Energy Science and Technology Focus Topic
Room: 203 - Session EN+BI+SS+SE-TuM

Catalysis for Energy Sustainability
Moderator: D.E. Ramaker, George Washington University

8:00am **EN+BI+SS+SE-TuM1 Size, Shape, and Support Effects in Oxidative Coupling Reactions**, ***C.L. Marshall***, *W. Setthapun, S. Mucherie,* Argonne National Laboratory, *H.S. Kim,* Northwestern University, *J.A. Libera, J.W. Elam,* Argonne National Laboratory, *P.C. Stair*, Northwestern University **INVITED**

In this paper we describe the characterization and catalytic performances in the reaction of ODH of propane over new nanostructured membrane catalysts composed of vanadium species supported on different metal oxides (Al2O3, Nb2O5, TiO2), which have been fabricated using the combination of anodic aluminum oxide (AAO) and atomic layer deposition (ALD).1 The aim of this study is to determine the role played by the nanostructured materials and the nature of the support oxide on the reactivity of these AAO membrane catalysts in terms of activity and selectivity to propylene.

8:40am **EN+BI+SS+SE-TuM3 Application of Single-Wall Carbon Nanohorns**, ***M. Yudasaka***, Advanced Industrial Science and Technology (AIST), Japan **INVITED**

The discovery of spherical aggregates of single-wall carbon nanohorns (SWNHs) was reported in 1999. The aggregates were called dahlia-like, bud-like, and seed-like SWNHs based on their forms. Since the dahlia-type aggregate (D-NHag) was obtained with the highest purity (about 90%) among the three types, SWNH applications have been studied mainly using the D-NHag. The individual SWNH has a structure similar to SWNTs, namely, a tube-like structure made of a graphene sheet, but with larger diameters (2-5 nm), shorter length (40-50 nm), and horn-shaped tips with a cone angle of about 19o. Studies of various applications of D-NHag revealed that they are a unique medium for adsorption, support, and storage of materials. This uniqueness mainly comes from mountain-valley structure of the D-NHag surfaces and wide inner-hollow spaces. The mountain-valley surface morphology was suitable for supporting material clusters with small sizes. The reason for this may be because migration on the SWNHag surface was suppressed, so coalescence of the clusters was avoided. In fact, the sizes of Pt-particles supported on D-NHag were small, about 1 nm. When the Pt/SWNHag was used as fuel-cell electrodes, the battery characteristics were significantly improved. The inside spaces of SWNHs were made accessible by making holes at the tips and defects of sidewalls. It was easy to incorporate various materials (C60, metals, inorganic and organic molecules including drugs, etc.) inside SWNHs in the liquid-phase at room temperature, where the incorporating quantities were controllable. The materials were moderately bound inside SWNHs, which enabled the rate-controlled release of the incorporated materials. It was also easy to individually disperse D-NHag in various solvents. They were well dispersed even in aqueous solutions, which will make possible biological applications of D-NHag. We previously reported that dexamethasone, a drug, was loaded in/on SWNHs in aqueous solutions and released in cell culture medium, exhibiting its drug effect in several ways. SWNH is quasi-SWNT, but, its usefulness is different from that of SWNT. We believe that D-NHag will be suitable for a catalyst support and material-delivery medium. Acknowledgement: I am grateful to all the collaborators, especially Professor Iijima, and JST for supporting this research through ICORP and SORST schemes.

[1] S. Iijima, et al., Chem. Phys. Lett. 309 (1999) 165.

9:20am **EN+BI+SS+SE-TuM5 Reducing Carbon Dioxide to Methane under Visible Light Illumination by Non-stoichiometric Mixed Phase Titania Thin Films**, ***L. Chen***, *M.E. Graham, P.A. DeSario, K.A. Gray*, Northwestern University

Non-stoichiometric mixed phased titania composites were deposited by reactive DC magnetron sputtering. Previously we[1-3] demonstrated that there are solid-solid interfaces with highly reactive interfacial sites created within mixed phase titania thin films, and we observed by EPR measurement that the bulk composition of the films was not fully stoichiometric. The objective of this study is to explore the role of non-stoichiometry in mixed phase titania in terms of photoresponse and photocatalytic performance in reducing CO_2 to methane. The control of oxygen partial pressure during film deposition yielded different levels of non-stoichiometry in films deposited mostly in the transition mode. Trace amounts of nitrogen were introduced during the sputtering process to stabilize the reactive sputtering process at the turning point of the transition mode and metallic mode and without incorporation in the films. The photocatalytic results showed that there was an optimal non-stoichiometry of titania films in terms of methane yield from CO_2 reduction. Under UV illumination, the best CO_2 conversion percentage was around 22%. In addition, both from reaction tests under visible light and the optical measurements, we determined that non-stoichiometric mixed phase titania films showed a strong light absorption shift into the visible range compared to commercial standard Degussa P25, which has a similar phase composition. SEM and TEM results showed film morphology with a high density of solid-solid interfaces developed in the films. Both EELS and XPS results identified the Ti^{3+} species in addition to Ti^{4+}. Most of the Ti^{3+} species were located at the interfaces of titania columns, where they might serve as the reactive interfacial sites for visible light harvesting or electron trapping.

[1] L. Chen, et al., Photoreduction of CO_2 by TiO_2 Nanocomposties Synthesized through Reactive DC Magnetron Sputter Deposition. Thin Solid Films, 2008. in review.

[2] L. Chen, et al., Fabricating Highly Active Mixed Phase TiO_2 Photocatalysts by Reactive DC Magnetron Sputter Deposition. Thin Solid Films, 2006. 515(3): p. 1176-1181.

[3] Hurum, D.C., et al., Probing reaction mechanisms in mixed phase TiO_2 by EPR. Journal of Electron Spectroscopy and Related Phenomena, 2006. 150: p. 155-163.

9:40am **EN+BI+SS+SE-TuM6 Variations in Metal-Ligand Effects on Pt in Pt_nM (M = Ru,Mo,Sn) Electrocatalysts as Exhibited by in situ XANES and EXAFS Measurements in Methanol**, ***D.E. Ramaker***, *F.J. Scott,* George Washington University, *S. Mukerjee*, Northeastern University

Metal-ligand effects on Pt are commonly utilized to decrease the CO poisoning of the anode in methanol as well as to increase the activity for oxygen reduction at the cathode. However, these effects are not clearly understood because of the general lack of information on the particle morphology (M island size, homogeneity, etc.) and CO or OH adsorbate coverages. In this work, in situ X-Ray Absorption Spectroscopy (XAS) measurements, in the near edge and extended regions (XANES and EXAFS) at the Pt L_3 edge, were carried out on three different carbon-supported electrocatalysts (Pt_3Mo, Pt_4Mo, and PtSn) in an electrochemical cell in 1 M $HClO_4$ along with 0.3 M methanol. The CO, OH, O, and H_{upd} relative adsorbate coverages on Pt are determined as a function of the applied potential via the ΔXANES technique and compared with comparable data reported for three different PtRu electrocatalysts (PtRu Etek, PtRu Watanabe, and Pt_3Ru) reported previously[1]. The average particle morphology of each catalysts is determined from EXAFS coordination numbers and a modeling technique.[1] The onset of the n-fold O atom coverage between 0.5 and 0.9 V (RHE) tracks essentially with the particle size. The more reactive Sn and Mo atoms interact more strongly with Pt, and hence the ligand effect for the M and MO_n islands are comparable, in contrast to that for Ru vs. RuO_n. Our results are correlated with the extensive electrochemical results found in the literature on similar Pt_nM catalysts. The results suggest that the strength of the ligand effect increases in the order $Ru < Mo, MoO_n < Sn, SnO_n \leq RuO_n$, where the relative Pt-CO bond strength is found to decrease and the Pt-OH bond strength increases with ligand effect. In the Sn and Mo bimetallics, the ligand effect is found to be sufficiently strong to allow CO replacement by H_2 at low currents.

[1] F. J. Scott, S. Mukerjee, and D. E. Ramaker, J. Electrochem. Soc. 154, A396-A406 (2007).

10:40am **EN+BI+SS+SE-TuM9 Controlling the Activity of Fuel Cell Electrode Materials by Tuning the Surface Electronic Structure**, ***J.K. Norskov***, Technical University of Denmark **INVITED**

The performance of low temperature fuel cells based on proton conducting membranes is severely hampered by an overpotential at the cathode where molecular oxygen combines with protons and electrons to form water. To understand the origin of this problem a method has been developed that allows a theoretical treatment of chemical reactions at the water-solid interface in the presence of an electrical bias on the basis of electronic structure calculations. Extensive density functional calculations have allowed an identification of the origin of the overpotential for the commonly used electrode material, platinum, as well as insight into the way alloying can change the surface electronic structure of platinum to reduce the overpotential. The reverse reaction, electrochemical water splitting, is also discussed, and it is shown that the performance of different classes of inorganic materials as electrocatalyst as well as the catalytic center for biological water splitting in photosystem II can be understood within the same conceptual framework.

11:20am **EN+BI+SS+SE-TuM11 Resolving the Electronic Properties of Catalytically Important Pd/Au Alloys at the Sub-Nanometer Level**, ***A.E. Baber***, *H.L. Tierney, E.C.H. Sykes*, Tufts University

Palladium/gold (Pd/Au) bimetallic alloys have been used to catalyze important processes such as the synthesis of vinyl acetate and hydrogen peroxide as well as some oxidative reactions (methanol, formic acid, CO).

Low temperature, ultra-high vacuum scanning tunneling microscopy (LT-UHV STM) is used not only to image bimetallic alloys, but also to spectroscopically probe the local electronic changes in both Pd and Au atoms when the two are alloyed. We have used STM to evaluate the surface composition of a real bimetallic alloy system and have found that the unique herringbone reconstruction of Au{111} provides entry sites for the incorporation of Pd atoms. We were able to differentiate between surface, subsurface and overlayer Pd atoms and study the temperature dependence of the preferred Pd destination. As the deposition temperature increases, the location of Pd changes from mostly overlayer to surface to subsurface. Scanning tunneling spectroscopy was used to examine the local density of states (LDOS) of individual Pd and Au atoms in both surface and subsurface sites in order to investigate the changes in the LDOS of a reactive metal alloyed in a more noble metal. It was found that in both surface and subsurface sites, Pd atoms displayed a LDOS very similar to the surrounding gold atoms, except for a small region at the band edge of the Au surface state in which the electron density was depleted. Pd atoms act as scattering sites for the surface electrons but do not fully quench the surface state. This is the first example of a simultaneous atomic-scale geometric and electronic characterization of a real PdAu catalytic system.

11:40am **EN+BI+SS+SE-TuM12 Water-Gas-Shift Reaction on Metal-Oxide Catalysts**, ***P. Liu***, *S. Ma, J.A. Rodriguez, J. Hrbek*, Brookhaven National Laboratory

The water-gas shift (WGS) reaction ($CO + H_2O \rightarrow H_2 + CO_2$) is a critical process in providing pure hydrogen for fuel cells and other applications. However, current industrial catalysts (Fe-Cr or Zn-Al-Cu oxides) are pyrophoric and require complex activation steps before usage. A fascinating puzzle has recently emerged: Au/CeO_2 and Au/TiO_2 nanomaterials show high activity for WGS catalysis. This is remarkable since in bulk form Au, ceria and titania are not known as WGS catalysts. The nature of the active phase(s) in these metal-oxide nanocatalysts is unclear at the present time, which impedes the design and optimization of WGS catalysts. We have carried out coordinated experimental and theoretical studies to address this problem. The experiments show that the model catalysts, $Au/CeO_2(111)$ or $TiO_2(110)$ and inverse CeO_2 or $TiO_2/Au(111)$, display activities comparable to good WGS catalysts (i.e., Cu(100) and Cu(111)). Theoretical calculations based on density functional theory (DFT) are also carried out to understand the active sites in the oxide-gold catalysts, by probing reaction scenarios on Au, titania, and $Au\text{-}TiO_2$ (Au/TiO_2 and $TiO_2/Au(111)$) catalyst model structure. In accordance with experiments, our calculations show a very high barrier for the dissociation of water on Au and the formation of very stable formate species on titania that prevents the production of H_2 and CO_2. The model $Au\text{-}TiO_2$ catalyst overcomes these bottlenecks: the moderate chemical activity of gold is coupled to the more reactive oxide. The dissociation of water takes place on the oxide easily, a reaction that extended surfaces and nanoparticles of Au cannot perform. CO adsorbs on gold sites located nearby (bifunctional catalyst). Then all the subsequent steps occur at the oxide-metal interface at a reasonable speed. Our results imply that the high activities of Au/CeO_2 and Au/TiO_2 nanocatalysts in the WGS reaction depend heavily on the direct participation of oxide-metal interface. The diversity of nanoparticle structures and the interplay with the support highlight the importance of identifying critical structural motifs to model catalyst function. This research was carried out at Brookhaven National Laboratory and supported by the US Department of Energy (Chemical Sciences Division, DE-AC02-98CH10886).

Nanometer-scale Science and Technology
Room: 311 - Session NS+NC-TuM

The Frontiers of Nanoscience
Moderator: M.C. Hersam, Northwestern University

8:00am **NS+NC-TuM1 The Missing Memristor Found: A Fundamental Element for Nanoelectronic Circuits**, ***R.S. Williams***, HP Labs **INVITED**

In 1971, Prof. Leon Chua of the UC Berkeley Electrical Engineering Department predicted from symmetry arguments for non-linear circuits that there should be a fourth fundamental passive circuit element to complement the capacitor, resistor and inductor. He called this element a memristor, a contraction for 'memory resistor', and showed that if it existed, it would have a great many interesting and useful properties. However, no one was able to construct such an element, so the idea faded away. On May 1 of this year, we announced that we had 'found' the missing memristor, and that the element we built indeed had the properties predicted by Chua when operated within a restricted parameter range. In this talk, I will describe the discovery of the memristor, what its properties are, how it is made, and how we have used it in a variety of hybrid integrated circuits with transistors, including nonvolatile random access memories and synaptic or "brain-like" circuits.

8:40am **NS+NC-TuM3 Driving Forces and Barriers in Formation of Nanostructured Assemblies at Surfaces**, ***D.L. Allara***, Pennsylvania State University **INVITED**

Much of the recent interest in micro- to nano-scale patterned molecular structures on substrates has arisen from applications ranging from molecule-based integrated logic circuits to “biochips.” In such structures the cascading details of hierarchial assemblies are critical. At the large scale the patterns are created as dictated by large scale needs such as circuit layouts or test probe spatial resolution while at the finest scale the structures may require precise single molecule placement and associated controlled local chemical and electrostatic environments. Throughout the hierarchical manifold of structures a wide range of chemical potential differences may exist in the components, leading to inherent instabilities, and large thermodynamic driving forces built into the processing conditions often result in unexpected nanostructures as subtle kinetic pathways steer the system into metastable and unexpected final states. These effects will be discussed with specific examples from our own work and selected work from other groups.

9:20am **NS+NC-TuM5 Linking Proteins, Particles, Wires and Dots with Ferroelectric Nanolithography**, ***D.A. Bonnell***, The University of Pennsylvania **INVITED**

Self assembly is a powerful strategy that utilizes chemical and physical forces to fabricate ensembles of nanostructures. The ultimate goal for some device strategies is to co assemble a variety of nanostructures with differing properties in arbitrary but pre defined configurations. Chemical self assembly alone presents serious challenges in this regard since it operates on one type of nanostructure: a layer of molecules, a lattice of particles, templated wires, etc. Ferroelectric Nanolithography is a directed assembly approach that positions nanostructures of various compounds into predefined functional configurations. The process relies on domain specific surface electronic structure and consequent reactivity. Starting from an understanding of the atomic structures of ferroelectric oxide surfaces, the origin of domain specific chemical reactivity will be illustrated with in situ thermal and optical SPM observations and with the deposition of metal and oxide nanoparticles. The use of electron beams and local electrodes to pattern ferroelectric substrates will be explained in terms of relevant electron/solid interactions. A critical aspect of both understanding assembly processes and characterizing device behavior is the ability to probe local electric, dielectric and ferroelectric properties. Scanning probe based techniques that access the frequency dependence of local properties will be described. Finally the lithographic approach will be illustrated with the fabrication of a molecular opto-electronic device made of 3nm – 50 nm metal particles, optically active porphyrins, and functionalized peptide tetramers on an oxide substrate. The generalization of the approach to include, for example, integration in hybrid systems and applications in flexible electronics will be summarized.

10:40am **NS+NC-TuM9 Complex Spin Structures on the Verge of Instability—Imaging and Manipulation by Spin-Polarized STM**, ***M. Bode***, Argonne National Laboratory **INVITED**

Within the recent years spin-polarized scanning tunneling microscopy has become a mature tool for high spatial resolution studies of spin structures down to the atomic scale. Together with its high surface sensitivity this makes SP-STM particularly suited for the investigation of complex antiferromagnetic or superparamagnetic surfaces which— because of the lack of macroscopic magnetization—could only be studied in some rare cases with very moderate spatial resolution in the past. One particularly graphic example is the two-dimensional atomic-scale antiferromagnetic (AFM) structure observed within a Mn monolayer on tungsten (110).[1] On the atomic scale SP-STM data reveal periodic stripes running along the [001] direction with an inter-stripe distance of 0:47 ± 0.03 nm, indicating row-wise AFM order. Large scale images reveal, however, that the magnetic amplitude is not constant but is modulated with a period of about 12 nm. Magnetic field-dependent experiments show that this modulation is caused by an AFM spin spiral. First-principles calculations identify a cycloidal spin spiral which is caused by the Dzyaloshinskii-Moriya (DM) interaction as the driving mechanism for this complex magnetic order. Due to thermal excitations this spin structure becomes unstable in nano-scale islands. Switching the magnetization of a magnetic bit by injection of a spin-polarized current offers the possibility for the development of innovative high-density data storage technologies. We show how individual superparamagnetic iron nanoislands with typical sizes of 100 atoms can be addressed and locally switched using a magnetic scanning probe tip, thus demonstrating current-induced magnetization reversal across a vacuum barrier combined with the ultimate resolution of spin-polarized scanning tunneling microscopy.[2] Our technique allows us to separate and quantify three fundamental contributions involved in magnetization switching (i.e., current-induced spin torque, heating the island by the tunneling current, and Oersted field effects), thereby providing an improved understanding of the switching mechanism.

[1] M. Bode et al., Nature 447, 190 (2007)

[2] S. Krause et al., Science 317, 1537 (2007).

11:20am **NS+NC-TuM11 Albert Nerken Award Lecture - Atomic Tool for Nanofabrication Based on Atomic Force Microscopy**, ***S. Morita****, *Y. Sugimoto,* Osaka University, Japan, *Ó. Custance,* NIMS, Japan, *M. Abe,* Osaka University, Japan, *P. Pou,* Universidad Autónoma de Madrid, Spain, *P. Jelinek,* Academy of Science of the Czech Republic, *R. Pérez,* Universidad Autónoma de Madrid, Spain **INVITED**

We have been developing a novel bottom-up nanostructuring system at room temperature (RT) based on ultra high vacuum (UHV) atomic force microscopy (AFM). It can image individual atoms, identify chemical species, and then manipulate selected atom species one-by-one to the designed site to assemble complex nanostructures consisted of multi atom species at RT under UHV environment. In this invited talk, we will shortly introduce principles of high-performance and high-resolution UHV-AFM, and then, introduce our recent results related to not only nanocharacterization but also nanofabrication based on UHV-AFM such as (1) site-specific force spectroscopy and force mapping related to chemical identification of individual atoms,[1-3] (2) vertical/lateral mechanical atom manipulation.[4,5] (3) atom interchange lateral/vertical manipulation and following assembly of embedded atom letters at RT.[6]

[1] Y. Sugimoto et al. "Real topography, atomic relaxations, and short-range chemical interactions in atomic force microscopy: The case of the Sn/Si(111)-(r3xr3)R30 surface", Phys. Rev. B 73 (2006) 205329.

[2] M. Abe et al. "Drift-compensated data acquisition performed at room temperature with frequency modulation atomic force microscopy", Appl. Phys. Lett. 90 (2007) 203103

[3] Y. Sugimoto et al. "Chemical identification of individual surface atoms by atomic force microscopy", Nature, 446 (2007) pp.64-67.

[4] N. Oyabu et al. "Mechanical Vertical Manipulation of Selected Single Atoms by Soft Nanoindentation Using Near Contact Atomic Force Microscopy", Phys. Rev. Lett. 90 (2003) 176102.

[5] Y. Sugimoto et al. "Mechanism for room-temperature single atom lateral manipulations on semiconductors using dynamic force microscopy", Phys. Rev. Lett. 98 (2007) 106104.

[6] Y. Sugimoto et al. "Atom inlays performed at room temperature using atomic force microscopy", Nature Materials, 4 (2005) pp.156-159.

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* Albert Nerken Award Winner

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Nanometer-scale Science and Technology
Room: 311 - Session NS+NC-TuA

Nanowires and Nanosize Effects
Moderator: H. Schift, Paul Scherrer Institut, Switzerland

1:40pm **NS+NC-TuA1 Optical Second Harmonic Generation from the Pt/Cu Bimetallic Nanowire Array on the NaCl(1 1 0) Faceted Template**, ***T. Nguyen***, *G. Mizutani*, Japan Advanced Institute of Science and Technology (JAIST)

We have fabricated bimetallic nanowire arrays as a new type of nano-material. We expect that the anisotropy at the interface in each bimetallic nanowire would raise the second harmonic generation (SHG) performance. In order to form bimetallic nanowire arrays we deposited Cu and Pt nanowires successively on the faceted NaCl(1 1 0) template by a shadow deposition method.[1] The sample preparation was carried out in an ultra-high vacuum chamber of the pressure of 1.3 x 10^{-7} Pa. TEM images of these samples showed the average width of nanowires of 20nm and the average spacing of about 40nm. We have also fabricated a sample with a SiO layer of 5nm thickness sandwiched between the Cu and Pt nanowires, in order to remove the effect of the interface between the two metallic nanowires. We have measured the azimuthal angle dependence of the optical second-harmonic (SH) intensity from these samples at the fundamental photon energy of 2.33 eV. The SH intensity from the sample with the sandwiched SiO layer is significantly lower than that from the bimetallic nanowire sample. The patterns of the SH intensity from both samples showed two-fold symmetry. Especially for the s-in/p-out polarization combination the SH intensity pattern from the Pt/Cu bimetallic sample was quite different from that of the Pt/SiO/Cu sample.

[1] A. Sugawara, G. G. Hembree, and M. R. Scheinfein, J. Appl. Phys. 82, 5662 (1997).

2:00pm **NS+NC-TuA2 Microcavity Modulation of Photoluminescence from GaN Nanowires**, ***J.P. Long***, *A.J. Makinen, B.S. Simpkins, M.A. Mastro, P.E. Pehrsson*, Naval Research Laboratory

Photoluminescence (PL) from single semiconducting nanowires (NWs) can exhibit considerable variability along a NW length and among NWs from the same growth batch. While the cause of the variability remains a subject of research and may be related to structural or chemical heterogeneities, here we report a purely optical source of variability caused by microcavity effects within the NW. Such effects must be considered whenever the transverse dimension of a transparent nanostructure exceeds $\sim\lambda/2n$, where λ is the free-space wavelength and n is the index of refraction. In our experiments, spatially and spectrally resolved micro-PL excited with 325-nm radiation was recorded at room temperature in a ~20-micron long GaN NW with a triangular cross section. An important feature of the NW was a gradual taper in width, from about 1 micron to less than tens of nanometers, that permitted recording the optical response as the NW width varied. The NW emitted band-gap radiation near 375 nm and a broad defect band beginning at ~475 nm and extending to longer wavelengths. The spectrally resolved PL exhibits periodic intensity modulations along the NW length. The periodicity is consistent with enhanced emission occurring when the PL wavelength satisfies the requirement for a transverse standing wave within the NW. We attribute the PL modulation to either or both of two mechanisms, namely a microcavity modulation of emission probability (the "Purcell effect") or a Fabry-Perot etalon effect that modulates the external radiation of internally generated PL.

2:20pm **NS+NC-TuA3 Doping PbSe Nanocrystals and Nanowires**, ***S.C. Erwin***, Naval Research Laboratory

We recently proposed that impurity doping in colloidally grown semiconductor nanocrystals is controlled primarily by kinetics, rather than by thermodynamics.[1,2] In this "trapped dopant" model, the diffusion of an impurity through a nanocrystal is negligible at colloidal growth temperatures. Therefore, an impurity can only be incorporated into a growing nanocrystal if it first adsorbs on the surface and is then overgrown. But this simple surface adsorption process is complicated by a competing process: the binding of the impurity by surfactant molecules, which are used in the growth solution to passivate the nanocrystal and control its growth. Here we use density-functional theory to study the interplay and outcome of these two processes for the doping of PbSe nanocrystals and nanowires by a number of candidate impurities (Mn, Cl, In, Cd, Tl, etc) in the presence of several widely used growth surfactants (oleic acid, trioctylphosphine, hexadecylamine). The results suggest that succesful doping requires making a trade-off between surface adsorption (which favors small impurities) and interior trapping (which favors large impurities). Moreover, the widely used surfactant oleic acid binds strongly to almost all impurities, suggesting that standard growth procedures may require modification for successful doping to be realized.

[1] S.C. Erwin, L. Zu, M.I. Haftel, Al.L. Efros, T.A. Kennedy, and D.J. Norris. Nature 436, 91 (2005).

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2:40pm **NS+NC-TuA4 Silicon Nanowire Resonators as Mass Sensors for a Specific Detection of Proteins**, ***S. Evoy***, *M. Belov, V.A. Wright, J.M. Buriak*, University of Alberta, Canada, ***N. Quitoriano***, *T. Kamins*, Hewlett-Packard Laboratories

Silicon nanowire resonators have been proposed as highly-sensitive transducers for the detection of molecular systems. High-quality nanometer scale resonators grown by the chemical vapor deposition (CVD) offer a potent approach for the production of cantilevered nanowires. Nanowire resonators were laterally grown from the sides of silicon posts using a CVD metal-catalyzed process. The diameters and lengths of the structures ranged from 40 to 400 nanometers and from 2 to 20 micrometers, respectively. An optical interferometric method was used to determine the resonant frequencies and quality factors of these resonators. Resonant properties of these devices at various temperatures and pressures are discussed. Nanowire resonators (with diameters 100 nanometers and lengths 3.3 micrometers) were functionalized using a monolayer of mercaptopropyltrimethoxysilane as a linker, followed by a functionalization with biotin. The attached biotin molecules enabled the specific attachment and detection of streptavidin molecules. Shifts of resonant frequencies by hundreds of kHz were observed, corresponding to an added streptavidin mass ranging from 1 to 3 femtograms. This work was supported by Alberta Innovation and Science and by Hewlett-Packard Laboratories.

3:00pm **NS+NC-TuA5 Solution Processed ZnO Nanowire and Heterostructure Arrays**, *K. Yong*, ***Y. Tak***, POSTECH, Korea

We researched an ammonia aqueous solution method for growing well-aligned ZnO nanowire arrays. Uniform ZnO nanowire arrays were grown on the seed layer coated silicon substrates in aqueous solution containing zinc nitrate and ammonia water by hydrothermal process. Synthesized ZnO nanowires were characterized using SEM, TEM, XPS, XRD and PL spectroscopy. Various parameters of ZnO nanowire growth, such as morphology of seed layer, pH, growth temperature, and concentration of zinc salt in aqueous solution were investigated. We also demonstrated the discrete controlled growth of ZnO nanowire length depending on sequential, tailored growth steps. Combining our solution method and general photolithography, we selectively grew ZnO nanowire arrays on patterned silicon substrate. Our concepts on controlled ZnO nanowire growth using a simple solution method would be applicable for various nano-device fabrications. Another part of this presentation is the fabrication of the ZnO nanowire heterostructure arrays. We prepared two kinds of the ZnO nanowire heterostructure, Co3O4/ZnO nanowire array and CdS/ZnO nanowire arrays using solution based deposition technique. Fabricated ZnO nanowire heterostructure arrays were characterized using SEM, TEM, XRD. Photocatalytic and photoelectrochemical property of the ZnO nanowire heterostructure arrays were tested.

4:00pm **NS+NC-TuA8 Asymmetric Functionalization of Gold and Silver Nanoparticles for Controlled Assembly**, ***J.-W. Park***, *R. Sardar, J.S. Shumaker-Parry*, University of Utah

We have developed a simple, inexpensive, versatile asymmetric surface functionalization approach for controlled assembly of gold and silver nanoparticles. The process is based on spatially localizing ligands on the nanoparticle surface and uses commercially available organic reagents. The localization of the ligands allows for controlled assembly and we are able to control interpaticle spacing using different types of linkers. We have used this approach to prepare dimers using an amide coupling reaction between localized ligands on two asymmetrically functionalized nanoparticles. In addition, we demonstrate the synthesis of dimers consisting of particles with different sizes. Without optimization, the dimer yield varies from ~30% to ~65% depending on the nanoparticle sizes. The dimers demonstrate remarkable stability in ethanol without further processing. We also can combine the asymmetrically functionalized nanoparticles with other materials such as polymers for additional organization. For example, we have covalently linked asymmetrically functionalized gold nanoparticles to polymer pendent groups to form one-dimensional nanoparticle chains. The lengths of the nanoparticle chains vary from 256 to 400 nm with regular interparticle spacing (2.7-5.4 nm) within the chains. The chains display distinct optical properties compared to individual nanoparticles. The dimers and chain assemblies are being investigated as tunable optical platforms for surface-enhanced Raman spectroscopy.

4:20pm **NS+NC-TuA9 Temperature Effects on the Formation of Thioether Self-Assembled Monolayers on Au(111)**, ***D.O. Bellisario***, *E.V. Iski, A.E. Baber, H.L. Tierney, E.C.H. Sykes*, Tufts University

Self-assembled monolayers (SAMs) offer many potential advantages to science and industry in the form of parallel nanostructure fabrication, lubricants for MEMS, corrosion protection and sensing. As such, being able to synthesize stable SAMs from different starting materials in a larger number of configurations will enable greater control over the systems for each of these applications. Due to the stability of metal-sulfur bonds, thiol (H-S-R) SAM formation has been studied extensively. In the case of thioethers (R-S-R), it has recently been shown that at temperatures up to 298 K in both ambient[1] and ultra-high vacuum[2] conditions, that the molecules still self-assemble on metal surfaces and exhibit long-range ordering, despite a weaker binding to the surface than thiols. Due to the presence of the additional hydrocarbon tail, thioethers form SAMs with a dramatically different geometry[2]; additionally, the weaker bonding reduces the stability of these systems relative to that of thiol SAMs. In this study it was found that in the Au(111)-$(C_{18}H_{37})_2S$ system, stability may be increased by elevation of the sample temperature to moderate values (400 K) during the monolayer formation. Furthermore, the gold surface reconstruction associated with increased adsorbate-substrate bond strength changes the ordering of thioether SAMs. This strong temperature dependence on the stablility of the thioether SAM's structure suggests that temperature may be an easily controllable parameter in the design and tuning of self-assembled monolayers for specific applications.

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[2] Stephen C. Jensen, A. E. Baber, H. L. Tierney and E. Charles H. Sykes ACS Nano, 2007, 1, 1, 22-29.

4:40pm **NS+NC-TuA10 Isolated Nanoscale Prochiral Reaction Assemblies on Pt(111)**, ***V. Demers-Carpentier***, *P.H. McBreen*, Laval University, Canada

Chiral surfaces can be used to achieve catalytic chirality transfer. The mechanism through which this occurs is one of very precise nanoscale assembly. In particular, it involves a constraint in which the substrate, prochiral, molecule is forced into contact with the catalyst surface uniquely via a specific enantioface. One method to achieve this is to chemisorb a chiral-modifier so as to form molecular chiral sites. Co-adsorption of the substrate then leads to 1:1 prochiral modifier-substrate complexes. We report a combined STM, HREELS and computational study of such 1:1 prochiral assemblies on Pt(111). The study reveals the existence of chemisorption induced strong C-H to O=C intermolecular hydrogen bonding between co-adsorbed ketones and aromatics on Pt(111). It also shows how this unforeseen interaction may be used to sensitively modulate both chemical reactivity at surfaces and nanoscale assembly at surfaces.

5:00pm **NS+NC-TuA11 Magic-Sized Superlattices in Boron Doped Diamond**, ***I.B. Altfeder***, *J. Hu, A.A. Voevodin,* Air Force Research Laboratory, *J. Krim*, North Carolina State University

We report scanning tunneling microscopy and transmission electron microscopy study of boron-doped nanocrystaline diamond. On surfaces of diamond grains our study revealed self-assembled nanoscale superlattices whose period is 12 nm. The analysis of data strongly suggests a structural origin of these superlattices that can be attributed to nanoscale self-organization of twinning boundaries. We found two different types of nanoscale superlattices exhibiting either one-dimensional or two-dimensional order. We speculate that the observed effect manifests ordering of boron impurities inside diamond.

5:20pm **NS+NC-TuA12 Tailoring Emission Properties of Nano Rare Earth Doped Oxides**, ***A. Kumar***, *S.B. Krishna, S. Seal*, University of Central Florida

Ceria (CeO2) is a rare earth metal oxide known for possessing less toxicity than many other metal oxides. Although the beneficial therapeutic properties of ceria nanoparticles have been explored, poor emission properties limit its application in imaging. The continuing quest to understand the interaction of ceria nanoparticles with cell requires better luminescent property of ceria, for which a nanoscale manipulation by doping has been reported. Europium is known for its strong emission and its atomic radii being close to that of cerium favors extensive solid solubility in ceria lattice. A systematic approach has been used to optimize emission intensity by varying the dopant concentration and annealing temperature. The doped oxide particles were synthesized by room temperature chemical precipitation technique. The size and morphology of the particles were characterized by high-resolution transmission electron microcopy (HRTEM). Strain induced on doping was calculated through X-ray Diffraction (XRD) from Williamson-Hall plot and is found to increase with the amount of dopant and decreases with annealing temperature. The emission property of europium doped ceria nanoparticles were studied by photoluminescence spectra. In order to disseminate the influence of surface chemical species, oxidation state, oxygen vacancy and strain on emission, X-ray photoelectron (XPS), Raman and Infra-red (IR) spectral characterizations were carried out. XPS results indicated that the ratio of Ce3+/Ce4+increases with dopant concentration and decreases with annealing temperature. Raman studies show a progressive shift to the higher energy due to local symmetry ordering with the temperature. Emission intensity varies with the wavelength of excitation and observed transitions indicate the presence of Eu3+ in different symmetry environments. The photoluminescence was found to be optimum at 15mol% Eu doped ceria and gets quenched with further doping concentration. Emission spectrum of the doped cerium oxide reveals peak characteristic to energy transfer from host to Eu3+ and this becomes more efficient on annealing. The present results are likely to have a profound impact not only for simultaneous therapeutic and imaging, but also on using ceria as carrier under physiological conditions. The study indicates that the enhanced photoluminescence is related to the manipulation of ceria lattice at nanoscale achieved through doping of suitable element.

Nanometer-scale Science and Technology
Room: Hall D - Session NS-TuP

Poster Session

NS-TuP1 Kinetic Control of Self-catalyzed Indium Phosphide Nanostructures, ***R.L. Woo***, *L. Gao, S. Kodambaka,* University of California, Los Angeles, *N. Goel, M.K. Hudait,* Intel Corporation, *K.L. Wang, R.F. Hicks*, University of California, Los Angeles

Nanowire research has gained tremendous momentum due to its potential applications in nano-electronics, photonics, solar cells, and thermoelectrics. Precise control of size, morphology, density, and uniformity is essential for realizing these commercial opportunities. Most indium phosphide nanowire research is prepared by vapor-liquid-solid (VLS) growth using gold catalysts. However, gold incorporation into the InP is unavoidable and can adversely affect optoelectronic properties. As an alternative, we have investigated the self-catalyzed growth of InP using liquid indium droplets in a metalorganic vapor-phase epitaxy (MOVPE) process. In this study, three distinct shapes were obtained depending on the growth conditions: nano-wires, cones, and pillars. The shape of nanostructures is determined by the relative rates of indium phosphide deposition via vapor-liquid-solid and vapor-phase epitaxial growth processes. At the meeting, we will discuss more details on the underlying mechanisms of the crystal growth process and the relationship between the deposition mechanism and the resultant shape of the nanostructure.

NS-TuP2 Polymer Transfer Printing for Chemical Patterns and its Application on Colloidal Assembly, ***Y.H. Kim***, Furukawa Electric Co. Ltd., Japan, *B.S. Kim, P.T. Hammond*, Massachusetts Institute of Technology

A new approach to directly organize colloidal particles into patterned arrays using templates coated with a layer-by-layer assembled polyelectrolyte multilayer was introduced. In this approach, a template using a UV-curable photo polymer was coated with polyelectrolyte multilayers, followed by a contact printing of an oppositely charged polyelectrolyte monolayer. The resultant topological template with both positive and negative charges provided a finely defined chemical nano-pattern to guide selective deposition of colloidal particles onto the patterned surface upon Coulombic attraction. For example, when negatively charged dilute colloidal suspensions were placed on the template, the particles were selectively adsorbed within positively charged grooves or holes. Additionally, we have demonstrated development of uniform PEG copolymer chemical patterns via polymer transfer printing and their applications on direct assembly of two different sets of particles to different surface regions. This effective method provides a flexible and versatile route to the development of composite colloidal structures which will present interesting technological applications in photonics, electronics and sensors.

NS-TuP3 Low-energy Electron Beam Calcination to Obtain Well-ordered Mesopores in Titanium dioxide Film, ***A. Hozumi***, *H. Taoda*, AIST, Japan

Mesoporous materials fabricated using organic surfactant molecules or block copolymers as structural directing agents has attracted much attention not only catalysts and adsorbents, but also insulating layers, chemical and gas sensors, and optical and electrical devices. In order to fabricate microdevices based on such well-ordered mesoporous materials, the control of morphologies and geometries in nano ~ micrometer scale is one of the key technologies for practical uses. In this study, we report on a facile and rapid template removal method at low temperature to obtain mesoporous titania film without cracking. Our approach demonstrated here, named “low-energy electron beam (LEEB) calcination,” is a novel calcination technique based on the decomposition and oxidation of organic fractions such as surfactants or block copolymers by LEEB irradiation under vacuum. Organic templates can rapidly be eliminated from precursor mesocomposite film within 30 min without distorting periodic mesostructure, resulting in the successful conversion to crack-free ordered mesoporous titania film. Our best rate by LEEB calcination is ~14 times faster than the result obtained by photocalcination using 172 nm vacuum UV light.

NS-TuP4 Structural and Morphological Evolution of Gallium Nitride Nanorods Grown by Chemical Beam Epitaxy, ***S.-Y. Kuo***, Chang Gung University, Taiwan, *F.-I. Lai,* Yuan-Ze University, Taiwan, *W.-C. Chen, C.-N. Hsiao*, National Applied Research Laboratories, Taiwan

The morphological and structural evolution is presented for GaN grown by chemical beam epitaxy on (0001) Al2O3 substrates. Their structural and optical properties are investigated by x-ray diffraction, scanning and transmission electron microscopy, and temperature-dependent photoluminescence measurements. While increasing the growth temperature and the flow rate of radio-frequency nitrogen radical, the three-dimensional growth mode will be enhanced to form the one-dimensional nanostructures. The high density of well-aligned nanorods with a diameter of 30–50 nm formed uniformly over the entire sapphire substrate. The x-ray diffraction patterns and transmission electron microscopic images indicate that the self-assembled GaN nanorods are a pure single crystal and preferentially oriented in the c-axis direction. In addition, the enhanced A1(LO) intensity of micro-Raman spectrum confirms the formation of strain-free GaN nanorods in consistent with XRD and HRTEM results. Particularly, the “S-shape” behavior observed in the temperature-dependent photoluminescence might be ascribed to the fluctuation in crystallographic defects and composition. Neither catalyst nor template is required in our epitaxial system make this technique feasible to develop nanodevices based on strain-free III-nitride nanorods.

NS-TuP5 Direct Measurements of the Interaction between Pyrene and Graphite in Aqueous Media by Single Molecule Force Spectroscopy: Understanding the pi-pi Interactions, ***Z. Wang***, *Y. Zhang, X. Zhang*, Tsinghua University, China **INVITED**

In this presentation, we have demonstrated the first direct measurement of the interaction between pyrene and a graphite surface at the single molecular level in aqueous media by AFM-based single molecule force spectroscopy (SMFS). As a model system driven by π- π interactions, pyrene derivatives can effectively absorb onto the surface of carbon nanotubes and graphite particles. For the investigation of the interaction between pyrene and graphite, we have connected a pyrene molecule onto an AFM tip via a poly(ethylene glycol) (PEG) chain. The use of PEG as a flexible spacer provides a means for differentiating the force signals based on the extension length and thereby for avoiding the disturbance of the nonspecific interaction between the AFM tip and substrate. To confirm the single molecular rupture events of pyrene desorbed from graphite, we have employed modified-freely jointed chain model to fit the force curves, and the fitting parameters are in accordance with that of a single PEG chain. Meanwhile, we have analyzed the distribution of the extension of the force peaks, and found that the most probable value is consistent with the PEG coutour length. The statistics of the height of the force peaks shows that the strength of interaction between pyrene and graphite is ~55 pN at the loading rate of 4.0 nN/s. To investigate the dynamic behavior of the interaction between pyrene and graphite, we have performed the SMFS experiment with different retraction velocities to obtain the dynamic force spectroscopy. This result indicates that there is no loading rate dependence at the experiment conditions, and implies that our experiments were carried out under a quasi-equilibrium condition. Therefore, the observed rupture force should equal the adhesion force between pyrene and graphite. This research may open a new route to directly study π- π interactions at a single molecular level, leading to understanding of the formation of supramolecular assemblies through π- π interactions.

NS-TuP7 Synthesis and Field Emission Properties of W18O49 Nanorods, *K. Yong,* ***S. Jeon***, POSTECH, Korea

In recent years, the assembly of 1-D nanostructures in the fabrication of transition metal oxides has received increasing attention due to their interesting potential applications. Among these metal oxide nanomaterials, the fabrication of tungsten oxide nanostructures have been intensively studied due to their promising physical and chemical properties. In current study, we report for the first time the synthesis of tungsten oxide nanorods from tungsten-compound material using a simple annealing of the W2N/Si substrate. W2N film was deposited on Si(100) substrate by chemical vapor deposition at 450 °C and then heating of the film at 600 ~ 700 °C produces a high density of tungsten oxide nanorods. The morphology, structure, composition and chemical binding states of the prepared nanorods were characterized by SEM, XRD, XPS, EDX and TEM measurements. XRD and TEM analysis showed that the grown nanorods were single-crystalline W18O49. According to XPS analysis, the W18O49 nanorods contained ~62% of W6+, ~28% of W5+, and ~10% of W4+. Field emission measurements showed a low turn-on field of 9.5 V/μm for the W18O49 nanorods, indicating that they can be used as potential field emitters.

NS-TuP8 Computational Simulation of Mechanical and Multi-Physics Behaviour of Micro and Nano-Structures, ***R. Said***, Simpleware Ltd., UK, *P.G. Young,* University of Exeter, UK, *B. Walker,* Arup, UK, *A. Abdul-Aziz,* NASA Glenn Research Center, *B. Notarberardino*, University of Exeter, UK

Computational simulation is increasingly proving to be a very effective and valuable tool in investigating materials behaviour at the micro and nano-scale level and in assessing its influence on the overall macro-scale properties. Well established computational techniques (based on numerical methods such as the Finite Element Method) can now be used to simulate mechanical, fluid dynamics, thermal or any combined (multi-physics) phenomena at the micro and nano-scale level. Crucial to the success of such a simulation is the ability to represent the 'micro-architecture' accurately and efficiently - which has proved to be a very challenging task so far. This paper will present an innovative image-based mesh generation technique that converts 3D images of micro and nano-structures (as provided by typical Micro/NanoCT scanners) directly into high fidelity computational models. The approach provides a deeper understanding than experimental tests, and achieves more realistic model results than via analytical approaches. Real-life applications will be presented, including the densification analysis of open celled foam, and the characterisation of composite materials. The aims of the paper is to demonstrate the potential of the proposed approach for understanding the nexus between micro-scale architecture and macro-scale properties, and illustrate the ability to simulate topologically complex problems with a high degree of accuracy but in a fraction of the time taken by other approximate methods. The ability to straightforwardly and robustly model the response of complex micro and nano-architectures provides powerful new tools for the material scientist to easily explore the influence of various parameters on the performance of novel complex material systems, which will be increasingly used in addition to and in combination with analytical modelling and experimental tests. These computational techniques will also be pivotal to the development of tools for material characterization of complex composites using inverse modelling techniques.

NS-TuP9 Fabrication of Three-Dimensionally Periodic Macroporous TiO_2 Thin Film for Photovoltaic Application, *S.B. Yoon, Y.H. Kim, K. Kim, B.-C. Woo,* Korea Research Institute of Standards and Science, *S.J. Chung,* Korea Research Institute of Biosience and Biotechnology, ***W.S. Yun***, Korea Research Institute of Standards and Science

Three-dimensionally (3D) periodic macroporous TiO_2 thin film was fabricated by using polystyrene sulfonate (PSS) nanoparticle as an organic template and titanium alkoxide as a TiO_2 precursor on fluorine-doped tin oxide (FTO) glass. Close-packed colloidal crystalline thin film composed of PSS nanoparticles was prepared by using 2D deposition technique. The TiO_2 precursor was immersed into the void space between PSS nanoparticles and subsequently in-situ hydrolysis and condensation were performed. The nanocomposite of PSS nanoparticles and amorphous TiO_2 was calcined to remove the organic materials and to crystallize the amorphous TiO_2 to anatase type at 450℃ under air flowing. Resultant anatase TiO_2 thin film was exhibited the 3D periodic macroporous framework with connecting windows. Photovoltaic cells composed of the Ru-dye coated 3D periodic macroporous anatase TiO_2 thin film were fabricated and their energy conversion efficiency was also investigated.

NS-TuP10 Vapour Phase Deposition of Aromatic Self-Assembled Monolayers, ***L. Kankate***, *H. Muzik, A. Turchanin, A. Gölzhäuser*, University of Bielefeld, Germany

Self-assembled monolayers (SAMs) with aromatic moieties recently caused a particular interest due to their applications in molecular electronics,[1] nanolithography[2,3] and biotechnology.[4] For high quality SAM-based devices and nanostructures, a reproducible fabrication of high quality SAMs is necessary. The traditional "wet" preparation of SAMs may suffer from solvent, ambient and substrate contaminations resulting in poor quality and degradation of the molecular assemblies. On the contrary, the preparation of SAMs in UHV can provide a high degree of control over the experimental parameters. We have studied the formation of 1,1'-biphenyl-4-thiol (BPT) and 4'-nitro-1,1'-biphenyl-4-thiol (NBPT) SAMs on gold surfaces by vapour deposition in UHV. The vapour deposited monolayers were characterized by mass spectrometry, X-ray photoelectron spectroscopy (XPS). and scanning tunnelling microscopy (STM). Based on this data, the deposition parameters were optimized. A comparison of vapor deposited SAMs with monolayers prepared from solution is presented.

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NS-TuP11 Characteristics of La-substituted Bismuth Titanate Ferroelectric Nanofibers by Electrospinning, ***K.T. Kim,*** University at Buffalo, the State University of New York, *C.I. Kim,* Chung-Ang University, Korea, *Y.K. Yoon*, University at Buffalo, the State University of New York

The bismuth layer-structured ferroelectrics have been known as high dielectric materials with attractive properties such as environmentally friendly lead-free composition and fatigue free characteristic. Specially, the La-substituted Bismuth Titanate ($Bi_{3.25}La_{0.75}$ Ti_3 O_{12} :BLT) has received the intensive attention for their excellent ferroelectric, crystalline properties as a promising dielectric for capacitors and memory devices.[1] Recently, there has been an intense research effort on one dimensional nano materials such as nanotube and nanofiber due to their unique structure and properties, such as high aspect ratio, large specific surface area and chemical/mechanical stabilities.[2] In this study, BLT nanofiber synthesis has been demonstrated using electrospinning and subsequent sintering. A composite solution consisting of a metal-organic decomposition solution of BLT and a binder of poly(vinylpyrrolidone) (PVP) has been electrospun in an electric field of 3×10^5 V/m to form nanofiber with a diameter of 120 nm. The BLT/PVP composite nanofiber has been calcined in air for 1 h at 500, 600, 700, 750, and 800 °C, respectively. The characteristics by X-ray diffraction, FT-IR, SEM and HR-TEM of the BLT/PVP composite nanofibers are reported.

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NS-TuP12 Nanostructured Glassy Carbon Supported GC/Pt Electrodes for Model Studies of Fuel Cell Relevant Electrocatalytic Reactions, ***Y.E. Seidel***, *A. Schneider, L. Colmenares, Z. Jusys, R.J. Behm,* Ulm University, Germany, *B. Wickmann, B. Kasemo*, Chalmers University of Technology, Sweden

In this contribution, we discuss the potential of nanostructured planar electrodes for model studies of electrocatalytic reactions relevant for Polymer Electrolyte Fuel Cell (PEFCs). The model electrodes consist of catalytically active Pt nanostructures of well-defined size and separation, which are supported on planar glassy carbon substrates.[1,2] They are fabricated employing colloidal lithography (CL)[1] or Hole-mask Colloidal Lithography (HCL),[2] or by micellar techniques, via deposition of metal loaded micelles and the subsequent removal of the polymer stabilizer.[3] Both techniques allow us to independently vary size and separation of the catalytically active nanostructures/particles. The resulting particle sizes are ca. 3-15 nm (micellar techniques) and 70-150 nm (CL, HCL), respectively. These nanostructured model electrodes allow direct and quantitative access to an important aspect of electrocatalytic reactions which so far has been largely neglected, to the influence of mesoscopic transport effects on the characteristics of electrocatalytic reactions. Using the reduction of O_2 and the oxidation of formaldehyde as examples it will be shown that mass transport effects not only modify the overall rate, but have significant effect also on the product distribution, e.g., on H_2O_2 formation. Possible contributions of the reactant transport to the overall reaction process will be discussed in a molecular picture.

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NS-TuP13 Dimer Ordering of M-TtertBuPc on Graphite, ***T. Takami***, *C. Carrizales, K.W. Hipps*, Washington State University

The growth and ordering of metal complexes of 2,9,16,23-tetra-tert-butyl-phthalocyanines (TtertBuPc) on graphite surface have been studied by scanning tunneling microscopy. A well-ordered molecular layer having the molecular plane lying parallel to the graphite substrate was obtained at the solution - graphite interface at room temperature. For Cu-TtertBuPc, dimer ordering similar to that reported previously on the Si(111)-r3Xr3-Ag surface[1] was partly observed. We will also discuss the effects of changing the center metal and/or the phthalocyanine to naphthalocyanine, and imaging and orbital mediated tunneling spectroscopy in ultrahigh vacuum (UHV).

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NS-TuP14 Optical Performance of EUV Lithography Mask with Silver Doped Zinc Oxide Absorber, ***H.Y. Kang***, *M.K. Kim, C.K. Hwangbo*, Inha University, Republic of Korea

The lithography performance of extreme ultraviolet lithography (EUVL) mask depends on the correct choice of absorber materials because it is directly related to imaging contrast, shadowing effect, focus shift effect, and thermal effect.[1] The optical constant of the absorber materials in the EUV region should have higher extinction coefficient for higher attenuation. Also, the absorber material should exhibit good conductivity, which can alleviate the charging effect during electron-beam patterning. In the past, a wide range of materials (Ti, TiN, Al–Cu, TaSi, Ta, TaN, Cr, etc) has been evaluated as possible conductive absorbing materials for EUVL mask.[2,3] The total thickness of the absorber stack by using the materials used to be greater than 80 nm because the available absorbing materials are limited and an anti-reflection coating is necessary to maximize pattern inspection efficiency at deep ultraviolet wavelength. It is reported that the large thickness of the absorber stack may cause a geometric shadow effect in an exposure step and as a result, the printed patterns are shifted and biased.[4] In this study, we propose a new absorber stack with a silver doped zinc oxide absorber layer. The optical constants of ZnO layers with various concentration of Ag at 13.5 nm are calculated. It is found that the optical constants of ZnO layers with high concentration of Ag show lower refractive index and higher extinction coefficient at 13.5 nm than those of TaN layer. Thus ZnO layers doped with Ag enables EUVL masks to be designed to have very small height difference between high reflecting and absorbing stacks, suggesting that the geometric shadow effect can be significantly reduced.

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[2] J. Y. Robic, P. Schiavone, V. Rodillon, R. Payerne, Microelectronic Eng 61–62, 257–263 (2002).

[3] P. Mangat, S. Hectora, S. Rosea, G. Cardinaleb, E. Tejnil, A. Stiverse, Proc. SPIE 3997, 76 (2000).

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NS-TuP15 Actinide Powder Characterization for Nuclear Forensics, ***W.S. Duncan***, *A.D. Neuman, C.C. Davis, T.A. Nothwang*, Los Alamos National Laboratory

Half of the Department of Energy's nuclear forensics scientists are expected to retire within the next 15 years but there continue to be around 10 confirmed cases of nuclear material trafficking each year.[1,2] The Interfacial Science team of LANL's Materials Science & Technology division is addressing this need for new nuclear forensics expertise by helping to create a database of actinide powder characteristics. This poster addresses physical characterization on a nanoscale level via microscopy and other methods in order to obtain microstructural and elemental composition as well as crystal structure of known powders.

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[2] McKenna, Phil. NewScientist.com news service. 16 February 2008. http://www.newscientist.com/article.ns?id=dn13336.

NS-TuP16 Template-Free Synthesis and Characterization of Copper Oxide Nanostructures, *K.-R. Lo*, ***C.-C. Chang***, National Taiwan University

As a relatively non-toxic p-type semiconductor and a classical example of excitonic solid, cuprous oxide may play an important role in the electronics industry as the dimensions of electronic devices continue to shrink. For example, devices made of nanometer-scale cuprous oxide are expected to be small and fast because the electrical signal can resonantly tunnel through the nanoscale cuprous oxide layers. In addition, cuprous oxide structures fabricated in the nanoscale may exhibit better antifouling and algicide effects, increase its overall water splitting capability for solar energy applications, and enhance its photocatalytic activity for degradation of organic pollutants under visible light. Nanoscale cuprous oxide structures were prepared in this study via a template-free synthetic approach in the ethylene glycol solution using different copper compounds as the precursor. SEM images and Auger spectra revealed that, instead of forming spherical particles, micro- to nano-sized aggregates of well-defined geometric shapes were obtained. These aggregates were made of nanocrystalline particles, as revealed in high-resolution TEM and diffraction studies, which self-assembled into organized solids. XPS spectra suggested that the crystallization and the self-assembling may take place via cuprophilic attraction. The shape and the dimensionality of the assemblage obtained can be controlled by adjusting reaction temperature and/or by using different surfactants. Chemical conversion of cuprous oxide to cupric oxide impaired the cuprophilic interaction, leading to dismantling of the assemblage at extended reaction time. The chemical process and the mechanism involved in the assembling and dismantling of the polycrystalline assemblage will be discussed.

NS-TuP17 Preferred Diameter Growth of Single-Walled Carbon Nanotube by using Sapphire Substrates, *K.-Y. Shin*, National Tsing Hua University, Taiwan, ***J.-S. Kao***, National Applied Research Laboratories, Taiwan, *K.-C. Leou, C.-H. Tsai*, National Tsing Hua University, Taiwan

Single-walled carbon nanotube (SWCNT) has been considered as an alternative material for nano-devices, such as carbon nanotube field-effect-transistor or nano-sensor. It has been found that the characteristics of the SWCNT-based device are affected by the band gap of the tube, which depends on its diameter and chirality. Preferred diameter growth of single-walled carbon nanotube (SWCNT) by using single crystal sapphire (0001) and sapphire (110-2) substrates is reported. The carbon nanotubes were grown by mono-layered iron catalyst from sapphire substrate and a mixture of methane and hydrogen at 900°C by chemical vapor deposition. Atomic force microscopy revealed that the particle size distribution of catalyst was varied with different orientation sapphire substrate. The micro-Raman spectra exhibited that the radial-breathing mode signals of SWCNTs grown by Fe (1nm) catalyst were shifted with different orientation sapphire substrates. A growth model based on minimum strain theory (i.e. O-lattice theory) and surface tension theory is proposed.

NS-TuP18 Green Synthesis and Mechanism of ZnSe Nanoflowers, ***Q. Dai***, Worcester Polytechnic Institute, *N. Xiao, B. Zou*, Jilin University, China, *W. Yu*, Worcester Polytechnic Institute

We introduce a nontoxic, simple, cheap and reproducible strategy, which meets the standard of green chemistry, for the synthesis of ZnSe nanoflowers. These green nanomaterials with a zinc blende structure can be readily scaled up and produced directly at ambient condition without affecting their qualities. A systematic study of the nanoflower formation process indicates the recently reported "limited ligand protection" mechanism cannot be employed to explain the formation of our nanoflowers. Instead, a new growth mechanism is proposed: Upon heating at high temperature, mononuclear Zn complexes convert to polynuclear Zn complexes with multiple Zn atoms. Each Zn atom grows into one ZnSe nanoparticle after the injection of Se solution. These nanoparticles closely connect and thus look like nanoflowers.

NS-TuP19 Fabrication of Porous Si Using Anodic Aluminum Oxide, ***N.Y. Kwon***, *K.H. Kim, J.M. Kwon, I.S. Chung*, Sungkyunkwan University, Korea

Porous Si templates with various pore patterns were obtained by etching underlying Si using an anodic aluminum oxide (AAO) mask. Si3N4 imprint stamps with a nano size matrix pillar (height : 50 nm) pattern were indented into Al film grown on Si wafer using an oil press method with the force of 5kN·cm-2. After indenting on Al thin film (thickness : 200 nm), we found that the periodic array with 30 nm depth was formed on Al thin film using scanning probe microscopy. The indented Al film was then anodized using two different anodizing conditions, namely, 0.3M oxalic acid of 4°C at 50V and 0.3M sulfuric acid of 10°C at 25V, and these conditions were suitable to define the matrix pore pattern. As pore's size and interval were decided by anodizing conditions, pre-patterning must set to anodizing condition to get regular pattern. We can control the size of pore and the interval of pore by modifying the aforementioned anodizing conditions. Thus, we can achieve a well organized Si porous template by transferring AAO pattern using ICP etcher with 30 W of rf power, 30 mTorr total pressure, 30 SCCM of CF4, and 4 SCCM of O2.

NS-TuP20 Fabrication and Characterization of One-Dimensional Semiconducting Nanowire That Use AAO, ***K.H. Kim***, *N.Y. Kwon, J.K. Hong, I.S. Chung*, Sungkyunkwan University, Korea

In this study, we attempted to fabricate and characterize one dimensional semiconducting nanowire(CdSe, Polypyrrole). It is well known that CdSe is n-type material, whereas polypyrrole is p-type material. The template used in the nanowire growth was AAO(Anodic Aluminum Oxide) template. After forming AAO template on Al foil, the oxidized underlying barrier layer was removed using a cathodic polarization method based on KCL(0.5mol, -5V, 4℃) solution. Then, nanowires with 50nm diameter and 300nm height were grown using the electroplating method. Finally, the nanowires were characterized using SPM(Seiko Instruments, SPA 300HV) by proving the conductive cantilever. I-V characteristics as a function of the temperature gives an activation energy which is useful to understand the conduction mechanism of semiconducting nanowires.

NS-TuP21 Nanofabrication by Near-Field Photochemical Modification of Phosophonic Acid Monolayers on Titanium Dioxide, ***G. Tizazu***, *G. Leggett, D.G. Lidzey*, University of Sheffield, UK

Phosphonic acid self assembled monolayers were formed on titanium oxide surfaces. Exposure of the samples to a UV light of wave length 244nm through a mask resulted in photo degradation of the monolayers in exposed areas leaving undegraded molecules in unexposed areas. Titanium oxide microstructures were produced by immersing the photo patterned samples in to a KOH solution. The phosphonic acid monolayers exhibited a surprising "switchable" character, performing as positive tone resists at low UV exposures but behaving as negative tone resists at high exposures. Backfilling the photo-degraded monolayers with a second phosphonic acid molecule with a different end group (for example an amine terminated adsorbate) yielded patterns consisting of regions with different chemical compositions. Aldehyde and amine modified fluorescent nanoparticles were attached to the chemically patterned surfaces, demonstrating their potential for fabricating complex functional architectures. Nanometre scale structures were produced by utilising a scanning near-field optical microscope (SNOM as the light source.

NS-TuP22 Nanopatterning by Near-Field Photodeprotection of 2-Nitrophenylpropyloxycarbonyl-Protected Aminosiloxane Monolayers on Glass, ***S. Alang Ahmad,*** University of Sheffield, UK, *L.-S. Wong,* University of Manchester, UK, *E. Haq, J. Hobbs, G. Leggett,* University of Sheffield, UK, *J. Micklefield*, University of Manchester, UK

Nanometre scale control of chemical reactivity is key for many applications of nanotechnology in biology, electronics, materials science, etc. Currently there are few methods for the selective initiation of chemical transformations with nanometre precision. Here we report a novel approach to nanopatterning in which a scanning near-field optical microscope coupled to a near-UV laser is used to selectively deprotect 2-nitrophenylpropyloxycarbonyl (NPPOC) protected aminosiloxane monolayers on glass. Initially, UV deprotection was studied for unpatterned samples using X-ray photoelectron spectroscopy and contact angle measurements. The resulting amine-terminated surfaces were activated with glutaraldehyde and then derivatized using a fluorinated adsorbate and aldehyde polymer nanoparticles. Contact angle and XPS measurements indicate extensive surface functionalisation. Next, micrometre-scale patterns were fabricated using mask-based exposure to light from a He-Cd (325 nm) or Ar-ion (364 nm) laser, and characterised by friction force microscopy. Nanoparticle patterns were formed by covalent attachment methods. Nanometre scale patterns were fabricated using near-field exposure, and characterised by FFM. The nanopatterns were derivatised with functionalised molecules, showing that high spatial resolution (ca 100 nm) was readily achievable, and also that extensive functionalisation of the patterns could also be accomplished.

Nanometer-scale Science and Technology
Room: 311 - Session NS+NC-WeM

Characterization and Imaging of Nanostructures
Moderator: R. Ruiz, Hitachi Global Storage Technologies Inc

8:00am **NS+NC-WeM1 Peter Mark Memorial Award Lecture: Probing the Order Parameter Dynamics and Energy Dissipation on a Single Defect Level: Hidden Dimensions of Scanning Probe Microscopy***, ***S.V. Kalinin****, Oak Ridge National Laboratory **INVITED**

The kinetics and thermodynamics of first-order phase transitions and reactions involving solids are universally controlled by defects. Examples are as diversified as nucleation centers in solid-state and electrochemical reactions, phase change and electrochemical memories, crystallization of metals, oxides, and polymers. The electronic and atomic structure of defects in solids has become accessible in exquisite detail with the advent of electron microscopy and spectroscopy techniques. In the last decade, the progress in AFM- unfolding spectroscopy and IETS has opened the pathway for probing thermodynamics and kinetics of single-molecule reactions, and vibrational modes within simple molecules. In comparison, the role of defects in solids on local phase transitions and order parameter dynamics has long remained beyond the experimental reach. In this presentation, I will summarize recent progress in spectroscopic multidimensional SPM techniques as applied for probing structure-property relationships on a single defect level using electric or thermal field confinement by an SPM tip. Ferroelectric materials provide a convenient model system in which bias-induced phase transition between two equivalent polarization states is reversible and is not associated with diffusion, mass, or significant heat exchange and strain effects. Spatially resolved mapping of local nucleation biases allows nucleation centers to be visualized, and corresponding thermodynamic and kinetic parameters to be reconstructed. The hysteresis loop fine structure provides additional information on defect-mediated domain dynamics and defect-domain interactions. The direct imaging of a single nucleation center on sub-100 nanometer level is demonstrated. In the second part of the talk, I demonstrate the approach for dissipation probing in SPM using non-sinusoidal signals (band excitation method). In all these examples, the 3- and 4D SPM techniques enabled by the recent advances in fast data acquisition electronics are the enabling step. Finally, I discuss potential pathways for extending these concepts from observation to control and communication with the nanoscale world. Research was supported by the U.S. Department of Energy Office of Basic Energy Sciences Division of Materials Sciences and Engineering and was performed at Oak Ridge National Laboratory which is operated by UT-Battelle, LLC.

8:40am **NS+NC-WeM3 Quantitative Evaluation of Carbon Nano Tubes by the Scanning Atom Probe**, ***O. Nishikawa***, *M. Taniguchi*, Kanazawa Institute of Technology, Japan

Quality of carbon nanotubes (CNT) strongly depends on the amount of impurities such as hydrogen, oxygen and others. However, few efforts have been paid for the quantitative evaluation of them. In order to evaluate the CNT at the atomic level point of view we mass analyzed various CNTs such as single walled CNT (SWCNT), double walled CNT (DWCNT) and multi walled CNT (MWCNT) utilizing the unique capability of the scanning atom probe (SAP).[1] In this mass analysis carbon atoms of the CNTs are field evaporated as positive ions of single atoms and clusters of few atoms. The mass to charge ratios of these ions are obtained by measuring their flight times from a specimen surface to an ion detector. One of the analyzed SWCNTs is grown by the high CO pressure process (Hipco) and other is synthesized by a direct-current arc-discharge method in He gas with Fe/Ni/S catalysis. The DWCNTs are commercially supplied. The MWCNTs are directly formed on a substrate of Ni-Cr-Fe alloy by thermal CVD at 650° using a mixture of acetylene, hydrogen and argon gases. CNTs are deposited on a W tip by silver paste. The amount of impurities is evaluated by counting the number of cluster ions forming mass peaks. For example, the numbers of C and H atoms forming the mass peak of 150 CH_3 clusters ions are 150 and 450, respectively. The number of C, H, O and other atoms are counted for all major mass peaks. The numbers of H, O and Na atoms in a Hipco SWCNT 3.7 %, 2.6 % and 0.1 % of the total number of detected atoms, respectively. Similarly, the amounts of the impurities in the CVD SWCNTs are 9 % of H, 0.7 % of O and 0.19 % of Na. The commercial DWCNTs contain fairly large amount of impurities with 20 % of H and 1.9 % of O. The MWCNT also contains a significant amount of impurities, 27 % of H, 4 % of O and 0.4 % of Na. Even if specimens are prepared by the CNT formed by an identical preparation process, most specimens show a different mass spectrum with different amount of impurities. However, many Hipco SWCNT specimens exhibit a similar mass spectrum. The binding between C atoms forming CNTs also evaluated. The mass spectrum with a large number of C^{2+} and C^{+} indicates that the C-C bonds of the CNT is strong and uniform. The relation between the binding state and the impurity content of the analyzed CNT will be discussed.

[1] O. Nishikawa, Y. Ohtani, K. Maeda, M. Watanabe and K. Tanaka: Mater. Char., 44, 29 (2000).

9:00am **NS+NC-WeM4 AgCl Monolayers on Au(111): Novel, Ultra-stable and Atomically-flat Surfaces**, ***E.V. Iski***, *M. El-Kouedi, D.O. Bellisario, E.C.H. Sykes*, Tufts University

Underpotential deposition (UPD) is a useful way of depositing up to one monolayer of a metal onto a more noble metal. We used this technique to deposit Ag onto Au(111) with and without the presence of chloride. Electrochemical scanning tunneling microscopy (EC-STM) revealed that, depending on the sample potential and hence the surface Ag coverage, Ag grows in a variety of ordered structures that can be atomically resolved. However, upon being removed from the electrochemical cell, these “chloride-free” Ag monolayers are subject to degradation by air. Interestingly, if the Ag layer is formed in the presence of trace amounts of chloride, the resulting AgCl layer is stable both in air and even at temperatures as high as 1000 K. X-ray photoelectron spectroscopy (XPS) was used to quantify the stoichiometry of the systems and both ambient- and EC-STM revealed that even after exposure to extreme temperatures the monolayer thick AgCl layer remained atomically perfect.

9:20am **NS+NC-WeM5 Atomic Scale Characterization of Charge Redistribution for Gallium Nanocluster Arrays on the Si(111)-7x7 Surface**, ***Q.H. Wang***, *M.C. Hersam*, Northwestern University

In recent years, the fabrication and characterization of nanocrystals with size-dependent properties has gained interest for both fundamental studies and technological applications ranging from magnetic storage to catalysis. Self-assembled arrays of uniform nanoclusters on the Si(111)-7x7 surface from In, Ga, and Al[1] have recently been observed. These nanoclusters share common characteristics: uniform atomic structure; high thermal stability; and self-assembly into well-ordered, large-area arrays. However, the electronic properties of these nanocluster arrays are not yet well understood. Experimental investigations thus far have focused on the behavior of individual nanoclusters rather than the delocalized properties of the nanocluster array as a whole. Meanwhile, a computational study of In and Al nanocluster arrays has predicted the formation of a spatially modulated 2D electron gas (2DEG) due to surface charge redistribution.[2] In this study, we report the observation of atomically resolved, delocalized 2D charge redistribution associated with Ga nanocluster arrays on the Si(111)-7x7 surface.[3] By using ultra-high vacuum scanning tunneling microscopy and differential tunneling conductance mapping, we correlate the topography of the Ga nanocluster array with its local density of states (LDOS). In the differential tunneling conductance maps, we observe the surface charge redistribution as distinct regions of increased LDOS forming an interconnected 2D network over the Ga nanocluster array. These results indicate that a delocalized 2DEG has been induced by the Ga nanocluster array. Furthermore, the close integration of the nanoclusters with the Si substrate can be discerned from differences in the LDOS between the faulted and unfaulted unit cell halves. Interestingly, the increased LDOS disappears abruptly over clean Si(111)-7x7 unit cells, suggesting a possible route for nanopatterning of the surface electronic structure via selective masking of the Ga nanocluster formation. These atomic-scale observations are likely to impact further fundamental studies of nanocluster arrays on Si and the development of potential nanoelectronic devices.

[1] J.F. Jia, X. Liu, et al., Phys. Rev. B, 66, 165412 (2002)

[2] L.X. Zhang, S.B. Zhang, et al., Phys. Rev. B, 72, 033315 (2005)

[3] Q.H. Wang and M.C. Hersam, Small, in press (2008).

9:40am **NS+NC-WeM6 QPlus AFM on Single Crystal Insulators with Small Oscillation Amplitudes at 5 K**, ***M. Maier***, Omicron NanoTechnology GmbH, Germany

The creation and investigation of nano-structures, molecules or atomic structures on insulating surfaces is a key approach for electronic decoupling from the substrate. It pushes AFM as an complementary imaging and spectroscopy technique to STM. Ideally, the used AFM probe should simultaneously or alternatively work in STM/STS modes without performance compromises on the latter. Based on a proven low temperature (5K) LT STM platform, we have integrated a QPlus[1] sensor, which employs a quartz tuning fork for force detection in non-contact AFM. For combined

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* Peter Mark Memorial Award Winner

STM operation, this sensor has key advantages over conventional cantilevers: (i) a solid metal tip for optimal STM/STS and (ii) high stiffness and high stability, i.e. low vibrational noise due to small self-resonance amplitudes. For quantitative force spectroscopy on insulating thin films or semiconductors, decoupling of tunneling current and piezo-electrically induced AFM signal is important. By measurements on Si(111) and Au(111) we prove that only a dedicated pre-amplification technique can solve this problem. In addition, extremely low signals require the first amplification stage to be very close to the sensor, i.e. to be compatible with low temperatures. STS measurements using a Niobium tunneling tip reveal the superconducting gap with a FWHM of approx. 2.5 meV and prove a probe temperature of approx. 5K. The high stiffness (1800 N/m) of the sensor allows for operation with extremely small amplitudes to (i) more precisely keep the sensor with a certain force interaction regime, (ii) increase sensitivity especially for short range forces and (iii) allow for force measurements during atom manipulation experiments without disturbing the manipulation event as such.[2] As benchmark measurement, we present atomic resolution imaging on single crystal NaCl with oscillation amplitudes down 100pm (peak-to-peak) in constant df imaging feedback. Optimal S/N ratio is achieved with a frequency noise down to 30mHz (peak-to-peak). We also present atomic resolution measurements on MgO(100), C60 molecules on Ag(111), and first evaluation measurements of the QPlus sensor in Kelvin Probe (KPM) mode operation.

[1] F. J. Giessibl, et al., Appl. Phys. Lett. 73, 3956 (1998)

[2] M. Ternes, et al., Science 319, 1066 (2008).

10:40am **NS+NC-WeM9 Nanoscale Characterization of Thin Film Coatings Using Annular Dark Field Scanning Transmission Electron Microscopy**, ***G. Acosta***, *R. Vanfleet, D. Allred, R. Turley*, Brigham Young University

When considering the optical performance of thin films in the Extreme Ultraviolet (EUV), developing an accurate physical description of a thin film coating is necessary to be able to successfully model optical performance. With the short wavelengths of the EUV, film interfaces and sample roughness warrant special attention and care. The surfaces of thin film samples are routinely measured by Atomic Force Microscopy, from which roughness can be determined. However, characterizing the quality of interfaces below the surface is much more challenging. In a recent study of scandium oxide thin films, High Resolution Transmission Electron Microscopy and Annular Dark Field Scanning Transmission Electron Microscopy (ADF STEM) were used to study the cross section of the samples. ADF STEM data analyzed along a path into the volume of the sample (normal to the interfaces) reveals information of sample density versus depth. This density-depth profile reflects the presence of subsurface film interfaces in the volume of the sample. Additionally, information from the ADF STEM profile can be used to gauge the roughness of the subsurface interfaces, which is used to refine the sample description during modeling. We believe this is the first use of ADF STEM in this capacity. This characterization technique may provide key insight to subsurface interface quality, which is particularly important when optimizing the performance of multilayer coatings in the EUV.

11:00am **NS+NC-WeM10 Electron Structure of InGaAs/GaAs Quantum Dots in Limit of Small Sizes**, *I. Filikhin, J. Nimmo, M.H. Wu,* ***B. Vlahovic***, North Carolina Central University

We model InGaAs/GaAs quantum heterostuctured objects, such as quantum dots (QD) and quantum rings (QR), in limit of small sizes. The electronic structure of these objects is restricted to a few electron and hole levels.[1] For QDs with small sizes, the effect of non-parabolicity of the conduction band becomes very important. In our model, this effect is taken into account using the Kane formula. In this study we apply an effective approach in which the combined effect of strains, piezoelectricity and interband interactions are simulated by an effective potential.[2] Based on our model, we performed an analysis of capacitance-gate-voltage data[1] and photoluminescence spectra for QDs, QRs and for double concentric QRs. We show that our approach reproduces both the few electron energy level spectra and the increase of the electron effective mass relative to the bulk value due to non-parabolicity. In this case the effective mass of excited states must be energy dependent and differs from the ground state value. Also, the non-parabolic effect visibly shifts the electron energy levels in comparison with parabolic models. We include heavy holes into the model of band structure using the effective potential approach. This model allows us to reproduce measured transition energies and Coulomb shifts for excitonic complexes (X-, X+, XX).[3] Ga and In material mixing in InGaAs/GaAs QD[4] is also taken into account in this study. We compare our results with those obtained by kp-calculations[5] and atomistic pseudopotential models.[3] We note that calculations that model QDs from first principles are of fundamental interest, but our effective potential method has strong application significance, which will be appreciated by industry, due to its efficiency and accuracy in calculating physical properties. This work is supported by the DoD: W911NF-05-1-0502.

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[2] I. Filikhin, et al. Phys. Rev. B 73, 205332 (2006).

[3] S. Rodt, et al. Phys. Rev. B 71, 155325 (2005); G. Narvaez et al. Phys. Rev. B 72, 245318 (2005).

[4] I. Kegel, et al. Phys. Rev. Lett. 85, 1694 (2000).

[5] J. I. Climente, et al., J. Phys.:Condens. Matter 17, 1573, (2005); A. Schliwa, et al., Phys. Rev. 76, 205324 (2007).

11:20am **NS+NC-WeM11 Characterization of Graphitic Coated Magnetic Nanoparticles used in Cancer Therapy**, ***S. Trigwell***, ASRC Aerospace, *A.S. Biris, Y. Xu, Z. Li, M. Mahmood,* University of Arkansas at Little Rock, *T.S. Nunney*, Thermo Fisher Scientific, UK

Graphitic carbon coated ferromagnetic nanoparticles of Co and Co/Fe with diameters of approximately 7 nm and cubic crystalline structures were synthesized by catalytic chemical vapor deposition (CCVD). X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis indicated that the metallic nanostructures inside the carbon shells were preserved in the metallic state and were not oxidized, which made them excellent candidates for electromagnetic radiation absorbers for biological thermal applications. Confocal microscope images revealed effective penetrations of the nanoparticles through plasmatic membranes into cultured HeLa cancerous cells both in the cytoplasm as well as the nucleus. Low RF radiation of 350 kHz triggered the cell death, a process that was application time and nanoparticle concentration dependant. Compared to nanostructures such as single wall carbon nanotubes, magnetic nanoparticles demonstrated higher specificity for RF absorption and heating.

11:40am **NS+NC-WeM12 Towards Automation in the Characterization of Nanostructured Materials and Devices**, *U. Schmidt, T. Dieing, M. Kress,* ***K. Weishaupt***, WITec GmbH, Germany

The characterization of nanostructured materials implies knowledge about their chemical and structural properties, leading to a growing demand for characterization methods for heterogeneous materials on the nanometer scale. However, certain properties are difficult to study with conventional characterization techniques due to either limited resolution or the inability to chemically differentiate materials without inflicting damage or using invasive techniques such as staining. By combining various analytical techniques such as Raman spectroscopy, confocal microscopy and AFM in one instrument, the same sample area can be analyzed with all implemented methods, leading to a better understanding of nanostructured materials. Raman spectroscopy, a chemical analysis technique, combined with confocal microscopy enables the unique Raman imaging of heterogeneous materials. The power of Raman imaging stems from the high chemical information content of molecular vibrational spectra. In the Raman spectral imaging mode, a complete Raman spectrum is recorded at every image pixel, leading to a two-dimensional array consisting of ten-thousands of complete Raman spectra. From this array images are extracted by analyzing various spectral features (sum, peak position, peak width, etc). Differences in chemical composition, although completely invisible in optical images, will be apparent in the Raman image and can be analyzed with a lateral resolution down to 200 nm. If higher resolution is required, by simply turning the microscope turret, the confocal Raman microscope can be transformed in to an AFM. Using this imaging technique, structures below the diffraction limit can be visualized from the same sample area. For the analysis of various devices formed on a support, an automated sample positioner with a travel accuracy better than 5 µm is incorporated in the instrument. Special scripting functions allow the automated execution of predefined measurement sequences on any user defined selection of measurement points on the sample, guaranteeing the most comprehensive surface analysis tool for systematic and routine research tasks.

Energy Science and Technology Focus Topic
Room: 203 - Session EN+AS+TF+VT+NC-WeA

Energy: Tools and Approaches
Moderator: T.A. Dobbins, Louisiana Tech University and Grambling State University

1:40pm **EN+AS+TF+VT+NC-WeA1 Continuous, In-Line Processing of CdS/CdTe Devices**, ***W.S. Sampath***, Colorado State University, *R.A. Enzenroth, K.L. Barth,* AVA Solar Inc., *V. Manivannan,* Colorado State University, *K. Barricklow, P. Noronha*, AVA Solar Inc. **INVITED**

A continuous, in-line process suitable for high throughput manufacturing of CdS/CdTe photovoltaic devices has been demonstrated. Utilizing this process, devices with efficiencies of 13% has been fabricated with a low iron soda lime glass (3"x3") with ant-reflection coatings. The process has been extended to large area devices (16" x16" substrate size). After CdCl$_2$ treatment, devices showed V_{oc} > 700 mV and J_{sc} > 20 mA/cm^2. This performance is similar to the performance of small area devices which showed good stability. Also we have employed many methods including Spectroscopic Ellipsometry (SE) as a non-destructive tool to characterize CdS/CdTe heterojunction specifically studying the effects of processing on the optical properties of the thin-film layers.

2:20pm **EN+AS+TF+VT+NC-WeA3 Molecular Dynamics and Experimental Investigations of Reversible Absorption of H$_2$, CH$_4$, and CO$_2$ in Calixarenes**, ***J.L. Daschbach***, *P.K. Thallapally, B.P. McGrail, L.X. Dang*, Pacific Northwest National Laboratory

Molecular solids based on calix[4]arenes have been shown to exhibit reversible absorption of small gas molecules, and remain stable, at temperatures above 400 K. As such, they are interesting as prototypical molecular systems for storing guests like hydrogen and methane, and potentially selectively trapping carbon dioxide in hydrocarbon based systems. We have conducted high-pressure and temperature gas absorption experiments with low density p-tert-butylcalix[4]arene (TBC4) in which calixarenes are slightly offset to form a skewed capsule with an estimated free volume of 235 Å^3. Hydrogen and methane absorption near 300 K were 1.0 and 2.2 wt% respectively. Carbon dioxide is absorbed at a 1:1 loading per TBC4 molecule at 3 atm. In recent work we have shown that the high density form of TBC4 will absorb CO$_2$ at 3 atm, undergoing a phase transformation in the process, and it can be reversibly cycled between these states using moderate combinations of temperature and pressure. Somewhat surprisingly, we have found that TBC4 can be loaded with up to two CO$_2$ per TBC4 molecule. We have used empirical molecular simulation techniques to study the dynamics of CO$_2$ and CH$_4$ in TBC4. The rattling motion of the absorbed small molecules have been characterized using velocity autocorrelation. The coupling to the host lattice is probed by temperature dependent calculations. The effects of increased loading are studied up to the 2:1 loading of CO$_2$, and clearly show differences in the host-guest coupling for molecules outside the cavities relative to the cage entrapped molecules. The free energy of absorption of CH$_4$ and CO$_2$ is studied under range of conditions by thermodynamic integration. These data support the experimental observations that these molecules can be reversibly absorbed at moderate pressures and temperatures.

2:40pm **EN+AS+TF+VT+NC-WeA4 Sustainable Energy and the Role of Advanced Electron Microscopy**, ***D.J. Stokes***, *B. Freitag, D.H.W. Hubert*, FEI Company, The Netherlands

Advanced electron microscopy, using the latest aberration-corrected and monochromated (scanning) transmission electron microscopes (S/TEM) is helping to bring new scientific and technological insights that are advancing progress in areas such as health, energy and the environment. Specifically, with global energy resources under increasing pressure, great efforts are being made to develop new nanomaterials that will lead to renewable energy sources and increased efficiency, to sustain energy supplies into the long term future whilst helping to preserve and protect the Earth's environment. To get there, we are being taken to atomic realms such that, to tailor new nanomaterials for specific functions, it is essential to precisely understand, accurately control and truly visualize structure-property relations at an unprecedented level. The atomic structure of nanomaterials and the energy needed for their function can be optimized by the fundamental understanding of catalytic behavior of nanoparticles and by a better understanding of the physical properties on the atomic level of systems such as solar cells, fuel cells and light sources (LEDs). This requires advanced tools that allow us to see down to the individual atoms and sense their chemical environment. It means having the ability to perform experiments in situ, to follow specific chemical reactions and physical processes, and there is a need to be able to do this in multi-dimensions, both spatial and temporal. We discuss and demonstrate the role of advanced electron microscopy in answering some of the most challenging and fundamental scientific questions in the field of catalysis, ranging from electron tomographic 3D reconstruction of the crystal facets of catalyst nanoparticles and aberration-corrected imaging correlated with density functional theory for elucidating precise atomic positions, to in situ studies of catalytic reactions for visualization of otherwise unseen intermediate nanostructures. These examples relate the nanostructures investigated to the property manifested by that particular structure, enabling us to gain new information about catalytic function.

3:00pm **EN+AS+TF+VT+NC-WeA5 Investigation of Low Temperature-Annealed TiO$_2$ Electrodes Prepared by Sol-Gel Technique for the Fabrication of Dye-Sensitized Solar Cells**, *M.F. Hossain, S. Biswas, M. Shahjahan, A. Majumder,* ***T. Takahashi***, University of Toyama, Japan

Dye sensitized solar cells (DSCs) are considered as a low cost alternative to conventional p-n junction solar cell devices. The high light-to-energy conversion efficiencies achieved with dye sensitized solar cells (DSCs) may be attributed to the nanoporous TiO$_2$ electrode. Among the various techniques for the preparation of TiO$_2$ photo-electrode, the relatively simple sol gel method is the most widely used because of its ability to obtain films with tailored properties on large, curved substrates, and also it is a low temperature process. Crystallinity is one of the key factors behind the photovoltaic performances of TiO$_2$; therefore achievement of better crystallinity at relatively low temperature is an important issue. In our present study, the titanium dioxide porous films were deposited on SnO$_2$:F coated glass by sol–gel technique; where, an alcoholic solution of tetra-buthylorthotitane was hydrolysed in a water/alcohol/acetic acid mixture. These films were transparent and crack free. For this investigation; annealing temperature and number of coating layers were varied. All the films were annealed at different annealing temperatures, ranging from 350 to 500°C. Sufficiently good crystalline samples were obtained by annealing at 350°C. The X-ray diffraction patterns of all TiO$_2$ films confirmed the anatase structure. The surface morphology of the films has been observed by atomic force microscope and field emission scanning electron microscope. The morphology of TiO$_2$ thin films strongly depends on annealing temperatures and number of coatings. Incident photon-to-current conversion efficiency is calculated for all the solar cells with different TiO$_2$ thin films to evaluate the economic viability of this technique. It has been observed that the photoelectric conversion efficiency of DSCs increases with the optimization of annealing temperature as well as with the increase of the numbers of layers.

Nanometer-scale Science and Technology
Room: 311 - Session NS+NC-WeA

Nanoscale Devices and Sensors
Moderator: S. Evoy, University of Alberta, Canada

1:40pm **NS+NC-WeA1 CNTFET: Carbon Nanotube Power Transistors**, ***B. Lim***, *B. Hunt, E. Wong, M. Bronikowski, S. Jung*, Atomate Corporation **INVITED**

The carbon nanotube field effect transistor [CNTFET] has the potential to deliver functional performance and efficiency that exceed silicon-based power devices by more than an order of magnitude. The high carrier mobility, high power density, high thermal conductivity, and low on-state resistance of the semiconducting single-walled carbon nanotube can result in a significantly smaller device that operates much cooler and consumes less power. Furthermore, new applications not possible with silicon MOSFET devices can be enabled because of unique characteristics of the CNTFET architecture. This talk will cover the innovative architecture of an early proof-of-concept CNTFET developed by Atomate and some of the challenges to commercial success and acceptance.

2:20pm **NS+NC-WeA3 Transition Between Particle Nature and Wave Nature of Hole in Single-Walled Carbon Nanotube Transistor by Gate Voltage**, ***K. Matsumoto***, Osaka University, Japan

We have succeeded in fabricating the convertible transistor which can operate as a resonant tunneling transistor (RTT) and also as a single hole transistor (SHT) using single-walled carbon nanotube (SWNT) by modulating the strength of the coupling between the electrode and the quantum island using the gate voltage that changes the thickness of Schottky barrier, in which RTT is the device using wave nature of hole and SHT is the device using particle nature of hole. The sample has a SWNT contacted to the source and the drain electrode by Ti metal. The distance between both electrodes is 73 nm. The gate electrode is in the back side of Si substrate. Contour plot of differential conductance characteristic as a function of gate voltage and drain voltage at 7.3 K is measured. When the gate voltage VG is relative low at around VG =-10 V to -15, the plot clearly shows the Coulomb diamond characteristic. This means the device shows the particle nature of hole. Additionally, line shape quantum levels are appeared at both sides of Coulomb diamonds. The Coulomb diamonds are getting blurred with negatively increasing gate voltage around VG=-15 V to -20 V. The quantum levels are, however, still remaining. Finally, at relative high gate voltage at VG=-20 V to -25 V, Coulomb blockade is lifted and Coulomb diamonds are disappeared. However, quantum levels are still remaining, and current oscillate owing to the resonant tunneling through quantum levels. Thus, only by modulating the gate bias, the device shows the Coulomb blockade phenomena, that means the particle nature of hoe at low gate bias, and also shows the coherent oscillation of hole that means the wave nature of hoe at negatively high gate bias.

2:40pm **NS+NC-WeA4 Charge Transport in SWCNT Transparent Contacts**, ***T.M. Barnes***, *J.L. Blackburn, R.C. Tenent, M.J. Heben, T.J. Coutts*, National Renewable Energy Laboratory

Single-wall carbon nanotube (SWCNT) networks exhibit high electrical conductivity and optical transparency, allowing their use as transparent electrical contacts in photovoltaics and other opto-electronic devices. They are particularly well suited to applications requiring a contact that is flexible, hole-conducting, or solution processible. We have shown in previous work that these materials function well as transparent contacts in a variety of organic and inorganic photovoltaic devices. However, their opto-electronic performance still lags that of the best transparent conducting oxides. Improving charge transport through the networks should enable higher conductivity and the use of thinner (and more transparent) networks. In this work, we focus on the conductivity mechanisms of transparent SWCNT networks as a function of the ratio of metallic to semiconducting tubes and chemical doping. Conductivity in SWCNT networks is influenced by a variety of factors. Junctions between the semiconducting and metallic tubes are thought to strongly affect network conductivity, but this is not well understood. Following the method of Arnold,[1] we have produced films that contain a range of tube conductivity types varying from strongly semiconductor enriched (96%) to strongly enriched in metallic tubes (96%) to study the effect of tube-type polydispersity on transport. Temperature dependant resistivity measurements are combined with spectrophotometry to characterize the networks revealing that both intentional and unintentional doping has a strong effect on network conductivity, regardless of tube-type. Tube-type and tube quality do appear to affect the high temperature stability of the conductivity. We present a model effectively describing the conductivity mechanism at low temperature and explore the factors controlling conductivity at higher temperatures.

[1] Arnold, M. S.; Green, A. A.; Hulvat, J. F.; Stupp, S. I.; Hersam, M. C., Sorting carbon nanotubes by electronic structure using density differentiation. Nature Nanotechnology 2006, 1, 60-65.

3:00pm **NS+NC-WeA5 A Single-Walled Carbon Nanotube Thermal Sensor Integrated with CMOS Circuitry**, ***M.R. Dokmeci***, Northeastern University, *S. Sonkusale*, Tufts University, *C.-L. Chen*, Northeastern University, *V. Agarwal*, Tufts University

In this paper we present Single-Walled Carbon Nanotube (SWNT) thermal sensor integrated with CMOS integrated circuits. The chip was fabricated using the AMI 0.5um CMOS Technology. Electrical measurements from the assembled SWNTs yield ohmic behavior with a two-terminal resistance of ~44KOhms. The SWNTs were incorporated on to the CMOS chip as a feedback element of a two-stage Miller compensated high gain operational amplifier. The measured small signal ac gain (~1.95) from the inverting amplifier confirmed the successful integration of carbon nanotubes with the CMOS circuitry. After assembly, the thermal behavior of the CNT-CMOS system yield a TCR value of -0.33 measured through the operational amplifier indicating that the SWNT device has potential applications in temperature sensing. This paper lays the foundation for the realization of next generation integrated nanosystems with CMOS integrated circuits. Recently, numerous approaches for the synthesis and device applications of nanoscale materials such as nanotubes and nanowires are being demonstrated. Despite the exciting preliminary success of nanowire research, one of the limitations is the absence of integration of the nanostructures with CMOS circuitry. The heterogeneous integration of nanostructures with readout electronics not only improves the signal to noise ratio, but also provides a means to record, buffer and amplify the measured signals on the same chip leading to highly sensitive nanostructure based nanosystems. The nanotube-CMOS assembly (based on Dielectrophoresis) utilized electrodes realized from the metal 3 layer of CMOS process and did not require any extra processing steps. SEM imaging results and the I-V measurements both confirm the controlled placement of nanotubes on to the electrodes attached to the CMOS circuitry. The measured ac gain of the operational amplifier (~1.95) matched the calculations well (2). SWNTs have a significant thermal response. The measured gain from the op-amp at 100ºC was ~1.26 which corresponded to a decrease in SWNT resistance. In summary, we have demonstrated a technology for integrating carbon nanotubes on to functional CMOS circuitry. The technique is simple, versatile and high yield with potential applications for the realization of nanotube based bio and chemical sensors fabricated on CMOS electronics.

4:00pm **NS+NC-WeA8 Coherence and Polarization Properties of Thermal Radiation Emitted by Metallic Nanowires**, ***L.J. Klein***, IBM TJ Watson Research Center, *Y.Y. Au, S. Ingvarsson*, University of Iceland, *H.F. Hamann*, IBM TJ Watson Research Center

We investigate the coherence properties of the thermal radiation emitted from resistively heated individual metallic nanowires. High aspect ratio nanowires are fabricated by e-beam lithography with widths from 60 nm up to 2 µm, dimensions well below the wavelength of the emitted thermal radiation. The coherence of thermal radiation is probed by self interfering the radiation from the nanowire with its image in a movable mirror. As the mirror approaches the nanowire, well defined interference fringes are observed. From the fringe visibility we extract the coherence length of the emitted thermal radiation. For nanowire width above 2 um the coherence length of the thermal radiation emitted by nanowires is similar to blackbody radiator. As the nanowire gets narrower an increased fringe visibility and higher coherence length is measured. A lower bound for the coherence length for thermal radiation is estimated to be 30 µm for very narrow metal nanowires well above 4 µm for the blackbody radiation.Furthermore the coherence length is increasing as the temperature of the nanowire is decreased. For very narrow nanowires the thermal radiation is polarized with very high extinction ratio. Either changing the width of the nanowire or the nanowire temperature the polarization can be rotated from a longitudinal to a tranversal direction to the long axis of the nanowire. Both the increased coherence and polarization of the thermal radiation can be related to correlation of the charge fluctuation and charge confinement in narrow structures. We discuss various approaches to further increase the coherence of the thermal radiation emitted by nanowires and their applications as sub-wavelength coherent infrared light sources.

4:20pm **NS+NC-WeA9 Microwave Conductance of Silicon Nanowires**, ***M. Lee***, *C. Highstrete*, Sandia National Laboratories, *A.L. Vallett, S.M. Eichfeld, J.M. Redwing, T.S. Mayer*, The Pennsylvania State University

The electrodynamic response of semiconductor nanowires across radio- to microwave frequencies is of great interest to both nanomaterial physics and high-frequency device applications of nanowires. It is of particular interest to highlight differences between nanowire and bulk characteristics of the same nominal material. We present measurements of conductance spectra on undoped, p-type, and n-type silicon nanowire (SiNW) arrays from 0.1 to 50 GHz at temperatures between 4 K and 293 K. Highly crystalline SiNWs were synthesized by VLS growth, assembled into arrays numbering between 11 to >50,000 NWs on co-planar waveguides, and measured using microwave vector network analysis. The complex conductance of all doped SiNW arrays was found to increase with frequency f following a sub-linear power law f^s, with $0.3 \leq s \leq 0.4$, and to agree with the expected Kramers-Kronig relation between real and imaginary parts of the conductance. This frequency dependence was independent of the number of SiNWs, while the conductance magnitude roughly scaled with the the number of SiNWs in the arrays. Such a sub-linear frequency dependent conductance is inconsistent with conventional Drude conductivity seen in bulk doped silicon, but is consistent with behavior found universally in disordered systems, although with an unusually small value of s. The magnitude of the microwave conductance was also observed to be sensitive to exposure to air, with p-type SiNWs becoming more conductive and n-type becoming less conductive upon venting the vacuum test chamber to air. We speculate that probable cause of the inferred disorder arises from Si/SiO_x interface states dominating the conduction due to the high surface-to-volume ratio and cylindrical geometry of the nanowires. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. Work at Penn State was supported in part by NSF MRSEC: Center for Nanoscale Science Grant # DMR-0213623, and NSF NIRT Grant # ECCS-0609282.

4:40pm **NS+NC-WeA10 A Quantitative Single-Molecule Analysis of Thioether Rotors and Motors**, ***E.C.H. Sykes***, *A.E. Baber, H.L. Tierney*, Tufts University

We have conducted a fundamental, single-molecule study of the motion of a set of thioethers supported on Au surfaces. These molecules constitute a simple, robust system with which to study molecular rotation as a function of temperature, applied field, and the proximity of neighboring molecules. Low-temperature scanning tunneling microscopy has allowed us to measure the rotational energetic barriers and pre-exponential factors of a set of thioethers. Our results reveal that ratcheting of the second carbon of the alkyl chain over the surface is responsible for the barrier. Through a series of controlled manipulation experiments we have switched the rotation on and off reversibly by altering either the electric field of the tip or by moving the molecules towards or away from one another. The thioether backbone constitutes an excellent test bed for studying the details of both thermally and electrically driven molecular rotation at the single-molecule level.

5:00pm **NS+NC-WeA11 Surface Modified Resonant Cantilevers for Specific Bacterial Detection**, ***A. Singh***, University of Alberta, Canada, *N. Glass, L. Gervais, M. Gel,* National Institute for Nanotechnology NRC, Canada, *M. Tolba, L. Brovko, M. Griffiths,* University of Guelph, Canada, *S. Evoy*, National Institute for Nanotechnology NRC, Canada

Bacteriophages are class of viruses that infect bacteria and use them as a host for replication. These phages are highly bacterial-strain specific and thus have the potential to be used as naturally sensitive and selective probes for the detection of pathogens. We have already reported the use of the biotin-streptavidin affinity to immobilize biotinylated phages onto gold surfaces. However, the need of genetic modification limits the versatility of this approach. Thus, there is a need to develop a simple universal process to immobilize phages onto sensor surfaces. We studied different surface modification protocols for gold substrates and their efficiency to capture phages and subsequently the bacteria was analyzed by using SEM and Fluorescence Microscopy. Wild type T4 phage was chosen as the model system for the study with E. coli EC12 strain as the host bacteria. Control experiments were performed with 3 non-host bacterial strains (E. coli 6M1N1, NP 30 and NP 10) to ensure specificity and selectivity of the system. The thiol binding chemistry on gold surfaces was utilized to modify the surface by using cysteine and cysteamine. The results revealed that the gold surfaces modified with cysteine or cysteamine and further activated by treatment with gluteraldegyde enables best phages density and bacteria capture as compared to other modifications. The SEM study for phage immobilization shows that a surface density of 15 ± 3 phages/µm2 was obtained. In our previous work, the biotin-streptavidin interaction was used to immobilize biotin expressing genetically-engineered phages which gave us a surface density of 10 ± 5 phages/µm2. Thus, the surface modification of the substrate enables a better phage density. The protocol was then duplicated on to a gold-coated cantilever surface, which again showed successful phage immobilization and subsequent bacterial capture. Microcantilever-based detection has been shown to have a mass sensitivity equivalent to that of a single bacterium. The shift in the resonance peaks of the cantilever, before and after the treatment of phage immobilized surface to bacteria, has been used as a measure to confirm bacterial capture. Thus, we illustrate a universal approach towards specific capture and detection of pathogenic bacteria, which could be potentially be employed in numerous sensing platforms such as microresonators, surface plasmon resonance, and quartz-crystal microbalance.

5:20pm **NS+NC-WeA12 Scanning Probe/Scanning Electron Microscope for In-Situ Nanoscale Experiments Based on a Thermally-Actuated, Piezoresistive Cantilever Sensor under Dynamic Frequency Control**, ***D.F. Ogletree***, Lawrence Berkeley National Laboratory, *Tzv. Ivanov, Y. Sarov, I.W. Rangelow*, Technical University of Ilmenau, Germany

A scanning probe microscope has been integrated into a variable-pressure scanning electron microscope for in-situ nanoscale experiments. The heart of the instrument is a self-sensing, self-actuated cantilever[1] oscillated at resonance for non-contact dynamic force or tapping mode imaging. We have employed piezoresistive readout and thermally driven bimorph actuation. The integrated Si tips have been formed at the end of the cantilever by a micro-machining process. A digitally-synthesized sine wave of variable frequency and amplitude excites the cantilever by driving an integrated resistor which generates thermal stress. Lever deflection is monitored by an integrated piezoresistive sensor, and the SEM is used to calibrate the sensor response. A commercial digital phase-lock loop controller[2] adjusts the drive signal to maintain a constant oscillation amplitude and fixed phase shift relative to the drive frequency. A lab-built piezo scanner including a lateral translation system and a commercial nanotranslator for the tip approach complete the system. The system performance and noise levels will be compared for operation at the first, second and third resonant modes of the cantilever sensor, and the effects of ambient gas pressure will be discussed.

[1] Ivo W. Rangelow, Microelectronic Engineering 83 (2006) 1449–1455.

[2] PLLpro, RHK Technology, Inc., Troy, Michigan, USA.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Novel nanostructured architectures are being explored for a wide range of applications including mimicking bioadhesive pads on insects and geckos, RF-microelectronics switches with robust compliant carbon nanotube films, and energy harvesting from friction by rubbing nanostructured piezoelectric coated fibers together. Developing an understanding of how these collections of nanostructured materials behave collectively requires experimental approaches at micron length scales. Experimental examination of the mechanics and tribology of materials in this intermediate regime can be influenced by macroscale phenomena (such as wear and interfacial transfer film formation during sliding) as well as phenomena more often associated with nanoscale contacts (such as significant adhesion contributions). In this talk, we will present tribological and mechanical analysis of columnar nanostructured poly-(p-xylylene) (PPX) thin films. Experiments are performed using nanoindentation and microtribology tools to examine the effects of load, counterface material, roughness, and transfer film formation on microscale tribological response. The PPX films are structurally anisotropic, consisting of nanowires oriented at various angles with respect to the surface normal. Sliding friction experiments performed at discrete angles with respect to the nanowire orientation resulted in relatively uniform friction behavior but significant differences in deformation response of the films. A simple mechanical model is proposed to explain the observed depth anisotropy. The value of monitoring both friction and contact depth simultaneously will be discussed and evaluated in context of materials exhibiting highly anisotropic mechanical properties.

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

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

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

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

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

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

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

Nanometer scale metallic contacts which can be directly deposited on planar substrates are of growing importance in view of future applications involving the integration of molecular electronics with current silicon technology. Here, a method which may provide well defined nanogap electrodes of predetermined spacing in a reproducible manner, without the need of sequential direct writing techniques, would be highly advantegous. We present a novel technique using direct high-resolution metal nanotransfer printing and demonstrate its capability to fabricate nanogap electrodes of predetermined spacing on a solid substrate such as silicon. The one-step transfer process is economical, simple and fast, and preserves the mold for manifold transfer. Using molecular beam epitaxy (MBE) a sandwich-like structure is grown with monolayer precision, comprising few nanometer thick GaAs layers embedded in AlGaAs. This structure is cleaved atomically flat perpendicular to the <110> crystallographic direction. Subsequently, the exposed GaAs layers are wet chemically etched thereby generating a 3D grating structure with nanometer-resolution at their edges. This structure serves as mold for nanotransfer printing: By coating the grating surface with a metallic thin film of PdAu/Ti (7/5 nm) and pressing the mold against a Si/SiO$_2$ substrate the patterned PdAu/Ti sandwich structure is directly transferred onto the surface. This one-step process does not require any flexible buffer layer or additional organic adhesion promoters. We report on a series of successful transfer experiments using different multi-line molds with varying aspect ratios and linewidths down to below 10 nm. In particular, we demonstrate electrically functional PdAu metal electrode pairs with separations down to 25 nm, featuring lead resistances of the order of kΩ and gap isolation in excess of 50 GΩ up to 2 Volts.

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

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

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

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

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

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

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

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

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

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

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

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

Nanometer-scale Science and Technology
Room: 311 - Session NS+NC-ThM

Nanoscale Assembly
Moderator: L.E. Ocola, Argonne National Laboratory

8:00am **NS+NC-ThM1 Confinement of Electrochemical Metal Deposition on the Nanometer Scale by a Hydrogen-Bonded Network/SAM Hybrid Structure**, ***C. Silien****, M.T. Räisänen,* University of St. Andrews, UK, *R. Madueño,* Universidad de Córdoba, Spain, *M. Buck*, University of St. Andrews, UK

The combination of supramolecular networks with thiol-based self-assembled monolayers (SAMs) offers interesting opportunities as the flexibility in surface functionalisation afforded by SAMs can be carried to an unprecedented level of precision. The scope for nanotechnological applications broadens even further by processing these hybrid systems in an electrochemical environment. Recently we have shown that an extended bimolecular network on Au(111) with a periodicity of 3.5 nm can be prepared from a solution of perylene-3,4,9,10-tetracarboxylic di-imide (PTCDI) and 1,3,5-triazine-2,4,6-triamine (melamine) and that this open hexagonal structure is sufficiently robust to act as template for thiol adsorption.[1] Proper control of the preparation parameters allows filling of the network pores without altering the framework. This leads to patterned self-assembled monolayers that reflect the periodicity and symmetry of the network with islands of thiol molecules kept apart by the PTCDI-melamine backbone. This hybrid structure can then be used as nanoscaled template for the electrodeposition of metal. Using scanning tunneling microscopy the underpotential deposition (UPD) of Cu was investigated where a monolayer of Cu is intercalated at the molecule-substrate interface. In contrast to continuous thiol SAMs where Cu UPD originates at major defects in the SAM and spreads by interfacial diffusion,[2] the hybrid structure acts as a barrier against interfacial diffusion and, thus, confines metal electrodeposition to the thiol-filled cells.[1] As a result a regular pattern forms where metal UPD islands are separated by the PTCDI-melamine framework.

[1] Madueño, R.; Räisänen, M.; Silien, C.; Buck, M. Nature 2008 (in print).

[2] Silien, C.; Buck, M. J. Phys. Chem. C 2008, 112, 3881-3890.

8:20am **NS+NC-ThM2 FIB Induced Self-Assembly of InAs Quantum Dots**

***M.J. Noordhoek**, J.Y. Lee, H. Mckay, A. Dehne, P. Rudzinski, J.M. Millunchick*, University of Michigan - Ann Arbor

The use of various patterning techniques for self-assembly of highly regular and dense quantum dot arrays are being pursued for applications in opto-electronics and quantum computing. In this work, we use a novel in-vacuo focused ion beam and growth system to pattern an array of holes on GaAs for subsequent deposition of InAs quantum dots. Exposure of GaAs(001) substrates to a 30keV 10pA beam of Ga+ ions as a function of pitch $140<L<547$nm and dwell time $200<t<1600$ microseconds results in well defined arrays of nanometer deep holes. The diameter ($20<d<60$nm) and depth ($0.7<z<4.4$nm) of these holes varies somewhat with dwell time and pitch according to atomic force microscopy. The fidelity of the hole array itself depends on dwell time per spot, and not as strongly on the pitch of the pattern. Growth of InAs upon these arrays shows that quantum dots nucleate exclusively at the hole edges. For example, holes spaced 140nm apart and fabricated with a dwell time of 1600 microseconds results in holes that are 38nm in diameter and 4nm deep. Growth of 1.8ML of InAs upon this pattern of holes results in multiple quantum dots that are on average 30nm in diameter nucleated around the edges. Deposition of additional InAs results in coalescence of these dots such that they cover the hole, resulting in quantum dots that are 60nm, much larger than quantum dots assembled without a pattern. Liquid nitrogen temperature photoluminescence studies show that the peak emission varies with deposited thickness and ion dose.

8:40am **NS+NC-ThM3 Fabrication and Characterization of Conjugated Organosilicon Nanostructures with UHV STM and X-Ray Spectroscopy**

***M.A. Walsh**, J.-C. Lin, J.-H. Kim*, Northwestern University, *K.H. Bevan,* Purdue University, *G.Y. Stokes, F. Geiger, S.T. Nguyen, M.J. Bedzyk, M.C. Hersam*, Northwestern University

Functionalized organic nanostructures on silicon present unique opportunities for integrating molecular electronic devices and sensors with conventional microelectronics. Of particular interest are 1-alkyne molecules since they have been shown to retain pi character following covalent attachment to the silicon surface, thus creating fully conjugated organosilicon nanostructures.[1] In an effort to quantify the structure and chemistry of 1-alkyne molecules mounted on silicon surfaces with atomic-scale spatial resolution, this study probes phenylacetylene and 1-bromo-4-ethynylbenzene adlayers on the Si(100)-2x1:H surface with ultra-high vacuum (UHV) scanning tunneling microscopy (STM) and complementary synchrotron X-ray techniques. UHV STM images reveal well-ordered one-dimensional nanostructures consisting of 1-alkynes that are aligned with the underlying silicon dimer rows. This observed alignment is consistent with the radical mediated chain growth reaction mechanism that has been previously observed for 1-alkenes on silicon. In an effort to provide further evidence in support of this mechanism, a suite of additional surface science techniques and theoretical calculations have been applied to this system. Specifically, the bromine tag on 1-bromo-4-ethynylbenzene can be probed with synchrotron X-ray radiation.[2] For example, X-ray photoelectron spectroscopy confirms that the bromine moiety remains intact following attachment to the silicon surface. Additional X-ray techniques, such as X-ray standing wave (XSW), X-ray fluorescence (XRF), and X-ray reflectivity (XRR), allow the bromine position to be triangulated with sub-angstrom precision. In particular, these X-ray measurements yield a bromine height of 8.85 angstroms above the bulk-like silicon, which agrees well with theoretical values determined by periodic density functional theory. The agreement between the theoretical and experimental results provides strong evidence for the expected sp2 hybridization of the terminal carbon-carbon bond. Overall, this study reveals 1-alkynes as a promising chemistry for forming conjugated organosilicon nanostructures on technologically relevant silicon surfaces.

[1] Cicero, R.L., M.R. Linford, and C.E.D. Chidsey, Langmuir, 2000. 16(13): p. 5688-5695.

[2] Basu, R., et al., Langmuir, 2007. 23(4): p. 1905-1911.

9:00am **NS+NC-ThM4 The Driving Forces Underlying the Formation of Chiral Domains of Fluorinated Diacids on HOPG**

*S.N. Patole, **C.J. Baddeley**, M. Schuler, D. O'Hagan, N.V. Richardson*, University of St Andrews, UK

Long chain hydrocarbons were designed and synthesized with carboxylic acid functionalities at each end and two amide linkages in the central region of the molecule. The amide linkages are separated by two –CHF- units. These units are each chiral centres and the molecules were synthesized as a racemic mixture of (R,R) and (S,S) species. We report an STM investigation of the adsorption of these molecules onto highly oriented pyrolytic graphite (HOPG) from phenyloctane solution. There are a number of motivations for this study. Firstly, we are interested in establishing control over 2-D assembly via intermolecular H-bonding interactions. Secondly, we assess the use of fluorine atoms as contrast agents in STM to aid the elucidation of structural aspects of complex molecule adsorption at surfaces. Thirdly, we are interested in the influence of chirality on the ordered adlayers produced on HOPG. The molecules adopt a flat lying geometry on graphite. The conformation of the central (fluorinated) section of the adsorbed molecular species differs significantly from the preferred geometry in the crystal structure. We demonstrate that the ordered molecular assemblies produced are dictated by a combination of effects including the preference of carbon backbones to align along high symmetry directions of HOPG; steric constraints imposed by the C-F bonds at the chiral centres and intermolecular H-bonding. We outline a heirarchy of effects which determine the lateral stacking and head-to-head interactions and explain the influence of stereochemistry on the molecular ordering. We conclude that enantiomerically pure 1-D domains are produced and examine the behaviour at the boundaries between domains of each enantiomer.

9:20am **NS+NC-ThM5 Potential-Controlled Force Curve Measurements between Electroactive Self-Assembled Monolayers**

***Y. Yokota**, T. Yamada,* RIKEN (The Institute of Physical and Chemical Research), Japan, *M. Kawai*, RIKEN and The University of Tokyo, Japan

It has been known that atomic force microscopy (AFM), in addition to providing topographic information, can be used to discriminate surface functional groups.[1] One of the most established methods is based on the surface sensitivity of the adhesion force between the tip and sample. Several groups have tried to electrochemically modify the interfacial properties by applying the appropriate potential.[2] We present the force curve measurements between electroactive ferrocene (Fc)-terminated Self-assembled monolayers (SAMs) under independent control of the tip and sample potentials. From the cyclic voltammetry of Fc SAM, the electronic states of Fc moieties in each force curve measurement were characterized.[3] The adhesion force of Fc SAM was drastically changed with the oxidation state of the Fc moieties (Fc or Fc^+). According to the previous wettability measurements, hydrophobicity of the Fc-terminated SAMs is decreased with the oxidation of Fc moieties.[4] Because the adhesion force in aqueous solutions is largely determined by hydrophobicity, the oxidation-state dependence of the hydrophobicity is responsible for the adhesion force change. We performed two control experiments using methyl (CH_3) and amino (NH_3^+)-terminated SAMs. Unlike in the case of Fc SAM, the force curves, both the approach and retraction curves, did not change with the applied potential. This indicates that the force curve measurements in this study are largely regulated by the effects of surface functional group rather than charging of double layer. Although Fc^+ and NH_3^+ SAMs contain almost the same amount of functional groups, their repulsive forces between the tip and sample considerably differed depending on the surrounding environment of counter anions. These results demonstrate that this AFM-based technique can be a powerful tool for investigating the ion pair formations.

[1] A. Noy et al., Annu. Rev. Mater. Sci. 27, 381 (1997).

[2] H.-C. Kwon et al., J. Phys. Chem. B 109, 10213 (2005).

[3] Y. Yokota et al., J. Phys. Chem. C 111, 7561 (2007).

[4] N. L. Abbott et al., Langmuir 10, 1493 (1994).

9:40am **NS+NC-ThM6 Self-Assembly of Nanostructures and Nanocomposites using De Novo Designed Helix- Loop- Helix Polypeptides**

***D. Aili**, K. Enander,* Linköping University, Sweden, *L. Baltzer,* Uppsala University, Sweden, *B. Liedberg*, Linköping University, Sweden

Self-assembly has emerged as a promising and powerful technique for fabrication of complex hybrid materials and nanocomposites. This contribution will discuss how folding of a set of de novo designed polypeptides can be utilized for the assembly of fibers, fibrous nanostructures and gold nanoparticles. The 42-mer polypeptides fold into four-helix bundles upon dimerization. The peptides are rich in either Glu or Lys which render them a high negative or positive net charge, respectively. Charge repulsion prevents homodimerization at neutral pH while promoting heterodimerization through the formation of stabilizing salt bridges. For the Glu rich polypeptide, homodimerization can be induced at acidic (pH<6) or by addition of certain metal ions, such as Zn^{2+}.[1] The polypeptides have a single Cys in the loop region to facilitate directed immobilization onto gold substrates. The Cys can also be utilized to connect two polypeptides via a disulphide bridge. The disulphide-linked polypeptides spontaneously and rapidly assemble into micrometer long fibers with a diameter < 5 nm as a result of a propagating association mediated by folding. In addition, the fibers have been observed to assemble into highly symmetric nano-rings. Furthermore, the polypeptides enable reversible, folding induced assembly of gold nanoparticles with defined interparticle distances.[1] Aggregation of polypeptide functionalized nanoparticles can be induced in a number of ways utilizing the highly specific interactions involved in both homodimerization and hetero-association. Furthermore, particle aggregation can be utilized to induce folding of the immobilized polypeptides. Helix-loop-helix polypeptides can also be utilized as a robust scaffold, or synthetic receptor, for biosensor applications.[2] The sensor scaffold was, as a proof of concept, site-selectively modified with a benzenesulfonamide moiety that provides a specific recognition site for Human Carbonic Anhydrase II (HCAII). Gold nanoparticles functionalized with the sensor polypeptide enabled simple colorimetric detection of HCAII.

[1] D. Aili, K. Enander, J. Rydberg, I. Nesterenko, F. Björefors, L. Baltzer, B. Liedberg, J. Am. Chem. Soc. 2008, 130, 5780-5788.

[2] K. Enander, G. T. Dolphin, L. Baltzer, J. Am. Chem. Soc. 2004, 126, 4464.

10:40am **NS+NC-ThM9 Non-IPR C_{60} Solids**, ***D. Löffler***, Universität Karlsruhe, Germany, ***N. Bajales***, Universidad Nacional del Litoral-CONICET, Argentina, ***M. Cudaj***, ***P. Weis***, ***A. Böttcher***, ***M.M. Kappes***, Universität Karlsruhe, Germany

Thin monodisperse films consisting of primarily non-IPR C_{60} isomers (IPR = Isolated Pentagon Rule) have been generated by depositing vibronically excited C_{60} ions on HOPG and subsequently sublimating the undesired IPR $C_{60}(I_h)$ isomer from the deposited mixture. The deposition procedure is based on UHV-compatible soft-landing of mass-selected carbon cluster ions on substrates (Low Energy Cluster Beam Deposition, LECBD). Beams of non-IPR C_{60} cations were produced by electron-impact mediated heating and ionization of various buckminsterfullerenes. The associated excitation processes activate the Stone-Wales rearrangement of carbon atoms in the cage (S-W), which creates non-IPR sites on C_{60} cages. The relative amount of these S-W isomers, C_{60} (S-W), deposited from the beam of hot C_{60} ions scales with the kinetic energy of electrons used for excitation/ionization. Essentially pure C_{60}(S-W) films were obtained simply by heating as deposited (mixed isomer) films up to ~600 K. This results in the thermal desorption of most IPR cages, $C_{60}(I_h)$. The topography of the resulting films, as studied by means of AFM, is governed by the aggregation of the C_{60}(S-W) cages and reflects intercage bonds constituted by non-IPR sites. These covalent intercage bonds are responsible for the higher stability of the C_{60}(S-W) films as mirrored by a sublimation offset at ~1100 K (compared to $C_{60}(I_h)$ which sublimes at ~ 550 K). In contrast to the characteristic doublet structure of the HOMO-derived band in C_{60} (I_h) films, the valence band of the C_{60}(S-W) films exhibits a triplet with a well distinguishable additional peak at a binding energy of ~2.6 eV. This results from electronic modifications induced by intercage bonds. The C_{60}(S-W) films exhibit a narrower HOMO-LUMO gap than found for $C_{60}(I_h)$ films.

11:00am **NS+NC-ThM10 Plasma Functionalized Surfaces for Chemically Directed Assembling of Luminescent Nanocrystals for Sensing and Optoelectronic Application**, ***E. Sardella***, CNR-IMIP, Italy, ***F.D. Liuzzi***, University of Bari, Italy, ***R. Comparelli***, ***N. Depalo***, CNR-IPCF, Italy, ***A. Agostiano***, University of Bari, Italy, ***M.L. Curri***, ***M. Striccoli***, CNR-IPCF, Italy, ***P. Favia***, ***R. d'Agostino***, University of Bari, Italy

Nanotechnology is increasingly oriented towards the fabrication of devices based on colloidal inorganic nanocrystals (NCs) arranged on a surface. Such interest is justified by the expectation that the controlled assembly of NCs, with relevant size-, shape-, and composition-dependent properties, will open access to unusual collective phenomena relevant to novel technological applications. The chemically-directed assembly of NCs onto substrates allow to obtain functionalities on multiple locations and levels. This approach requires the introduction of suitable functionalities at the NC surface, in order to tune their reactivity without altering the original structural and the chemical-physical properties, also at the interface with substrate, where the NC assembly will take place.[1,2] Several strategies are currently employed to drive NCs assembly onto different substrates, with some limitations. In this work alternative plasma based routes are considered in order to fabricate functionalized substrates with an accurate control on the surface treatment depth. Plasma technology is used to produce customized surfaces irrespectively to the material composition, also to define patterns for the subsequent NC immobilization.[3] The obtained functionalized surface are then exploited to assembly red emitting CdSe@ZnS core shells NCs. The results have successfully demonstrated the effectiveness of such an assembling approach, thus envisioning promising application for the nanostructured materials in optoelectronic and sensing field.[4] Acknowledgements: PRISMA-INSTM 05MADA1 and EC NaPa-NMP4-CT-2003-500120 projects are acknowledged for the financial support.

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11:20am **NS+NC-ThM11 Insertion of Block Copolymers Into the Lithographic Process**, ***P.F. Nealey***, *J.J. de Pablo*, University of Wisconsin-Madison **INVITED**

Self-assembling materials spontaneously form structures with well-defined dimensions and shapes at length scales of interest in nanotechnology. In the particular case of block copolymer materials, the thermodynamic driving forces for self-assembly are small and low-energy defects can get easily trapped. At issue is the extent of direction or guidance required to meet criteria related to perfection and registration for use of such materials in nanofabrication. We explore and develop new materials and processes for advanced lithography in which self-assembling block copolymers are integrated into and advance the performance of the patterning process for semiconductor manufacturing and data storage applications. Through fundamental understanding of the physics and chemistry of interfacial phenomena associated with equilibrating block copolymer films in the presence of lithographically defined chemically nanopatterned substrates, we synthesize and assemble materials to enable fabrication at length scales (3-20 nm) currently not possible. Essential attributes of existing manufacturing practices must be retained, including pattern perfection, registration and overlay, and the ability to pattern device-oriented geometries, but with additional qualities including resolution enhancement and precise control over the shapes and dimensions of patterned features.

Biomaterial Interfaces
Room: 202 - Session BI+TF+MI+NS+NC-ThA

Plasmonics and Magneto/Plasmonics Aimed at Biosensing
Moderator: F. Höök, Chalmers University of Technology, Sweden

2:00pm **BI+TF+MI+NS+NC-ThA1 Optical Meta Materials and Nano Plasmonics**, ***X. Zhang***, University of California, Berkeley **INVITED**

Recent theory predicted a new class of meta structures made of engineered sub wavelength entities - meta "atoms" and "molecules" which enable the unprecedented electromagnetic properties that do not exist in the nature. For example, artificial plasma and artificial magnetism, and super lens that focuses far below the diffraction limit. The metamaterials may have profound impact in wide range of applications such as nano-scale imaging, nanolithography, and integrated nano photonics. I'll discuss a few experiments that demonstrated these intriguing phenomena. We showed, for the first time, the high frequency magnetic activity at THz generated by artificially structured "meta molecule resonance", as well as the artificial plasma. Our experiment also confirmed the key proposition of super lens theory by using surface plasmon. We indeed observed optical superlensing which breaks down so called diffraction limit. I'll also discuss nano plasmonics for imaging and bio-sensing. The surface plasmon indeed promises an exciting engineering paradigm of "x-ray wavelength at optical frequency".

2:40pm **BI+TF+MI+NS+NC-ThA3 Gold and Silver Nanocrescents as Tunable Substrates for Surface Enhanced Infrared Absorption Spectroscopy**, *R. Bukasov*, ***J.S. Shumaker-Parry***, University of Utah

Controlling the size, shape, and orientation of metal nanoparticles in order to tune and optimize the particles' optical properties for specific applications remains a challenge in the field of plasmonics. Tuning the localized surface plasmon resonance (LSPR) wavelength as well as the localized field enhancements is especially important for spectroscopy applications such as surface enhanced Raman spectroscopy (SERS) and surface enhanced infrared absorption spectroscopy (SEIRA). Although SERS has receive a lot of attention with the engineering of nanoparticle-based substrates, the activity in SEIRA development has been less, most likely due to the lack of tunable substrates for the IR spectral region. We describe the development of gold and silver nanocrescents as tunable substrates for SEIRA studies. We use nanosphere template lithography to fabricate gold and silver crescent-shaped structures which exhibit multiple, polarization-sensitive plasmon resonances that are tunable from the visible through the infrared. Large electromagnetic field enhancements are expected due to the sharpness of the crescent's tips and the ability to bring these sharp tips into close proximity to each other. Using the crescent-shaped structures as substrates, we demonstrate the importance of spectral tunability for maximizing signal enhancements in SEIRA. The nanocrescent area normalized SEIRA signal enhancement increases from 7,700 to 46,000 with an increase in the extent of overlap of the nanocrescents' LSPR frequency with the frequency of the probed molecular vibration. The broad tunability of the nanocrescents' LSPR properties makes the structures excellent candidates for a range of spectroscopic and sensing applications including SEIRA.

3:00pm **BI+TF+MI+NS+NC-ThA4 Use of Angle-Resolved SPRi for the Characterization of Protein Binding and Agglomeration Dynamics**, ***M.S. Golden***, *J.A. Ruemmele, A. Whitty, R.M. Georgiadis*, Boston University

Transient protein-protein interactions are essential on almost every level of cellular function. In addition, protein aggregates play various roles in cell signaling pathways and have been implicated in the onset of many neurodegenerative conditions such as Alzheimer's disease. Although various structures of protein complexes have been widely studied, the mechanisms involved in protein binding events are not clearly understood, and the transient dynamics of this formation have proven difficult to study. Investigation of the mechanisms of protein agglomeration and binding, however, is essential to elucidating the role of these structures in diseases. Here we exploit the multi-array quantitative capabilities of angle-resolved surface plasmon resonance imaging (SPRi) to perform kinetic and thermodynamic measurements of protein-protein interactions. Specifically, the agglomeration and small molecule inhibition of Tumor Necrosis Factor (TNF) family members whose primary role is the regulation of immune cells is under investigation. Surface fabrication techniques coupled with multi-channel microfluidic delivery will be employed in order to introduce protein binding partners and small molecules to the surface. Effects of density, orientation, and heterogeneity of surface immobilized protein molecules on protein binding efficiency and kinetics will be investigated and optimum surface fabrication conditions will be identified. In addition, a unique multi-wavelength SPRi approach will be implemented to simultaneously determine dielectric constants and thicknesses of protein layers on a surface. These studies will therefore allow aggregate and nonaggregate structures at the surface to be clearly differentiated. The results of these fundamental studies will allow a broader understanding of how proteins act cooperatively.

3:20pm **BI+TF+MI+NS+NC-ThA5 Sensitivity Enhancement of Surface Plasmon Resonance Imaging by Nanoarrayed Organothiols**, ***P. Lisboa***, *A. Valsesia, I. Mannelli, P. Colpo, F. Rossi*, JRC-European Commission, IHCP, Italy

The implementation of sensor platforms providing high sensitivity of detection is a crucial step for the design of the new analytical device generation for biosensor developments. Designing platform with active/non-actives region at nanoscale has shown already a drastic increase of detection sensitivity.[1,2] The use of organothiols to create nanopatterns has been already studied showing that this type of chemistry is indicated to produce chemical contrasts for bio-applications.[3] In this work, the effect of organothiols-nanopattern in Surface Plasmon Resonance imaging (SPRi) detection was studied. The gold surface of the SPRi chip was divided in two areas, one modified with a chemical nano-contrast based in two different organothiols (thiolated polyethylene oxide (PEO) and Mercaptohexadecanoic acid (MHD) and the other modified uniformly with MHD. The SPRi study was based on the detection of the immunoreaction between Human IgG and anti-Human IgG (Ab specific) by comparing the results obtained with nanostructured and uniform carboxylic surface. First Human IgG was immobilised on the chip and after the recognition of different concentrations of anti-Human IgG was realised. The achieved SPRi signal was higher in the case of the nanostructured areas for all the tested concentrations. Since the active surface with carboxylic functionalities presented only 3% of the total area, one would expect the detection signal to be 3% of the signal obtained for the uniform MHD surface. The fact that the signal from the nanostructures is higher than in the MHD surfaces in SPRi detection is related to an amplification of signal due to the 2D crystalline character of the structures. This type of arrangement presents the geometry of a photonic crystal leading to the interaction between the Surface plasmon polaritron modes and the regular modulation of the dielectric constant of the surface above the gold film modifying the plasmon effect and consequently increasing the measured reflectivity. These results indicate that SPRi detection performance can be improved by the rational functionalisation of the prism surface with 2D crystalline nanopatterns. Moreover adhesive – nonadhesive nanopatterns are recognized to be good platforms for the correct immobilization of the biomolecules on biosensing surfaces.

References

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[2] A. Valsesia, et al., Langmuir 2006, 22, 1763.

[3] P. Lisboa, et al., Applied Surface Science, 2006, 253, 4796.

4:00pm **BI+TF+MI+NS+NC-ThA7 New Developments in Magneto-Plasmonic Devices**, ***C. Clavero***, *J.R. Skuza, K. Yang, R.A. Lukaszew*, College of William and Mary **INVITED**

In recent years Surface Plasmon Resonance (SPR) sensors have been extensively used in bio-sensing applications. SPR is a charge density oscillation at the boundary between a metal and a dielectric material that gives rise to highly confined fields at the interface. As a consequence the SPR excitation condition is very sensitive to changes in refractive index in the dielectric medium and hence to bio-molecules adsorbed at the metal surface. Nevertheless, the required detection sensitivity for low concentrations of small molecules exceeds current SPR sensors. A new kind of sensors combining plasmonic and magneto-optical (MO) properties, i.e. magneto-plasmonic devices, is being actively investigated. In particular, Au-Co-Au trilayers have been found to increase sensitivity in this type of biosensors.[1] This is due to MO activity enhancement in the Co film caused by the high electro-magnetic field created by SPR.[2] We will report on Au-Co-Au thin film tri-layers grown on glass using UHV magnetron sputtering. The optimization of growth conditions and accurate control of films thickness is critical to achieve a remarkable increase in MO activity and hence in overall sensitivity. A practical issue in these multilayer systems is the bad adhesion of Au to glass causing degradation of the sensor when exposed to a water flux. We will show how to circumvent this problem by inserting Cr or Ti thin buffer layers. A different approach to magneto-plasmonic materials, namely fabrication of Au-Co nano-composite materials in thin film form, will also be presented. These materials are expected to exhibit enhanced MO response due to localized surface plasmon resonances (LSP) within the Co nano-particles and also considerable reduction of light absorption associated with ferromagnetic materials thus increasing the overall sensitivity of the bio-sensor. Parameters such as shape, size and inter-particle distance can be tuned to control the optical and magnetic properties of the material. Au-Co nano-composite materials in thin film form were obtained by magnetron sputtering co-deposition of Au and Co where parameters such as Au and Co concentration, deposition temperature and film thickness were accurately controlled. Finally, different optical configurations for the excitation of the surface plasmon resonance will be discussed.

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4:40pm **BI+TF+MI+NS+NC-ThA9 Grafting Thermoresponsive Polymers on Gold Nanoparticles with Atom Transfer Free Radical Polymerization**, ***S. Chakraborty***, *V.H. Perez-Luna*, Illinois Institute of Technology

Thermoresponsive polymer brushes on colloidal gold were formed through Atom Transfer Free Radical Polymerization (ATRP) of N-isopropylacrylamide (NIPAAM) in aqueous media. In this approach, the “grafting from” technique was used with Atom Transfer Radical Polymerization (ATRP) to grow polymer chains from the surface of gold nanoparticles (~20nm). ‘Grafting from’ using the ATRP technique enables more uniform/homogenous coverage of polymer chains on the surface of gold nanoparticles. Other advantages of ATRP are the growth of polymer chains without chain termination or chain transfer and that the presence of an active initiator site at the end of the growing polymer chain facilitates synthesis of block copolymers. In the present work, PNIPAAM was grown from the surface of nanoparticles with the help of 2-bromopropionyl bromide as the initiator. The reaction was carried out at room temperature under inert atmosphere and aqueous conditions. The system was found to exhibit thermoresponsive behavior with increase in temperature above 32oC. This behavior could be exploited to develop aggregation based assays. The hybrid polymer-gold nanoparticle system was characterized using Optical Absorption Spectroscopy, Fourier Transform Infra-Red Spectroscopy (FTIR) and Dynamic Light Scattering (DLS). These analytical techniques confirmed the growth of polymer chains in the reaction scheme yielding the final product. The ability to make block copolymers with this metal-polymer hybrid system opens up a wide range of applications such as drug delivery systems, detection assays and bioseparations.

5:00pm **BI+TF+MI+NS+NC-ThA10 Reconfigurable Core-satellite Nanoassemblies as Molecularly-Driven Plasmonic Switches**, *D.S. Sebba, J.J. Mock, D.R. Smith, T.H. LaBean,* ***A.A. Lazarides***, Duke University **INVITED**

Colloidal metal nanoparticles support localized surface plasmon resonances that are sensitive to the presence of molecules, materials, and other polarizable particles that assemble in their near fields. Biomolecule nanoparticle conjugates have been implemented in various molecular detection applications in formats that allow monitoring of plasmonic response. Each specific format has vulnerabilities as well as advantages. For instance, monolayers of immobilized particles functionalized with receptors respond sensitively to target molecules and can be used to track kinetics, but are equally sensitive to non-specific adsorbates, a disadvantage shared with traditional, thin film surface plasmon resonance (SPR). Other formats, such as target induced particle aggregation offer strong plasmon modulation, but involve a complex bulk phase process that presents a significant barrier to quantitative interpretation of the optical data. Here, we report plasmon modulation in pre-formed, few particle assemblies linked by reconfigurable DNA nanostructures. The investigation is motivated by the potential of reconfigurable few particle assemblies to provide control of plasmon coupling, and ultimately, to yield a signal that is distinguishable from plasmonic variations associated with non-specific interactions. In the coupled system upon which we report, DNA nanostructures tether satellite particles to a core particle of like or unlike composition. The DNA nanostructures use duplex DNA to control interparticle separation and are responsive to target strands that modulate interparticle helix length. The reconfigurable assemblies are characterized structurally using dynamic light scattering and transmission electron microscopy and optically using elastic scattering spectroscopy. We demonstrate that DNA nanostructures provide molecular control of interparticle separation by correlating measured plasmonic signals with simulated signals derived from models based upon measured structural parameters. In order to study the sensitivity of core-satellite spectral response to colloid material properties, single assembly scattering spectroscopy and multi-color CCD image analysis are used to monitor perturbation of the core plasmon resonance induced by assembly of satellites of various composition.

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

Biological and Molecular Applications of Nanostructures
Moderator: P. Kingshott, The University of Aarhus, Denmark

2:00pm **BO+NS+BI+NC-ThA1 Fabrication of Nanoscale Bioarrays for the Study of Cytoskeletal Protein Binding Interactions Using Nano-Imprint Lithography**, ***M. Schvartzman***, *M. Palma, J. Abramson, J. Sable, J. Hone, M.P. Sheetz, S.J. Wind*, Columbia University

Recent advances in solid-state nanofabrication technology now make it possible to fabricate structures in the size regime of biomolecules, i.e., ~ tens of nanometers and below. We are developing a system that mimics biological spatial order by using nanofabricated structures which are organized into hierarchical arrays in which structural parameters, such as spacing and orientation, are systematically varied, and which provide multiple protein binding sites with nanometer-scale separations. The aim of the work is to study the dependence of large cytoskeletal protein binding on the geometrical arrangement of extracellular matrix (ECM) proteins and integrins. Nanoscale patterns are formed in arrays containing metal dots 5 - 10 nm in diameter, which are functionalized with linker molecules that specifically interact with individual protein binding sites. These dots can be arranged individually, in pairs, or in more complex patterns based on the structure of the molecules under investigation. In particular, we are interested in understanding of the importance of the spacing between integrin cytoplasmic tails on the binding of other proteins, such as talin, that are involved in the building of focal adhesion (FA) complexes by which the actin cytoskeleton attaches to the ECM. The nano-arrays fabrication process uses thermal nanoimprint lithography and pattern transfer by Au/Pd deposition and lift-off. For the lift-off process for such small features and relatively thin resist layer, an angle evaporated metal hard mask is deposited after the NIL step, followed by resist descum. A post-lift-off annealing step at 400 – 500 oC results in further reduction of feature size and a high degree of uniformity. Spheroidal dots are formed with diameters ~5 - 10 nm. The pattern is functionalized with fibronectin RGD motif through a biotin-avidin-biotin linkage. Total-Internal-Reflectance Fluorescence (TIRF) is used for the monitoring of the bio-functionalization with fluorescene labeled molecules. In-vitro study of cells spreading on the patterned and bio-functionalized surfaces is performed on the patterns with different geometries. This presentation will describe the fabrication arrays of ultra-small metal features using NIL technology, functionalization and implementation of these arrays in the study of the fundamentals of cell behavior, representing a new example of the enormous impact of nanofabrication on the life sciences.

2:20pm **BO+NS+BI+NC-ThA2 Universal Method for Forming Various Metal Particles as Multiplexed Labels for Electron Microscopy in the Backscattering Mode**, ***H. Takei***, *H. Kim, K. Yasuda*, Kanagawa Academy of Science and Technology, Japan

Scanning electron microscopy is a powerful technique in terms of resolution, three dimensional rendition of the object and use of ease. Life science is one among many fields for which SEM is an indispensable tool, and it continues to find new uses. One way to enhance its utility in the field of life science is to multiplex labeling as carried out routinely with fluorescence microscopy; labels with different emission spectra. For this purpose, one approach would be to use particles made from different metals because different metals backscatter electrons differently in accordance to the atomic weight. In the backscattering mode, particles made from different metals can be readily distinguished by the brightness of the image so that labeling each type of the particle with distinct biomolecules such as an antibody or DNA would allow one to observe distributions of distinct molecular species simultaneously, as with multiplexed fluorescence labeling, albeit at much higher resolutions. What is needed is thus a method to produce various metal particles at will. For this purpose, we will demonstrate a universal method consisting of formion of a dense monolayer of monodisperse Latex spheres with a self-assembling technique and then evaporating a metal that can be readily evaporated or sputtered. With the above method, the sphere adsorption is accomplished through mild physisorption so that application of mild sonication to surface bound metal particles in the presence of a liquid such as water leads readily to re-dispersal of Latex sphere coated with the metal. We show that resulting particles made from different metals such as gold, silver, nickel or aluminum can be readily distinguished. The sphere size used ranges typically from 50 to 100 nm with the deposition thickness anywhere between 5 to 20 nm. Beside its flexibility with respect to the type of metal that can be used, another advantage of this method lies with a fact that particles can be surface-modified while still adsorbed on a surface. This is particularly advantageous from the perspective of rinsing after each surface treatment protocol. It should be mentioned that because particles are covered only on one side, two types of surfaces, metal and exposed polystyrene, can be selectively used for surface modifications; if necessary two sides can be modified with two distinct species at the same time to give higher functionalities.

2:40pm **BO+NS+BI+NC-ThA3 Nanoscopic Presentation of Peptides at Cell Interfaces**, *J.P. Spatz*, ***V. Hirschfeld-Warneken***, MPI for Metals Research and U. of Heidelberg, Germany **INVITED**

Engineering of cellular environments has become a valuable tool for guiding cellular activity such as differentiation, spreading, motility, proliferation or apoptosis which altogether regulates tissue development in a complex manner. The adhesion of cells to its environment is involved in nearly every cellular decision in vivo and in vitro. Its detailed understanding and defined control also opens new strategies for medical technologies with respect to, e.g., stem cell regulation, tissue scaffolds, cell selection due to their disease state, artificial blood vessels, or immunology. Our approach to engineer cellular environments is based on self-organizing spatial positioning of single signaling molecules attached to inorganic or polymeric supports, which offers the highest spatial resolution with respect to the position of single signaling molecules. This approach allows tuning cellular material with respect to its most relevant properties, i.e., viscoelasticity, peptide composition, nanotopography and spatial nanopatterning of signaling molecule. Such materials are defined as “nano-digital materials” since they enable the counting of individual signaling molecules, separated by a biologically inert background. Within these materials, the regulation of cellular responses is based on a biologically inert background which does not trigger any cell activation, which is then patterned with specific signaling molecules such as peptide ligands in well defined nanoscopic geometries. This approach is very powerful, since it enables the testing of cellular responses to individual, specific signaling molecules and their spatial ordering. Detailed consideration is also given to the fact that protein clusters such as those found at focal adhesion sites represent, to a large extent, hierarchically-organized cooperativity among various proteins. Moreover, “nano-digital supports” such as those described herein are clearly capable of involvement in such dynamic cellular processes as protein ordering at the cell’s periphery which in turn leads to programming cell responses.

3:20pm **BO+NS+BI+NC-ThA5 Bioadhesive/Bioresistant Nanopatterns: Fabrication, Characterization and Investigation of Their Effect on Enhancing Biomolecule Affinity Reactions**, ***I. Mannelli***, *A. Valsesia, P. Lisboa, P. Colpo, F. Rossi*, European Commission Joint Research Centre, Italy

Fabrication and characterisation of nanopatterned surfaces are topics of many past and present research studies. Recently many techniques have been investigated for the fabrication of nanopatterned surfaces. Among them colloidal lithography combined with plasma polymer deposition and/or self-assembly has shown to be a flexible technology for producing large area nanostructured surfaces. At the same time investigations have increasingly focused on the behavior of biomolecules (i.e. protein, nucleic acid) when interacting with surfaces and/or particles with nanometre dimensions. Although many studies have been done on the surface/biomolecule interaction mechanisms and the conformation changes that molecules undergo after the interaction with macroscopic surfaces it is much less well understood how the biomolecules interact with surfaces that have been previously functionalised with nanofeatures. In particular little is known about the interactions which occur with features with dimensions comparable with those of the biomolecules themselves and how, after the interaction, the native molecule conformation changes. We have optimized a procedure for fabricating nanopatterned surfaces at the sub500 nm scale in which a hexagonal close packed array of bioadhesive gold nanoareas are embedded in an anti-fouling matrix (PEO-like polymer). The surfaces fabricated in this way were characterized by AFM analysis and their interaction with amino functionalised Au nanoparticles were investigated. The AFM images show the crystalline arrangement of nanopattern array and the localization of the H_2N-Au nanoparticles in the bioadhesive areas. A SPR Imaging system was used to perform kinetics studies on the adsorption and interaction behaviour of biomolecules on these surfaces. At the same time, the detection performance of these surfaces when employed as a transduction platform for studying biomolecule interactions has been investigated. To do this, a recognition biomolecule was immobilized on the surface and the affinity reaction with a specific target molecule was monitored in real time by means of the SPRi system. The investigated surfaces showed an enhancement of the affinity reaction efficiency with respect to the non structured surfaces. The results obtained show that nanostructuring the surfaces makes it possible to improve the binding site accessibility of the immobilized biological probes without significantly modifying the native biomolecule conformation.

4:00pm **BO+NS+BI+NC-ThA7 Control and Separation of Proteins in a Nanofluidic FET Device, using pH Gradient and Valence Charge**, ***Y.-J. Oh***, University of New Mexico, *D.R. Bottenus, C.F. Ivory*, Washington State University, *S.M. Han*, University of New Mexico

We have fabricated Si multiple internal reflection infrared waveguides embedded with a parallel array of nanofluidic channels (100 nm W ×500 nm D) and studied field-effect-transistor (FET) flow control and separation of proteins, using scanning laser confocal fluorescence microscopy (SL-CFM) and multiple internal reflection Fourier transform infrared spectroscopy (MIR-FTIRS). For fluidic FET, a DC potential is applied to a highly doped gate area in the mid-section of nanochannels, in addition to a longitudinal electric field along the nanochannels. The gate potential controls the surface charge on SiO_2 channel walls and therefore their ζ-potential. Depending on the polarity and magnitude, the gate potential can accelerate, decelerate, or reverse the flow of proteins. In addition, our MIR-FTIR analysis demonstrates that fluorescein dye molecules, used here as a pH indicator, are hydrogenated and dehydrogenated in response to the gate bias and subsequent pH shift. Using fluorescein, we have thus measured a pH shift caused by the surface charge modulation and longitudinal electrical field. We observe that this pH shift is further influenced by water electrolysis occurring at the electrodes that drive the electroosmotic flow as well as at the gate where a leakage current unavoidably flows through a thermal SiO_2 layer. Using this pH manipulation and generating a pH gradient along the nanochannels, we have conducted isoelectric focusing and separation of proteins with different isoelectric points (Ip). In this presentation, we will further discuss protein separations, using transverse electromigration based on their different valence charges in relation to the surface charge on channel walls.

4:20pm **BO+NS+BI+NC-ThA8 High Throughput Device for Surface Modification Studies**, ***S. Saxer***, *S. Tosatti, S. Zuercher,* ETH Zurich, Switzerland, *K. Gademann,* EPF Lausanne, Switzerland, *M. Textor*, ETH Zurich, Switzerland

Surface coatings are often used to control the degree of the interaction between the material and the surrounding environment. Paints and lacquers are the most common and widespread coatings. Recent developments in the process of micro- and nanostructures lead to the demand of thinner coatings, which maintain the aspect ratio and preserve the fine structures. Such conditions can be fulfilled by the use of self-assembled monolayers.[1] Due to the large spectrum of applications are nowadays high-throughput approaches required to screen through a large number of parameters, ranging from the substrate up to the different assembly conditions (temperature, solvent, pH). We designed a surface modification screening platform (SuMo-device), which allows the parallel execution of different surface–modification experiments while allowing a single measure for the adlayers characterization, thus enhancing the efficiency of the experiment. The seventy wells (working area/well: $7mm^2$; Volume/well: 20μmL) provided by the SuMo-device, were verified with solutions having different concentrations of the grafted copolymer; poly (L-lysine)-grafted-poly ethylene glycol, which is known to adsorb electrostatic to different metal oxide substrates and to render the surface resistant against non-specific protein adsorption (non-fouling), and thus resulting in adlayers with different coverage and thickness.[2] A secondary adsorption of fluorescein isothiocyanate labeled fibrinogen (FITC-fbg) enables to test the non-fouling behavior and therefore the quality of the polymer layer, by the measurement of the fluorescence with a microarray scanner.[3] A standard evaluation procedure was introduced to enable a quantification of the fluorescent response. The Limit of Detection (LOD) was calculated from the standard curve and requires a minimum FITC-fbg concentration of 0.002mg/mL (incubation: 1 h at 25°C). The fluorescence data were compared and found to correlate with layer thickness (ellipsometry) and with the in situ mass adsorption curve obtained by optical biosensor devices. Thus, we conclude that our approach offers a faster and more efficient way to screen between different possible coatings strategies, similarly to drug discovery processes.

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4:40pm **BO+NS+BI+NC-ThA9 Nanopatterned Functional Surfaces by Electron Beam Lithography of Plasma Assisted Chemical Vapour Deposited Polymers**, *F. Bretagnol, A. Valsesia,* ***G. Ceccone***, *D. Gilliland, P. Colpo, F. Rossi*, European Commission, Joint Research Centre Italy

We presents a method for the fabrication of well defined chemically active nano-patterned surfaces. Electron-beam lithography is applied on plasma-deposited polymers in order to create sub-micron carboxylic functional areas over a non-bio-adhesive matrix. Characterization of the patterned surface demonstrates that this technique can be used to fabricate chemically active features with lateral size down to 200 nm. Moreover, experiments with a model protein (bovine serum albumin) on the patterned surfaces show preferential adhesion on the active region indicating the ability of this method for the design of biosensing platforms.

5:00pm **BO+NS+BI+NC-ThA10 Application of Plasma Polymerised Microchannel Surfaces for IEF**, ***M. Salim***, *B. O'Sullivan, S.Y. Ow, P.C. Wright, S.L. McArthur*, The University of Sheffield, UK

The emerging proteomics field has triggered the development of many bioanalytical tools and technologies. Since biological samples are usually present in small quantities and volume, there is a high priority for the analytical tools to be able to process these minute samples. The use of microfluidics for this purpose has thus emerged. Plasma polymerisation has been shown to be an attractive method to coat microchannel surfaces. Here, we apply the plasma surface modified microchannels for on-chip IEF protein separation (separation based on the isoelectric points of the proteins). A common problem associated with the use of non-coated glass or fused silica substrates in IEF is the high electroosmotic flow (EOF) and high extent of protein adsorption. Therefore, coated microchannel surfaces are usually introduced to reduce the EOF and reduce protein adsorption, and improve the resolution of the separation. Lower EOF can also permit IEF separation in short channel lengths. In this study, we investigate the applicability of plasma polymerised tetraglyme surface for IEF-facilitated protein separation at a 2.2 cm channel length, since it exhibits slower EOF compared to non-coated microchannel surfaces, and is low-fouling. Comparisons were also made to non-coated microchannels and other types of plasma polymers, i.e. plasma polymerised acrylic acid and plasma polymerised allylamine coated surfaces. IEF performed on the low-fouling plasma polymerised tetraglyme microchannel surface was shown to exhibit better separation compared to non-coated microchannel, as observed from the clearer formation of focused protein bands. Also, due to the presence of protein and carrier ampholytes adsorption in both plasma polymerised acrylic acid and allylamine coated microchannels, these surfaces may not be suitable for IEF protein separation over a wide range of pH, with the separation resolutions decreasing after repeating experimental runs.

5:20pm **BO+NS+BI+NC-ThA11 Plasma Deposited Polyethylene Oxide as a Platform for Proteins and Stem Cells Microarrays**, *L. Ceriotti*, JRC, Ispra, Italy, *L. Buzanska*, JRC, Ispra, Italy and Polish Academy of Science, *H. Rauscher, I. Mannelli*, ***L. Sirghi***, *D. Gilliland, M. Hasiwa, F. Bretagnol, A. Ruiz, S. Bremer, S. Coecke*, JRC, Ispra, Italy, *P. Colpo*, Joint Research Center, IHCP, Italy, *F. Rossi*, JRC, Ispra, Italy

In this work we fabricated and characterized microarrays of proteins of the extra cellular matrix (ECM) for stem cells adhesion studies. Plasma deposited poly(ethylene) oxide (PEO-like) film coated glass slides has been chosen for its dual properties, being protein and cell repellent in wet conditions and protein adhesive in dried conditions. The microarrays were created by direct microspotting of the proteins on the PEO films with optimized printing buffer by using a non-contact printing technology. The stability and the quality of the spots of fibronectin used as model protein were assessed by Time of Flight- Secondary Ion Mass Spectrometry (ToF-SIMS) and ellipsometry was used to determine the amount of protein immobilized on each spot after rinsing of the substrate with water. It was found that when fibronectin is spotted at a concentration higher than 84 μmg/ml, the protein forms a monolayer with a density of 112 ± 4 ng/cm^2 with a low surface coverage but quite regular spatial distribution as confirmed by Atomic Force Microscopy (AFM) measurements. The active conformation of the spotted fibronectin as a function of the spotted concentration was verified by performing an immunoassay with antibodies specific for the fibronectin RGD sequence by Surface Plasmon Resonance (SPR) imaging. Human Umbilical Cord Blood Neural Stem Cells (HUCB-NSCs) were cultured on different ECM protein arrays (fibronectin, laminin, collagen I, collagen III and collagen V) showing a protein type and concentration dependent adhesion and growth on the micro-spots. No cells were found in-between the spots thanks to the anti adhesive properties of the PEO-like film. The cell nuclei were stained for cell counting and preliminary specific cell staining was performed to evaluate the differentiation stage of HUCB-NSCs on fibronectin spots. The array platform developed in this study provides a promising approach to investigate in a high throughput manner how insoluble factors patterned on the surface influence stem cell adhesion and development.

Nanomanufacturing Focus Topic
Room: 309 - Session NM+MS+NS+NC-ThA

Nanomanufacturing II: Nanostructures
Moderator: J. Murday, University of Southern California

2:00pm **NM+MS+NS+NC-ThA1 Superionic Electrochemical Patterning of Metallic Nanostructures**, ***P.M. Ferreira***, *N.X. Fang, K. Hsu, K. Jacob, A. Kumar, P. Schultz*, University of Illinois, Urbana **INVITED**

Nanoscale metallic nanostructures find widespread and critical application in many micro and nanoscale technologies. Processes such as electrochemical and electro-discharge machining lack the fine control to obtain sub-micron resolution. As a result, such structures are generally fabricated using indirect patterning techniques, resulting expensive, lengthy multi-step manufacturing operations. In this presentation, we introduce a new means of directly patterning metal films into metallic nanostructures. The process, Solid-State Superionic Stamping (S4), uses a patterned solid-electrolytic stamp or mold to directly create metallic nano- and microstructures through electrochemical anodic dissolution. As a result, it requires very small mechanical forces and no contaminating liquids, and is capable of producing structures with nanoscale precision over large areas. This presentation will discuss the mechanism that underpins the process; characterize its capabilities in creating silver and copper nanostructures; discuss the fabrication of stamps, and some applications that such a process enables. The presentation will conclude with a description of the process technology under development and directions for future research.[1]

[1] This research was supported by NSF through the Center for Chemical-Electrical-Mechanical Manufacturing Systems (Nano-CEMMS) under Grant DMI-0312862, the Office of Naval Research under grant N00173-07-G013 and the University of Illinois through the Grainger Foundation grant. We are grateful that part of this work was carried out in the Center for Microanalysis of Materials, University of Illinois, which is partially supported by the U.S. Department of Energy under grant DEFG02-ER45439.

2:40pm **NM+MS+NS+NC-ThA3 Designing Semiconductor Nanocrystals for Optoelectronic and Biological Applications**, ***M. Bawendi***, Massachusetts Institute of Technology **INVITED**

Semiconductor nanocrystals, aka quantum dots, have become the prototypical material for the emergence of new properties when dimensions are reduced to the nanometer range. The size dependent properties of excitons and multiexcitons in quantum dots, coupled with a material that can be engineered and processed from solution, has led to potential applications in fields that include emissive displays, solar energy conversion, and biological and biomedical fluorescence imaging. A fundamental understanding of exciton processes is critical for any of these applications to become realized. The design and synthesis of well characterized materials is obviously key, not only of the functional inorganic particle itself, but also the ligand shell that protects it and couples it chemically to molecules and matrices of interest. This talk will review some of the chemistry and photophysics of quantum dots and then explore the fundamental properties and challenges behind broadly applying quantum dots as light emitters and light absorbers in devices and for biological imaging.

3:20pm **NM+MS+NS+NC-ThA5 Controlled Assembly and Nanoscale Doping of Semiconductor Quantum Dots Using Focused Ion Beams**, ***J.F. Graham***, *C.D. Kell*, University of Virginia, *J.L. Gray*, University of Pittsburgh, *J.A. Floro, S.A. Wolf*, University of Virginia, *L. Bischoff*, Research Center Dresden-Rossendorf Inc., Germany, *R. Hull*, University of Virginia and Rensselaer Polytechnic Institute

Self-assembled semiconductor quantum dots are a candidate for use in potential nanoelectronic device architectures such as quantum cellular automata and magnetic spin exchange switches. It is possible to grow quantum dots (QDs) with relatively uniform size-distributions using heteroepitaxial techniques, but in order to apply QDs in such nanoelectronic devices they must also be spatially ordered into patterns of varying complexity. In addition, the QDs must posses the magnetic or electronic properties required for device operation. We have previously demonstrated the use of Ga$^+$ focused ion beam (FIB) templating of Si surfaces prior to growth in order to fabricate patterns of Ge(Si) QDs of any desired complexity. Our current work employs a mass-selecting FIB with liquid metal alloy ion sources, enabling the generation of a wide range of separated species in focused beams, to template QD structures and electrically or magnetically dope them at a dot-by-dot level for nanoelectronic device applications. Ions can be selected according to isotope mass and charge state by using a mass-selecting Wien filter. Suitable alloy sources then provide the ability to template a Si substrate with electrically non-invasive ions (i.e. Si or Ge) and implant dopant ions for electronic or magnetic activation (e.g. with B or Mn), with resolution of

< 50nm and doses down to a few ions per dot. Key technical issues we are addressing include i) the attainable limits of spatial resolution and the dot-by-dot implantation dose, ii) comparisons between Ga and Si ion templated growth, iii) physical alignment between a templating ion beam and a dopant implantation ion beam and iv) procedures for eliminating unwanted exposure of adjacent areas of the sample to implantation ions.

4:00pm **NM+MS+NS+NC-ThA7 Semiconductor Nanowires: From Materials Science to Device Physics**, ***L. Samuelson***, Lund University, Sweden **INVITED**

In the general trend towards the use of self-assembly for realization of ultra-small devices on the 10nm-scale, semiconductor nanowires (NWs) have emerged as one of the most interesting candidates. In this talk I will describe different materials science aspects of NW growth, with a focus on III-V NWs grown epitaxially on a single-crystalline substrate as a top-down guided bottom-up growth of NWs . I will present recent progress in studies of structural properties of such NWs, including the importance and control of the stacking sequence of subsequent layers in NWs. I will then describe the controlled formation of axial and radial heterostructures, which is of great importance for the use of NWs for basic physics studies as well as for applications in electronics and photonics. As examples of recent physics studies of NWs I will describe transport via single and multiple quantum dots and optical studies of excitonic recombination in single quantum dots in NWs. Finally, I will give an update on the progress in realizing electronic as well as photonic devices using NWs, and will here primarily present progress in technology and performance of wrap-gate field-effect transistors. I time allows I will conclude with some visions for where I think NW-based science and technology may be heading in the future.

4:40pm **NM+MS+NS+NC-ThA9 Surface Plasmon Enhanced Photoluminescence from Noble Metal/CdS Hybrid Semiconductor Nanowires**, ***W. Luo***, *S.C. Kung, W.V. Veer, R.M. Penner, J.C. Hemminger*, University of California, Irvine

Surface plasmon enhanced techniques provide promising methods to improve the light emission efficiency of semiconductor materials. In this talk, we present the growth of noble metal/CdS hybrid semiconductor nanowires, and the plasmon-enhanced photoluminescence from these nanowires. In our previous studies, we demonstrated the straightforward fabrication of ordered linear arrays of spherical silver nanoparticles with gaps between the individual nanoparticles of less than 10 nm on highly oriented pyrolytic graphite (HOPG) surfaces using physical vapor deposition (PVD) under controlled experimental conditions. These silver nanoparticle arrays were capable of supporting very strong surface plasmon resonances, which was demonstrated by our polarized surface enhanced Raman scattering experiments. In this presentation, we describe experiments where following the PVD growth of Ag or Au nanoparticle arrays on HOPG surfaces, we electrochemically deposit cadmium around these nanoparticle arrays to form hybrid nanowires as thin as 50-60 nm in width. Further annealing of these hybrid nanowires in H_2S at temperatures of 300-320°C enables the formation of CdS nanowires around the Ag or Au nanoparticle cores. Using this combined PVD/electrochemistry/chemical modification approach we have been able to generate ordered 2-D arrays of hybrid semiconductor nanowires that are as small as 100 nm in diameter and 100s of microns in length. Under light illumination, the surface plasmon supported by the Ag or Au nanoparticle cores enhances the photoluminescence of the outer CdS nanowires.

5:00pm **NM+MS+NS+NC-ThA10 Metal Oxide Nanowires by Near Field Electrospinning**, *M. Rinaldi, F. Ruggieri*, University of L'Aquila, Italy, ***L. Lozzi***, CNISM and University of L'Aquila, Italy, *S. Santucci*, CNR-INFM and University of L'Aquila, Italy

The growth of metal oxide nanowire is an important challenge for the realization of nanostructured devices, as for example highly sensitive gas sensors.[1] A very easy method to deposit metal oxides is the electrospinning.[2] This simple and low cost technique allows the growth of very thin nanofibers, whose diameter can be varied from 50 nm to about 1 μm. It is based on the effect of an electric field on a charged liquid (polymer or solution) ejected from a nozzle. The charged jet is accelerated by the electric field, dries and is deposited onto a grounded substrate, forming nanofibers. Generally the nozzle-substrate distance is about 10-15 cm and the applied voltage is about 10-15 kV. Unfortunately this method does not allow easily the growth of well ordered nanofibers. In the present study TiO2 nanofibers were electrospun with a novel approach of electrospinning called NFES (Near-Field Electrospinning), in which the tip-substrate distance is strongly reduced to few millimetres, decreasing also the applied bias voltage to few hundreds of volts.[3] Significant advancement in collecting aligned electrospun nanofibers has been made with this improved technique that complements conventional electrospinning by providing the feasibility of controllable deposition for sub-100-nm nanofabrication. Well aligned TiO2 nanofibers were grown onto a silicon dioxide substrate. These nanofibers were up to several millimetres long with a diameter of about 200-400 nm. The scanning electron microscopy showed the presence of microcystallites, whose crystalline nature was confirmed by X-ray diffraction measurements after a thermal process, also used for removing the polymer. The chemical composition was investigated by X-ray photoemission spectroscopy showing that the nanofibers are composed by stoichiometric TiO2 crystallites.

[1] S. Piperno, M. Passacantando, S. Santucci, L. Lozzi, S. La Rosa, J. Appl. Phys., vol. 101, (2007) 124504.

[2] W.E. Teo and S. Ramakrishna, Nanotechnology, vol. 17, (2006) R89.

[3] D. Sun, C. Chang, S. Li, and L. Lin, Nanoletters, vol 6, (2006), p. 839.

5:20pm **NM+MS+NS+NC-ThA11 Luminescent Rare-Earth Doped Metal Oxide Nanostructures**, ***Y. Mao***, *J. Dorman, J.P. Chang*, University of California at Los Angeles

Advanced luminescent materials have practical applications in nearly all devices involving the artificial production of light and considerable research has been carried out to synthesize new luminescent materials. Their luminescent properties have been shown to be dependent on the size and morphology of the crystallites, hence materials with dimensions in the nanometer regime emerges as promising materials. These attributes make them viably applicable in nanoscaled electronics, photonics, display and advanced bioanalysis. In this talk, we present our recent work on the fabrication of rare-earth doped metal oxide nanostructures, including $Er:Y_2O_3$ nanotubes (NTs) and nanoparticles (NPs) and $Er:La_2(Zr_xHf_{1-x})_2O_7$ NPs, by hydrothermal and molten-salt syntheses.[1,2] The formation of nanostructures were probed in-situ by time-resolved synchrotron x-ray diffraction and absorption spectroscopy to delineate the process-structure-property relations. The as-synthesized nanostructures were further characterized by electron microscopy and various spectroscopy[3] to be single crystalline, with well controlled size distributions around 100-400 nm in outer diameter and 2-5 μm in length for $Er:Y_2O_3$ NTs, around 80 nm in diameter for $Er:Y_2O_3$ NPs, and around 15 nm in diameter for $Er: La_2(Zr_xHf_{1-x})_2O_7$ NPs. The erbium coordination number and local bonding environment were shown to dictate the measured photoluminescent characteristics, including photoluminescence and cathodoluminescence. Specifically, these 0-100% erbium-doped oxide nanostructures have sharp and well-resolved photoluminescent behavior in the near-infrared region, outstanding green and red upconversion emissions, and excellent cathodoluminescent properties. These properties make these nanostructures promising for applications in display, bioanalysis and telecommunications.

[1] Mao, et al. Synthesis and luminescence properties of erbium-doped Y_2O_3 nanotubes, J. Phys. Chem. C, 112, 2278 (2008).

[2] Mao, et al. Molten salt synthesis of highly luminescent erbium-doped yttrium oxide nanoparticles, submitted (2008).

[3] Mao, et al. Correlation between luminescent properties and local coordination environment for erbium dopant in yttrium oxide nanotubes, J. Appl. Phys. in press (2008).

Nanometer-scale Science and Technology
Room: 311 - Session NS+NC-ThA

Nanolithography and Manipulation
Moderator: J.N. Randall, Zyvex Labs

2:00pm **NS+NC-ThA1 Pattern Error Correction and Density Multiplication by Lithographically Guided Self Assembly**, ***R. Ruiz***, *E.A. Dobisz, D.S. Kercher, T.R. Albrecht,* Hitachi Global Storage Technologies Inc., *H. Kang, F.A. Detcheverry, J.J. de Pablo, P.F. Nealey*, University of Wisconsin **INVITED**

Patterned media for storage applications at densities beyond $1Tb/in^2$ requires fabrication of periodic patterns at 27nm full pitch and smaller. Templating patterns at these dimensions is particularly challenging when considering the stringent quality restrictions imposed by storage applications in terms of feature size distribution, line edge roughness, placement and long-range ordering. We present here a guided self-assembly approach that combines e-beam lithography with block copolymer self-assembly. E-beam lithography is used to pre-pattern a guiding substrate defining features with registration and long-range orientational and translational order. A block copolymer film is applied on top of the guiding pattern. The uniformity of the self-assembled features effectively corrects noise and non-uniformities introduced by the e-beam and the e-beam resist. We use image processing to quantify the pattern quality rectification achieved by the block copolymer. We also use this guided self-assembly approach as a pattern density multiplier. The self-assembled pattern can be used to multiply the density of e-beam features by at least a factor of four. This density multiplication approach enables the possibility to pattern features at resolutions not accessible by state-of-the-art e-beam lithography but still taking full advantage of its registration and long-range ordering properties.

2:40pm **NS+NC-ThA3 Patterning Self-Assembled Monolayers of Thiols Down to the sub-10 nm Scale by Scanning Tunneling Microscopy**, ***C. Shen**, M. Buck*, University of St. Andrews, UK

While self-assembled monolayers (SAMs) have opened up unprecedented opportunities for surface functionalisation and patterning, the generation of structured SAMs on the ultrasmall length scale remains a challenge. In this range scanning probe microscopies such as scanning near field optical microscopies (SNOM), STM and AFM play a crucial role as patterning tools. Depending on the techniques, different schemes of modification are applied, e.g., load and field induced modification for AFM and STM, respectively. Here we report our studies on STM based patterning using SAMs of (methyl-biphenyl-4-yl)-alkane thiols (BPn SAMs) on Au(111). Since these systems form layers of excellent structural quality they are promising systems for nanolithography. Patterns were generated by displacement of BPn molecules by alkane thiols. In contrast to the common approach, STM patterning was performed at voltages well below those of field induced disruption of the SAM. Since these rather gentle conditions of SAM modification do not result in major changes of the STM tip, the resulting SAM patterns could be analysed at molecular resolution. Lines as thin as 2.5 nm and dots below 20 nm2 can be straightforwardly produced. It is found that the structure of BPn SAM is reflected in its displacement behaviour. For example, (methyl-biphenyl-4-yl)-ethane thiol (BP2) which exhibits a rectangular unit cell exhibits a patterning anisotropy with a preferential displacement and differences between alternating rows of molecules along the <11-2> directions.

3:00pm **NS+NC-ThA4 A Novel Nanolithography Technique for Formation of Uniform Nanostructures**, ***W. Wu**, D. Dey, O. Memis, A. Katsnelson, H. Mohseni*, Northwestern University

A novel nanolithography technique—Nanosphere Photolithography (NSP)—was demonstrated to generate a large area of highly uniform nanoholes or nanoposts of photoresist by utilizing the monolayer of hexagonally close packed silica microspheres as super-lenses on top of photoresist. Both our simulation and experimental results show that the size of the nanostructures generated is almost independent of the sphere sizes and hence extremely uniform patterns can be obtained. We also show that large areas of highly uniform nanoholes (~250 nm) and nanoposts (~300 nm) in multi metal stacks with the period of 1 um using the broadband wavelength of light centered about 400 nm. The nanoholes diameter in metal layers could be tuned by changing the under-cut strength. Using this method, the nanoholes with bottom diameters as small as 50 nm could be produced. The period and size of the nanostructures could be tuned independently by changing proper parameters. We were also able to generate nanostructures within desired patterns by combining the NSP technique with standard photolithography masks during exposure. Our simulation results show that the sizes of the nanostructures can be further reduced using shorter wavelengths. This technique establishes a new paradigm for high throughput nano-lithography, allowing rapid, economical and simple creation of large areas of uniform nanostructures.

3:20pm **NS+NC-ThA5 Fabrication of Large Area Glass Submicron Pattern by Multibeam Interference Lithography and Reactive Ion Etching**, ***H.S. Jee***, University at Buffalo, *A.P. Zhang*, Zhejiang University, China, *R. Burzynski*, Laser Photonics Technology Inc., *K.T. Kim, P.N. Prasad, Y.K. Yoon*, University at Buffalo

Large area glass submicron patterns are important because of its advantages and great potentials for the applications of nanoimprint molding, diffraction mask patterning, gratings, diffractive waveguide devices, microfluidic channels, and lab on a chip. In this work, we use multibeam interference lithography using photoresist to fabricate two dimensional (2-D) submicron patterns covering a large glass substrate area and nano pattern transfer to the glass substrate using subsequent reactive ion etching (RIE). Three plane wave laser (532nm) beams are utilized for interference pattern on a SU-8 thin film layer. Reactive ion etching is appropriate for the large area pattern transfer with high aspect ratio pattern with appropriate RIE power and gas control. The glass etching rate and shape with various reactive ion etching conditions are reported for the nanoscopic patterns. This profile shows uniform pattern transfer in the large area substrate with fidelity. The proposed glass submicron patterning approach provides the advantages of both low cost and precise tailoring of submicron geometry, appropriate for mass production.

4:00pm **NS+NC-ThA7 STM Atom and Molecule Manipulation: Realizing Single Molecule Switches and Devices**, ***S.-W. Hla***, Ohio University **INVITED**

Scanning tunneling microscope (STM) manipulation of single atoms and molecules on surfaces allow construction of novel quantum structures on an atom-by-atom basis and demonstration of single molecule devices on a one molecule at-a-time basis. STM is not only an instrument used to '/see/' individual atoms by means of imaging, but also a tool used to '/touch/' and '/take/' atoms/molecules or to '/hear/' their vibration by manipulations. Therefore, it can be considered as the '/eyes', 'hands'/ and '/ears'/ of the scientists connecting our macroscopic world to the exciting atomic and nanoscopic world. In our research projects, we combine STM manipulation schemes with a variety of tunneling spectroscopy measurements to address several critical issues covering both fundamental understanding, and demonstration of novel atoms/molecules based nano-devices. In this talk, our recent results of single atom/molecule manipulations using a low-temperature STM will be presented. The presentation will include atom manipulation on 3-D nanoclusters, comparative lateral force measurement to move individual atoms, manipulation of nanoscale bio-molecules to realize a multi-step single molecule switch, manipulation of Kondo effect in zero and two-dimensional molecular systems, and charge transfer molecular switching.

4:40pm **NS+NC-ThA9 Nanopatterning of Functional Polymers by Thermal Dip-Pen Nanolithography**, ***W.K. Lee***, Naval Research Laboratory, *W.P. King*, University of Illinois, Urbana-Champaign, *L.J. Whitman*, National Institute of Standards and Technology, *P.E. Sheehan*, Naval Research Laboratory

Thermal dip-pen nanolithography (tDPN) uses a heated AFM cantilever coated with an ink to melt, deposit, and align the ink on a substrate.[1] tDPN has proven particularly effective for depositing polymers.[2,3] The polymer thickness and lateral dimensions may be tuned by adjusting the tip heating power and the writing speed to allow layer-by-layer deposition. The deposited polymer is aligned along the writing direction apparently due to shear between the tip and substrate. Many different functional polymers have been successfully deposited on silicon oxide surfaces, including a temperature-responsive polymer [poly(N-isopropylacrylamide), known as pNIPAAM], a semiconducting polymer [poly(3-dodecylthiophene)], a piezoelectric polymer [poly(vinylidene fluoride)], and a light-emitting polymer [poly(9,9-dioctylfluorenyl-2,7-diyl)]. We will present our characterization of a deposited polymer. For example, pNIPAAM nanostructures by tDPN patterned in surface parallel form along the writing direction and undergo a hydrophilic-to-hydrophobic phase transition induced by temperature that allows the structures to controllably capture and release proteins.[3] Moreover, we will demonstrate how a universal polymer carrier "ink" may be used to deposit a wide range of materials that could not be deposited under ordinary conditions. Finally, we will describe the deposition and nanostructuring of aromatic molecules which may not be accessible by other scanning probe lithographic techniques.

[1] Sheehan et al., Appl. Phys. Lett., 85, 1589 (2004).

[2] Yang et al., J. Amer. Chem. Soc., 128, 6774 (2006).

[3] Lee et al., Soft Matters, accepted for publication (2008).

5:00pm **NS+NC-ThA10 Selective Assembly of DNA-Templated Nanostructures for the Application to Nano-Device**, ***H.J. Kim**, Y. Roh, B. Hong*, Sungkyunkwan University, Korea

The nanowires using the conjugation of DNA and metal (e.g., Ag, Au, Cu and Pd) are essential building blocks to realize the nanometer-scaled electronic devices and are being extensively investigated to apply to nano-scale electronic devices. However, there are remaining some problems for realization of DNA device such as fixing on specific location and aligning with uniform interval. We report an approach to selectively align and uniformly separate λ-DNA molecules and thus DNA-templaed gold nanowires (AuNWs) on SiO2 surface using surface-patterning technique by combination of self-assembly and conventional microfabrication processes. We also utilized the photolithography and plasma ashing methods to create molecular patterns comprised nano-scale patterned 3-(aminopropyl)triethoxysilane (APS) region and micron-scale octadecyltrichlorosilane (OTS) region that the key for highly selective assembly is the high-quality molecular layers. DNA was attached only on the APS region defined by the amine groups, but not on the surface of the OTS region. By surface-pattering technique, we could obtain DNA molecules and thus DNA-based AuNWs aligned parallel and selectively at 10 µm intervals on a Si substrate. We used atomic force microscopy (AFM) to analyze the configuration of AuNWs.

surface-pattering technique, plasma ashing, λ-DNA molecule, gold nanowires (AuNWs), APS, and OTS.

5:20pm **NS+NC-ThA11 High Resolution STM Imaging and Manipulation of Multi-decker Porphyrin**, ***H. Tanaka***, Osaka University, Japan, *T. Ikeda*, Kyushu University, Japan, *M. Takeuchi*, NIMS, Japan, *S. Shinkai*, Kyushu University, Japan, *T. Kawai*, Osaka University, Japan

Supramolecular chemistry has emerged as a powerful strategy for construction of molecular-based devices with advanced functions and well-defined nanometer-scale structures. Structural determination of supramolecular aggregates is of great importance and mainly performed by means of NMR and/or X-ray crystal analysis. One of the convincing ways to evaluate or even visualize the structure, other than those just mentioned, is scanning probe microscopy. A large number of studies have been reported for ultrahigh vacuum scanning tunneling microscopy (UHVSTM) measurements of porphyrins, phthalocyanines, their mixtures, and covalently linked multi-porphyrins. In spite of submolecular/atomic resolution, the number of reports on high resolution UHVSTM images of supramolecules is still limited, due to the lack of suitable deposition method for such molecules without decomposition. We have overcome this difficulty by developing a pulse injection technique as a novel deposition method of fragile biomolecules, such as DNA/RNA/protein and supramolecules, such as porphyrin oligomers/macrocycles. Here we focus on the molecular system of multi-decker (double-decker(DD) and triple-decker(TD)) porphyrin on Au(111). The DD molecules are known to form highly ordered adlayers on HOPG. We have found that both DD and TD, deposited by pulse injection method, form highly ordered adlayers on Au(111). We also successfully observed rotation of topmost porphyrin of both DD and TD. To the best of our knowledge, there have been no reports of STM where such movement of “molecular bearing” (not rotation of entire molecular unit over the surface) has been detected in this way.

Friday Morning, October 24, 2008

Nanometer-scale Science and Technology
Room: 311 - Session NS+NC-FrM

Nanoscale Processes
Moderator: N.A. Burnham, Worcester Polytechnic Institute

8:20am **NS+NC-FrM1 Synthesis of Controlled (/n,m/) Identity Single-Walled Carbon Nanotubes**, ***L. Pfefferle***, *C. Zoican*, Yale University **INVITED**

Advanced electronic applications using single-walled carbon nanotubes (SWNT) require uniform property SWNT that are not degraded by compositional variation (/n,m/ plurality) or side wall damage induced by cleaning or separation processes. The lack of uniform (/n,m/) identity SWNT with a low level of side-wall defects presents a major hurdle to device development. Thus, the ultimate goal of nanotube synthesis is to produce specific (/n,m/) nanotubes at high selectivity. In this talk we will discuss methods for controlling the diameter and /n,m/ identity of a nanotubes produced in synthesis. Many investigators have shown that the use of a second metal or transition metal oxide in the catalyst can anchor small domains of the active phase or alter their morphology to narrow the distribution of nanotubes identities produced. In addition such methods can produce highly enriched semiconducting or metallic samples. In some of these catalyst systems using CO disproportionation as the growth reaction, changing reaction temperature can dramatically vary the diameter of the nanotubes produced. We will show our recent work and that of others using X-ray absorption spectroscopy to explore the interaction between the catalyst components and how the size of the active phase varies and is related to the nanotubes diameters observed. Longer term, in order to gain almost pure n,m identity nanotubes in an economically viable manner, regrowth of specific (/n,m/) nanotube would be the most effective technique. We have recently demonstrated regrowth of SWNT chopped into short “seeds”, filled with iron or nickel functionalities and activated in a simple reaction step prior to the regrowth. Our exploratory results from the regrowth processes to be described in this talk resulted in a significant increase in SWNT weight, while at the same time showing a clear potential for retaining the (/n,m/)-distribution of the seed. This methodology offers advantages (e.g. scalability, fidelity, and does not require specialized seed cutting or functionalization) compared to other recent pioneering demonstration of SWNT regrowth by the Smalley research group.[1,2]

[1] Smalley, R. E.; Li, Y.; Moore, V. C.; Price, B. K.; Colorado, R., Jr.; Schmidt, H. K.; Hauge, R. H.; Barron, A. R.; Tour, J. M., Single Wall Carbon Nanotube Amplification: En Route to a Type-Specific Growth Mechanism. /Journal of the American Chemical Society /*2006,* 128, (49), 15824-15829.

[2] Wang, Y.; Kim, M. J.; Shan, H.; Kittrell, C.; Fan, H.; Ericson, L. M.; Hwang, W.-F.; Arepalli, S.; Hauge, R. H.; Smalley, R. E., Continued growth of single-walled carbon nanotubes. /Nano Letters /*2005,* 5, (6), 997-1002.

9:00am **NS+NC-FrM3 Fullerene Growth on N-adsorbed Cu(001) Nanopatterned Surfaces**, ***T. Iimori***, *B. Lu*, University of Tokyo, Japan, *K. Sakamoto*, Chiba University, Japan, *K. Nakatsuji*, University of Tokyo, Japan, *F. Rosei*, University of Quebec, Canada, *F. Komori*, University of Tokyo, Japan

Nitrogen (N)-adsorbed Cu(001)-c(2x2) nanopatterned surfaces are used as templates to guide the growth of low-dimensional C_{60} molecular nanostructures. The detailed nucleation and growth behaviors are studied by in situ scanning tunneling microscopy(STM). At room temperature, on the 0.3 ML-N-covered surface, where 5x5 nm^2 patches of the c(2x2)-N surface are squarely arranged and bare Cu(001) surface. In other word, the bare Cu surface forms a nanogrid. Here ML is defined as the Cu atom density of the clean Cu(001) surface. During the initial stages of growth, C_{60} molecules preferentially adsorb on the bare Cu regions on a partially N-covered grid surface. Subsequently a two-dimensional molecular nanomesh is formed after C_{60} covers all the bare Cu regions. Further deposition leads to C_{60} growth on the c(2x2)-N areas until the first molecular layer is completed. For N-saturated surface with trench structures, the <010> steps of these structures serve as initial anchoring sites for C_{60} growth. From there, the growth proceeds two-dimensionally until a single C_{60} layer is achieved due to island coalescence. In contrast, no nucleation site was observed when the <110> steps were predominant on the surface. At least up to 6 mono-molecule layer, the growth proceeds layer-by-layer i.e., the overlayer morphologies are directed by the underlying substrate pattern in both (partially and fully N-covered) surfaces. Four rotational domains are observed for the quasi-hexagonally close-packed C_{60} overlayer with a nearest-neighbor C_{60}-C_{60} distance of 1.02 nm. It is found that the interaction between C_{60} and the c(2x2)-N surface is fairly weak, likely to be dominated by van der Waals forces, whereas the C_{60}-Cu interface is chemisorbed. Site-specific electronic effects between these two regions can be resolved by STM even for thick films.

9:20am **NS+NC-FrM4 Nanochemical Equilibrium Involving a Small Number of Molecules: a Prediction of a Distinct Confinement Effect**, ***M. Polak***, *L. Rubinovich*, Ben-Gurion University, Israel

This study explores theoretically features unique to the chemical equilibrium in a nano-confined reaction mixture, which is closely related to newly developed routes for the synthesis of organic molecules and inorganic nanoclusters. Remarkable modifications in the equilibrium state of a closed small system compared to its (macroscopic) thermodynamic limit (TL) are predicted for several model reactions. Thus, canonical ensemble based statistical-mechanical formulation and computations show that a decrease in the overall number of molecules can lead to significant enhancement of the equilibrium extent of exothermic reactions. In particular, plots of lnK vs. 1/T exhibit below a certain temperature an increase in the slope, relative to the TL case, by a factor equal to the sum of the ingredient stoichiometric coefficients. In order to exemplify the smallness effect on K, the reaction $2AB(ad)=A_2(ad)+B_2(ad)$ on a surface is modeled for different overall number of molecules with emphasis on the roles of fluctuations and off-stoichiometric effects. The modeling is extended to the gaseous phase using the "harmonic oscillator-rigid rotor" approximation for the exothermic reaction $2NO(g)=N_2(g)+O_2(g)$, demonstrating the generality of the confinement-smallness effect. The enhancement is significant also in case of the addition reaction A+B=C, taking place in a closed tetrahedral "cage" as a model for a molecular capsule. The computations show that the temperature range of variations in the lnK vs. 1/T slope (from ΔH^o to $2\Delta H^o$) strongly depends on the reaction exothermity. These phenomena are relevant to reactions taking place under certain conditions in a confined nano-space, such as catalytic nanoreactors ranging from molecular capsules and micelles[1] to zeolite cavities[2] and carbon nanotubes.[3] While in catalysis the system is typically open, in nanoreactors there can be situations, such as the occurrence of rapid pre-equilibrium or "product inhibition", in which the reaction mixture is confined effectively. Then, conclusions of the closed system present modeling should be valid and taken into account as an appreciable contribution to the reaction equilibrium yield.

[1] T. S. Koblenz, J. Wassenaar, and J. N. H. Reek, Chem. Soc. Rev. 37, 247 (2008).

[2] B. Smit, and T. L. M. Maesen, Nature 451, 671 (2008).

[3] D.A. Britz et al., Chem. Commun. 37 (2005).

9:40am **NS+NC-FrM5 Epitaxial Growth of InP Nanowires on Silicon**, ***L. Gao***, *R.L. Woo*, *R.F. Hicks*, University of California, Los Angeles

Semiconductor nanowires have potential applications in new and high-performance one-dimensional devices. Epitaxial growth of high-quality semiconductor nanowires on Si surfaces is ideal for utilizing semiconductor nanowires within the frame of mainstream silicon technology. We have achieved epitaxial growth of InP nanowires on Si(111) and Si(100) surfaces by metalorganic vapor phase epitaxy (MOVPE). The silicon surfaces are wet cleaned before growth. Indium droplets are deposited onto the silicon surface as the seeds for InP nanowire growth. By finely controlling the experimental conditions, InP nanowires prefer to grow in the <111> directions of the silicon substrates, which makes it possible to grow vertical InP nanowires on Si(111) surface. By restraining the growth of non-vertical nanowires, the growth of all vertical nanowires can be achieved on Si(111) substrate. TEM and PL studies of as-grown InP nanowires will also be presented.

10:00am **NS+NC-FrM6 Structure and Electron Transport within Self-Assembled Monolayers (SAMs) of Discotic Molecules on Au-substrates**, ***A. Bashir***, Ruhr Universität Bochum, Germany, *X. Dou*, Max Plank Institute of Polymer Research Mainz, Germany, *Z. Wang*, *D. Käfer*, *G. Witte*, Ruhr Universität Bochum, Germany, *K. Müllen*, Max Plank Institute of Polymer Research Mainz, Germany, *Ch. Wöll*, Ruhr Universität Bochum, Germany

Hexa-peri-hexabenzocoronene (HBC) and HBC-derivatives can self-assemble in form of columnar film structures, which have recently attracted a significant amount of attention with regard to one-dimensional charge transport. The HBC molecules are known to form the large ordered columnar rows studied by various methods. In previous work the preparation of vertically oriented columnar rows has been achieved by employing a zone casting technique.[1] Here, we demonstrate another approach to fabricate such columnar system by an immersion process, where one-dimensional columns are formed by the self organization of discotic HBC molecules modified by thiol (-SH) anchors adsorbed on Au(111) substrates. The molecular arrangements and charge transport of such columnar films is investigated by scanning tunneling microscopy (STM) and current imaging tunneling spectroscopy (CITS). The HBC self-assembled monolayer (SAMs) are found to consist of long range ordered domains consisting of equidistant paired rows. Each row consists of a one-dimensional column of closely packed stacked HBC units. The periodicity between these rows amounts to be twice than the diameter of the HBC-molecules. From the STM data and the molecular orientation obtained from near-edge x-ray absorption spectroscopy (NEXAFS) a structural model is derived. The current-voltage (I-V) characteristics measured by locally positioned STM tip above the HBC-SAM at 298 K and at 80 K exhibit a pronounced temperature dependence, indicates the presence of an additional charge transport mechanism including a hopping between the adjacent HBC disks aside from direct tunneling

[1] Simpson, C. D.; Wu, J.; Watson, M. D.; Müllen, K., From graphite molecules to columnar superstructures - an exercise in nanoscience. Journal of Materials Chemistry 2004, 14, (4), 494-504.

10:20am **NS+NC-FrM7 Nanoscale Ballistic Heat Conduction in Silicon**, *L.J. Klein*, IBM TJ Watson Research Center, *M. Ashegi*, Stanford University, ***H.F. Hamann***, IBM TJ Watson Research Center

Today's electronic devices operations are affected by thermal issues determined by physical dimensions that are smaller or comparable to the mean free path of phonons in silicon. Controlling and understanding heat dissipation on nanometer scale can improve the thermal efficiency and power management of electronic circuits. Here we investigate heat conduction on nanometer scale employing metallic nanoheater with dimensions ranging from 100 nm up to 5 um. The nanoheaters are used both for heat generation and also for local temperature measurement. We investigate how the thermal resistance of individual nanoheaters and heat conduction across gaps ranging from 100 nm to 400 nm is changing as the sample temperature is varied from room temperature down to 30 K. As the temperature is lowered the phonon mean free path increases by more than 2 orders of magnitude compared with room temperature value and ballistic heat conduction (localized heating effects) start to play an important role. The thermal resistance of nanoheaters is a complex interplay between the thermal conductance of silicon substrate, localized heating effect and interface thermal resistance and their relative contribution changes as the phonon mean free path increases. A simple model considering the spreading thermal resistance, the interface thermal resistance, and the localized heating effect is proposed and used to model the experimental results. While for large heaters, the phonon mean free path is comparable to the size of the hot spots even at low temperature, for the small heaters, the mean free path is much larger than the heater size, and the localized heating effect plays a significant role in the total thermal resistance. The ballistic heat transport impact on nanoscale heat conduction has been evaluated in terms of heater size and phonon mean free path.

10:40am **NS+NC-FrM8 Understanding the Factors Driving Performance and Reproducibility for Spray-Coated Single Wall Carbon Nanotube Transparent Conductive Films**, ***R.C. Tenent***, *J.L. Blackburn, T.M. Barnes, M.J. Heben*, National Renewable Energy Laboratory

Transparent and electrically conducting films of single wall carbon nanotubes (SWCNT) have been shown to be useful for integration into a variety of opto-electronic devices including solution-processed photovoltaics (PV). Several techniques have been introduced for the deposition of SWCNT networks including vacuum filtration, spin coating, ink jet printing and spray coating. We believe that spray coating represents the most cost effective technique for integrating transparent conductive SWCNT network films into large scale manufacturing. While a variety of groups have reported spray deposition techniques for SWCNT networks, there has been little detailed discussion of the issues relating to performance, reproducibility, and suitability for large scale manufacturing. A number of factors influence the electronic and optical properties of SWCNT networks. These factors include the tube source, purification protocol, ink formulation procedure (e.g. sonication power, duration, and choice of surfactant), the deposition method itself, and post-deposition processing. Our current work is focused on understanding the interplay of these factors in the spray coating process for SWCNT thin films. We pay special attention to optimizing film performance and reproducibility for photovoltaic applications. These studies have facilitated the reproducible fabrication of high performance organic photovoltaic devices on our SWCNT electrodes with efficiencies comparable to devices fabricated on traditional transparent conducting oxide films, such as indium tin oxide.

11:00am **NS+NC-FrM9 Electron Beam Irradiation Induced Mass Transport in Indium Filled Indium Oxide Tubular Nanoarrow Structures**, ***M. Kumar***, *V. Singh, B.R. Mehta, J.P. Singh*, Indian Institute of Technology Delhi

Indium filled indium oxide tubular nanoarrows have been synthesized on silicon substrates by using simple horizontal tube furnace kept at 960°C and atmospheric pressure. Indium oxide powder mixed with carbon (1:1) in the presence of reducing ambient has been used for the growth of indium oxide nanotubular structures. A constant flow of Ar gas at the rate of 200 ml/min. was maintained during the growth. The transmission electron microscopy (TEM) studies show the presence of indium inside the indium oxide tubular base extended with octahedron tip. The octahedron tip is sharp and has the diameter as low as 10 nm. High resolution TEM studies reveal that the structures are crystalline in nature and growth direction to be <100>. The bottom-vapor-solid growth mechanism has been used to explain the role of reducing ambient in self catalytic growth of indium filled indium oxide tubular nanoarrows. The electron-beam-induced mass transport of indium filled in indium oxide nano structures has been studied using TEM with the background pressure of specimen chamber at 10^{-7} mbar and room temperature. The electron beam current has been varied from 0.8 µA to 24.7 µA to study the onset of phase transformation of indium from solid to liquid in different nanotube structures having diameter ranging from 30 nm to 150 nm. The electron-beam irradiation results in the melting and transport of indium inside the tubular structures. The real time imaging in TEM measurements have been used to study the mass transport properties. The synthesis of indium filled indium oxide tubular nanoarrows and the observed indium transport may have the potential nanotechnological applications.

11:20am **NS+NC-FrM10 Etch Stop Control and Low-Damage Atomic-Layer Etching of HfO2$_2$ using BCl$_3$ and Ar Neutral Beam**, ***J.B. Park***, *S.D. Park, W.S. Lim, G.Y. Yeom*, SungKyunkwan University, Korea

The downscaling of metal-oxide-semiconductor field-effect transistors (MOSFETs) has created the need for high-dielectric-constant k materials to replace SiO$_2$ for reducing the gate-leakage current while maintaining the gate-dielectric capacitance. Therefore, there have been many studies on the dry etching of HfO$_2$ using halogen-based plasma etching for applications to MOSFET devices. A precise etch rate is required in the plasma etching for HfO$_2$ instead of a high etch rate due to the low thickness of the material. Moreover, an extremely high etch selectivity over the under layer material is required. In addition, the damage on the etched surface is intolerable. However, the conventional plasma-etching processes tend to physically damage the surface of the devices by creating surface defects, including structural disruption, an intermixing layer, or stoichiometry modification, and increasing surface roughness, due to use of energetic reactive ions to achieve vertical etch profiles. In addition, these halogen-based plasma etchings showed finite etch selectivity between HfO$_2$ and the under lying materials. These problems decrease the device performance. Atomic-layer etching (ALET) may be the most suitable method for etching HfO$_2$ in next-generation MOSFET devices because it may etch HfO$_2$ with no physical damage and with atomic-scale etch controllability. The etch characteristics of HfO$_2$ by ALET were investigated using a BCl$_3$./Ar neutral beam. The effect of ALET on surface modification and etch-depth control was also examined. Self-limited etching of HfO$_2$ could be obtained using BCl$_3$ ALET. This was attributed to the absorption of BCl$_3$ by the Langmuir isotherm during the absorption stage and the vaporization of hafnium-chlorides/boron oxychlorides formed on the surface during the desorption stage. In addition, the surface composition of HfO$_2$ was not altered by etching during ALET.

11:40am **NS+NC-FrM11 Assessment and Characterization of Exposures to Airborne Nanoparticles at Research Centers**, ***S.J. Tsai***, *E. Ada*, University of Massachusetts Lowell, *J. Isaacs*, Northeastern University, *M. Ellenbecker*, University of Massachusetts Lowell

As part of ongoing efforts for the respiratory protection of researchers in the Center for High Rate Nanomanufacturing, nanoparticle exposure levels in various nanoparticle research laboratories were measured. The exposure assessments studied were associated with the use of nanoparticles during various machines processing and handling solid nanoparticles. Background particle number concentrations and particle size distributions varied significantly among the laboratories. Breathing zone particle number concentrations and particle size distributions were not significantly different from those of background when the process or handling was performed inside a laboratory fume hood or an effective local exhaust hood. However, high workers' breathing zone particle number concentrations were measured for a few operations that were performed without proper local exhaust ventilation. A TSI Fast Mobility Particle Sizer was used to measure airborne particle concentration from 5 nm to 560 nm in 32 size channels. Air samples were also collected on TEM grids placed on polycarbonate membrane filters and particles were characterized by transmission electron microscopy and scanning electron microscopy. Measurement locations were the room background, the researcher's breathing zone, and the source location. Airborne particle concentrations measured at breathing zone locations were analyzed to characterize exposure level. Elevated concentrations at the source location compared to the background concentration were found in most laboratories. Typically, nanoparticle agglomerates were formed at particle sizes ranging from nanometer to micrometer. Nanoalumina particles with individual particle size less than 100 nm formed airborne particle agglomerates as small as 200 nm and as large as above a few micrometers. Exposure levels to airborne nanoparticles were affected by the properties of nanoparticles (size, shape, density), humidity and the airflow pattern of the environment. Our study is committed to ensuring that nanoparticle research is carried out in a healthful and environmentally beneficial manner. Complete results will be fully discussed in the presentation.

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