of Resonant-Frequency Techniques for AFM Nanomechanical Mapping, D.C. Hurley, J.P. Killgore, A.B. Kos, NIST, A. Gannepalli, R. Proksch, Asylum Research**
Contact-resonance force microscopy (CR-FM) is an emerging AFM technique for quantitative imaging of near-surface nanoscale mechanical properties. In CR-FM, the resonant frequency f of the cantilever is measured when the tip is in contact with the sample. Mechanical-property values are obtained from the frequency data with the use of models for the vibrating cantilever and the tip-sample contact. Contact-resonance measurements

* NSTD Recognition Award

were originally made at a fixed sample position with off-the-shelf electronics. However, to achieve sufficient speed for CR-FM imaging, it has been necessary to develop new instrumentation approaches. Here we describe work to directly compare three methods for CR-FM imaging: the SPRITE (Scanned Probe Resonance Image Tracking Electronics) approach developed at NIST, the DART (Dual AC Resonance Tracking) approach developed by Asylum Research, and the BE (Band Excitation) method originally developed at Oak Ridge National Laboratory and implemented by Asylum Research. Each method enables contact-resonance frequency mapping but achieves it through different practical implementations. First, we will discuss the concepts on which each method is based. Next, results of comparison experiments will be presented in which images were acquired with each method in succession on the same AFM instrument. A variety of specimens were imaged to probe the strengths and limitations of each method. For example, we found that DART could operate at higher scan speeds, while SPRITE and BE were better able to track very asymmetric peaks that presumably originate from nonlinear tip-sample interactions. Both DART and BE provide values of the resonance quality factor Q in addition to the resonant frequency f , while currently SPRITE measures f only. Despite these differences, the methods yielded similar results in many cases. The availability of a broader array of frequency mapping tools will ultimately facilitate the widespread application of CR-FM to nanoscale materials science.

11:20am **NS+AS+MN-WeM11 Single Molecule Structural Transitions of Water Polymer Chains in a Nanoscale Confined Space Studied by COIFM, B.I. Kim**, Boise State University

Interfacial water structures have been investigated in an ambient environment between two silica surfaces using a newly developed cantilever based optical interfacial force microscope (COIFM). As the gap distance decreases between the tip and the substrate, a remarkable oscillatory behavior is observed in normal and friction forces. Our further analysis suggests that water molecules confined between tip and substrate in an ambient environment form a bundle of water chains through hydrogen bonding. Each chain length is analyzed by a model called "freely jointed chain" (FJC) model in which the individual segments can rotate freely. The bundle of water chains experiences multiple layering transitions (without single layer transition) from $l = 36$ diameters to $l = 12$ diameters as the tip approaches the surface. The analysis shows that the number of links (l) decreases by 5,4,3,3,3,3,4,5 in water diameters. The result indicates that, as the gap between the tip and the substrate decreases, the interfacial water molecules favor multilayer transitions to stepwise, single layer transitions. The multilayer transitions consist of a sequential reduction of total chain length by integer number of water diameters. The loss of one water diameter in overall chain length represents a highly cooperative transition, whereas the loss of two additional water diameter along the sigmoidal shape is reminiscent of a well-known two state transition. As a model to describe these transitions, a kink is introduced in the chain by rotating one water molecule 90 degrees while maintaining the number of hydrogen bonds in the chain. The other remaining molecules still follow the freely jointed chain model.

Tribology Focus Topic

Room: Tesuque - Session TR+MN+NS+SS-WeM

Influence of Atmosphere, Temperature, and Materials on Friction

Moderator: J.D. Schall, Oakland University

8:00am **TR+MN+NS+SS-WeM1 'Demystifying' Gas Phase Lubrication: Tribochemistry, Third Bodies and Competition, I.L. Singer**, Naval Research Laboratory **INVITED**

Gas phase lubrication, also called vapor phase lubrication, refers to processes in which the gas surrounding a sliding (or rolling) contact contributes to lubrication [1]. It has wide ranging applications from internal combustion engines to MEMS. Some gases simply condense on surfaces, others decompose and deposit lubricating films on the surface, e.g. hydrocarbon films decompose and deposit graphite. Some can be made to react on the surface, as do various monomers that tribopolymerize and form lubricious third bodies at the contact. Alternatively, gases can react with the surface to form films; the most ubiquitous example is the oxide film formed on metals, which prevents (on earth, but not in outer space) surfaces from weld upon contact. Reaction films have been studied extensively by surface scientists; less well understood are tribofilms, films formed by rubbing action. Another important component to the lubrication process is film removal, which can occur during sliding or rolling; the competition between film formation and film removal always needs to be considered. In some

cases, gas lubrication provides low friction and low wear; in other cases, it can increase friction and wear. In this talk, I will review gas phase lubrication processes and present several gas phase lubrication studies that still mystify me.

[1] For overview, see http://nfsafresh.org/wiki/index.php?title=Gas_Phase_Lubrication

8:40am **TR+MN+NS+SS-WeM3 Understanding Vapor Phase Lubrication Mechanism of Alcohol for MEMS and Other Materials, S.H. Kim**, Pennsylvania State University

9:00am **TR+MN+NS+SS-WeM4 Mechanistic Aspects of Vapor Phase Lubrication of Silicon, M.T. Dugger, J.A. Ohlhausen, S.M. Dirk**, Sandia National Laboratories

The lubrication of silicon surfaces with alcohol vapors has recently been demonstrated [D.B. Asay, et. al, Langmuir 24 (2007) p.155]. With a sufficient concentration of pentanol vapor present, sliding of a silica ball on an oxidized silicon wafer can proceed with no measurable wear. The initial results of time-of-flight secondary ion mass spectrometry (ToF-SIMS) analysis of wear surfaces revealed a reaction product having thickness on the order of a monolayer, and with an ion spectrum that included fragments having molecular weights of 200 or more that occurred only inside the wear tracks. The parent alcohol molecule (pentanol) has molecular weight of 88 amu, suggesting that reactions of adsorbed alcohols on the wearing surfaces allowed polymerization of the alcohols to form higher molecular weight species. In addition to pin-on-disk studies, lubrication of silicon surfaces with pentanol vapors has also been demonstrated using MicroElectroMechanical Systems (MEMS) devices. Extraordinary increases in the operating life of MEMS devices have been observed with vapor phase lubrication. Devices with thermal actuators as well as electrostatic actuators have been successfully operated, demonstrating that the heated surfaces of the thermal actuators do not form prohibitively large amounts of reaction product from the alcohol vapor. The same reaction product between pentanol and the silicon surface observed in pin-on-disk tests has also been found on MEMS contacting surfaces using ToF-SIMS analysis.

Recent investigations of the reaction mechanisms of the alcohol molecules with the oxidized silicon surfaces have shown that wearless sliding requires a concentration of the alcohol vapor that is dependent upon the contact stress during sliding, with higher stress requiring a greater concentration of alcohol. Different vapor precursors including those with acid functionality, olefins, and methyl termination also produce polymeric reaction products, and can lubricate the silica surfaces. Doping the operating environment with oxygen was found to quench the formation of the polymeric reaction product, and demonstrates that polymer formation is not necessary for wearless sliding.

9:20am **TR+MN+NS+SS-WeM5 Tribological Study of Octadecylphosphonic Acid Self-Assembled Monolayers Across Velocity Regimes, O. Matthews, S. Barkley, Luther College, C. Bouxsein, M. Deram, N. Eigenfeld, St. Olaf College, A. Poda, W.R. Ashurst, Auburn University, B. Borovsky, St. Olaf College, E. Flater**, Luther College

Microelectromechanical systems (MEMS) are critically-limited by interfacial phenomena such as friction and adhesion. The most common method of reducing friction between MEMS surfaces is the use of molecularly-thin self-assembled monolayer (SAM) coatings. Typically silicon MEMS have been coated with silane-based SAMs, such as octadecyltrichlorosilane (OTS), and have resulted in some modest improvement in device performance and lifetime. Continued progress in the development of MEMS may require new materials systems to be implemented. Through a collaborative effort, we investigate the frictional properties of octadecylphosphonic acid monolayers deposited on aluminum oxide surfaces across speed regimes. Measurements using an atomic force microscope (AFM) and a nanoindenter-quartz crystal microbalance are performed each with a microsphere-terminated probe. This allows for a comparative study with similar contact sizes, pressures, surface roughness, and interfacial chemistry. Speeds between the different instruments range from microns per second to meters per second. Preliminary AFM friction vs. load and friction vs. velocity measurements are presented, with the goal of investigating phosphonate SAM/ metal oxide systems as alternative MEMS materials.

9:40am **TR+MN+NS+SS-WeM6 Triboelectrification and Triboplasma Generation and its Application for Surface Modification, S.V. Singh, P.K. Michelsen, Y. Kusano**, Technical University of Denmark

Triboplasma gas discharges are often induced by triboelectrification around a sliding contact. Only an empirical classification is available for triboelectrification, whereas a detailed physical mechanism behind it is still unknown. Laboratory triboplasmas are mostly characterized by using

optical diagnostics, and the optical emissions are reported to be observed mostly in ultraviolet region, corresponding to nitrogen emission lines. These measurements do not directly address triboelectrification. Here we present the evidence of electrostatic charging at the sliding contact and gas break down between the contacts through electrical measurements. Furthermore, the applicability of triboplasma for surface modification on polymeric materials was studied. Two capacitive probes were used for the investigation of a triboelectrification and triboplasma generated in a pin-on-rotating disk apparatus. These probes were mounted above the disk and on the pin, respectively. Measurements show a clear evidence of tribocharging, charge decay and triboplasma generation. Several combination of sliding contact materials with tendency to gain opposite charging and different sliding speeds, as high as 1000 rotation per minute, were carefully chosen. In addition, influence of different gas environment and pressure were investigated. Triboplasma induced surface modifications were characterized by water contact angle and X-ray photoelectron spectroscopy measurements.

10:40am **TR+MN+NS+SS-WeM9 Friction at Cryogenic Temperatures, S.S. Perry**, University of Florida **INVITED**

There are a number of applications where operation over a wide temperature range is required for device success. These extreme conditions are often the motivation for variable temperature studies in tribology; however, a paucity of relevant tribology data exists for temperatures below 273 K.

In the range from 300 K to 100 K the friction coefficient of various solid lubricants has recently been shown to increase with decreasing temperature. Molecular scale measurements employing an atomic force microscope over a temperature range from 140 K to 750 K at a vacuum level of 2×10^{-10} torr have identified a temperature activated behavior of the friction and friction coefficient for the solid lubricants graphite and molybdenum disulfide. These molecular scale experiments were performed under conditions for which interfacial sliding was confirmed, interfacial wear was absent, and the role of adsorbed contaminants could be dismissed.

The potential influence of interfacial wear as well as the mechanism underlying the measured temperature dependence will be discussed.

11:20am **TR+MN+NS+SS-WeM11 In-Situ Scanning Auger Analysis of a Tribological Wear Scar in UHV Conditions, B.P. Miller, O.J. Furlong, W.T. Tysoe**, University of Wisconsin-Milwaukee

Lubrication of sliding copper-copper interfaces for use in brushes in electrical motors provides a particular challenge. Not only is a reduction in friction and wear required, but also allowing for high conductivity through the contact. Therefore, a self-limiting tribofilm is essential. The following explores the surface chemistry and tribology of dimethyl disulfide (DMDS) on copper surfaces to establish whether it is sufficiently reactive to potentially form a tribofilm near room temperature as required for lubrication of the sliding copper-copper contact in an electric motor. The surface chemistry and decomposition pathways of DMDS on copper surfaces are analyzed using temperature-programmed desorption (TPD), reflection-absorption infrared spectroscopy (RAIRS) and X-ray photoelectron spectroscopy (XPS). It is shown that DMDS reacts to form methyl thiolate species on the copper surface at room temperature. After heating to about 430K, methane and C₂ hydrocarbons desorb leaving molecular sulfur adsorbed onto the surface. A UHV tribometer chamber was equipped with a scanning electron gun having a ~100 micron diameter spot size. DMDS was dosed in the gas phase while performing friction measurements so that *in-situ* elemental analysis of the wear scar could be made. An increase in the sulfur signal is witnessed inside compared to outside of the tribological wear scar. A depth profile Auger analysis of the sample showed selective diffusion of sulfur into the bulk only inside the wear scar attributed to tribologically induced effects. This novel method of analysis can give important insights into the fundamentals of tribological systems.

11:40am **TR+MN+NS+SS-WeM12 First Principles Calculations and Atomistic Simulations of Tribology at Sliding Molybdenum Disulfide Surfaces, T. Liang, S.R. Phillpot, S.B. Sinnott**, University of Florida

Molybdenum disulfide is the most commonly used solid lubricant coating in aerospace applications. In this work, we carry out first principles density functional theory (DFT) calculations of the potential energy surface between two MoS₂ surfaces and examine the influence of oxidation on the results. In addition, we present the results of a recently developed empirical many-body potential for Mo and S systems and examine nano-scale friction between sliding MoS₂ surfaces using classical molecular dynamics (MD) simulations. In particular, MD simulations of interfacial sliding at various loads, temperatures and sliding directions are carried out. The loads and friction forces are extracted to calculate the friction coefficient of the MoS₂ as a function of temperature, and the results are compared to experimental

pin-on-disk measurements of MoS₂ coatings and atomic force microscopy measurements on single crystal MoS₂ surfaces. The results from both the DFT calculations and the MD simulations help us to better understand the origins of lubricity on MoS₂.

Wednesday Afternoon, October 20, 2010

Energy Frontiers Topical Conference
Room: Mesilla - Session EN+NS-WeA

Nanostructures for Energy Conversion & Storage I
Moderator: S. Agarwal, Colorado School of Mines

2:00pm EN+NS-WeA1 **Electrochemical Performance of Nanostructured Sn Thin Films as Anodes of Thin film Li-ion Battery.** C.S. Nimisha, G. Venkatesh, T. Dhivya, G. Mohan Rao, N. Munichandraiah, Indian Institute of Science, India

Nanostructured Sn thin films have been prepared by rf sputtering and thermal evaporation on to silicon substrates for evaluating the electrochemical performance to use as anode layer of thin film Li-ion battery. The scanning electron microscopy (SEM) shows different film morphologies for evaporated and sputtered films which directly control the electrochemical performance. Crystallinity of the deposited films were ensured by X-ray diffraction (XRD). Bio-Logic SA potentiostat / Galvanostat (model:VPM3) is used for testing electrochemical performances. Sn thin films prepared by thermal evaporation from Sn granules of 99.99% purity resulted in films with nanograins of ~200nm size homogeneously distributed over the surface. Whereas films made by rf sputtering from Sn target (99.99% purity) with Ar as sputtering gas at a pressure of 5×10^{-3} mbar, resulted in highly porous film surface with 'nanobead' (~50nm size) formation inside the edges.

For electrochemical studies half cells were assembled using lithium as counter and reference electrodes in 1M LiAsF₆ dissolved in ethylene carbonate and dimethyl carbonate electrolyte. Charging was done with a constant current density of $10 \mu\text{A} / \text{cm}^2$ up to 1.2 V, followed by discharging at $10 \mu\text{A} / \text{cm}^2$ down to 0.2 V. The capacity obtained from both evaporated and sputtered films clearly shows the three plateau regions of lithiation and delithiation for both evaporated and sputtered films. From the evaporated film, a discharge capacity of $83.6 \mu\text{Ah}/\text{cm}^2$ is obtained, whereas from sputtered film a much higher capacity of $886 \mu\text{Ah}/\text{cm}^2$ is obtained.

We speculate that the increased surface area of the rf sputtered Sn film due to the porous nature and the presence of nano beads, resulted in higher capacities than the evaporated Sn films, which have relatively bigger sized grains. Also the presence of more nano sized features in the sputtered film surface reduces the pulverization of Sn films during cycling since the absolute volume change would be minimized. The reduction in diffusion length for Li-ion and increased effective surface area ensures higher discharge capacity from rf sputtered Sn films compared to evaporated films. The higher discharge capacity obtained from rf sputtered Sn thin films makes it ideal candidate for integrating as anode layer of thin film Li-ion battery.

2:20pm EN+NS-WeA2 **Lithographically Defined Porous Carbon Electrodes.** R. Polsky, B. Burckel, X. Xiao, C.M. Washburn, M. Roberts, B. Bunker, Sandia National Laboratories, A. Raub, S. Brueck, University of New Mexico, S. Brozik, D.R. Wheeler, Sandia National Laboratories

Pyrolyzed Photoresist Films (PPF) have electrochemical properties similar to glassy carbon electrodes with the unique feature that they can be lithographically defined to create microstructures and microfeatures. Previously we reported that the near atomically flat surface of PPF results in the deposition of gold nanoparticles (1-3 nm) with narrow size distributions. [1] Herein we describe the fabrication of porous carbon structures using interference lithography (IL) to generate 3-D structures in PPF that contain five patterned layers with microporous hexagonal lattices (~ 800 nm in diameter). [2] Because IL is a maskless approach porous carbon structures are able to be patterned over large volumetric areas (2.5 X 2.5 cm). We demonstrate the porous carbon structures can be used as a highly adaptable electrode material suitable for the deposition of metal nanoparticles (Au, Ag, and Pt) and conducting polymers with possible applications in such areas as fuel cells, ultracapacitors, and biosensors.

References

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2:40pm EN+NS-WeA3 **Designing Inorganic Nanostructures for Solar Cells and Energy Storage Devices.** Y. Cui, Stanford University INVITED

The capability of synthesizing materials with nanometer size and shape control has enabled exciting opportunities to engineer materials for controlling and understanding electronic, photonic, mechanical and ionic

processes, which are important for applications such as energy conversion and storage devices. In this talk I will show two examples on how we design nanoscale materials towards high performance photovoltaics and energy storage devices. In the first example, nanocone- and nanodome-shaped substrates are designed for efficient photon management and charge carrier separation, which result in significant improvement of solar cell power efficiency compared to the flat film devices. Second, nanowires are exploited to maximize efficiency of simultaneous electron and ionic insertion with facile strain relaxation, which enable novel ultrahigh capacity storage capacity materials towards next generation of high energy density batteries.

4:00pm EN+NS-WeA7 **Synthesis of Rare Earth Ion Co-Doped Core-Shell Nanostructures for Improved Energy Generation Efficiency.** J.A. Dorman, J. Hoang, J.H. Choi, J.P. Chang, University of California, Los Angeles

The development of rare-earth ion (RE) doped phosphors allows for the conversion of photons at various wavelengths to those at energies similar to that of the photovoltaic band gap. Work has been shown that through the incorporation Er³⁺ and Yb³⁺ into complex metal oxides, specifically yttrium based compounds, both energy upconversion and downconversion can be utilized to convert absorbed photons to a more desirable energy for Si based solar cells. However, both photoluminescence and energy transfer mechanisms are highly susceptible to the local crystal environment, including the overall crystal field and surrounding molecules. The addition of a shell layer increases luminescence by decreasing the effect of surface quenching sites while promoting energy transfer between layers.

This work focuses on the synthesis of core-shell nanostructures while controlling the luminescence spectrum through the spatial distribution within the particle architecture using a combination of wet chemical synthesis and atomic layer deposition (ALD). Y₂O₃: Er³⁺, Yb³⁺ core nanoparticles (NPs) were synthesized using the molten-salt synthesis. Enhanced luminescence was observed after deposition of a high quality shell of Y₂O₃: Yb³⁺, roughly 5-10 nm thick, by radical enhanced ALD. However, the deposited shell layer has a slightly lower density, as shown in TEM imaging. The downconversion and upconversion luminescence spectra was collected for Y₂O₃:Er³⁺, Yb³⁺ NPs, 1 mol % Er³⁺ and the Yb³⁺ mol % ranging from 0 to 8 %, with a 980 nm diode excitation. The various NPs cores emitted strongly in the green (532 nm) and red (650 nm) upconversion luminescence and IR (1540 nm) downconversion luminescence, the ²H_{11/2}, ⁴S_{3/2}→⁴I_{15/2}, ⁴F_{9/2}→⁴I_{15/2} and ⁴I_{13/2}→⁴I_{15/2} transitions, respectively. A systematic luminescent red shift, ~2 nm, was observed when comparing the core to core-shell structures for all samples. Visible luminescence occurs via an energy transfer process, requiring two absorbed photons (red) and three absorbed photons (green), between the Yb³⁺ ²F_{5/2} and Er³⁺ ⁴I_{11/2} and ⁴I_{13/2} energy levels. The proposed energy transfer mechanism incorporates the interaction between RE ions at the core-shell interface based on the local binding environment modeled using enhanced x-ray absorption fine structure (EXAFS) spectroscopy. Additionally, the energy transfer coefficients are extracted using the excitation lifetimes and the red-to-green ratio is correlated to key spectroscopic parameters, such as the Judd-Ofelt parameters and branching ratio. These values can be compared to the bulk Y₂O₃ luminescence and the actual measured lifetimes, 200 ms (green) and 600 ms (red), as the figure of merit.

4:20pm EN+NS-WeA8 **High Figure of Merit Nanostructured Bulk Thermoelectrics from Doped Pnictogen Chalcogenide Nanoplate Crystals.** R.J. Mehta, C. Karthik, B. Singh, Y. Zhang, E. Castillo, T. Borca-Tasciuc, G. Ramanath, Rensselaer Polytechnic Institute

Nanostructured pnictogen chalcogenides are attractive for realizing high thermoelectric figure of merit (ZT) materials for solid-state refrigeration and electrical power harvesting from heat. Here, we report a scalable surfactant-assisted microwave synthesis approach to realize bulk assemblies of sulfur-doped nanostructures with 25% to 250% higher room temperature ZT than the non-nanostructured bulk counterparts of both n- and p-type nanostructured bulk materials with room temperature ZT ~ 1. We synthesized ~5- to 20-nm-thick single-crystal hexagonal sulfur-doped nanoplates of the pnictogen chalcogenides in a microwave oven, followed by compaction and sintering to obtain bulk nanostructured pellets. The n-type material was obtained from single-component nanostructure assemblies of bismuth chalcogenides, while the p-type material was obtained by mixing bismuth telluride and antimony telluride nanostructures. Electron spectroscopy shows that <1% sulfur doping from thioglycolic acid, used as a nanoplate-sculpting and surface-passivating agent, increases the power factor $\alpha^2\sigma$ to ~5% greater than that of the state of the art alloys. Electron microscopy analyses reveal that measured k values as low as 0.5 – 1.4 W/mK, which are ~50% lower than bulk alloys, are due to 50-100 nm

grains with intragrain structural modulations with characteristic wavelengths between 3-10 nm. Our findings open up completely new possibilities for realizing novel high ZT thermoelectric materials through the assembly of doped single-crystal nanostructures.

4:40pm **EN+NS-WeA9 Core-Shell Nanodielectrics through Hybrid Wet Chemistry/Laser Process for Embedded Energy Storage Capacitors**, *B. Rajesh*, University of Houston, *N. Badi*, University of Houston and Integrated Micro Sensors, Inc., *A. Bensaoula*, *R. Supparesk*, *T.R. Lee*, University of Houston

Extensive interest is being invested into the research of nanodielectrics because of their promising applications in energy storage solutions as both discrete and embedded capacitors. They are useful in integral passive technology for miniaturization, improvement of power distribution and as decoupling capacitors. Their applications include, but are not limited to, high speed computing boards (servers, routers, super computers) and module boards (cell phones, PDA, note book computers). We fabricated high capacitance density dielectrics for flexible electronics by embedding core-shell type gold-silica nanoparticles in a polymer matrix using a coupled sol-gel procedure with laser engineering technique.

We report on fabrication of nanodielectric capacitors based on core-shell nanoparticles embedded in polyvinyl pyrrolidone (PVP) dielectric matrix. We developed a process chain to optimize the use of PVP as dielectric and measured its dielectric constant (K) as 7 at 10 KHz and breakdown field as 130V/ μm . Monodispersed core-shell nanoparticles (NPs) are prepared with two different structures: 1) 35nm gold core – 95nm silica shell and 2) coating 35nm gold NPs with polymer compatible self assembled monolayer (SAM). Pre-processing is performed to uniformly disperse the NPs in a polymer matrix and to selectively form the polymer shell around each of the nanoparticles. Post-processing is carried out to spin coat on substrates and to cure under UV light to make capacitor slabs.

The results from SEM and AFM analysis, thermal and frequency response, breakdown dielectric strength and dielectric loss of the films for different loadings of NPs will be reported in the talk. K value of 20 and breakdown field of 50V/ μm were measured for a dielectric with 10% loading of Au/SiO₂ NPs. Resulting capacitance value of 11.5nF/In² is in par with commercially available capacitor devices. It is worth mentioning that currently manufacturers use ceramic based dielectric material which makes it hard to manufacture (reproducibility, stability and cost) and shows limited flexibility (a requirement in modern printed circuit board technologies) due to high ceramic loading. Our fabricated nanodielectrics have the advantage of ease of fabrication and high flexibility due to the low metal loading.

It is forecasted that the effective permittivity of the dielectric and thereby the K value increases with loading of NPs till a percolation threshold is reached and then rapidly decreases with further loading. Future research is aimed at using other inexpensive metal NPs like silver and testing different polymers for best desirable characteristics of the capacitors.

5:00pm **EN+NS-WeA10 Characterization of Vertical InN Nanorods and InN-GaN Core-Shell Structures Grown by Merged Metal Organic Hydride Vapor Phase Epitaxy**, *V.U. Chaudhari*, *D. Wood*, *R. Krishnan*, *T.B. Song*, *T.J. Anderson*, University of Florida

The pseudobinary solid solution Ga_xIn_{1-x}N alloys exhibits a direct band gap in the range 3.4 to 0.7 eV and thus suitable for optoelectronic device applications. Recent simulations from our group have also suggested this alloy could produce high efficiency thin film photovoltaic devices on the order of 18% efficiency, similar to CIGS devices. The use of nanorod structures for light emitting and absorbing applications promises relatively high junction area, crystalline quality, and collection efficiencies. In addition, the nanorod assemblies are less rigid, and thus open to flexible substrates. The synthesis of nanorods with specific orientation, however, remains a challenge.

The synthesis of self-assembled, vertical InN nanorods and InN-GaN core shell nanostructures on Si without the need for a catalyst or template is reported. This self-catalyzed approach has made it possible to grow nanorods with uniform yet tunable diameter without any patterning of the substrate. The synthesis is performed in a Merged Metal Organic Hydride Vapor Phase Epitaxial growth system. This system allows growth of Ga_xIn_{1-x}N by either metal organic CVD, using trimethylgallium, trimethylindium and NH₃, or hydride VPE in which the metal organic precursor is reacted with HCl. This presentation summarizes properties of the nanorods grown in the temperature range 560 to 600 °C at atmospheric pressure in N₂. As revealed by transmission electron spectroscopy, the grown nanorods are defect-free, single crystal showing the wurtzite structure. Scanning electron microscopy and X-ray diffraction results reveal growth in vertical direction with (002) preferred orientation. The InN-GaN core shell structures exhibited a polycrystalline GaN shell with (002) and (101) preferred orientations. This particular behavior of GaN is attributed to the high growth rates used. Annealing studies of these microstructures under

ammonia atmosphere showed the absence of alloy formation with virtually no inter-diffusion of In and Ga.

5:20pm **EN+NS-WeA11 Fabrication of InAs/GaAs Nanocomposites Using Ion Implantation**, *M.V. Warren*, *C. Uher*, *R.S. Goldman*, University of Michigan, Ann Arbor

The controlled formation of semiconductor nanocomposites offers a unique opportunity to tailor functional materials with a variety of novel properties. In particular, nanocomposites consisting of InAs nanostructures embedded in GaAs have been proposed for high efficiency photovoltaics and high figure-of-merit thermoelectrics. A promising approach to nanocomposite synthesis is matrix-seeded growth, which involves ion-beam-amorphization of a semiconductor film, followed by nanoscale re-crystallization via annealing [1]. In earlier studies of In⁺ implantation into GaAs, the formation of InGaAs alloys upon annealing was reported [2-4]. Due to the large size difference between In and Ga, it is likely that phase separation occurs, especially for high indium fraction InGaAs alloys. Therefore, we are examining the possibility of selective formation of InAs-rich nanocrystals in a GaAs matrix using high dose In implantation into GaAs. However, Profile Code simulations suggest that the retained In dose in GaAs, $4.5 \times 10^{20} \text{ cm}^{-3}$, is limited by sputtering. To increase the concentration of implanted In, we have developed a sputter-mask method, for which a sacrificial layer with sputter yield lower than that of GaAs is used to prevent sputtering of GaAs:In. Using 100kV ions with fluences ranging from 3.8×10^{15} to $3.8 \times 10^{17} \text{ cm}^{-2}$, we have implanted In⁺ ions into GaAs with 50 nm sputter-masks consisting of AlAs. Following implantation, the films were annealed at 500 to 600°C for 30 to 60 s. We will discuss the influence of In⁺ dose and annealing conditions on the nucleation and growth of InAs, as well as the influence of nanostructuring on the temperature dependence of the resistivity and Seebeck coefficient of the implanted structures.

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Nanometer-scale Science and Technology

Room: La Cienega - Session NS+EM+EN-WeA

Photonic and Plasmonic Materials and Devices

Moderator: P. Cheng, Cornell University

2:00pm **NS+EM+EN-WeA1 Spatially-Resolved Study of Luminescence and Composition in III-Nitride Nanowires**, *G.T. Wang*, *Q. Li*, Sandia National Laboratories

Given the strong interest in III-nitride-based nanowires for optoelectronic and energy applications, a better understanding of their optical properties and structure-composition is required, particularly at nanoscale spatial resolutions, which could shed light into issues such as the nature and distribution of radiative defects and alloy compositional variations. Here, we present a spatially-resolved, correlated study of luminescence and composition in GaN, Al(Ga)N/GaN, and InGaN/GaN core-shell nanowires grown by metal-organic chemical vapor deposition. For GaN nanowires, a surface layer exhibiting strong yellow luminescence (YL) near 566 nm in the nanowires was directly revealed by high resolution, cross-sectional cathodoluminescence (CL) imaging, compared to weak YL in the bulk. In contrast, other defect related luminescence near 428 nm (blue luminescence) and 734 nm (red luminescence), in addition to band-edge luminescence (BEL) at 366 nm, were observed in the bulk of the GaN nanowires but were largely absent at the surface. As the nanowire width approaches a critical dimension, the surface YL layer completely quenches the BEL. The surface YL is attributed to the diffusion and piling up of mobile point defects, likely isolated gallium vacancies, at the surface during growth. AlGaIn/GaN and AlN/GaN core-shell nanowires were observed to exhibit stronger BEL and weaker YL as compared with bare GaN nanowires, which may relate to the passivation of nanowire surface states. InGaIn/GaN core-shell nanowires were also investigated by correlated CL and cross-sectional scanning TEM (STEM). Dislocation-free InGaIn layers with up to ~40% indium incorporation were achieved on GaN nanowires. The indium composition distribution in the InGaIn layers were qualitatively correlated to the strain energy density distribution as calculated by finite

element analysis models. The observed high indium incorporation and high crystalline quality in the heteroepitaxial InGaN layers is attributed to strain-relaxed growth on the nanowires. Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin company, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

2:20pm NS+EM+EN-WeA2 Photonic Crystal Cavities and Vertical Confinement to Increase the Conversion Efficiency of a Thermophotovoltaic Cell, C. Shemelya, T. Vandervelde, Tufts University

For many years researchers have attempted to efficiently harvest waste heat and transform it into a usable energy via thermophotovoltaics (TPVs). The low quantum efficiency (QE; i.e. the probability that a photon will be absorbed) in most TPV cells is probably the biggest limiting factor in achieving an economically viable device and directly affects the conversion efficiency (CE; i.e. the probability that a photon will be converted into a carrier that is collected). In many cases, top of the line TPV cells might only have a CE of 20%. Recent advances in micro-/nano-fabrication techniques have enabled the creation of novel structures to enhance the absorption and, therefore, the conversion of the incident thermal photons. In particular, photonic crystals (PhC) interface enhancements have been shown to increase the efficiency of photon to current conversions for infrared photodetectors. The addition of a back reflecting layer, or vertical confinement layer can further increase conversion efficiencies. Here, we report on the enhancement of photon conversion by integration of PhC structures and vertical confinement layers into the TPV cells. To this end, photonic crystals consisting of rods of either air or dielectric surface-passivation material are placed into the base semiconductor TPV cells to increase duration of thermal photon absorption, resulting in significantly enhanced QE and CE. The use of photonic crystals and vertical confinement in augmenting the conversion efficiency of TPV cells is applicable for most IR wavelengths, making this a widely useful technology. The ability to harvest waste heat for energy will help make many processes and/or systems more energy efficient, which will be a critical component in ushering in an era of energy independence.

2:40pm NS+EM+EN-WeA3 Unconventional and Broadband Plasmonics, T.W. Odom, Northwestern University **INVITED**

Breakthroughs in photonics and optoelectronics demand actively controlled materials that are inexpensive, robust, and scalable. The interaction of light with surface plasmons—collective oscillations of free electrons—in metal nanostructures has resulted in exceptional displays of enhanced optical transmission, collimation of light through a subwavelength aperture, and negative permeability and refraction at visible wavelengths. The structures that display these phenomena typically consist of ordered arrays of particles or holes with sizes of the order 100 nm. Surface plasmons can interact with each other over much longer distances, however, and thus the ability to organize nanoscale materials over multiple length scales could lead to new plasmonic metamaterials with novel optical properties.

This talk will describe how superlattices and low symmetry plasmonic lattices provide an important first step to meet these goals. We will introduce new soft nanolithography tools for creating new plasmonic structures, including PEEL (a procedure combining Phase-shifting photolithography, Etching, Electron-beam deposition, and Lift-off) and solvent assisted nanoscale embossing (SANE). These methods can achieve arrays of 50-nm features simultaneously over 6-in² areas without needing electron, ion, or photon-based lithographies. We will then discuss how the optical properties of the plasmonic crystals and the nanoparticle arrays can be engineered and then manipulated by external factors to produce large optical responses.

4:00pm NS+EM+EN-WeA7 Controlling Plasmon Enhanced Photoconduction in Porphyrin-Gold Nanoparticle Assemblies, D.J. Conklin, S.U. Nanayakkara, T.-H. Park, University of Pennsylvania, J.T. Stecher, M.J. Therien, Duke University, D.A. Bonnell, University of Pennsylvania

Recently we demonstrate plasmon-induced electronic transport in hybrid metal nanoparticle-molecular devices that realized enhancements of up to a factor of 200. This was realized in a hybrid structure that consists of an array of gold nanoparticles linked by (porphinato)zinc(II) oligomers. Here we examine the role of metal particle size, spacing, molecular length and radiation power on the photoconductive properties. Controlling these parameters allows the relative roles of nano antennae focus increasing effective photon flux and hot electron distribution to the current enhancement to be compared.

This phenomenon offers a pathway to selectively enhance specific optical energies or to design a hybrid structure that can simultaneously enhance a

range of optical wavelengths. Applications in optical devices and a range of photovoltaics could exploit this new phenomenon [ACS Nano, 2010, 4 (2), pp 1019-1025].

4:20pm NS+EM+EN-WeA8 From Red-Coloured Coatings to Light Trapping in Solar Cells: on the Tunability and Control of the Surface Plasmon Resonance Behaviour, M. Creatore, H. Takeke Beyene, M. Ponomarev, M.C.M. van de Sanden, Eindhoven University of Technology, Netherlands

The combination of (noble) metal nanoparticles (NPs) with dielectrics is an on-going research subject, due to the generated surface plasmon resonance (SPR) effect, relevant in several technological applications such as color filters, optical switching devices and sensors, to name a few.

In this contribution, we report on the tunability and control of the surface plasmon resonance behaviour through the engineering of metal NP/dielectric interfaces for two applications, i.e. thickness- and viewing angle- independent red- coloured decorative coatings and light trapping enhancement in silicon- based tandem thin film solar cells. Both studies have been carried out by making use of a vacuum chamber where plasma-enhanced chemical vapour deposition for the dielectric layer and magnetron sputtering for the metal NP deposition are combined.

Multilayer structures composed of gold NPs sandwiched between SiO₂ layers represent a valid solution for the independent control of NP size and density: while a constant NP size guarantees a narrow surface plasmon frequency, an increased NP density leads to an enhancement in the absorption [1]. A multi-diagnostic approach consisting of spectroscopic ellipsometry, transmission electron microscopy and Rutherford backscattering analysis has allowed the characterization of the deposited coatings: gold NPs (diameter 10-15 nm) with a surface area coverage of 26% and sandwiched between 40 nm- thick SiO₂ layers, exhibit a red colour, whereas the color intensity (i.e. from cool to warm deep red) increases with the layer number, i.e. NP density.

While in this first application the main mechanism contributing to extinction is *absorption*, for an efficient sun light management/ trapping within a solar cell, *scattering* plays a dominant role. In particular, for amorphous (a-Si:H)/microcrystalline (μ c-Si:H) silicon tandem solar cells a promising approach consists in the incorporation of an intermediate layer (e.g. ZnO) sandwiched between the top a-Si:H and the bottom μ c-Si:H cell, able to efficiently scatter photons of a specific frequency range back to the top cell or forward to the bottom cell. In this respect, copper NPs (30-150 nm diameter) when coupled to ZnO layers, are responsible for the generation of a plasmon peak at 700 nm, which shifts towards higher wavelengths with an increase in NP size, therefore showing its potential towards low energy photon forward scattering into the bottom μ c-Si:H cell.

[1] H. T. Beyene, F.D. Tichelaar, P. Peeters, I. Kolev, M.C.M. van de Sanden, M. Creatore, accepted for publication in Plasma Processes and Polymers (2010).

4:40pm NS+EM+EN-WeA9 Index-Matching at the Nanometer Scale, G. Broenstrup, C. Leiterer, N. Jahr, B. Hoffmann, F. Talkenberg, Institute of Photonic Technology, Germany, S.H. Christiansen, Max Planck Institute for the Science of Light, Germany

Silicon nanowires (SiNW) show high potential as future building blocks for photonic devices. They show strong resonant enhancement effects resulting in high absorption efficiencies and even higher scattering efficiencies. Since both effects are based on the same underlying physical principles the resonant enhancement of the absorption as well the resonant enhancement of the scattering of light occurs at the same wavelength. These large scattering efficiencies could result in an increased reflectivity of structures based on these SiNWs.

To overcome the increased scattering efficiencies we show an index matching core-shell approach.

The SiNWs are wrapped with a thin oxide layer with a refractive index smaller than the refractive index of silicon. The thickness of the wrapping layer is formed using atomic layer deposition (ALD), which allows to control the thickness of the layer at the Angstrom scale. The microstructure is analyzed using transmission electron microscopy (TEM).

The scattering behavior of these individual SiNWs with an oxide layer are measured using an optical microscope with a coupled spectrometer. The experimental data is analyzed using an extended Mie theory.

It will be shown, that this method can be used to tune the absorption efficiencies and the scattering separately to different wavelengths.

5:00pm **NS+EM+EN-WeA10 20 μ s Photocurrent Response from Lithographically Patterned Nanocrystalline Cadmium Selenide Nanowires**, S.-C. Kung, W.E. van der Veer, F. Yang, K.C. Donovan, R.M. Penner, University of California, Irvine

Lithographically patterned nanowire electrodeposition (LPNE) provides a method for patterning nanowires composed of nanocrystalline cadmium selenide (*nc*-CdSe) over wafer-scale areas. We assess the properties of (*nc*-CdSe) nanowires for detecting light as photoconductors. Structural characterization of these nanowires by X-ray diffraction and transmission electron microscopy reveals they are composed of stoichiometric, single phase, cubic CdSe with a mean grain diameter of 10 nm. For *nc*-CdSe nanowires with lengths of many millimeters, the width and height dimensions could be varied over the range from 60 to 350 nm (*w*) and 20 to 80 nm (*h*). Optical absorption and photoluminescence spectra for *nc*-CdSe nanowires were both dominated by band-edge transitions. The photoconductivity properties of *nc*-CdSe nanowire arrays containing \sim 350 nanowires were evaluated by electrically isolating 5 μ m nanowire lengths using evaporated gold electrodes. Photocurrents, i_{photo} , of $10\text{--}100\times i_{\text{dark}}$ were observed with a spectral response characterized by an onset at 1.75 eV. i_{photo} response and recovery times were virtually identical and in the range from 20 to 40 μ s for 60×200 nm nanowires.

5:20pm **NS+EM+EN-WeA11 Efficient, Single Layer Organic Light-Emitting Devices Based on a Graded Composition Emissive Layer**, N.C. Erickson, R.J. Holmes, University of Minnesota

We demonstrate efficient electrophosphorescence from devices comprised of a single organic active layer. High efficiency is realized by combining both hole- and electron-transporting host materials (HTM and ETM, respectively) into a single, graded composition emissive layer with the green emitter, *fac*-tris(2-phenylpyridine) iridium (III). The composition of the host-material is continuously graded to realize 100% HTM at the anode, and 100% ETM at the cathode. A peak external quantum efficiency of $\eta_{\text{EQE}}=(19.3\pm 0.4)\%$ is realized in the forward-viewing direction at a luminance level of 600 cd/m^2 , corresponding to a power efficiency of $\eta_p=(66.5\pm 1.3)\text{ lm/W}$. This performance is similar to that realized in more conventional and complex, multi-layered structures. The graded composition of the structure balances electron and hole injection and transport leading to efficient exciton formation, permitting high efficiency using a single active layer. The graded composition architecture may be further utilized to realize simple, efficient organic light-emitting devices for use in display and lighting applications.

Tribology Focus Topic

Room: Tesuque - Session TR+NS+SS-WeA

Mechanical & Chemical Effects on Friction and Wear

Moderator: S.S. Perry, University of Florida

2:00pm **TR+NS+SS-WeA1 Quantitative Assessment of Sample Stiffness and Sliding Friction from Force Curves in Atomic Force Microscopy**, J.R. Pratt, G.A. Shaw, NIST, L. Kumanchik, University of Florida, N.A. Burnham, Worcester Polytechnic Institute

It has long been recognized that the angular deflection of an atomic force microscope (AFM) cantilever under "normal" loading conditions can be profoundly influenced by the friction between the tip and the surface. It is shown here that a remarkably quantifiable hysteresis occurs in the slope of loading curves whenever the normal flexural stiffness of the AFM cantilever is *greater* than that of the sample. This situation arises naturally in cantilever-on-cantilever calibration, but also when trying to measure the stiffness of nanomechanical devices or test structures, or when probing any type of surface or structure that is much more compliant along the surface normal than in transverse directions. Expressions and techniques for evaluating the coefficient of sliding friction between the cantilever tip and sample from normal force curves, as well as relations for determining the stiffness of a mechanically compliant specimen are presented. The model is experimentally supported by the results of cantilever-on-cantilever spring constant calibrations. The cantilever spring constants determined here agree with the values determined using the NIST electrostatic force balance within the limits of the largest uncertainty component, which had a relative value of less than 2.5%. This points the way for quantitative testing of micromechanical and nanomechanical components, more accurate calibration of AFM force, and provides nanotribologists access to information about contact friction from normal force curves [1].

1. J. Appl. Physics **107**, 044305 (2010), doi:10.1063/1.3284957

2:20pm **TR+NS+SS-WeA2 Nanotribological Properties of Polyzwitterionic Brushes**, Z. Zhang, A.J. Morse, S.P. Armes, University of Sheffield, UK, A.L. Lewis, Biocompatibles UK Ltd., UK, G.J. Leggett, University of Sheffield, UK

The frictional properties of surface grown zwitterionic polymer brushes: poly(2-(methacryloyloxy)ethyl phosphorylcholine) (PMPC) have been characterized using friction force microscopy (FFM) in different liquid media.

1. Effect of molecular weight and solvent on the frictional properties

For brushes thicker than 192 nm, the coefficient of friction decreased with increasing brush thickness, while for brush layers with smaller thicknesses, the coefficient of friction varied little with molecular weight. It is suggested that water molecules bound to PMPC chains act as an interfacial lubricant; as brush thickness increases, the amount of bound water increases and the coefficient of friction decreases. This hypothesis is supported by comparative studies of the approaching parts of force-displacement plots acquired for PMPC brush samples with different molecular weights under water. In particular, it was found that thicker brushes exerted a greater repulsive force to the AFM probe. Gold-coated probes were used throughout this part to avoid any complication might be caused by tip surface chemistry. FFM has also been used to investigate the consoolvency behaviour of PMPC. Friction force was measured for PMPC brushes with a dry thickness of 307 nm while immersed in alcohol/water binary mixtures with different compositions. A distinct increase was observed in the coefficient of friction at an ethanol-water ratio of 90:10, and a 2-propanol-water ratio of 70:30, but not for methanol/water mixtures. This result is induced the loss of conformational change of the polymer brush, which induced the loss of hydration layer.

2. Influence of solvent and tip chemistry on the contact mechanics

To study the contact mechanics of tip-sample interactions in FFM, AFM probes were chemically functionalized by deposition of three different types of self-assembled monolayer of dodecanethiol ($\text{C}_{11}\text{H}_{23}$) or mercaptoundecanoic acid (C_{10}COOH), or cysteamine (C_2NH_2). In alcohol solvents, friction force acquired using acid- or CH_3 - functionalized tip has a linear relationship with the applied load, but nonlinear for amine-terminated tip. It is also noted that the coefficient of friction is highest in 2-propanol for all three types of probe, which again suggests that conformation of PMPC brush is one of the key factors. In aqueous medium, the friction-load relationships were nonlinear and characterized by the Derjaguin-Muller-Toporov model of contact mechanics. Coefficient of friction measured by amine-functionalized probes were greater than that of acid-functionalized probes, and than CH_3 - ones, which was attributed to the interaction between polymeric chains and probes.

2:40pm **TR+NS+SS-WeA3 Atomic-scale Processes in Friction and Wear: From Diamond to Graphene**, R.W. Carpick, University of Pennsylvania **INVITED**

Nanoscale friction and wear are primary limitations for small-scale devices such as atomic force microscopy (AFM) probes and micro- or nano-electronic mechanical systems with contacting surfaces, and is also relevant to understanding friction and wear in larger-scale contacts. We first present studies that quantify the nanoscale volume loss in sliding wear using AFM and periodic *ex-situ* transmission electron microscopy (TEM) imaging. Novel carbon-based AFM tip materials, including ultrananocrystalline diamond and diamondlike carbon, exhibit superior wear resistance compared to conventional materials (silicon and silicon nitride)¹⁻³. We then present results from wear tests performed inside of the TEM using modified *in-situ* indentation techniques. This permits real-time visualization of the contact geometry and shape evolution of a single asperity with sliding over a countersurface. This allows us to measure wear with a higher degree of precision than previously possible. Insights comparing the wear resistance of carbon-based and Si-based materials, particularly in the context of atom-by-atom wear processes, will be discussed⁴. Finally, we will discuss how nanoscale friction in graphene and other atomically-thin sheets is governed by the high flexibility intrinsic to the atomic scale⁵.

1. *Prevention of nanoscale wear in atomic force microscopy through the use of monolithic ultrananocrystalline diamond probes*. J. Liu, D.S. Grierson, J. Notbohm, S. Li, S.D. O'Connor, K.T. Turner, R.W. Carpick, P. Jaroenapibal, A.V. Sumant, J.A. Carlisle, N. Neelakantan & N. Moldovan, **Small**, in press (2010).

2. *Ultra-low nanoscale wear through atom-by-atom attrition in silicon-containing diamond-like-carbon*. H. Bhaskaran, B. Gotsmann, A. Sebastian, U. Drechsler, M. Lantz, M. Despont, P. Jaroenapibal, R.W. Carpick, Y. Chen & K. Sridharan, **Nature Nanotechnology** **5**, 181-185 (2010).

3. *Wear resistant diamond nanoprobe tips with integrated silicon heater for tip-based nanomanufacturing*. P.C. Fletcher, J.R. Felts, Z. Dai, T.D. Jacobs,

H. Zeng, W. Lee, P.E. Sheehan, J.A. Carlisle, R.W. Carpick & W.P. King, *ACS Nano*, accepted (2010).

4. *On the application of transition state theory to atomic-scale wear*. T.D. Jacobs, B. Gotsmann, M.A. Lantz & R.W. Carpick, *Tribol. Lett.*, accepted (2010).

5. *Frictional characteristics of atomically-thin sheets*. C. Lee, Q. Li, W. Kalb, X.-Z. Liu, H. Berger, R.W. Carpick & J. Hone, *Science* 328, 76-80 (2010).

4:00pm **TR+NS+SS-WeA7 Lubricin Reduces Microscale Cartilage Wear**, *J.M. Coles, D.P. Chang*, Duke University, *L. Zhang, G.D. Jay*, Brown University / Rhode Island Hospital, *F. Guilak, S. Zauscher*, Duke University

Articular cartilage is the load bearing surface of mammalian joints. Relatively little wear occurs in cartilage and the tissue is able to sustain millions of loading cycles despite limited regenerative capacity. Though many studies of cartilage friction and lubrication have been performed, often with a stated goal of understanding cartilage wear prevention, very few have measured wear directly and none have directly assessed the effects of synovial fluid constituents in mediating wear. Here we show that the synovial fluid glycoprotein lubricin reduces microscale cartilage wear in vitro. We used colloidal probe microscopy to induce wear and use the change in the average height of the surface as a measure of worn volume. The height change in locations worn in the presence of lubricin was significantly less than in those worn in the control solution. These data indicate that lubricin is important for cartilage preservation physiologically and may have implications for treating or preventing joint disease.

4:20pm **TR+NS+SS-WeA8 Friction of Metallic Nanoparticles: The Influence of Particle Morphology, Orientation and Air Exposure**, *D. Dietzel, T. Moeninghoff, C. Herding, M. Feldmann, H. Fuchs*, Westfälische Wilhelms-Universität Muenster, Germany, *C. Ritter, U.D. Schwarz*, Yale University, *A. Schirmeisen*, Westfälische Wilhelms-Universität Muenster, Germany

The contact area dependence of the interfacial friction experienced during the translation of the antimony is studied under different conditions using the tip of an atomic force microscope as a manipulation tool [1]. In vacuum a dual behavior in the friction-area curves is found had been found earlier, characterized by the observation that some particles exhibit friction below the detection limit while other similarly sized particles showed constant shear stress values [2]. New investigations with improved sensitivity confirm the reproducibility of this effect and that neither the particle's morphology nor their relative orientation towards the substrate lattice change this behavior. In contrast, we find that a temporary exposure to ambient air can lead to a drastic increase in the particle's friction.

[1] A. Schirmeisen and U. D. Schwarz, *ChemPhysChem* 10 (2009) 2358

[2] D. Dietzel et al., *Physical Review Letters* 101 (2008) 125505

4:40pm **TR+NS+SS-WeA9 Modeling Materials in Contact using Molecular Simulation**, *J.D. Schall, R.V. Petrach*, Oakland University
INVITED

Molecular dynamics (MD) simulation has become an extremely powerful tool for materials science research due to the wealth of atomic level information it provides. In this talk an overview of the MD simulation method will be given. Then a number of applications where MD simulations have been applied to study materials in contact will be discussed. Topics will include the tribology of amorphous carbon films in the presence of hydrogen, and recent work involving the indentation of free-standing graphene sheets. In simulation of the tribology of amorphous carbon, chemical reactions between opposing films were monitored and used to elucidate the mechanisms for enhanced friction and wear properties and to discover the mechanisms of transfer layer formation. These simulations illustrate the need for surface passivation of amorphous carbon films in applications where low friction is desired. We have also investigated the role of silicon on the properties of these films using a parametrization of Brenner's second generation reactive empirical bond order potential for Si-C-H interactions. Recent results of the simulation of indentation of free-standing graphene films will be shared.

5:20pm **TR+NS+SS-WeA11 Modeling Tribochemistry of DLC vs DLC in the Presence of Water**, *J.A. Harrison, P.T. Mikulski, M.T. Knippenberg*, United States Naval Academy

Because the structure and properties of diamond-like carbon (DLC) can vary depending upon deposition conditions, the tribological response of DLC (and diamond) is very sensitive to environmental conditions. For instance, the presence of water vapor has been shown to negatively impact the friction performance of hydrogenated DLCs but to improve the performance of nanocrystalline and ultrananocrystalline DLCs.

Tribochemical reactions of the water with the DLC are thought to be at the heart of this long-standing puzzle.

With that in mind, we have been working to develop a potential energy function that is capable of modeling DLC in the presence of water. To be realistic, such a potential energy function should be able to model tribochemical reactions that may occur as a result of the sliding. In addition, because H, C, and O have very different electronegativities, the potential energy function must be capable of modeling charges and fluctuating charges that arise from electronegativity differences in a realistic way. This talk will outline our efforts at potential development and present some preliminary results of DLC friction in the presence of water.

**Supported by The Air Force Office of Scientific Research.

5:40pm **TR+NS+SS-WeA12 Effects of Impact and Sliding Forces on Failure Behavior of a DLC Coating**, *J.F. Su, L. Wang, X. Nie*, University of Windsor, Canada

The wear and tribological properties of diamond-like carbon (DLC) coatings have been investigated and well documented under various laboratorial and industrial conditions. However, investigations into failure behavior of the coatings when subjected to cyclic impact-sliding loads are scarce. In this study, an inclined ball-on-plate impact-sliding tests were used to evaluate the fatigue cracking and peeling failure behavior of a DLC (a-C:H) coating and a TiN coating as comparison. By adjusting the impact velocity of a steel impacting ball that is connected to and driven by air cylinder, various dynamic impact loads can be obtained. The impact load vs. time curves were recorded and showed three stages, i.e., impact loading stage, vibration stage and quasi-static sliding stage for each impact-sliding cycle. Four loading combinations of impact/static forces (50N/100N, 100N/100N, 50N/200N and 100N/200N) were used in the tests. The test results showed that the DLC coating performed better than the TiN coating under the impact forces but worse under the sliding stages where the quasi-static force was applied by the air cylinder.

Thursday Morning, October 21, 2010

Biomaterial Interfaces

Room: Taos A - Session BI2+NS-ThM

Quantitative Sensing at Biointerfaces

Moderator: E.O. Reimhult, University of Natural Resources and Applied Life Sciences, Switzerland

10:40am **BI2+NS-ThM9 Membranes on Solid Surfaces, A.P. Shreve,** Los Alamos National Laboratory **INVITED**

Lipid assemblies on solid substrates provide a means of integrating biological and non-biological systems. They serve as a basis for a number of technological applications, particularly biological sensing and imaging platforms. They also provide important materials for the study of fundamental biophysical processes, and additionally are a platform for the study of the structure and dynamics of low-dimensional complex fluids. Working with a number of collaborators [1-4], we have been investigating how lipids interact with variously textured and functionalized solid surfaces, with an emphasis on the use of optical microscopy and spectroscopy as means of interrogating structure, dynamics and function within membrane assemblies on surfaces. Selected examples from recent and ongoing work will be discussed, including the use of diffusion measurements to infer the nature of membrane interactions with nanotextured surfaces, preparation and characterization of controlled multibilayer architectures, study of how electrostatic interactions with surfaces affect the structure and asymmetry of membranes, the interaction of functionalized nanoparticles and nanomaterials with membranes, and the development and characterization of multicomponent membranes on patterned nanoporous and nanostructured substrates. All of these topics are related to long-term interests in the application of solid-substrate supported lipid assemblies in sensing and characterization of biological systems.

[1] T.H. Yang, C.K. Yee, M.L. Amweg, S. Singh, E.L. Kendall, A.M. Dattelbaum, A.P. Shreve, C.J. Brinker, A.N. Parikh, "Optical detection of ion-channel-induced proton transport in supported phospholipid bilayers," *Nano Letters* 7 (2007) 2446. [2] A.E. Oliver, E.L. Kendall, M.C. Howland, B. Sanii, A.P. Shreve, A.N. Parikh, "Protecting, patterning, and scaffolding supported lipid membranes using carbohydrate glasses," *Lab on a Chip* 8 (2008) 892. [3] A.P. Shreve, M.C. Howland, A.R. Sapuri-Butti, T.W. Allen, A.N. Parikh, "Evidence for leaflet-dependent redistribution of charged molecules in fluid supported phospholipid bilayers," *Langmuir* 24 (2008) 13250. [4] J.H. Werner, G.A. Montaña, A.L. Garcia, N.A. Zurek, E.A. Akhadov, G.P. Lopez, A.P. Shreve, "Formation and dynamics of supported phospholipid membranes on a periodic nanotextured substrate," *Langmuir* 25 (2009) 2986.

11:20am **BI2+NS-ThM11 2010 AVS Albert Nerken Award Lecture - AlGaIn/GaN High Electron Mobility Transistor Based Sensors for Bio-Applications, F. Ren***, S.J. Pearton, B.H. Chu, C.Y. Chang, University of Florida, W.J. Johnson, Nitronex, A. Dabiran, P.P. Chow, SVT Associates **INVITED**

It is highly desirable to have a programmable, single chip sensor with an array of sensors for different purposes that is handheld and capable of wireless communication. This kind of sensor can be very useful for environmental, safety, and biomedical applications. For example, the sensor can be programmed in the doctor office for specific uses to give it to patients to use at home, transmitting the sensing results to their doctor directly to monitor the effectiveness of prescribed medicines. Thus, patients can get better, prompt and adequate health care. It can also reduce the number of unnecessary visits to the emergency room and the cost of the national health system. AlGaIn/GaN high electron mobility transistor based sensors are good candidates for low cost, handheld, and wireless chemical and biomedical sensor due to their excellent thermal as well as chemical stability and sensitivity to the changes of ambient. We have demonstrated AlGaIn/GaN HEMT based individual sensors for protein, DNA, kidney injury molecules, prostate cancer, pH values of the solutions, pH in the exhaled breath condensate, and mercury ions with specific surface functionalizations. Recently, we integrated ZnO nanorods with AlGaIn/GaN HEMT to detect glucose. This approach offers a possibility of integrating AlGaIn/GaN HEMT based sensors with ZnO nanorod sensors on a single "smart sensor chip" for bio-sensing applications.

* Albert Nerken Award Winner

Nanometer-scale Science and Technology

Room: La Cienega - Session NS-ThM

Nanowires and Nanoparticles

Moderator: L. Bartels, University of California at Riverside

8:00am **NS-ThM1 Enantioselective Separation on Chiral Au Nanoparticles, N. Shukla, M. Bartel, N. Ondeck, A.J. Gellman,** Carnegie Mellon University

The surfaces of chemically synthesized Au nanoparticles have been modified with D- or L- cysteine to render them chiral and enantioselective for adsorption of chiral molecules. Their enantioselective interaction with chiral compounds has been probed by optical rotation measurements when exposed to racemic propylene oxide. The ability of optical rotation to detect enantiospecific adsorption arises from the fact that the specific rotation of polarized light by R- and S-propylene oxide is enhanced by interaction Au nanoparticles. The enhancement of the specific optical rotation of polarized light by R- and S-propylene oxide is sensitive to excitation wavelength. Longer the excitation wavelength, smaller is the specific rotation of polarized light. This effect is related to previous observations of enhanced circular dichroism by Au nanoparticles modified by chiral adsorbates. More importantly, chiral Au nanoparticles modified with either D- or L- cysteine enantioselectively adsorb one enantiomer of propylene oxide from a solution of racemic propylene oxide, thus leaving an enantiomeric excess in the solution phase. Au nanoparticles modified with L- cysteine (D- cysteine) selectively adsorb the R-propylene oxide (S-propylene oxide). A simple model has been developed that allows extraction of the enantiospecific equilibrium constants for R- and S-propylene oxide adsorption on the chiral Au nanoparticles.

8:20am **NS-ThM2 Unique Optical Properties in Wet - Chemically Etched Silicon Nanowires, V.A. Sivakov, B. Hoffmann, F. Voigt, G. Broenstrup, F. Talkenberg,** Institute of Photonic Technology, Germany, G. Bauer, University of Oldenburg, Germany, S.H. Christiansen, Max Planck Institute for the Science of Light, Germany

Silicon nanowire (SiNW) ensembles with vertical and zig-zag architectures have been realized using wet chemical etching of bulk silicon wafers (p-Si(111) and p-Si(100)) with an etching hard mask of silver nanoparticles that are deposited by wet electroless deposition on polystyrene patterned silicon surfaces.

Strong visible (red-orange) room temperature photoluminescence has been observed in wet chemically etched heavily (10²⁰ cm⁻³) and lowly (10¹⁵ cm⁻³) doped SiNWs. Our observations strongly suggest that visible light emission at room temperature of SiNWs is a result of the rough sidewall structure that can be such that nanoscale features form that make quantum confinement most probable. Significant light absorption (over 90% in a range between 300-2000 nm) was observed in the SiNWs covered by the TCO (Al doped ZnO) thin layers performed via Atomic Layer Deposition. The strong absorption, less reflection of visible and infra-red light and room temperature photoluminescence of the SiNW ensembles strongly suggest that such a material has a real potential to be applied in the fields of optoelectronics, photonics, sensoric and photovoltaics. The morphology, crystallographic and surface structure, and optical properties of SiNWs will be presented and discussed in details.

8:40am **NS-ThM3 Size, Composition and Support Effects in Nanocatalysis: I. Bridging the Sub-Nanometer and Nanometer Size Range & II. Coupling the Studies of Model and "Real" Catalysts, S. Vajda,** Argonne National Laboratory

The elucidation of the size/composition/shape/structure and function correlation is instrumental for the design of new catalysts. Uniform particles are prerequisites for such studies, making size-selected clusters of few atoms to several nm in size as ideal model systems. The experiments are based on 1) size-selected cluster deposition, 2) electron microscopy and 3) *in situ* synchrotron X-ray characterization under working conditions (scattering and absorption), combined with 4) mass spectroscopy of

products. DFT calculations performed by our collaborators are instrumental at the understanding of the catalytic properties of these materials. In this presentation, examples will be given on bridging the size gap between the sub-nanometer and nanometer cluster size regime and on coupling studies of model size-selected [1-3] and "real"- with wet chemical methods prepared [4-6] catalysts. Processes discussed will include dehydrogenation, Fischer-Tropsch synthesis and partial oxidation of alkenes. For example, our studies led to the identification of a new class of silver-based direct propylene epoxidation catalyst which works at considerably lower temperatures than existing ones [1]. The role of the size in catalyst's activity and the evolving morphology of silver nanoclusters under epoxidation conditions will be addressed [1-3], followed by the discussion of strong size, composition and support effects in dehydrogenation [4,5], hydrogenation [6] and Fischer-Tropsch reactions.

[1] Y. Lei, F. Mehmood, S. Lee, J. P. Greeley, B. Lee, S. Seifert, R. E. Winans, J. W. Elam, R. J. Meyer, P. C. Redfern, D. Teschner, R. Schlögl, M. J. Pellin, L. C. Curtiss, and S. Vajda, *Science* **328**, 224 (2010)

[2] S. Vajda, S. Lee, K. Sell, I. Barke, A. Kleibert, V. von Oeynhausen, K.-H. Meiwes-Broer, A. Fraile-Rodríguez, J. W. Elam, M. J. Pellin, B. Lee, S. Seifert, R. E. Winans, *J. Chem. Phys.*, **131**, 121104 (2009),

[3] L. M. Molina, S. Lee, K. Sell, G. Barcaro, A. Fortunelli, B. Lee, S. Seifert, R. E. Winans, J. W. Elam, M. J. Pellin, I. Barke, A. Kleibert, V. von Oeynhausen, Y. Lei, R. J. Meyer, J. A. Alonso, A. Fraile-Rodríguez, S. Giorgio, C. R. Henry, K.-H. Meiwes-Broer, and S. Vajda, *Catal. Today*, invited, under review

[4] M. Di Vece, S. Lee, X. Wang, B. Lee, S. Seifert, R.E. Winans, M. Neurock, G. Haller, L. D. Pfefferle, and S. Vajda, in preparation

[5] M. Di Vece, S. Lee, R. Si, B. Ricks, S. Seifert, R.E. Winans, M. Flytzani-Stephanopoulos, and S. Vajda, in preparation

[6] S. A. Wyrzgol, S. Schäfer, S. Lee, B. Lee, M. Di Vece, X. Li, S. Seifert, R. E. Winans, M. Stutzmann, J. A. Lercher, and S. Vajda, 2010, *Phys. Chem. Chem. Phys.* feature article, on-line April 27, 2010

9:00am **NS-ThM4 Electrochemistry of Surface-Passivated Nanocrystals**, *P. Szymanski, A.Y. Kopsosov, V.I. Klimov, M. Sykora*, Los Alamos National Laboratory

We have combined electrochemical and optical measurements to investigate the effects of charging on the optical properties of semiconductor nanocrystals (NCs). We show that cyclic voltammetry with simultaneous monitoring of absorption and photoluminescence is necessary to accurately determine the energy offset of the NC conduction-band minimum. The combination of electrochemical and optical studies also reveals the different location of charges - surface vs. NC core. The studies of photoluminescence dynamics show that carrier relaxation dynamics is significantly enhanced in charged NCs. In addition, we have studied the effect of inorganic passivating layers on the NC charging. The addition of a shell with a wide band gap, such as ZnS, creates an energetic and kinetic barrier for charging the nanocrystal core under an applied potential. We find that a significant shift in the charging potential can occur with shell thicknesses as thin as 2 monolayers. Our results demonstrate the broad applicability of spectroelectrochemical methods for characterizing materials of potential interest in photovoltaic and light-emitting devices.

9:20am **NS-ThM5 Single-nanoparticle Catalysis at Single-turnover Resolution**, *P. Chen*, Cornell University **INVITED**

Metal nanoparticles can catalyze many chemical transformations for energy conversion, petroleum processing, and pollutant removal. Characterizing their catalytic activity is important, but challenging in ensemble measurements due to their morphology dispersions and variable surface active sites. Using single-molecule microscopy of fluorogenic reactions, we monitor the redox catalytic reactions on the surface of individual Au-nanoparticles in an aqueous environment in real time at single-turnover resolution. We find that for catalytic product generation, all Au-nanoparticles follow a Langmuir-Hinshelwood mechanism, but individual nanoparticles show drastically different reactivity. And for product dissociation, three nanoparticle subpopulations are present that show differential selectivity between parallel dissociation pathways. Individual nanoparticles show large temporal activity fluctuations, attributable to both catalysis-induced and spontaneous dynamic surface restructuring that occurs at different timescales at the surface catalytic and product docking sites. Individual Au-nanoparticles also show reactant-concentration dependent dynamic surface switching between a low reactivity state and high reactivity state. Strong size dependences are also observed in the catalytic activity, selectivity, and dynamics of these Au-nanoparticles. Smaller particles are more reactive but bind the reactant weaker. Larger particles are less selective in the parallel reaction pathways. The smaller particles are more prone to dynamic surface restructuring, whose activation energies and timescales are quantified. The

results exemplify the power of the single-molecule approach in revealing the interplay of catalysis, heterogeneous reactivity, and surface structural dynamics in nanocatalysis.

10:40am **NS-ThM9 Size Effects in the Synthesis of Ge and Ge/Si Nanowire Heterostructures**, *S.A. Dayeh, S.T. Picraux*, Los Alamos National Laboratory

Progress in the synthesis of semiconductor nanowires has prompted intensive discussions of the science of their growth and the technological applications they promise. Fundamental aspects of their growth have been postulated for nearly five decades for larger diameter nanowires and debated more recently in detailed growth studies for different materials systems. Here, we exploit an extreme level of control over diameter, morphology, and placement in VLS synthesized germanium nanowires to establish systematic size effects on their growth at small diameters, down to sub-10 nm, where quantum effects become relevant. We observe reproducible reduction in Ge nanowire growth rates with decreased diameter coupled to a measured increase in the Ge equilibrium solubility¹ for the same wires, validating the role of the Gibbs-Thomson effect in nanowire growth at small diameters. We show how this sets a practical thermodynamic limit on the lowest achievable nanowire diameters (~ 3 nm) and present comprehensive studies of the effects of temperature, pressure, and the introduction of dopant precursors on the size dependences and cutoff diameters for nanowire growth. We also discuss methods to control and eliminate Au diffusion during the growth of Ge/Si core/shell heterostructures. Single crystal core/multi-shell Ge/p+Ge/Si nanowires were grown using such a process and their transport properties benchmarked. Using field-effect transistors as a test-bed for their transport properties, we observe up to 2X mobility enhancement in such heterostructured nanowires without Au diffusion and obtain record geometry-normalized on-currents for p-type FET devices of up to 430 $\mu\text{A/V}$. These studies provide an in-depth understanding for the control of the growth of Ge/Si nanowires and for exploiting their bandgap engineering possibilities for unique nanoscale device performance.

¹ E. Sutter et al., 2010 (to be published).

11:00am **NS-ThM10 Formation and Characterization of Metallic Glass Nanowire**, *K.S. Nakayama, Y. Yokoyama, T. Ono, M.W. Chen, K. Akiyama, T. Sakurai, A. Inoue*, Tohoku University, Japan

Metallic glasses have exciting potential for structural, chemical, and magnetic applications with the sizes ranging from micrometer to centimeter, but the fabrication and characterization down to nanoscale remains an important challenge. Progress has been hindered by the lack of bottom-up methodologies to produce amorphous nanostructures. Recently, we show the self-organized amorphous nanowires that are formed on the fracture surfaces of bulk metallic glasses [Nakayama et al., *Nano Lett.* **8**, 516-519 (2008)]. However, it is difficult to control their morphologies because they were created by instantaneous fracture processes. Here we report the controlled formation and mechanical characterization of individual amorphous nanowires. We find that they have a high strength with the excellent flexibility where the elastic modulus is much smaller than that of the bulk owing to the hyper-excess free volume in nanowire. The nanowire composed of amorphous materials leading to outstanding mechanical properties would offer a new paradigm for development in nanotechnology and materials science.

11:20am **NS-ThM11 Diameter Dependence of the Minority Carrier Diffusion Length in Semiconductor Nanowires**, *A. Soudi, Y. Gu*, Washington State University

Carrier transport in semiconductors is of both fundamental and technological significance, as it not only reflects fundamental aspects such as electron-phonon interactions, but also controls electronic and optoelectronic device characteristics. Minority carrier transport is particularly important, as it determines the performance of p-n junction based devices. A fundamental understanding of carrier transport properties, especially those of minority carriers, provides a critical basis for material engineering and device design efforts.

In advancing semiconductor nanowire-based device technologies, a quantitative knowledge of carrier transport parameters, such as the carrier diffusion length, is required for a rational design of devices with controlled performance. From a fundamental perspective, in semiconductor nanowires, the one-dimensional confinement of carriers and phonons, together with the high surface-to-volume ratio, can render carrier transport characteristics significantly different from those in the bulk. Here, using the near-field scanning photocurrent microscopy technique, we have directly measured the minority carrier diffusion length in single ZnO nanowires. In particular, a near-field scanning optical microscope was used to locally generate minority carriers in single nanowire Schottky diodes; the spatial variations of the resulting photocurrent images near the Schottky contact were used to

obtain the minority carrier diffusion length, L_D . The diameter dependence of L_D suggests a *diameter-dependent* surface electronic structure, particularly an increase in the density of mid-bandgap surface states with the decreasing diameter. This diameter dependence of the surface electronic structure might be a universal phenomenon in wurtzite-type nanostructures, and is critical in interpreting and understanding the effects of surfaces on various material properties.

11:40am **NS-ThM12 Photocatalytic Deposition of Pt or Ag Nanoparticles on Ordered Linear Arrays of TiO₂ Nanoparticles**, *J. Taing, J.C. Hemminger*, University of California, Irvine

TiO₂ nanoparticles are generated on step edges of highly oriented pyrolytic graphite (HOPG) via physical vapor deposition of Ti followed by air oxidation. Deposition of Ti on HOPG while the substrate is held at 900 K results in nanoparticle growth exclusively at the graphite step edges. Since the steps on high quality HOPG are long (>1 micron) and very parallel, the result is highly ordered arrays of nanoparticles. Photodeposition of Pt on the TiO₂ nanoparticles results in the decoration of the TiO₂ with Pt nanoparticles (≤ 5 nm). Photodeposition of Pt is accomplished by submersion in an aqueous solution of 0.25 mM K₂PtCl₄ and 0.5 mM trisodium citrate followed by photolysis with TiO₂ bandgap radiation (365 nm radiation from a 200 W Mercury lamp). Similarly, Ag nanoparticles can be deposited by photolysis of the sample in an aqueous solution of 0.25 mM Ag(NO₃)₃ and 0.5 mM trisodium citrate. Scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM), x-ray dispersive spectroscopy (EDS), and x-ray photoelectron spectroscopy (XPS) characterize the morphology, crystal structure, and chemical identity of the nanoparticles. Images of decorated TiO₂ nanoparticles are included in the supplement.

Thursday Afternoon, October 21, 2010

Nanometer-scale Science and Technology
Room: La Cienega - Session NS+BI-ThA

Biomolecular Templates & Bioinspired Nanomaterials

Moderator: B. Borovsky, St. Olaf College

2:00pm NS+BI-ThA1 Bio-functionalization of Nanopatterned Surfaces and their Integration with DNA Nanostructures, M. Palma, J.J. Abramson, E. Penzo, A. Gorodetsky, R. Wang, M.P. Sheetz, C. Nuckolls, J. Hone, S.J. Wind, Columbia University

The ability to control biomolecules on surfaces with nanometer resolution is of great interest in the field on nanoscience and nanotechnology. DNA nanoarrays, in particular, are of interest in the study of DNA-protein interactions, for biodiagnostic investigations and as a tool to drive self-organization of nanomaterials on surfaces. In this context, achieving a highly specific nanoscale assembly of oligonucleotides at surfaces is critical.

Here we describe different strategies to control the immobilization of single- and double-stranded DNA, as well as DNA nanostructures (DNA "origami"), on nanopatterned surfaces, with features down to the sub-10nm regime.

Using electron-beam and nanoimprint lithography we fabricated sub-10nm metal dots arranged in multiple configurations on Si or glass substrates. We have developed strategies for the selective bio-functionalization of these patterns, at the single nanodot level: each step of the biochemical functionalization has been monitored by Fluorescence Microscopy. The bio-functionalization approach used allowed for the formation of non-sterically hindered DNA nanodomains where the dsDNA attached to the dots maintains its native conformation, as confirmed by restriction enzymes studies. This allowed us, moreover, to follow the activity (at surfaces) of a restriction enzyme in real time and at the nanoscale: the monitoring of protein-DNA interactions with such biological nanoarrays will be discussed.

We will highlight the broader utility and application of such nanopatterned surfaces for the self-organization of DNA nanostructures. In-situ hybridization between the complementary strands on DNA nanostructures and on functionalized nanodots has been achieved, resulting in the ordered placement of the origami on the dot patterns, as demonstrated by Atomic Force Microscopy (AFM) imaging, both in liquid and in air.

Finally, we will discuss the application of DNA origami as functional scaffolds for the assembly of different nanomaterials (e.g Au nanoparticles and carbon nanotubes): highly complex arrangements can be created with high resolution and high throughput, opening the possibility for the realization of electronic devices at the molecular scale.

2:20pm NS+BI-ThA2 De Novo Nanostructure Design: from Protein Folding to Self-Assembled-Templated Nanomaterials, M. Ryadnov, National Physical Laboratory, UK

Rational design of self-assembled nano-to-micro scale structures offers an efficient tool for molecular nanotechnology improving our ability to engineer nanostructured materials at whim. Such attention is driven by the need for approaches leading to specialist nanostructures whose properties can relate to particular biological functions. Critical in this respect becomes the hierarchical nature of self-assembly rendering the process a "bottom-up" strategy in challenging different levels of nanostructural complexity [1].

Generic protein folding motifs are proving to be instrumental for prescriptive nanoscale engineering. Of particular demand are nanostructures which can be made functionally and architecturally amenable in cellular environments. In this report, bioinspired nanoscale designs based on peptide self-assembling systems possessing antimicrobial [2], cell-supporting [3], encapsulating[4] and tuneable morphological[5] properties will be discussed.

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2. Ryadnov, M. G., Mukamolova, G. V., Hawrani, A. S., Spencer, J. & Platt, R. (2009) RE-coil: An antimicrobial peptide regulator. *Angew. Chem. Int. Ed.* 48, 9676-9679.

3. Ryadnov, M. G., Bella, A., Timson, S. & Woolfson, D. N. (2009) Modular design of peptide fibrillar nano- to microstructures. *J. Am. Chem. Soc.*, 131, 13240-13241.

4. Ryadnov, M.G. (2007) A self-assembling peptide polyanoreactor. *Angew Chem Int Ed Engl.* 46, 969-972.

5. Ryadnov, M. G. & Woolfson, D. N. (2003) Engineering the morphology of a self-assembling protein fibre. *Nature Mater.*, 2, 329-332.

2:40pm NS+BI-ThA3 Rare Earth Nanoparticles to be used as Both Fluorescent Probes and MRI Contrast Agents, L. Axelsson, M. Åhrén, L. Selegård, F. Söderlind, Linköping University, Sweden, P. Nordblad, Uppsala University, Sweden, M. Lindgren, Norwegian University of Science and Technology, Norway, K. Uvdal, Linköping University, Sweden
Nanotechnology continuously explores new fields, and nanomedicine presents an entirely new research area with unlimited possibilities. For the last 20 years, gadolinium complexes have been used clinically as contrast enhancing agents for Magnetic Resonance Imaging (MRI). Simultaneously, Quantum Dots (QDs), with its excellent photostability and high quantum yield, are developed to replace organic fluorophores for medical diagnosis. The aim of this study is to develop nanopropbes that possess both the magnetic properties suitable for a contrast agent, and luminescent properties.

We have designed a novel nanomaterial of gadolinium oxide nanoparticles doped with europium (Eu:Gd₂O₃) or terbium (Tb:Gd₂O₃). Using nanoparticles, the local signal intensity in MRI can be increased compared to Gd complexes with only one Gd ion per complex. When introducing luminescent europium or terbium ions into the gadolinium oxide nanocrystal, fluorescent properties are added, creating a bifunctional nanocrystal. In addition to the favorable size for biomedical applications, nanoparticle contrast agents can bring advantages such as longer rotational correlation time to obtain increased relaxivity, and surface-coating possibilities for attaching targeting molecules. This will enable tailored design of a new generation of contrast agents. We present highly crystalline, 5 nm large nanoparticles, showing typical Eu³⁺ or Tb³⁺ fluorescence with a long luminescent lifetime. The strength of both europium and terbium ions is the suitable properties for excitation in an ordinary confocal microscope, which makes them promising as components when designing nanopropbes for cell studies. Relaxation measurements show relaxivity ratios in the same range as the pure Gd₂O₃ nanoparticles. The nanoparticles present a promising bifunctional core material, acting as a platform when developing advanced nanopropbes for future applications in biomedical imaging.

3:00pm NS+BI-ThA4 Plasma Polymerized Amino Acids used for Bio-Assisted Fabrication of Nanostructures, R. Jakubiak, Air Force Research Laboratory, K. Anderson, Georgia Institute of Technology, J. Slocik, UES, Inc., M. McConney, Georgia Institute of Technology, J. Enlow, UES, Inc., T. Bunning, R. Naik, Air Force Research Laboratory, V. Tsukruk, Georgia Institute of Technology

Plasma-enhanced chemical vapor deposition (PECVD) allows deposition of conformal, ultrathin, and uniform polymer coatings from gaseous, liquid or solid precursors onto a variety of materials. Our process uses a modified afterglow plasma reactor operated at room temperature where plasma polymerization occurs downstream from plasma generation. This allows controllable retention of the precursor's functionality needed for surface-induced biomineralization on soft or delicate substrates that cannot withstand high temperature or multiple wet-chemistry treatments. Amine-functionalized substrates, derived from the plasma polymerization of L-tyrosine, enabled biomineralization of gold nanoparticles from a solution of gold chloride. Templated gold nanoparticle coatings were formed by the placement of a shadow mask on the substrate during plasma deposition creating a micropatterned plasma polymerized tyrosine film. Subsequent gold chloride exposure created a gold nanoparticle network replica of the initial micropattern. Similar processing conditions were used to biomineralize titania on highly order three-dimensional structures.

3:40pm NS+BI-ThA6 Molecular Shuttles for 'Smart Dust' Biosensors, Active Self-Assembly, and Protein-Resistant Coatings, H. Hess, Columbia University
INVITED

Biomolecular motors, such as the motor protein kinesin, can serve as biological components in engineered nanosystems. Initially, a nanoscale transport system termed molecular shuttle has been explored by others and us as a model system. The development of this system has revealed a number of challenges in engineering at the nanoscale, particularly in the guiding, activation, and loading of these shuttles. Overcoming these challenges requires the integration of a diverse set of technologies, and continues to illustrate the complexity of biophysical mechanisms.

A proof-of-principle application of the developed technologies is a "smart dust" biosensor for the remote detection of biological and chemical agents, which is enabled by the integration of recognition, transport and detection into a submillimeter-sized microfabricated device.

The application of nanoscale forces introduces an interesting element into self-assembly processes by accelerating transport, reducing unwanted connections, and enabling the formation of non-equilibrium structures. The formation of nanowires and nanopools from microtubules transported by kinesin motors strikingly illustrates these aspects of motor-driven self-assembly.

Finally, a critical aspect of the design of these hybrid systems is the controlled adsorption of proteins. In pursuit of this goal of controlled adsorption, we have utilized kinesin motors as probes of residual protein adsorption to non-fouling coatings and achieved the detection of a few adsorbed molecules per square micrometer (adsorbed mass on the order of pg/cm²). Furthermore, we have developed a Random Sequential Adsorption model which successfully explains residual protein adsorption as the result of randomly occurring "bald" spots on a surface covered with PEG-chains.

4:20pm NS+BI-ThA8 Probing Biomineralization Protein Interactions with Hydroxyapatite Using SFG and NEXAFS Spectroscopy, T.M. Weidner, M. Dubey, N.F. Breen, J. Ash, J.E. Baio, University of Washington, C. Jaye, D.A. Fischer, National Institute of Standards and Technology, G.P. Drobny, D.G. Castner, University of Washington

The structural integrity of hydroxyapatite (HAP) in tooth enamel is maintained through the saliva environment that is supersaturated with calcium and phosphate salts. The biomineralization protein statherin adsorbs onto HAP surfaces with high binding affinity. It regulates HAP growth and prevents the buildup of excess HAP on the tooth surface by inhibiting spontaneous calcium phosphate growth. Owing to the importance of the underlying physiological processes and a general interest in biomineralization mechanisms, the binding of statherin to HAP has attracted significant interest in the biomaterials community. Sum frequency generation (SFG) spectroscopy can probe protein orientation and secondary structure at the solid-liquid interface and we have recently shown it can address specific protein regions with atomic resolution when combined with isotopic labeling.¹ Near edge X-ray absorption fine structure (NEXAFS) spectroscopy can give valuable information about the structure and binding chemistry of proteins on surface. We have combined both techniques to characterize the structure of the binding domain of statherin, SN15, a short peptide with 15 residues (Ac-DSSEENKFLRRIGRFG-OH) adsorbed onto a model HAP surface. Protein adsorption was verified using X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry. SFG confirmed a loosely helical secondary structure of SN15 on HAP. Deuteration was used to specifically probe the orientations of the hydrophobic leucine and isoleucine side chains with SFG in situ. Side-chain orientations were determined using ratios of the symmetric and asymmetric CD₃ stretching modes. The leucine chain was tilted 120° from the surface normal (pointing towards the surface) and the isoleucine was tilted 5° from the surface normal. For the first time, element labels were employed to probe individual side chain orientations with NEXAFS spectroscopy. Para- and perfluorination of the phenylalanine rings F7 and F14 allowed us to precisely measure their orientations using angle dependent NEXAFS data. The tilt angles from the surface normal were determined to be 26° for F7 and 35° for F14.

[1] T. Weidner, N. F. Breen, K. Li, G. P. Drobny, D. G. Castner, submitted.

4:40pm NS+BI-ThA9 Assembly of Nanoparticles for Patterning and Functional Materials in Nature's Way at Liquid-Liquid Interfaces, L. Isa, E. Amstad, M.H. Textor, E.O. Reimhult, ETH Zurich, Switzerland

An interesting aspect of the self-organization in Nature resulting in precise patterning of hierarchically structured materials is that the "synthesis" and patterning of the materials occur at liquid amphiphilic interfaces such as membranes. That particles can be organized and change the properties of liquid interfaces has long been known and explored as e.g. Pickering emulsions in foams, food processing and other large-scale, bulk materials applications. However, self-assembly of nanometer-sized colloids with defined surface properties at liquid-liquid interfaces is also a process with huge potential for the fabrication of controlled two-dimensional nanoscale structures and patterns as well as "nanomaterials". This is due to three key factors: a) the particles are trapped at the interface, but b) retain lateral mobility and c) exhibit specific interactions, which when properly understood and controlled lead to assembly of controlled structures. We have recently explored both how the oil-water interface can be used for unprecedented control of the assembly of nanoparticle patterns and transferred to substrates for low-cost nanolithography, and how tailored core-shell nanoparticles with functional cores can be assembled at such interfaces.

I will describe how self-assembly at the liquid-liquid interface (SALI) can be used for the deposition of non-close-packed crystalline arrays of NPs for lithographic masks and the physical control parameters for the successful application of this method. Our approach allows us to control the spacing of particles in a wide range; we have demonstrated reproducible and

homogeneous patterns with spacing between 3 to 20 particle diameters using colloids from 40 to 500 nm over chip-sized areas. The use of bimodal size distributions at controlled ratios also allows for induced phase separation and thus hierarchically ordered patterns to emerge.

By optimization of a simple Schäfer-type deposition setup and the choice of the proper oil phase, the particle patterns can be transferred to a substrate with few limitations. We will demonstrate use of the deposited particle patterns to fabricate a range of nanostructures for electrochemical and nanoplasmonic biosensing which previously could not be fabricated by particle lithography, and this at a fraction of cost to other available patterning techniques.

5:00pm NS+BI-ThA10 Characterization of Folate Receptor Targeting Drug Loaded PLGA-Lipid Hybrid Nanoparticles, S. Sandoval, A. Liberman, J. Yang, S. Aschemeyer, L. Zhang, W.C. Trogler, A.C. Kummel, University of California, San Diego

The response rate of breast cancer to first line chemotherapies is encouraging, but 20-30% of patients develop chemoresistance to these drugs, and consequently, have a cancer reoccurrence 7-10 months after their last treatment. Chemoresistance is believed to be due to drug efflux proteins responsible for the removal of many commonly used anti-neoplastic agents. One possible way to overcome these drug efflux pumps is to give higher doses of chemotherapy, but high doses of such agents commonly lead to chemocytotoxicity. Targeted PLGA-Lipid hybrid nanoparticle (NP) drug delivery systems have been developed that can deliver high doses of chemotherapy agents specifically to breast cancer cells. A practical cancer targeting drug delivery system will reduce the overall amount of chemotherapy agents given to patients for a given amount of targeted NPs endocytosed by cancer cells. Biodegradable NPs were synthesized using a novel nano-precipitation lipid-polymer hybrid platform which also allows for the encapsulation of hydrophobic chemotherapy drugs within the NPs. Using this method, drug free NPs have been shown to have an average diameter size of 81.78 nm (PDI: 0.25), while single loaded NPs, with Paclitaxel or Doxorubicin, show an average size between 72.33 to 89.64 nm (PDI: 0.242 to 0.339), signifying that the synthesis technique creates consistent sub 100nm particles. The majority of all NPs show a zeta-potential value of > -30 mV consistent with the NPs having sufficient repulsive interaction to be mono-dispersed in solution under physiological conditions. Folate receptors are often over expressed on the surfaces of cancer cells; therefore, folic acid was incorporated to the surface of these NPs as a cancer targeting ligand. Previous studies have shown that HeLa cells, a cervical cancer cell line, over expresses folate receptors. Immunofluorescence studies show that folic acid coated PLGA-Lipid hybrid NPs are readily endocytosed by HeLa cells compared to non-targeted NPs. Cytotoxicity studies will determine the increased effectiveness of drug delivery with targeted PLGA-Lipid hybrid NPs vs. untargeted PLGA-Lipid hybrid NP in cell lines and in animal models.

5:20pm NS+BI-ThA11 Controlled Surface Modification of Ultra-stable Superparamagnetic Iron Oxide Nanoparticles, E. Amstad, M.H. Textor, E.O. Reimhult, ETH Zurich, Switzerland

Biocompatibility, magnetic properties and ease of synthesis renders iron oxide nanoparticles (NPs) attractive for many especially biomedical applications such as magnetic resonance (MR) contrast agents, triggered drug release and cell separation. Good NP stability under physiologic conditions and controlled surface chemistry are key to successful application not only in the biomedical field but also for assembly into various materials.

NPs with close control over the interfacial chemistry and good stability at high salt concentrations and elevated temperatures can only be achieved if dispersants are irreversibly bound to the NP surface. The dispersant binding affinity is determined by its anchor group. Low molecular weight dispersants which consist of one high affinity anchor covalently linked to poly(ethylene glycol) (PEG) spacers have been proven well suited to sterically stabilize Fe₃O₄ NPs. However, we found that electronegatively substituted catechols such as nitrocatechols vastly outperform the well-known and often used catechol anchors such as DOPA and dopamine. Because of the optimized binding affinity of nitrocatechols, PEG-nitrocatechol coated Fe₃O₄ NPs remained stable under physiologic conditions up to 90 °C whereas e.g. PEG-dopamine stabilized Fe₃O₄ NPs started to agglomerate below body temperature.^[1] Further investigations showed that the optimal binding affinity of nitrocatechols to Fe₃O₄ is closely related to a redox reaction between Fe²⁺ located at the Fe₃O₄ NP surface and nitrocatechols, which leads to electron delocalization in the adsorbed catechol ring, and a close to covalent bond of nitrocatechols to Fe₃O₄ surfaces. Irreversible binding of PEG-nitrocatechols to Fe₃O₄ NPs allowed us to closely control and investigate the influence of dispersant layer thickness by varying the nitrocatechol-PEG molecular weight. Furthermore, NPs could easily be functionalized by co-adsorbing differently end-functionalized dispersants on the Fe₃O₄ NP surface.^[2]

In summary, nitrocatechols have a close to optimal binding affinity to Fe_3O_4 surfaces. This optimized binding affinity not only leads to ultra-stable PEG-nitrocatechol coated superparamagnetic Fe_3O_4 NPs but also allows for close control over the hydrodynamic diameter and interfacial chemistry, factors which crucially determine NP performance especially in biomedical applications.

[1] E. Amstad, T. Gillich, I. Bilecka, M. Textor, E. Reimhult, *Nano Letters* **2009**, *9*, 4042.

[2] E. Amstad, S. Zurcher, A. Mashaghi, J. Y. Wong, M. Textor, E. Reimhult, *Small* **2009**, *5*, 1334.

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 Schreiner, P.R.: NS-TuA4, 8
 Schroeter, B.: EN+NS-WeM11, 15
 Schwarz, U.D.: NS+AS+MN-WeM9, 17; TR+NS+SS-WeA8, 24
 Schwendemann, T.C.: NS+AS+MN-WeM9, 17
 Seal, S.: NS-MoA10, 5
 Sehun Kim, S.: NS-TuP3, 10
 Seidel, J.: NS-MoM9, 1
 Selegård, L.: NS+BI-ThA3, 28
 Seyller, T.: EN+NS-WeM11, 15
 Sfeir, M.Y.: NS-TuA1, 8

- Shaw, G.A.: TR+NS+SS-WeA1, 23
 Sheehan, P.E.: GR+NS-MoA9, 4; NS-TuM6, 6
 Sheetz, M.P.: NS+BI-ThA1, 28
 Shemelya, C.: NS+EM+EN-WeA2, 22
 Shenoy, V.B.: GR+NS-MoA6, 3
 Shiao, M.H.: NS-TuP25, 13
 Shiffler, D.A.: NS-TuA3, 8
 Shih, C.K.: IS+AS+NS+MI-WeM1, 15
 Shreve, A.P.: BI2+NS-ThM9, 25
 Shukla, N.: NS-ThM1, 25
 Silver, R.M.: NS-TuM3, 6
 Singer, I.L.: TR+MN+NS+SS-WeM1, 18
 Singh, B.: EN+NS-WeA8, 20
 Singh, S.V.: TR+MN+NS+SS-WeM6, 18
 Sinnott, S.B.: TR+MN+NS+SS-WeM12, 19
 Sivakov, V.A.: EN+NS-WeM11, 15; NS-ThM2, 25
 Slocik, J.: NS+BI-ThA4, 28
 Snow, E.: GR+NS-MoA7, 3
 Söderlind, F.: NS+BI-ThA3, 28
 Song, H.: NS-TuP5, 10
 Song, T.B.: EN+NS-WeA10, 21
 Soudi, A.: NS-MoM10, 2; NS-ThM11, 26
 Starodub, E.: GR+NS-MoA10, 4
 Stecher, J.T.: NS+EM+EN-WeA7, 22
 Stiles, P.L.: NS-TuP2, 10
 Strano, M.: NS-TuA9, 9
 Su, C.Y.: NS-TuP25, 13
 Su, J.F.: TR+NS+SS-WeA12, 24
 Subrahmanyam, A.: NS-MoM2, 1
 Sullivan, S.L.: NS-TuM1, 6
 Supparesk, R.: EN+NS-WeA9, 21
 Sutter, P.: NS+AS+MN-WeM4, 17
 Suzer, S.: NS-TuP8, 11
 Sykes, E.C.H.: NS-TuM9, 7
 Sykora, M.: NS-ThM4, 26
 Szymanski, P.: NS-ThM4, 26
- **T** —
 Taing, J.: NS-ThM12, 27
 Takeke Beyene, H.: NS+EM+EN-WeA8, 22
 Talkenberg, F.: EN+NS-WeM11, 15;
 NS+EM+EN-WeA9, 22; NS-ThM2, 25
 Tenent, R.: NS-MoM3, 1
- Textor, M.H.: NS+BI-ThA11, 29; NS+BI-ThA9, 29
 Therien, M.J.: NS+EM+EN-WeA7, 22
 Thevuthasan, S.: NS-MoA10, 5
 Tierney, H.L.: NS-TuM9, 7
 Tkachenko, B.A.: NS-TuA4, 8
 Todorovic, M.: NS+AS+MN-WeM9, 17
 Toriz, G.: NS-TuP21, 12
 Toth-Fejel, T.: NS-TuM3, 6
 Tratnyek, P.G.: NS-MoA9, 4
 Triscone, J.-M.: NS-MoM5, 1
 Trogler, W.C.: NS+BI-ThA10, 29; NS-TuP19, 12
 Tsai, M.Y.: NS-TuP10, 11
 Tseng, Y.-C.: NS-TuM10, 7
 Tsukruk, V.: NS+BI-ThA4, 28
 Tysoe, W.T.: TR+MN+NS+SS-WeM11, 19
- **U** —
 Uher, C.: EN+NS-WeA11, 21
 Uvdal, K.: NS+BI-ThA3, 28
- **V** —
 Vail, M.A.: NS-TuA11, 9
 Vajda, S.: NS-ThM3, 25
 van Buuren, T.: NS-TuA4, 8
 van de Sanden, M.C.M.: NS+EM+EN-WeA8, 22
 van der Veer, W.E.: NS+EM+EN-WeA10, 23
 Vandervelde, T.: NS+EM+EN-WeA2, 22
 Venkatesh, G.: EN+NS-WeA1, 20
 Voigt, F.: NS-ThM2, 25
 Von Ehr, J.R.: NS-TuM3, 6
- **W** —
 Wallace, R.M.: NS-TuM3, 6
 Walton, S.G.: GR+NS-MoA9, 4
 Wang, C.M.: NS-MoA9, 4
 Wang, D.: GR+NS-MoA9, 4
 Wang, G.T.: NS+EM+EN-WeA1, 21
 Wang, H.: NS-MoA10, 5
 Wang, L.: TR+NS+SS-WeA12, 24
 Wang, R.: NS+BI-ThA1, 28
 Wang, W.: EN+NS-WeM2, 14
 Warren, M.V.: EN+NS-WeA11, 21
 Washburn, C.M.: EN+NS-WeA2, 20; NS-TuA7, 8
 Wei, Z.: GR+NS-MoA9, 4
- Weidner, T.M.: NS+BI-ThA8, 29
 Whang, D.M.: NS-TuP11, 11
 Wheeler, D.R.: EN+NS-WeA2, 20; NS-TuA7, 8
 Wiemer, C.: NS-TuP17, 12
 Wiesendanger, R.: NS+AS+MN-WeM5, 17
 Wiest, L.A.: NS-TuA11, 9
 Willey, T.M.: NS-TuA4, 8
 Wind, S.J.: NS+BI-ThA1, 28
 Wolak, M.A.: EN+NS-WeM12, 15
 Wolden, C.A.: NS-MoM3, 1
 Wong, S.S.: NS-TuA1, 8
 Wood, D.: EN+NS-WeA10, 21
- **X** —
 Xiao, X.: EN+NS-WeA2, 20
 Xiao, Z.: NS-TuA12, 9
 Xue, J.: EN+NS-WeM5, 14
- **Y** —
 Yabutani, H.: NS-TuA8, 9
 Yakes, M.K.: GR+NS-MoA9, 4
 Yamada, T.: NS-TuA8, 9
 Yang, C.: NS-TuA8, 9
 Yang, C.C.: NS-TuP25, 13
 Yang, F.: NS+EM+EN-WeA10, 23
 Yang, J.: NS+BI-ThA10, 29; NS-TuP19, 12
 Yang, S.: NS-MoA8, 4
 Yang, Y.S.: NS-TuP12, 11
 Yelton, W.G.: NS-TuP7, 11
 Yeom, G.Y.: NS-TuP9, 11
 Yeon, J.K.: NS-TuP9, 11
 Yilmaz, E.: NS-TuP8, 11
 Yokoyama, Y.: NS-ThM10, 26
 Yu, P.: NS-MoM9, 1
- **Z** —
 Zaki, N.: NS+AS+MN-WeM4, 17
 Zalalutdinov, M.: GR+NS-MoA7, 3
 Zanini Gadioli, G.: NS-TuP27, 13
 Zauscher, S.: TR+NS+SS-WeA7, 24
 Zavadil, K.R.: NS-MoM4, 1
 Zhang, L.: NS+BI-ThA10, 29; TR+NS+SS-WeA7, 24
 Zhang, Y.: EN+NS-WeA8, 20
 Zhang, Z.: TR+NS+SS-WeA2, 23