Biomaterial Interfaces
Room: K - Session BI+NS-MoM

Nanoparticles and Self Assembly
Moderator: A. Chilkoti, Duke University, V. Perez-Luna, Illinois Institute of Technology

8:20am **BI+NS-MoM1 Self-assembling and Biofunctionalization of Plasmonic Gallium and Gold Nanoparticles on Semiconductors for Label Free Bio- and Chemo-sensing**, *M. Losurdo,* IMIP-CNR, Italy*, P.C. Wu,* Duke University*, G.V. Bianco, M. Giangregorio,* IMIP-CNR, Italy*, T.H. Kim,* Duke University*, G. Bruno,* IMIP-CNR, Italy*, **A.S. Brown***, Duke University

Biorganic functionalization of gold thin films and nanocluster mesoscalar assemblies and their resulting optical properties have immense applications ranging from biosensing to nanomedicine. The appealing property is the surface plasmon resonance of those bio-metal ensembles that can be tailored not only by the metal nanoparticles geometry but also by the nature of the biomolecules and the chemistry of the interface. This characteristic is being exploited for realizing nanoscale optical chemosensors and biosensors based on localized surface plasmon resonance of metal nanoparticles.

In this contribution we present and discuss bio- and chemo-functionalization of a novel system based on plasmonic gallium (Ga) nanoparticles (NPs) self-assembled on a large variety of semiconductor substrates including Si, SiC, GaN and GaAs. The advantages of this system for a plasmonic metal/semiconductor sensing platform are presented and compared to the standard gold (Au) nanoparticles system.

The Ga and Au NPs are directly deposited on semiconductors by evaporation and/or plasma sputtering.

For both systems Ga (NPs)/semiconductor and Au(NPs)/semiconductor we discuss semiconductor surface treatments affecting the interface chemistry and the dynamics of interface phenomena playing a role in tailoring the surface plasmon resonance.

Those systems have also been functionalized by bio-molecules, e.g., antigens and antibodies for biosensing and by porphyrins for gas sensing to nitric oxide (NO).

The peculiarity of our study is the exploitation of Plasmonic spectroscopic ellipsometry (HORIBA UVISEL, Jobin Yvon) for the optical monitoring of the plasmon resonance tuning in real time during the nanoparticles deposition on semiconductor surfaces and for the functionalization of metal nanoparticles by anchoring biomolecules to the semiconductor nanostructures.

For these plasmon-enhanced semiconductor nanoscale sensors, the degree of coverage by the porphyrin and/or protein, the aggregation, the type of binding and orientation of biomolecules on a semiconductor nanostructures surface is important for the sensing activity. Therefore, plasmonic ellipsometry is used to investigate the interplay among the nanostructures size and shape, the functionalizing solution concentration and dipping time, the mechanism of anchoring of the functionalizing molecules.

Data are corroborated by atomic force and electrical force microscopies.

This work is supported by the 7FP European Project NanoCharM_Multifunctional NanoMaterial Characterization exploiting ellipsometry and polarimetry

8:40am **BI+NS-MoM2 Geometry and Interactions: How Shape and Intermolecular Interactions Direct the Self-Assembly of Cage Molecules on Au{111}**, ***J.N. Hohman**, M. Kim, P. Zhang, E.I. Morin,* The Pennsylvania State University*, V.E. Balema,* The Sigma Aldrich Corporation*, P.S. Weiss*, The Pennsylvania State University

The self-assembly of cage molecules on metal surfaces enables the manipulation of interface chemistry while eliminating an entire class of defect modes commonly associated with straight-chain molecules such as the n-alkanethiols. The adamantanethiols and carboranethiols have similar geometries and unit cells on Au{111}, but exhibit striking differences in their behavior. We attribute these differences to their contrasting electronic structures and consequent intermolecular interactions. We have characterized the SAMs of positional isomers of several carboranethiols and adamantanethiols by scanning tunneling microscopy, cyclic voltammetry, grazing-incidence Fourier transform infrared spectroscopy, Kelvin probe microscopy, and contact-angle goniometry. We discuss how geometry and intermolecular interactions play competing roles in determining monolayer assembly and stability.

9:00am **BI+NS-MoM3 On the Role of Supramolecular Nanostructure in determining Interfacial Energy and Biological Interactions**, ***F. Stellacci***, Massachusetts Institute of Technology **INVITED**

It is know that specific molecules can spontaneously arrange on various surfaces forming two-dimensional poly-crystalline mono-molecular layers called self-assembled monolayers (SAMs). These organic coatings are used to impart targeted optical, electronic and biological properties to surfaces. Very often SAMs composed of more than one type of molecule (mixed-SAMs) are used to simultaneously impart multiple properties. Scanning tunneling microscopy (STM) studies have shown that, in mixed SAMs, molecules phase-separate in domains of random shape and size.

We will show that when mixed SAMs are formed on surfaces with a radius of curvature smaller than 20 nm they spontaneously phase-separate in highly ordered phases of unprecedented size. The reason for this supramolecular phenomenon is purely topological and can be rationalized through the “hairy ball theorem”. In the specific case of mixed SAMs formed on the surface of gold nanoparticles, the molecular ligands separate into 5 Å wide phases of alternating composition that encircle or spiral around the particle metallic core. This new family of nano-structured nano-materials shows new properties solely due to this novel and unique morphology. For example, we will show that the cell uptake of these particles strongly depends on the particle’s composition and the ligand shell morphology.

9:40am **BI+NS-MoM5 Can We Make Alkanethiol SAM's on Surface of Gold Nanorods?**, ***S. Chakraborty**, S. Lee, V. Perez-Luna*, Illinois Institute of Technology

Gold has been a fascinating element that drew the interest of people since early origins of human history. However, it is just over the last two decades that it gained a resurgence of interest, in conjunction with the advent and development of nanotechnology. Gold nanoparticles have a wide variety of bio-applications such as labeling, sensing, and targeted drug delivery. A directed assembly of gold nanoparticles in the form of nanowires or networks is extensively used as nanodevices. Nanoparticles come in a variety of shapes; spheres, rods and cubes being the frequently observed ones. Surface functionalization facilitates tailoring of the gold surface for various applications. The objective here is to investigate the surface modification of gold nanorods by chemisorption of alkanethiols.

An important property of gold nanorods is their *aspect ratio,* which is defined as the width-height ratio. The lateral surface and edge surface mostly comprise of [100[and [111[surfaces respectively. By appropriate choice of capping agents, the anisotropic surfaces can be tailored for different applications. One of the most-successful methods for synthesis of gold nanorods relies on the use of cationic surfactant CetylTrimethyl Ammonium Bromide (CTAB). CTAB provides stability, size and shape control. The displacement of CTAB allows fuctionalization with other molecules. In this work, the displacement of CTAB is carried out with alkanethiols of varying chain length, viz. 16-mercaptohexadecanoic acid, 11- mercaptoundecanoic acid, 3-mercapto propionic acid. An indirect investigation method is used to analyze the behavior of gold nanorods. Planar surfaces with the same crystalline structures as gold nanorods (111 and 110) are selected for the experiment. Surface modification of planar surfaces is conducted in two steps: formation of CTAB bilayers by immersing planar substrates followed by displacement of CTAB bilayers with alkanethiols.

The experimental studies are characterized by contact angle measurements, fourier transform infrared spectroscopy and cyclic voltammetry. The displacement of CTAB is confirmed by decrease in the contact angle upon formation of carboxyl terminated surfaces and concomitant appearance of stretching band of carboxyl groups. Cyclic voltammetry studies are carried out to calculate the free energy of adsorption of the alkanethiol layers on gold surfaces. Results indicate that longer chain alkanethiols perform better in terms of displacing the CTAB layer from the gold surfaces. The displacement of CTAB is possible on both the lateral and edge surfaces.

10:00am **BI+NS-MoM6 Size-selective Placement of Nanoparticles on a Single Particle Level**, ***P. Bhadrachalam**, S.J. Koh*, University of Texas at Arlington

We present a new nanoparticle placement technique in which single nanoparticles of different sizes recognize different target positions on a substrate and exactly one nanoparticle of specific size is placed on each target position in a self-limiting way. We demonstrate this by using ~50nm and ~20nm colloidal Au nanoparticles (AuNPs) as a model system, where the ~50nm particles are first electrostatically guided onto targeted substrate locations and then the ~20nm particles to different target locations on the same substrate. The electrostatic guiding structure was defined using CMOS-compatible fabrication processes and subsequent functionalization of surfaces using self-assembled monolayers (SAMs) of organic molecules. Using appropriate guiding structure, we present >90% success rate of ~50nm AuNPs placement onto substrate locations targeted for ~50nm AuNPs only. Theoretical calculations for ~20nm AuNPs, which was carried out by solving the non-linear Poisson-Boltzmann equation, revealed that the self-limiting single-particle placement is due to an increase of the free energy barrier after the placement of one nanoparticle onto a targeted substrate location, which prevents the approach of other nanoparticles to the already occupied position. The size-selective placement of single nanoparticles can be explained by dependence of the free energy barrier changes upon the sizes of nanoparticles and guiding structures. The same approach may also be useful for size-selective and single-entity-level placement of other nanoscale building blocks such as nanowires, proteins, and DNA.(Supported by NSF CAREER (ECS-0449958), ONR (N00014-05-1-0030), and THECB (003656-0014-2006))

Nanometer-scale Science and Technology
Room: L - Session NS+BI-MoM

Nanowires and Nanoparticles I
Moderator: L.E. Ocola, Argonne National Laboratory

8:20am **NS+BI-MoM1 Zirconia Nanoplatelets for use in Dental Restoratives**, ***K. Coulter****, V.Z. Poenitzsch, S. Wellinghoff, B. Furman, M. Rubal, D. Nicolella, K. Chan*, Southwest Research Institute

Photopolymerizable composites containing very high volume fractions (>50%) of radio-opaque nanoplatelets in a low polymerization shrinkage, liquid crystalline (LC) monomer mixture are being developed as dental restoratives. The LC monomer promotes the organization of the nanoplatelets into either a smectic or columnar, colloidal liquid crystal structure with significantly enhanced strength. Further, theoretical calculations suggest that the tetragonal form of the yttria-stabilized zirconia nanoplatelets that SwRI is producing by a roll-to-roll, e-beam evaporation process can be induced to transform into a less dense monoclinic form in the presence of the hydrostatic tensile stresses expected at a growing crack tip within the composite resin. This transformational volume expansion coupled with the inherent ductility of the surrounding LC polymer matrix results in substantial improvements in dental composite wear resistance. SwRI has successfully coated onto a 200nm pitch, nanoembossed PET film in single run lengths of hundreds of meters, a 10 nm alkali halide release layer to produce a 50nm thick zirconia film of tetragonal crystal form which is subsequently removed by dissolving the alkali halide layer in water. The nanoembossed pattern transfers to the zirconia layer to produce nanoplatelets. three specific problems have been encountered including: (1) producing tetragonal zirconia of consistent morphology in different ca 100 meter runs, (2) complete fracture along the nanoembossed pattern, (3) color in the zirconia, most probably resulting from oxygen depletion and sub-4+ zirconia oxidation states. In this paper we will present the fabrication process and challenges in producing the nanoplatelets and present some of the preliminary composite data.

8:40am **NS+BI-MoM2 Formation of Metallic Nanoclusters on TiO_2 by Deposition and Sputtering**, ***A.B. Arjad****, J.A. Yarmoff*, University of California, Riverside

The discovery that Au nanoclusters are catalytically active when supported in an oxide matrix[1] has led to an abundance of surface studies, particularly those concentrating on metal nanoclusters deposited on single crystal TiO_2. For example, STM showed that Au clusters grow on TiO_2(110) without a wetting layer and that the size of the clusters increases as more metal is deposited.[2] We previously used low energy alkali ion scattering to interrogate such clusters grown by evaporation, measuring the neutral fraction of the backscattered ions with time-of-flight spectroscopy.[3] We were able to show that the neutralization depends on the electronic structure of the clusters, and therefore changes as a function of cluster size. Our group also demonstrated a novel method for the production of nanoclusters by Ar^+ sputtering a thin Au film deposited on TiO_2.[4] As this initial work was performed with Au, it is not clear whether nanoclusters displaying quantum size effects could be fabricated by sputtering other materials. In the work presented here, Ag and Pt are evaporated onto TiO_2(110) and thin films of these metals are sputtered. The materials are then interrogated via the scattering of 2.5 keV Na^+. It was found that while both Pt and Ag form nanoclusters by evaporation, only Pt forms nanoclusters after sputtering. This may be due to differences in the surface free energy of the metals, or of the propensity of Ag to oxidize. Future efforts will include temperature programmed desorption to test the chemical activity of the metal nanoclusters, as well as the use of other substrates.

[1] M. Haruta, et al., J. Catal. **144**, 175 (1993).

[2] M. Valden, X. Lai and D.W. Goodman, Science **281**, 1647 (1998).

[3] G.F. Liu, Z. Sroubek and J.A. Yarmoff, Phys. Rev. Lett. **92**, 216801 (2004).

[4] P. Karmakar, G.F. Liu, Z. Sroubek and J.A. Yarmoff, Phys. Rev. Lett. **98**, 215502 (2007).

9:00am **NS+BI-MoM3 Towards Emergence of New Function by Engineering Materials: Colloidal Nanocrystals as Building Blocks for Nanocomposites and Assemblies**, ***M.L. Curri***, CNR IPCF, Italy **INVITED**

Increasing attention has been devoted to the properties of materials in nanophase state, which are highly dependent on their size and shape and can be dramatically different from those of the corresponding bulk phase materials. Such geometry dependent characteristics result essential for design novel functional materials with tailored characteristics, revealing a high impact on fundamental aspects as well as on potential technology applications. Fine tuning of the nanomaterial electronic, optical, magnetic, thermal, mechanical, and chemical properties opens possibilities for their wide applications in several technological fields. In this sense the basic nanosized building blocks of such complex structures play a crucial role and the extent to which nanocrystals (NCs) and nanoparticles (NPs) can be fabricated, engineered and their properties tailored is central. Chemical strategies are now able to provide highly processable NCs, possessing an adjustable interface with the external environment, able to tune their specific chemical reactivity towards the surroundings1. Equally decisive is the scheme used to convey the instruction for assembly and organization into the inorganic NPs. Assembly can be spontaneous (self assembly), guided by the intrinsic information coded into the building blocks, and/or driven by external stimuli, templates, chemical and/or physical forces.1,2 The complexity of the formed structures depend on a variety of factors, ranging from the type of the single structural component, the length scale along which the structured material is achieved, the kind of mechanism ultimately involved for the creation of the final architectures. The NC based structures, either hierarchical organized or nanocomposite in nature, can show original emergent properties which cannot be readily envisioned from the building block original properties, while can be observed to arise in the originated mesostructure of nano-objects.3 The potential to design and fabricate such nanostructured materials with unprecedented functionality open the routes for applications in biomedical, optical, electronic, catalytic and light energy conversion systems.

1. E. Fanizza, P. D. Cozzoli, M. L. Curri, M. Striccoli, E. Sardella, A. Agostiano (2007) Adv.Funct. Mater. 17 201-211.

2. M. L. Curri, R. Comparelli, N. Depalo, E. Fanizza, M. Striccoli "Patterning and Assembling of Inorganic Nanocrystals" in Nanomaterials: Inorganic And Bioinorganic Perspectives Edited by C. M. Lukehart and R. A. Scott, Chichester, UK: John Wiley & Sons, Ltd, pp 327-356,

3. J. Y.Kim, C. Ingrosso, V. Fakhfouri, M. Striccoli, A. Agostiano, M. L. Curri, J. Brugger (2009) Small 5 1051-1057.

9:40am **NS+BI-MoM5 The Direct Writing of Nanoscale Patterns of Nanoparticles and Polymer–Nanoparticle Composites**, ***P. Sheehan****, W.-K. Lee,* Naval Research Laboratory*, W. King, Z. Dai*, University of Illinois, Urbana-Champaign

In thermal Dip Pen Nanolithography (tDPN), a heatable AFM cantilever regulates the deposition of an ink through controlled melting, much like a nanoscale soldering iron. Control over writing is exceptional—deposition may be turned on or off and the deposition rate easily changed without breaking surface contact. Moreover, the technique may be performed in UHV and is compatible with standard CMOS processing. tDPN has been successful at depositing materials ranging from semiconductors to insulators to metals at speeds up to 200 µm/s.

Recently, we have become interested in directly depositing nanoparticles-polymer composites. Nanoparticles and nanoparticles–polymer composites offer many new capabilities that could greatly advance nanoelectronics, data storage, biosensors, and optical imaging applications. However, these applications often require that the nanoparticles or composites be formed into nanostructures that are precisely deposited on a surface or in a device. This requirement has spurred the development of many new nanolithographies but, to date, they have exhibited relatively low resolution (>~100 nm), a lack of generality to a range of materials, or the requirement of many serial processing steps. With tDPN, we can deposit with nanoscale precision a wide range of polymers (PMMA, P(VDF-TrFE), polyethylene) that contain metallic nanoparticles, semiconducting nanoparticles, or small molecules. An oxygen plasma can remove the polymer to reveal evenly dispersed nanoparticles or, for some combinations, precisely-placed 10 nm wide rows of nanoparticles. The flexibility and precision of this approach should greatly speed the advent of AFM tip based nanomanufacturing.

10:00am **NS+BI-MoM6 Synthesis and Structural Characterization of Fe-O Nanonetworks**

***G.C. Franco**, C.V. Ramana*, University of Texas at El Paso

Iron (Fe) oxides and hydroxides have been the subject of numerous investigations for many years. Fe oxides and hydroxides find application in chemical catalysis, magneto-electronics, energy storage and conversion, and nuclear industry. The properties and phenomena of these materials are influenced by the morphology and size. The present work is performed to grow high-quality and ordered structure Fe oxides by simple wet-chemical method at a relatively low temperature. Fe oxides and hydroxides have been prepared in aqueous media by precipitation of iron nitrate and ammonium hydroxide. Their growth and structural characteristics have been investigated using x-ray diffraction (XRD) and high-resolution scanning electron microscopy (HRSEM). The approach is preparing different solutions of Fe particles in suspension and acetic acid at different concentrations and subject to heat treatment at 100 °C. XRD analyses indicate that the solids obtained from aqueous stage exhibit goethite (α-FeO(OH)) with average particle size 2-3 nm, while the samples with acetic acid addition shown hematite (α-Fe_2O_3) with average size ~20 nm. HRSEM images confirm the presence of particles ~100 nm in samples with no acetic acid. HRSEM indicate that the samples with acetic acid exhibit nanoparticles ~20 nm with small spots within the particles. In addition, SEM shows the presence of net-shaped structures and particles with high-dense porosity within the nano-regime depending on the concentration of acetic acid. The experiments also confirm that Fe oxide nano-particles and networks are stable to a temperature of 500 °C. The results obtained on the growth, structure, and properties of the grown Fe-based nanomaterials will be presented and discussed in detail.

10:40am **NS+BI-MoM8 Synthesis of Shape Controlled Sinter Resistant Nanoparticles**

***N. Shukla**, M. Nigra, A.J. Gellman*, Carnegie Mellon University

We report synthesis of shape controlled, sinter resistant, core shell nanoparticles. The synthesis conditions allow control of the shell shape and the preparation of hexagonal shells and spherical shells. The 3D structures of these particles have been studied using angle resolved high resolution TEM. 2D cross sectional TEM images show that the cores are not positioned at the centers of the shells. By rotating the nanoparticles and monitoring the apparent motions of the cores in the 2D cross sectional images it is possible to determine the radial position of the core with respect to the center of the shell. The distribution of core positions within the core shell structures is bimodal. These observations suggest that the Fe shells grow on the Pt cores by a nucleation process rather than layer-layer growth.

11:00am **NS+BI-MoM9 Fabrication and Characterization of Carbon Nanostructures; Optical, Mechanical and Chemical Properties**

***H. Fredriksson**, T. Pakizeh,* Chalmers University of Technology, Sweden*, J. Cardenas,* University of Oslo, Norway*, M. Käll, B.H. Kasemo, D. Chakarov*, Chalmers University of Technology, Sweden

Nanosized carbon particles are present in many different context and applications. Examples include, aerosols and interstellar dust, inks, lubricants, composite materials and electronics. Investigations of the physical properties of such nanocarbons are therefore well motivated. We present a systematic investigation of the optical, mechanical and chemical properties of graphite and amorphous carbon nanostructures with different size. Hole-mask colloidal lithography and oxygen reactive ion etching is used to fabricate supported carbon nanostructures with well-defined diameters ranging from ~100 to 350 nm and heights from ~50 to 200 nm. Optical absorption/extinction spectra of these samples, as well as finite difference time domain (FDTD) calculations, reveal resonant absorption of visible light, both for the graphitic and for the amorphous carbon structures. The spectral maxima of the absorption peaks are correlated to the nanostructure diameters and heights. These optically resonant nanostructures are then further investigated using Raman spectroscopy, and compared with measurements from macroscopic graphite crystals. We show that the limited size has little influence on the mechanical properties of the graphite, i.e. the nanostructures have the mechanical properties of crystalline graphite. However, a slight enhancement of the Raman scattering intensity, correlated to the resonant absorption in the nanostructures is observed. Upon increasing the laser power we also observe distinct peak-splits and -shifts as well as increasing anti-Stokes signal intensity, suggesting selective heating of the nanostructures. Furthermore, the correlation between size and optical absorption have been used to follow the oxidation-driven size decrease of amorphous carbon nanostructures, relevant as model systems for investigations of soot oxidation. It is shown that the peak characteristics (spectral position and amplitude) are very sensitive signatures of the nanostructure size and that this can be used to accurately measure very low oxidation rates, using simple optical absorption techniques.

11:20am **NS+BI-MoM10 Microscopic and Spectroscopic Studies of Photoactive Supermolecular Porphyrin Assemblies**

***U.M. Mazur**, K.W. Hipps, B.C. Wiggins, B.A. Friesen*, Washington State University

Synthetic porphyrins form excitonically coupled ring- and rod-shaped nanostructures, which are of interest for their potential applications in optoelectronic devices and solar cells. Nanorods produced from the sodium salt of tetrakis(4-sulfonatophenyl) porphyrin, TSPP, dissolved in acidic aqueous solutions, were deposited onto Au(111) substrates and were imaged by scanning probe microscopy. Ambient and UHV scanning tunneling microcopy, STM, images revealed individual rods with diameters of 25-40 nm and lengths of hundreds of nanometers. High resolution STM images of TSPP on Au(111) showed that the rods are composed of disk-like building blocks approximately 6.0 nm in diameter. We speculate that the disks are formed by a circular *J*-aggregation of 14-16 overlapping electronically coupled porphyrin chromophores and that this circular porphyrin organization is driven by nonplanar distortions of the porphyrin diacid. X-ray photoelectron spectroscopy, XPS, was employed to investigate the structural changes in TSPP associated with the protonation of the porphyrin ring and aggregation. Scanning tunneling spectroscopy, STS, results indicate high conductivity of TSPP nanorods that can be attributed LUMO based conductivity in the nanorods.

Our results shed light not only on the structural model for TSPP basic aggregate unit but also on the conduction mechanism within the TSPP nanorod structure.

11:40am **NS+BI-MoM11 Solid-State Tunneling Spectroscopy of Individual Nanoparticles**

***R. Subramanian**, P. Bhadrachalam, V. Ray, S.J. Koh*, University of Texas at Arlington

Semiconducting nanoparticles are increasingly finding innovative applications in many areas of science and technology such as bio-medicine, solar-energy harvesting, and photonics. For effective use of nanoparticles for these applications, it is necessary to know their electronic structures and efficient and accurate techniques to measure them are desired. We present a new technique to directly probe the energy levels of individual semiconducting nanoparticles in which the units to measure the electronic structures are fabricated using CMOS-compatible processes. This technique not only enables us to probe energy levels of an individual nanoparticle, but allows carrying out many such measurements from numerous units fabricated with a single-batch parallel processing. The energy levels were directly obtained with the I-V measurement through double barrier tunnel junctions that were formed when the nanoparticles were placed between vertically separated source and drain electrodes. The band gap (E_g~1.92eV) and energy level spacings (ΔE ~ 130meV, ΔE_{p-d}~ 96meV and ΔE_{d-f}~ 103meV) were measured directly from the current-voltage and differential conductance spectra for colloidal CdSe nanoparticles (~7nm). Measurements for core-shell semiconducting nanoparticles (such as InP/ZnS) will also be presented. (Supported by NSF CAREER (ECS-0449958), ONR (N00014-05-1-0030), and THECB ARP (003656-0014-2006))

Nanometer-scale Science and Technology
Room: L - Session NS+BI-MoA

Nanowires and Nanoparticles II
Moderator: L. Bartels, University of California at Riverside

2:00pm **NS+BI-MoA1 Shape Control and Assembly of Colloidal Metal Nanocrystals**, *P. Yang*, University of California - Berkeley, ***Henzie***, University of California, Berkeley **INVITED**

Colloidal metal nanoparticles are emerging as key materials for catalysis, plasmonics, sensing, and spectroscopy. Within these applications, control of nanoparticle shape lends increasing functionality and selectivity. Shape-controlled nanocrystals possess well-defined surfaces and morphologies because their nucleation and growth are controlled at the atomic level. An overall picture of shaped metal nanoparticles will be presented, with a particular focus on solution-based syntheses and assembly for the noble metals. General strategies for synthetic control will be discussed, emphasizing key factors that result in anisotropic, nonspherical growth such as crystallographically selective adsorbates and seeding processes. The application of such nanoparticles and their arrays in SERS will be discussed.

2:40pm **NS+BI-MoA3 Properties of InP/InAs/InP Core-Shell Nanopillars Grown by Metalorganic Vapor-Phase Epitaxy**, ***V. Evoen***, *L. Gao, S. Chowdhury, R. Woo, B. Liang, M. Pozuelo, S. Prikhodko, M. Jackson,* University of California, Los Angeles, *N. Goel, M. Hudait,* Intel Corporation, *D. Huffaker, M. Goorsky, S. Kodambaka, R. Hicks*, University of California, Los Angeles

Compound semiconductor nanowire devices are of great interest due to their size-dependent electrical and optical properties and their potential applications in nano-electronics. In this study, we demonstrate the growth of InP/InAs/InP core-shell nanopillars by metalorganic vapor-phase epitaxy (MOVPE). Indium droplets were used to catalyze crystal nucleation at low temperature. At 400°C and a V/III ratio of 86, hexagonal pillars were grown with smooth side walls and average widths and heights of 45 and 70 nm, respectively. Scanning and transmission electron microscopy, electron backscattered diffraction, and selected area electron diffraction revealed that the pillars were single crystal wurtzite and were bounded by {1,-1,0,0} sidewalls. Indium arsenide quantum wells were deposited on the nanopillars at 395°C and a V/III ratio of 120, and then capped with a thin layer of InP. The thickness of the quantum well was ~5 nm. Photoluminescence spectra at 77 K yielded a single intense band at 1750 nm (0.7 eV) with a full width at half maximum of 350 nm. These results indicated that there was phosphorus and arsenic intermixing with formation of an InAsxP1-x alloy. Further growth experiments varying temperature, V/III ratio, and hydrogen interrupt time succeeded in shifting the photoluminescence peak closer to the band gap for InAs. Detailed measurements of the optical and electrical properties of the core-shell nanopillars will be presented at the conference.

3:00pm **NS+BI-MoA4 Synthesis of Vertically Aligned and Patterned Silicon-Carbon Core Shell Nanotubes**, ***J. Song***, *R. Vanfleet, R.C. Davis*, Brigham Young University

Here we report the first synthesis of silicon-carbon core-shell nanotubes (SiCNTs). The SiCNTs are formed by coating a vertically aligned and patterned carbon nanotube(CNT) forest with low pressure chemical vapor deposition (LPCVD) of silicon. The carbon nanotube forests were grown from a patterned thin film Fe catalyst resulting in high aspect ratio three dimensional microscale structures up to 500 microns tall with vertical sidewalls. The density of the nanotubes in the forests is very low; the nanotubes fill only about 1 percent of the space by volume. Silicon LPCVD layers (~30 nm thickness) are deposited conformally, coating the nanotubes and significantly increasing the mechanical strength of the structure. By adjusting the silicon deposition temperature, amorphous or crystalline silicon shells can be formed. This combination of silicon LPCVD on VACNTs yields a unique fabrication approach resulting in porous three dimensional silicon structures with precise control over shape and porosity.

3:40pm **NS+BI-MoA6 Structure and Electron Transport through Molecules Assembled in Multi-Component Molecular Gradient Layers**, ***N. Ballav***, *P. Morf,* Paul Scherrer Institute, Switzerland, *F. Nolting,* Swiss Light Source, Switzerland, *F. Wrochem, H.-G. Nothofer, A. Yasuda, J. Wessels,* Sony Deutschland GmbH, Germany, *T.A. Jung*, Paul Scherrer Institute, Switzerland

Surface molecular gradients are essential for the fast screening of molecular and cellular adhesion and motion in assays and have been used to relate molecular binding with the biological response for functional biomolecular entities. They are being used for optimizing the properties of bio-interfaces, bio-chips, bio-assays, and bio sensors, and for controlling wettability to induce movement in water droplets. Herein we present a new method to fabricate self-assembled monolayer (SAM) based multi-component molecular gradients comprising constituents with specific head or tail groups attached to different molecular backbones. We demonstrate for the first time how local (STM) and non-local (NEXAFS) methods can be combined with theoretical calculations (DFT) to draw conclusions on structure, orientation and local processes, in particular electronic conductance in the gradient layer (1). Our achievement goes beyond previous works in the ability to visualize molecular gradient layers and to study the anisotropy of physicochemical properties with laterally changing composition.

4:00pm **NS+BI-MoA7 Reduction, Morphology, and Conductivity of Pd Nanoparticles on Pyridine-Terminated Self-Assembled Monolayers**, ***C. Silien***, University of Limerick, Ireland, *M. Buck, S. Francis, M. Caffio, B. Wang, R. Schaub,* University of St Andrews, UK, *D. Lahaye, N.R. Champness*, University of Nottingham, UK

Metallization of organic self-assembled monolayers (SAMs) is generally impeded by the penetration of metal through the film. A two-step scheme, involving coordination of metal ions and electrochemical reduction in separate solutions [1], was recently proposed to circumvent the problem, opening up new opportunities for the preparation of low-dimensional metal structures on SAMs. This strategy was further investigated using SAMs of newly designed pyridine-terminated molecules (ω-(4-pyridine-4-yl-phenyl)-alkanethiol, PyPn, with n=2,3) [2], which combine the high structural integrity and quality of biphenyl-based SAMs [3,4] with the chemical functionality afforded by the pyridine moiety. Pd adlayers on PyPn SAMs on Au(111) were prepared by reduction of Pd^{2+} either directly from solution or following the two-step scheme [1]. Scanning tunneling microscopy (STM) revealed that, in both cases, and independently of the alkane spacer length, Pd systematically organizes into nanoparticles that are weakly bonded onto the pyridine moieties (*i.e.*, easily displaced with tunnel current of the order of a few pA), exhibit a narrow height distribution around 2.4 nm and display a Coulomb gap of ~ ±0.20 V. These data strongly suggest that the Pd nanoparticles are not contacted with the Au substrate. Moreover, the nanoparticle coverage can be increased up to a monolayer, revealing that it is more favorable to generate new nanoparticles than to add material to existing ones. It is proposed that Pd^{2+} reduction is not mediated by structural defects in the SAM. Lateral diffusion of Pd adatoms and nanoparticles occurs on the SAM and explains the morphology of the Pd adlayer.

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4:20pm **NS+BI-MoA8 Estimation of Thermal Conductivity of Si and Oxide-Covered-Si Nanowires by Molecular Dynamics Simulation**, ***T. Saegusa***, *K. Eriguchi, K. Ono,* Kyoto University, Japan, *H. Ohta*, University of California, Santa Barbara

Nanowires (NWs) have attracted much attention because they are expected to be applicable to various devices such as the field-effect transistors, solar cells, and thermoelectric devices. The reason is that in nanostructures, we can see some peculiar phenomena which are not observed in bulk materials. One of the phenomena is the lower thermal conductivity of NWs [1]. The thermal conductivity of NWs is one to two orders of magnitude lower than the bulk value (~168 W/mK at 300K). This is appreciated to occur by confinement of the phonon propagation. The phonons are prevented by surface scattering due to the small wire radius. This means that surface atoms may have a great influence on material properties. Experimental observations of the thermal conductivity by P. Yang's group [1] as well as theoretical studies by different approaches such as Boltzmann transport equation, Monte Carlo (MC) method for phonon propagation [2], and molecular dynamics (MD) simulations [3] have been published. In addition, Hochbaum *et al*. experimentally observed the reduction of thermal conductivities in Si-NWs fabricated by electroless etching, where silicon NWs were coated by native oxides [4]. These studies indicate thermal conductivities are very sensitive to surface structures.

In this paper, we present the thermal conductivity of naked Si-NWs and oxide-coated Si-NWs at 300 K, evaluated by employing direct nonequilibrium MD simulation with the Stillinger-Weber interatomic potential model for Si/O systems. The thermal conductivity was obtained for various cross sections (2-8 nm^2) and lattice orientations (<100>, <111>, and <110>). The thermal conductivity for naked Si-NWs with cross sections of 2-8 nm^2 at 300 K was 2-10 W/mK, which was in good agreement with that for <100>Si-NWs (1-2 W/mK) obtained from equilibrium MD simulation by Volz *et al*. [3] and from MC simulation by Chen *et al*. [2]. We found the small dependency of thermal conductivity on the lattice orientation. In case of oxide-coated Si-NWs, the thermal conductivity was reduced as the thickness of Si-oxides increased. To check our simulation results, we also analyzed the strain in Si-NW due to surface oxidized layers. Detailed simulation results and analytical approach for various surface structures or cross-sections will be shown at the conference.

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4:40pm **NS+BI-MoA9 Temperature Dependence of Carbon Nanofiber Resistance**, ***H. Yabutani***, *T. Yamada, T. Saito, C. Yang*, Santa Clara University

To assess their potential for interconnect applications, the interplay between electrical and thermal transport in carbon nanofibers (CNFs) under high-current stress is examined. Current-voltage measurement results obtained during each stress cycle reveal temperature-dependent behavior of CNF resistance, the analysis of which is the subject of this paper.

To minimize the contact resistance between gold electrode and CNF, tungsten is deposited on each electrode using focused ion beam [1]. For each test device, we apply stressing current progressively, *i.e*., in the first cycle, a small current is applied for three minutes, and in the second cycle, a slightly larger current is applied for another three minutes, etc. Using this scheme, we obtained a decrease in average resistance with increasing stressing current for each stress cycle. In ref. [2], we presented a heat transport model that takes into account Joule heat generation, dissipation, and diffusion during current stressing. In this model, the CNF temperature along its length was determined as a function of stressing current. Since the increase in temperature originates from Joule heating, and since we established that current stressing has little effect on the total resistance at ambient temperature prior to breakdown [1], this result suggests that the reversible resistance change due to Joule heating is a result of change in bulk CNF properties at elevated temperatures.

The mechanism for CNF bulk resistance decrease with temperature was discussed in the context of transport in disordered media [3]. Our CNF devices have impurities and/or lattice defects, which often serve to trap carriers. Thermal energy releases these carriers from the trap centers, giving rise to lower resistance. Thus transport is controlled by thermal activation of these trapped carriers and their subsequent re-trapping as the temperature is lowered. The same mechanism would account for the observed decrease in resistance as the temperature increases with increasing stressing current due to Joule heating.

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5:00pm **NS+BI-MoA10 Relative Stability of Aromatic Self-Assembled Monolayers Formed by Thiols and Selenols**, ***K. Szelagowska-Kunstman***, *P. Cyganik*, Jagiellonian University, Poland, *B. Schüpbach, A. Terfort*, Goethe-Universität Frankfurt, Germany

Aromatic self-assembled monolayers (SAMs) are considered a model system for molecular electronics applications.[1] However, potential use of these monolayers in real devices is limited by significant concentration of structural defects,[2] which disturb functions of the metal-molecule-metal junction. One of strategies we propose to optimize structure of aromatic SAM's is selection of proper headgroup atom binding SAMs to the substrate.[3,4]

In this presentation we report on stability of two analogous aromatic SAMs bound to the Au(111) substrate by S or Se atom. To compare stability of both systems we analyze exchange of molecules constituting complete SAM monolayer during incubation in solution containing other aliphatic thiol or aliphatic selenol molecules.[5] The exchange experiments have been performed by comparing not just a single SAM but two entire homologue series of BPnS (CH_3-$(C_6H_4)_2$-$(CH_2)_n$-S-, n = 2-6) and BPnSe (CH_3-$(C_6H_4)_2$-$(CH_2)_n$-Se-, n =2-6) molecules on Au(111) surface. Quantitative control of the exchange process was obtained using Infrared Reflection Adsorption Spectroscopy. These data will be discussed together with our recent microscopic study which found that binding by selenium atoms improve significantly the ordering of these SAMs and influences molecule-substrate interaction.[4] Obtained results clearly indicate higher stability of SAMs based on selenols in comparison to their thiol analogs.

References

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Nanometer-scale Science and Technology
Room: L - Session NS+TR-TuM

Modeling Nanoscale Phenomena
Moderator: S.B. Sinnott, University of Florida

8:20am **NS+TR-TuM2 Tribological Behavior of Nanostructured Materials Predicted from Molecular Dynamics Simulations**, ***E. Bucholz***, *T. Liang, S.R. Phillpot, S.B. Sinnott*, University of Florida

Nanostructured materials such as fullerenes and nanotubes have been of much interest to tribologists since the discovery of C_{60}, buckminsterfullerene, in 1985. Characterized by weak van der Waals (vdW) forces that govern the interactions between these nanostructured materials, low friction coefficients are obtained through combinations of rolling, sliding, and rotating at the sliding interface. This presentation will report on the tribological properties of onion-like carbon (OLC) fullerenes with and without a residual diamond core as a solid lubricant between two sliding, diamond-like carbon (DLC) surfaces. The molecular dynamics (MD) simulations presented here utilize the reactive empirical bond order (REBO) potential for short range interaction coupled with the Lennard-Jones (LJ) potential for long range vdW interactions Within these simulations no discernable difference is predicted between the OLC fullerenes with a diamond core and those without. Further, the frictional behavior of these systems is highly dependent on the interactions that take place between the fullerenes and the DLC substrates. Without the formation of bonds with the substrates, the OLC fullerenes in the simulations are able to roll providing extremely low frictional forces, but as bonds begin to form, the OLC fullerenes begin to slide which causes a significant increase in the observed friction. The presentation will also report on the mechanical properties of molybdenum disulfide (MoS_2) nanotubes and their response when used as solid lubricants between two sliding Mo surfaces. Variations in number of nanotube layers, temperature, and compressive load are examined in order to characterize each system. The authors acknowledge the support of the National Science Foundation Grant No. CMMI-0742580.

8:40am **NS+TR-TuM3 High Pressure at Small Scales in Tribology and Piezoelectronics: Insights from First-Principle Molecular Dynamics**, ***M.H. Müser***, University of Western Ontario, Canada **INVITED**

At very small scales, many solids have the ability to sustain extremely large pressures before wearing off, i.e., up to a few GPa. Some materials, deposited on top of such hard solids, undergo chemical changes at these pressures, thereby changing their mechanical or electrical properties dramatically. In my talk, I will discuss how first-principle molecular dynamics can be used to analyze the mechanisms responsible for changes in the response functions of the deposited materials. Specific examples will be zinc phosphates (ZPs), in their function as anti-wear additives in commercial lubricants, and doped pnictogen solids (DPSs), when used in non-volatile electronic memory or in programmable switches. Molecular dynamics reveals when and why ZPs show "smart material" properties and anticipate the possibility for DPSs to be switched with nanoscale piezoelectronic actuators.

9:20am **NS+TR-TuM5 Optical Energy Density Inside Metallic Nano-Apertures**, ***P. Zhu***, *H. Craighead*, Cornell University

We use numerical methods and calculate the optical energy density inside a sub-micron sized hole surrounded by metallic cladding as light wave travels through it. Such information is important in the use of Zero-Mode-Waveguides (ZMWs) [1], where the diameter of the apertures is less than the wavelength of the light. In ZMWs, it has been postulated the evanescent wave inside the aperture defines the illumination volume, which is a function of the illumination wavelength and the aperture cut-off wavelength, which is in-turn a function of the aperture-diameter. Although the cut-off wavelength of a circular hole in an infinitely thin perfect conductor is a monotonically increasing function of the hole diameter [2], we see from our calculation result that, inside apertures surrounded by aluminum cladding, optical energy density increases until it reaches a peak as aperture diameter increases, and then levels off as aperture becomes more transmitting. This result suggests that, in order to achieve the best signal-to-noise ratio in fluorescent single-molecule experiments involving ZMWs, there is an optimal aperture diameter for each wavelength and application.

[1] Levene et al, “Zero-Mode Waveguides for Single-Molecule Analysis at High Concentrations, Science, Vol 299, 2003.

[2] Jackson, J. D., Classical Electrodynamics, 1998.

9:40am **NS+TR-TuM6 Field Amplification in Surface-Enhanced Raman Scattering**, *E.J. Adles*, ***S. Franzen***, *D.E. Aspnes*, North Carolina State University

Surface-enhanced Raman scattering (SERS) is experiencing renewed popularity as a result of the present interest in nanostructures and reported observations of SERS from single molecules. However, the detailed reasons for enhancements, which have been reported to be as much as 10^{14}, remain unclear. We address the issue from a fundamental perspective that has provided insight into the physics of second-harmonic generation and other nonlinear-optical processes, considering metallic spherical inclusions for simplicity. One obvious result, although it contradicts many statements in the literature, is that resonant-plasmonic enhancement of both incident and emitted waves by the same sphere is impossible, since the sphere cannot simultaneously exhibit plasmonic resonances at the frequencies w_o and w_R of the driving and Raman fields, respectively. The presence of an adjacent inclusion nominally resonant at the other frequency does not resolve the issue due to coupling by the longitudinal (Coulomb) interaction. However, under certain circumstances amplification can occur at a second frequency by means of a resonance activated by a renormalization of the effective mass of the bonding electrons of the molecule due to their longitudinal interactions with the sphere. Local configurations in deposited thin films where this could occur would likely be extremely rare, but cannot be ruled out completely.

Tuesday Afternoon, November 10, 2009

Nanometer-scale Science and Technology
Room: A8 - Session NS1+PV-TuA

Organic Photovoltaics I
Moderator: P. Sharps, Emcore Corporation

2:00pm **NS1+PV-TuA1 Probing Polymer Photovoltaics: Imaging Photocurrents and Controlling Morphology in Organic Solar Cells**, ***D.S. Ginger***, University of Washington **INVITED**

Organic solar cells are a potential low-cost alternative to conventional inorganic photovoltaics. The most successful organic solar cells rely on nanoscale phase separation between different components to achieve high efficiencies. Understanding and controlling nanoscale film structure has thus become the central challenge that affects every aspect of the field, from the optimization of new low-bandgap polymers to early efforts to scale up manufacturing of polymer solar cells. Our group has pioneered several scanning-probe methods, including time-resolved electrostatic force microscopy (trEFM) and photoconductive atomic force microscopy (pcAFM), as tools to characterize active organic solar cells. We discuss applications of these tools to study several model polymer systems, including the local origin of the photocurrent in polyfluorene blends, the effect of annealing on the formation of hole transport, electron transport and photocurrent collection networks in the archetypal polythiophene (P3HT) fullerene (PCBM) system, and the role that mesoscopic PCBM crystallites play in polyfluorene-copolymer/PCBM cells during solvent-vapor annealing. These data show the power of scanning-probe methods in correlating morphology with performance, and underscore the need to model these devices as fully 3D networks, rather than as uniform 2D semiconductor slabs.

2:40pm **NS1+PV-TuA3 Nanoscale Confinement Induced 3-D Chain Alignment of Poly (3-hexylthiophene) for Organic Solar Cells**, ***M. Aryal***, *K. Trivedi, W. Hu*, University of Texas at Dallas

Organic semiconducting polymers are of wide interests for many applications in organic solar cells, field effect transistors, light emitting diodes, and biosensors. The optical and electrical properties of these polymers are anisotropic which largely depends on their nanoscale morphology, crystallinity and the direction of chain configuration. Furthermore, control over direction of chain orientation is essential as certain devices prefer chain alignment in certain directions as determined by device structures, e.g. vertical alignment for solar cells where vertical charge transport occurs, while for FETs, lateral orientation along the channel is preferred instead. Though the significant progress has been made by the development of varieties of techniques for control of nanoscale morphology, crystallinity and orientation of polymer chains for years, the perfect crystallization and preferred chain ordering in nanoscale regime still remains challenging. We report the fabrication of highly-ordered nanostructure arrays of nanopillars and nanogratings in poly (3-hexylthiophene) (P3HT) using nanoimprint lithography and show 3-D chain ordering by x-ray diffraction (XRD) analysis. We have proved for the first time that nanoscale confinement exerted by the mold can induce only one possible configuration of the chain network in the three dimensional P3HT nanostructures during thermal nanoimprint process. Such monodical 3-D chain configuration strongly depends on the geometry of the nanoconfinement. Interestingly the configuration is arranged in a favorable way for solar cell and FET applications, e.g. vertical chain alignment, and π-stacking along gratings.

In this report, uniform 80 nm thin films of rerioregular P3HT were prepared on a Si substrate. The nanograting of 200 nm height, 65 nm wide gratings at a period of 200 nm while hexagonal array of nanopillars of 150 nm high nanopillars with 80 nm diameter were fabricated using nanoimprint lithography. The P3HT nanostructures were characterized by SEM and crystallization and chain orientation were studied by both in-plane, out-of-plane and in-plane grazing incident XRD. The chain ordering of thin film, nanopillar and nanograting structures are proved to be entirely different. The conjugated polythiophene backbones which are horizontal to the substrate in the thin film are reordered into vertical direction in the imprinted structures of P3HT. The interaction of hexyl side chains with hydrophobic mold surface in turn results π-stacking along nanogratings. We will present XRD results analysis and expect to present solar cell device results using these imprinted P3HT nanostructures.

3:00pm **NS1+PV-TuA4 Porphyhrin-Gold Junctions in Molecular Optoelectronics**, ***S.U. Nanayakkara***, University of Pennsylvania, *P. Banerjee*, University of Maryland, *D. Conklin*, University of Pennsylvania, *T.-H. Park*, University of Michigan, *M.J. Therien*, Duke University, *D.A. Bonnell*, University of Pennsylvania

Photo-conductance in novel multi-chromophoric molecules with porphyrin centers has been measured. This class of molecules is fully conjugated optical absorption properties that induce hole mediated conductivity with delocalization lengths on the order of 8 nm. Conjugated linker groups that terminate with a thiolate functionality (on one or both sides of the molecule) enable facile, co-valent attachment to a gold surface. We have attached these multi-chromophoric molecules between surface-bound Au nanoparticles and have measured transport as a function of varying laser excitation wavelengths. Additionally, we have measured spatially varying, charge transport in individual molecules within a tunneling junction utilizing a laser-coupled ultra-high vacuum scanning tunneling microscope. The wavelength dependent conductance will be discussed within the context of the molecule-Au junction.

4:00pm **NS1+PV-TuA7 Torsional Defects in Conjugated Polymers: Modeling and Nanostructured Photovoltaic Materials**, ***S.B. Darling***, *M. Sternberg*, Argonne National Laboratory **INVITED**

Conjugated polymers represent a promising class of organic semiconductors with potential applications in a variety of molecular devices. Poly(3-alkylthiophene)s, in particular, are garnering interest due to their large charge carrier mobility and band gap in the visible region of the spectrum. Defects play a pivotal role in determining the performance of polymer electronics, and yet the function of specific types of defects is still largely unknown. Density functional theory calculations of alkyl-substituted oligothiophenes are used to isolate the effect of static inter-ring torsion defects on key parameters such as electronic coupling between rings and band gap. These polymers are often modeled with very short backbones and without their side chains. These results demonstrate the shortcomings of this approach for modeling torsional disorder and identify a minimal acceptable model.[1] Two experimental systems, one based on block copolymers and the other on a hybrid oxide nanotube-polymer system, with nanoscale morphology rationally designed to minimize torsional disorder will also be discussed. Results have potential implications both for the fundamental understanding of intramolecular charge transport and for improving processing in organic optoelectronic devices.

[1] Use of the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract #DE-AC02-06CH11357.

5:00pm **NS1+PV-TuA10 Locally Probing the Efficacy of Photoinduced Charge-Generation and Trap Clearing in Pentacene-Based Thin-Film Heterojunctions and Transistors using Electric Force Microscopy**, ***J. Luria***, Cornell University, *A. Gorodetsky, C. Nuckolls*, Columbia University, *J.A. Marohn*, Cornell University

Pentacene and its derivatives are leading candidates for many organic electronics applications including electron donors in organic photovoltaics. Charge trapping, which is associated with device degradation in both photovoltaics and transistors, remains poorly understood even in this comparatively well studied class of materials. Northrup and Chabinyc [1] have carried out ab initio studies showing that reactions of holes with hydrogenated and oxygenated pentacene is a plausible charge trapping mechanism. Jaquith et al. [2] demonstrated a dependence of trap formation rate on hole concentration in pentacene, which is consistent with traps forming by a defect-mediated chemical reaction, and showed that traps could be cleared by the application of light. Coffey and Ginger [3] have shown that the fastest charging rates under illumination in polymer/fullerene films do not occur at phase interfaces, as widely assumed. Charge generation at the donor-acceptor interface in organic heterojunctions also remains poorly understood.

To resolve such open questions, we have developed a general approach to illuminating samples (from above) in an electric force microscope. We will describe studies where variable-wavelength light is utilized to clear traps in polycrystalline pentacene transistors. We will also discuss investigations into image charge generation in bis(thienyl)-pentacene/PCBM bulk heterojunction thin films.

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[3] D.S. Ginger and D.C. Coffey, *Nat. Mater.* **5**, 735 (2006).

5:20pm **NS1+PV-TuA11 A New Look at Si Inversion-Layer Solar Cells, Meeting Ground for Inorganic, Molecular and Organic Electronics**, ***R. Har-Lavan***, *O. Yaffe*, *D. Cahen*, Weizmann Institute of Science, Israel

We suggest a near-ambient temperature, simple and potentially low-cost approach to fabricate semiconductor solar cells. To this end we use a monolayer of organic molecules that self-assembles onto n-Si, to passivate and buffer the Si surface. The direct binding of the molecules to the oxide-free Si surface also provides a strong interface dipole and effectively reduces the semiconductor's electron affinity by as much as 0.7 eV. A thin layer of a conducting polymer with a high work function, that is spin-coated on top of the molecular layer plays a threefold role:

the high work function induces inversion in the Si and leads to an n-p^+ homojunction in the Si;

with n~1.5 refractive index the polymer acts as an anti-reflective coating to the Si.

because it protects the molecular monolayer, subsequent metal deposition and encapsulation is now possible.

Good and stable interface passivation along with strong inversion allow minority carriers, generated by absorbed sun light, to move laterally within the inverted Si top layer and to be collected by a minimal area metal grid, deposited on the conducting polymer. For the same reason (lateral conductance) photo-current losses, due to polymer sheet resistance, are minimized. Not only are cells fabricated without high temperature steps, the use of small organic molecules appears to convey here a unique advantage over inorganic passivation or buffer layers. The approach, which includes no or minimal (for metal grid) high vacuum steps, should be applicable to other inorganic absorbers, amorphous materials and thin films to improve photovoltaic solar energy conversion.

5:40pm **NS1+PV-TuA12 Modification and Characterization of Transparent Conducting Oxides for Generation III Nanostructured Photovoltaics**, ***D. Placencia***, *N. Armstrong*, University of Arizona

Indium-Tin oxide (ITO), Indium-Zinc oxide (IZO), and Antimony-doped tin oxide (ATO) substrates were modified with ca. 3-5 nm gold nanoparticles to characterize their effect on the performance of Generation III organic photovoltaics (OPVs). This talk will focus on the presumed mechanism for their deposition, their impact on rates of electron transfer (solution), and OPV device performance parameters. ITO, IZO, and ATO thin films were deposited via magnetron sputtering and modified through a deposition-precipitation protocol. X-ray, UV photoelectron, and polarization modulated infrared reflection absorption spectrocopies were used to characterize the interfacial composition, work function changes, and the molecular nature of Au NP nucleation and growth. Planar heterojunction OPVs were created to evaluate the efficacy of oxide modification with metal nanoparticles, as an intermediate step towards the improvement of charge collection at the organic/oxide interface in organic solar cells.

Nanometer-scale Science and Technology
Room: L - Session NS2-TuA

Templated Self-Assembly
Moderator: N.A. Burnham, Worcester Polytechnic Institute

2:00pm **NS2-TuA1 Size-selective Templated Self-Assembly of Particles**, *C. Kuemin*, ETH Zurich, Switzerland, *E. Loertscher, A. Rey, A. Decker*, IBM Research GmbH, Zurich Research Laboratory, Switzerland, *N.D. Spencer*, ETH Zurich, Switzerland, ***H. Wolf***, IBM Research GmbH, Zurich Research Laboratory, Switzerland

The special properties of nanoscale objects, such as metal and semiconductor nanoparticles, nanowires, or nanotubes, make them promising building blocks of novel optical and electronic devices. The systematic fabrication of devices usually requires the integration of these heterogeneous materials into a larger, ordered structure. More complex device architectures may, in addition, entail the selective assembly of several different types of small objects into pre-defined locations or demand an assembly with the correct orientation when such objects are nonspherical.

Serial pick-and-place techniques are no longer economical at these length scales. Self-assembly mechanisms can arrange a large number of objects in parallel, but will mainly produce homogeneous monolayers limited to the characteristic length-scale of the assembled objects (e.g. the diameter of the particles). Templated assembly on the other hand, provides an adequate strategy for the massively parallel arrangement of particles into designed patterns of arbitrary structure. With selective assembly sites, integration of different components becomes feasible.

Here we show concepts and experimental implementations for the selective templated self-assembly of spherical particles of different size. Particles between 200 and 500 nm in size are assembled selectively into predetermined locations on a template. We use capillary assembly from aqueous suspensions onto templates with topographic features that are selective for a certain particle size. The templates are prepared in poly(dimethylsiloxane) (PDMS) molded from a topographically patterned master. The master is a Si wafer patterned by electron beam lithography.

As a model system for the templated self-assembly of nonspherical objects we use Au nanorods.

2:20pm **NS2-TuA2 Templated Self Assembly of 6 nm Gold Nanoparticles by Means of micro-Trough Technique**, ***L.E. Ocola***, Argonne National Laboratory, *A. Chao*, Illinois Mathematics and Science Academy

This paper demonstrates that combining top-down electron beam lithography and bottom-up colloidal chemical assembly leads to large scale placement of nanoparticles on arbitrary flat substrates. We report on the templated self-assembly of 6 nm gold nanoparticles using template geometries that lend themselves to induce self-assembly at distances significantly larger than typical trench geometry constraints. We can obtain oriented and ordered arrays of 6 nm gold nanoparticles that extend hundreds of nanometers away from any template boundary. The goal is to be able to create oriented arrays of nanoparticles over hundreds of microns. We have developed a micro-Trough technique where we define a specific area on where to create an equivalent of a Langmiur Blodgett trough directly on a sample surface. Using this technique we overcome liquid current effects usually encountered in traditional colloid dispersion deposition techniques. Progress in templated self-assembly will lead to novel nanophotonic and chemical sensing devices, along with the means to extend top-down nanofabrication below the 10 nm barrier.

2:40pm **NS2-TuA3 Focused Ion Beam Templating and Doping of Si(Ge) Nanostructures**, ***J.F. Graham***, *C.D. Kell, J.A. Floro*, University of Virginia, *R. Hull*, Rensselaer Polytechnic Institute

An important application of the focused ion beam (FIB) is nanoscale modification of surfaces for directed self-assembly of nanostructures. In previous work, we have demonstrated Ga^+ FIB patterning of Si(100) substrates followed by epitaxial deposition, resulting in templated nucleation of Ge quantum dots (QDs) and SiGe quantum dot molecules (QDMs). Such positional control of QD growth using FIBs should be useful in fabricating potential, QD-based nanoelectronic devices like quantum-dot cellular automata and spin exchange switches. However, since Ga is a *p*-type dopant in Si, patterning with Ga^+ ions from a conventional liquid metal ion source (LMIS) leads to uncontrolled doping of the Si substrate. Moreover, Ga can behave as a surfactant during epitaxial growth of Si and Ge. In this work, we use electrically non-invasive ions for FIB-templated growth in order to avoid Ga doping and as a means to investigate fundamental mechanisms involved in templated nucleation of QDs. We employ a mass-selecting FIB and alloy LMISs to work with ions which are unobtainable from elemental sources. Ions of particular importance for non-invasive patterning include Si (obtained from a AuSi LMIS) and Ge (from a AuGeMn LMIS). In addition, the use of B ions (from an AsPdB LMIS) is explored as a potential method of producing auto-doped, templated QDs. These techniques are establishing a platform for nanoscale control of the formation, position and doping of epitaxial QD arrays of any desired complexity.

4:00pm **NS2-TuA7 Clathrin: A Protein Scaffold for Biotemplating 2-D and 3-D Nanostructures**, ***A.P. Schoen***, *S.C. Heilshorn*, Stanford University

Nature has evolved numerous methods for the self-assembly of nanoscale architectures with high levels of precision. Biomolecules such as DNA, bacterial membranes, viral particles, and proteins all exhibit stunning regularity and reproducibility in the structures they can achieve, making them ideal templates for the patterning of inorganic nanostructures. While some success has been realized in patterning materials from these biological templates, they generally have been limited to simple 0-D or 1-D structures. In contrast, proteins have the ability to form 2-D and 3-D structures, and the immense library of naturally available proteins encourages the development of new techniques to reproducibly template these materials.

Using clathrin as a model protein, we are developing flexible biotemplating protocols to interface protein structures with a variety of inorganic materials. The intracellular transport protein clathrin is composed of three semi-flexible arms that form a pinwheel structure with three-fold symmetry. Clathrin provides a framework that offers access to a variety of architectures, both 2-D and 3-D, such as sheets, tetragons, and geodesic spheres depending on the environmental conditions (pH, concentration, buffer ionic strength) during assembly. The ability of this single protein to assemble into multiple structures makes clathrin an ideal model system for investigating the underlying kinetic and thermodynamic principles of self-assembly. To interface these biological templates with inorganic materials, we design bi-functional peptide linkers that serve as molecular bridges between the clathrin protein and inorganic materials. Rational design of these bi-functional peptide linkers includes a conserved clathrin-binding motif fused to an inorganic-binding peptide sequence. This newly developed strategy enables great flexibility to interface a single protein biotemplate with a variety of different inorganics without requiring any direct modifications to the template. The ability of a single protein biotemplate to assemble into multiple 2-D and 3-D protein nanostructures and to interface with a variety of inorganic materials makes this modular, self- assembling system applicable to a broad range of applications.

4:20pm **NS2-TuA8 Assembly of Block Copolymer Micelles on a Lithographically Modified Surface**, ***A. Pearson***, *R.C. Davis*, Brigham Young University

Block copolymer self-assembly is a promising method of creating ordered arrays with feature sizes smaller than possible by conventional lithography techniques. Block copolymer micelle patterning has proven to be a versatile method of creating hexagonal arrays of metal nanoparticles with sizes less that 10 nm and spacing that can be adjusted by changing the molecular weight of the block copolymer used. In order to use these nanoparticles for many lithographic applications, registration of the nanoparticles with other surface patterns is essential. Here we exploit the self-aligned assembly of PS-P2VP block copolymer micelles with both topographical and chemical surface patterns to achieve micelle registration. Specifically e-beam lithography and plasma etching of SiO_2 surfaces was used to create recessed boxes and ovals where controlled numbers of micelles were deposited by dip coating. Chemical patterning was used to selectively place micelles in the recessed patterns with low micelle adsorption in the non-recessed regions. Gold nanoparticles were formed from the micelles by adding $HAuCl_4$ to the micelles in solution prior to deposition. After dip coating , an oxygen plasma etch removes the polymer, leaving gold nanoparticles. Scanning electron and atomic force microscopy were used to measure nanoparticle alignment.

Surface Science
Room: C1 - Session SS1+PS+TF+AS+NS-TuA

Non-Thermal Chemistry / Ion, Electron Processes
Moderator: A.V. Walker, University of Texas at Dallas

2:00pm **SS1+PS+TF+AS+NS-TuA1 Growth and Purification of Nanostructures Deposited by Electron Beam Irradiation: A Surface Science Perspective**, ***H. Fairbrother***, *J. Wnuk*, *J. Gorham*, *S. Rosenberg*, Johns Hopkins University, *T. Madey*, Rutgers, *W.F. van Dorp*, *K. Hagen*, Delft University of Technology, The Netherlands

Focused electron beam induced processing (FEBIP) of volatile organometallic precursors has emerged as an effective and versatile method of fabricating metal-containing nanostructures. However, to improve the materials properties of FEBIP nanostructures, provide information that can aid in the rational design of new precursors and improve the modeling of the FEBIP process it is necessary to better understand the molecular level processes associated with the electron stimulated decomposition of organometallic precursors. To address this issue, we have employed a UHV-surface science approach to study the electron induced reactions of dimethyl(acetylacetonate) gold(III) ($Au(acac)Me_2$), a common precursor used for Au deposition in FEBIP, adsorbed on solid substrates. Surface reactions, reaction kinetics and gas phase products were studied using incident electrons in the energy regime between 40-1500 eV, using a combination of XPS, RAIRS and MS. XPS data indicate that electron irradiation of $Au^{III}(acac)Me_2$ is accompanied by the reduction of Au^{III} to a metallic Au^0 species embedded in a carbon matrix while MS reveals the concomitant evolution of methane, ethane and hydrogen. The electron stimulated decomposition of the $Au^{III}(acac)Me_2$ precursor can be described by a first-order decay process with respect to the surface coverage, with a rate constant that is proportional to the electron flux and a total reaction cross-section of $\approx 3.6 \times 10^{-16}$ cm^2 at an incident electron energy of 520 eV. As a function of the incident electron energy, the maximum deposition yield was observed at ≈175 eV. Our results are consistent with the idea that those carbon atoms removed as volatile species from the $Au^{III}(acac)Me_2$ precursor during FEBIP are associated with methyl groups attached to the central Au atom. In related studies we also studied the effects of atomic oxygen and atomic hydrogen on Au-containing carbonaceous films deposited by electron beam irradiation of $Au(acac)Me_2$, as a potential route to purify FEBIP deposits. Atomic oxygen was found to be the more effective of the two radical treatments in removing carbon, although a surface layer of gold oxide was formed. Subsequent exposure of this overlayer to atomic hydrogen rapidly removed the oxide, resulting in a pure Au film. AFM analysis of FEBIP deposits before and after radical treatment support the idea that carbon abatement is accompanied by a decrease in particle size.

2:20pm **SS1+PS+TF+AS+NS-TuA2 Surface Morphology Control and 3D Structure Development with Cryogenic Assisted Electron Beam-Induced-Deposition**, ***M. Bresin***, *K.A. Dunn*, University at Albany SUNY

Electron beam-induced-deposition (EBID) of platinum-containing materials was performed at cryogenic temperatures. Deposit morphology, microstructure and nanostructure have been characterized by scanning and transmission electron microscopy (SEM and TEM), and shown to be controllable by the electron fluence used for EBID. 3D structures were developed using a multilayer deposition method, facilitating the creation of hanging, suspended or incorporated-gap structures.

Experiments were performed using an FEI Nova 600 Nanolab dual beam system with a LN2 cryogenic stage, enabling substrate temperatures of -155±5oC. A gaseous platinum precursor (MeCpPtMe3) was first condensed onto the cooled substrate using a capillary-style gas injection system (GIS). Condensate thicknesses between 100nm-3mm were produced by adjusting the GIS-substrate gap and precursor crucible temperature. Next, gas flow was terminated and the condensate was irradiated with an electron beam to induce precursor decomposition. When the substrate was returned to room temperature, any unreacted precursor desorbed and was removed by the pumping system, while irradiated regions showed clear evidence of successful deposition. The morphology of the deposited material depended on exact deposition conditions, and exhibited several distinct types absent from deposits made by conventional (room temperature) EBID.

3D structures were developed with a multilayer deposition method. In this method, multiple layers were used to take advantage of the electron penetration depth within the condensate, through which the depth of deposition could be controlled. An initial layer was first condensed and a region was deposited with the electron beam to act as a substrate-anchoring site. A second condensed layer was then applied such that electrons could only penetrate to the top of the initial condensed layer. The electron beam was then shifted, to deposit a section partially over the anchoring region (in the initial layer) with the remainder over unreacted area. After reheating, part of the second deposit was found to have adhered to the anchoring region, while the rest hung over vacuum. Using similar process, structures were also developed to create embedded gaps or tunnels.

Taken together, these observations have important implications for the creation of arbitrarily large or complex structures previously untenable by EBID fabrication. The growth mechanism and potential applications will be discussed, from nanotechnology to osteointegration.

2:40pm **SS1+PS+TF+AS+NS-TuA3 Nanoscale Patterning and Graphene Film Deposition on Si using Low-energy Electron Beams**, ***T.M. Orlando***, *D. Sokolov*, *D. Oh*, *K. Shepperd*, Georgia Institute of Technology **INVITED**

The physics and chemistry associated with desorption induced by electronic transitions, particularly electron stimulated desorption (ESD), is the basis for many electron-beam induced processes in materials growth, etching, and lithography. We have demonstrated experimentally and theoretically that the total ESD yield of adsorbates can be a function of the incident low-energy electron-beam direction. We refer to this phenomena as Diffraction in Electron Stimulated Desorption (DESD). We have also explored three graphene growth strategies which utilize low-energy electron beams and non-thermal reactions. The first uses electron beam irradiation in conjunction with chemical vapor deposition techniques to grow graphene directly on Si substrates. This approach utilizes unsaturated hydrocarbon precursor molecules and can be carried out at relatively low temperatures. The second involves electron-stimulated removal of oxygen and organic fragments from graphene-oxide flakes positioned on patterned Si substrates. This may allow for damage-free reduction of graphene-oxide to graphene. The third involves electron-beam removal of defects from graphene expitaxially grown from SiC(0001) substrates.

4:00pm **SS1+PS+TF+AS+NS-TuA7 A Study of the Nucleation of Focused Electron Beam Induced Deposits: Growth Behavior on the Nanometer Scale**, ***W.F. van Dorp***, Delft University of Technology, The Netherlands, *J.B. Wagner, T.W. Hansen, R.E. Dunin-Borkowski,* Danish Technical University, Denmark, *K. Hagen*, Delft University of Technology, The Netherlands

Focused electron beam-induced deposition (FEBID) is a technique where adsorbed precursor molecules are dissociated by a focused beam of electrons to define metallic or semi-conducting patterns. Control over the process has developed to the extent that the amount of deposited material can be controlled nearly to the level of single molecules. Currently, the highest resolution that is reported is 0.7 nm [1] using the precursor $W(CO)_6$. At this scale, deposits contain no more than a few molecules on average. Our ultimate goal is to develop the ability to deposit single precursor molecules in a consistent manner.

We perform our FEBID experiments in environmental scanning transmission electron microscopes (E-STEM) with a beam energy of 200 keV and a 0.2 nm probe. The annular dark field (ADF) signal is used for the imaging of the deposits. By recording the ADF signal during deposit growth we are able to monitor the growth process in situ. Thin, electron transparent graphite is used as a substrate and typical precursor gas pressures at the sample during the deposition were 10^{-3} to 10^{-5} Torr.

In the present study we used $Me_3PtMeCp$, a Pt-precursor that is often used in FEBID experiments [2]. To improve on the currently achieved resolution, it is important to study the nucleation stage of deposits. When using a graphite substrate we found that there is a significance difference in deposition behavior between the $W(CO)_6$ and $Me_3PtMeCp$ precursors. Where the typical growth behavior for $W(CO)_6$ is to form nm-sized or even sub-nm sized deposits, the deposits fabricated from $Me_3PtMeCp$ are a few nanometers in diameter and consist of individual sub-nm sized grains. We report on our study of this difference in growth behavior and strategies to increase the writing resolution.

[1] W.F. van Dorp, C.W. Hagen, P.A. Crozier, P. Kruit, Nanotechnology 19 (2008) 225305

[2] A. Botman, M. Hesselberth, J.J.L. Mulders, Microelectron Eng 85 (2008) 1139

4:20pm **SS1+PS+TF+AS+NS-TuA8 Direct Local Deposition of High-Purity Pt Nanostructures by Combining EBID and ALD**, ***A.J.M. Mackus,*** Eindhoven University of Technology, the Netherlands, *H.J.J.L. Mulders, A.F. de Jong,* FEI Electron Optics, the Netherlands, *M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, the Netherlands

Due to its ability to directly deposit nanostructures with sub-10 nm lateral dimensions electron beam induced deposition (EBID) has the potential to become a key nanomanufacturing technology. The technique suffers however from incomplete decomposition of the precursor gas and consequently a low material purity. Platinum EBID yields typically only a purity of ~15 at.% and a resistivity value orders of magnitude higher than bulk resistivity which reduces the functionality of the material for most nanoprototyping applications such as adding electrical contacts to nanodevices. In this contribution we propose a novel approach for the fabrication of high-purity Pt nanostructures based on a combination of the patterning capability of EBID and the high material quality obtained by atomic layer deposition (ALD). The latter technique yields submonolayer control of the film thickness and in the case of Pt ALD high purity (~100%), low resistivity (13±1 μΩcm) films [1]. The developed approach comprises seed layer deposition by EBID and area-selective ALD growth. For specific conditions the thermal ALD process of Pt ($MeCpPtMe_3$ precursor, O_2 gas) was found to start selectively on an EBID seed layer with a thickness equivalent to one monolayer Pt. It was established that the deposits have a uniform thickness and a high purity value (>93%), whereas the method has the potential to achieve sub-10 nm lateral dimensions. In addition to the approach and the material properties the underlying reaction mechanism of the (area-selective) Pt ALD process will be discussed, including aspects such as the role of dissociative chemisorption of O_2 molecules on Pt and the formation of H_2O, CO_2, and CH_4, reaction products.

[1] H.C.M. Knoops, A.J.M. Mackus, M.E. Donders, M.C.M. van de Sanden, P.H.L. Notten, and W.M.M. Kessels, *Electrochem. Solid-Sate Lett.* **12**, G34 (2009)

4:40pm **SS1+PS+TF+AS+NS-TuA9 Anionic Surface Processes Induced by Low-Energy Electrons**, ***P.A. Rowntree***, University of Guelph, Canada **INVITED**

The historical development of surface chemistry has largely been based on the use of free-energy-driven processes; an enormous volume of literature exists that details the search for chemical control over these processes using the classical parameters of temperature, surface composition and reagents. However, as the interest in controlling the processes grows, and the need to produce structurally resolved reactive systems increases, alternative non-thermal mechanisms are increasingly being explored in order to drive the interfacial processes into reaction channels chosen by the needs of the operator instead of the principles of thermochemistry. Our specific interest is in the control of surface processes using low-energy electrons as specialty 'reagents' that can be delivered to surfaces in a highly controlled manner, and interact with surface species according to understandable and reproducible mechanisms. The overall goal is to understand and manipulate these mechanisms to selectively interact with target molecules of our choosing to modify surfaces according to our needs.

This presentation will focus on two aspects of this 'manipulative' approach to surface chemistry. The first is our recent development of ways to selectively control where incident electrons interact with the organic monolayers that are deposited on Au(111) surfaces. These chemically homogeneous monolayers have a highly uniform electronic structure along the length of the chains, such that it is normally not possible to strongly enhance the dissociation probabilities at any given site. We have found that it is possible to selectively enhance the rupture of C-H bonds at the methyl terminations of these films by coupling the incident electron flux with anionic excitonic states of rare gas solids that are adsorbed on these methyl terminations. The energy+charge transfer process that leads to bond rupture is extremely sensitive to the incident energy as well as the chemical nature of the target species, thus enhancing the selectivity of the local modifications to the organic surface. A second set of processes will be discussed that involves the electron-induced decarbonylation of metal carbonyls adsorbed on organic surfaces to produce atomic metal deposits. We have shown that low-energy electrons can induce surface polymerization reactions in $Fe(CO)_5$ films that lead to apparent CO-elimination cross-sections greater than 1 nm^2. This strong coupling to dissociative processes allows us to develop thin metal overlayers without the substrate damage that is usually associated with using thermal evaporation or sputtering processes.

5:20pm **SS1+PS+TF+AS+NS-TuA11 Condensed Phase Electron-Stimulated Reactions: Desorbed Anions and Retained Radicals**, ***Y. Shyur****, J. Wang, S. Lau, E. Krupczak, C. Arumainayagam*, Wellesley College

Studies of low-energy electron-induced processes in nanoscale thin films serve to elucidate the pivotal role that low-energy electron-induced reactions play in high-energy radiation-induced chemical reactions in condensed matter. While electron-stimulated desorption (ESD) experiments conducted during irradiation have yielded vital information relevant to primary or initial electron-induced processes, analyzing the products following low-energy electron irradiation can provide new insights into radiation chemistry. We have used post-irradiation temperature-programmed desorption to identify labile radiolysis products as demonstrated by the first identification of methoxymethanol as a reaction product of methanol (CH_3OH) radiolysis. Although low-energy electron-induced oligomerization reactions have been previously reported for molecules such as thiophene and cyclopropane, our electon-induced studies of CCl_4 represent the first study to specifically identify the products of such reactions, demonstrating the utility of post–irradiation temperature programmed desorption experiments to study the radiation chemistry of condensed matter. Results of post-irradiation studies have been used not only to determine the identity of radiolysis products, but also to determine the dynamics of electron-induced reactions. By comparing our post-irradiation results to previous electron stimulated desorption studies of anion production during irradiation of condensed CF_2Cl_2 and CF_3I, we examine the relationship between desorbed anions and retained radicals during dissociative electron attachment in the condensed phase.

5:40pm **SS1+PS+TF+AS+NS-TuA12 Cluster-induced Desorption and Ionization of Biomolecules for Application in Mass Spectrometry**, ***M. Dürr***, Hochschule Esslingen, Germany, *C. Gebhardt, A. Tomsic, H. Schröder, K. Kompa*, MPI für Quantenoptik, Germany

Mass spectrometry of biological macromolecules has developed into a key technology for fast routine analysis in biotechnology. A critical issue is the efficient transfer of non-volatile biomolecules out of their sample solution into the gas phase in combination with their concomitant ionization. Here we show that a beam of neutral molecular clusters consisting of 10^3 to 10^4 SO_2 molecules can be used for the desorption and ionization of biomolecules. Cluster impact on arbitrary surfaces pre-treated with biomolecules efficiently creates cold, desolvated, gas phase biomolecular ions as large as 6000 u without any need for preparation of the biomolecules in a special matrix or post-ionization after desorption. Since the cluster provides not only the energy for the desorption process but also a transient matrix during the process, the molecules are found to be desorbed without any fragmentation.

As revealed by means of molecular dynamics simulations, high kinetic temperatures in the order of a few thousand Kelvin are reached during cluster impact on the surface. However, these extreme conditions prevail only for some picoseconds, since shattering of the initial cluster leads to very fast energy dissipation. Already after 20 ps, the SO_2 cluster fragments have reached a temperature colder than the original temperature of the adsorbates. This fast energy dissipation excludes efficient energy transfer into the vibrational degrees of freedom relevant for the cleavage of the relatively large biomolecules and thus allows for their soft, fragmentation-free desorption.

Nanometer-scale Science and Technology
Room: Hall 3 - Session NS-TuP

Nanometer-scale Science and Technology Poster Session

NS-TuP1 Capture and Characterization of Nanoparticles at Trace Levels in Semiconductor Process Gases, ***J. Feng***, *M. Raynor, D. Davia, A. Seymour, R. Torres*, Matheson TriGas Inc.

Particulate contamination in process gases used in semiconductor fabrication can have harmful effects on device morphology, performance, reliability and yield. There are significant challenges in the measurement of particles in process gases, especially trace level nanoparticles <50 nm in reactive and corrosive gases. Optical particle counters and condensation nucleus counters are frequently used in inert gases to provide real time data on particle levels and size distributions. However these devices may not provide accurate size measurement or be compatible with reactive gases. Further, they don't give any information on the composition of the particles, which may be important for determining the contamination source. An alternative method is to capture the particulate contamination on sampling filters and perform post microscopic analysis. This approach has been previously used for environmental particulate sampling but has not been widely applied to reactive semiconductor gases. In this work, a sampling system with nanopore-sized (NPS) membrane filter for capturing particles from difficult-to-measure gases is described, initially tested with a nanoparticle source in nitrogen and then applied to reactive process gases such as HBr. Feasibility of capturing iron oxide nanoparticles (30-50 nm) introduced into purified nitrogen via a particle shaker inert gas was demonstrated on NPS alumina filter. Sampling with HBr required compatibility testing of the filter membrane. Results indicated that the NPS alumina filter is capable of withstanding the corrosive effects of HBr, provided the sampling system and gas are properly dried. Membranes were analyzed using various surface analysis techniques such as AFM and SEM. Before collecting samples, blanks were collected to ensure that the delivery system was clear of any contamination. Typical results of contaminant particles from reactive gases such as HBr are presented. These data provide information on the particle content and form in the source container and delivery lines and efficiency of filters in removing particles from the flowing gas. SEM images of particles captured from a filtered gas sources via a delivery system show the presence of clusters of small particles, indicating that the particles may have an affinity for one another in the gas phase. SEM-EDS provides compositional data of the particles detected. The data show that in the case of HBr, the particles are mainly mixed metal bromides. The elements detected compare well to those detected by hydrolysis metal sampling with ICP-MS. Such information can assist in locating the source of particles and eliminating such sources

NS-TuP4 Large area Room-Temperature Nanoimprint using Liquid-phase HSQ Resin with PDMS Mold, ***Y. Kang***, *M. Okada, Y. Haruyama, K. Kanda, S. Matsui*, University of Hyogo, Japan

Nanoimprint lithography (NIL) is a very useful technique to make nanostructure devices with low cost and high throughput. So far, we reported room-temperature NIL (RT-NIL) using hydrogen silsesquioxane (HSQ) as a resin. However, the issue of a higher imprinting pressure than those of thermal NIL and UV NIL still remain to be addressed in NIL using spin-coated HSQ as the replication material. We attribute these disadvantages to evaporation of the solvent contained into HSQ during the spin-coating.

To overcome the above problem, we reported a Nanoimprint technique using liquid-phase HSQ as a replication material alternative to HSQ resin formed by conventional spin-coating. A low imprinting pressure and HSQ residual layer with less than 10 nm thick were achieved by using liquid-phase HSQ. But the HSQ-coated substrate is required to heat up around 90 ^{o}C to evaporate the solvent contained in the HSQ resin while the pressure was held. And a large area imprinting was difficult because the organic solvent in the HSQ evaporated only through the side-gap between SiO$_2$/Si mold and HSQ coated Si substrate. To address these problems, we used Poly(dimethyl siloxane) (PDMS) mold instead of SiO$_2$/Si mold. Because PDMS is a porous gel, the organic solvent in the HSQ solution can be evaporated through PDMS mold.

The new imprint technique using liquid-phase HSQ with PDMS mold is as follows. First, the PDMS mold was fabricated by spin-coating a mixture of base resin and hardener resin (Dow Corning Co. Sylgard 184) on the SiO$_2$/Si master mold. Following, PDMS coated substrate was baked at 70 ^{o}C for 15 min to cure the PDMS. After curing of the PDMS, the PDMS mold was demolded from the SiO$_2$/Si master mold. Next, HSQ solution was dropped onto a Si substrate. Following, the PDMS was pressed onto the Si substrate with 1MPa pressure. And then, the organic solvent in the HSQ solution was evaporated through the pores of PDMS. The imprinting temperature, pressure and time were RT, 1MPa, and 10 min, respectively. In this experiment, we used two kinds of HSQ, one is the caged HSQ (Dow Corning Co. Fox-16) and another is the ladder HSQ (Tokyo Ohka Kogyo Co. OCD T-12). Finally, the PDMS mold was removed from the Si substrate, and then HSQ patterns were successfully replicated on a 4 inch wafer in full area.

NS-TuP5 Electron Microscopy Characterization of Hexagonal Molybdenum Trioxide (MoO$_3$) Nano-Rods, ***I.B. Troitskaia***, *V. Atuchin*, Institute of Semiconductor Physics, Russia, *G.C. Franco*, University of Texas at El Paso, *D.A. Ferrer*, University of Texas at Austin, *M.A. Ramos, C.V. Ramana*, University of Texas at El Paso

MoO is an interesting material for application in solid state microbatteries,electronic information displays, and optical memory and sensor devices. MoO$_3$ exhibits several polymorphs and, hence, the controlled growth and structure of MoO$_3$ are highly important. The successful efforts to synthesize metastable hexagonal phase (*h*–MoO$_3$) have been very limited, partly due to the complications in stabilizing the metastable-phase as compared to the thermodynamically stable a -MoO$_3$. As such, the physicochemical properties of the metastable *h*–MoO$_3$ phase are largely unknown, in spite of the fact that metastable structures often demonstrate new or enhanced activity when compared to thermodynamically stable phases. Here, we demonstrate a simple low-temperature chemical method to produce metastable *h*-MoO$_3$ nanorods and their excellent structural characteristics. Hexagonal MoO$_3$ samples were prepared via the precipitation of molybdenum oxide from an ammonium paramolybdate solution, by the addition of nitric acid. The structure of *h*-MoO$_3$ nano-rods was examined in detail using high-resolution scanning electron microscopy (HR-SEM) and high-resolution transmission electron microscopy (HR-TEM). A drop of the nanorods diluted in ethanol was added onto a carbon-coated TEM grid, and allowed to evaporate for analysis on a FEI Tecnai TF20 (200kV) equipped with a STEM unit, high-angle annular dark-field (HAADF) detector and X-Twin lenses. The SEM data reveal that the nano-rod *h*-MoO$_3$ crystals have the shape of straight hexagonal rods with an aspect ratio ~60. The HR-TEM results confirm the hexagonal structure of the MoO$_3$ nanocrystals. Computations of the observed TEM data along with x-ray diffraction pattern further confirm the stability of the nano-structure of *h*-MoO$_3$ rods. The results obtained are presented and discussed.

NS-TuP6 A Photochemically Initiated Chemistry for Coupling Underivatized Carbohydrates to Gold Nanoparticles, ***X. Wang***, Portland State University, *O. Ramström*, KTH - Royal Institute of Technology, Sweden, *M. Yan*, Portland State University

Biofunctionalized metal nanoparticles provide a sensitive platform for the analysis and detection of molecular recognitions in biological system. The remarkably sensitive optoelectronic properties of metal nanoparticles make nanoparticle-based materials a powerful tool to study fundamental biorecognition processes. Here we present a new and versatile method for coupling underivatized carbohydrates to gold nanoparticles (Au NPs) via the photochemically induced reaction of perfluorophenylazide (PFPA). A colorimetric model system based on the carbohydrate-modified Au NPs was furthermore constructed for the sensitive detection of carbohydrate-protein interactions. Treating mono-, and di-mannose-modified Au NPs with Concanavalin A (Con A) lead to a distinct color change of the Au NP solution, which was directly associated with the surface plasmon resonance shift upon nanoparticle aggregation. The coupling chemistry is highly efficient and is applicable to a wide range of carbohydrate structures.

NS-TuP7 Fabrication of Quantum Dots Utilizing Multi-Coated Self-Assembled Monolayer, ***N.Y. Kwon***, *K.H. Kim, I.S. Chung*, Sungkyunkwan University, Korea

We have created various nano-gaps by controlling the number of self-assembled molecular coating. The generated nano-gaps were used to yield quantum dots with a precise size and placement. First, Au electrodes with an unique shape were obtained using a conventional lithography. Then, self-assembled multilayer, composed of alternating layers of α, ω - mercaptoalkanoic acids (~2 nm) and copper (II) ions, were deposited on Au electrode patterns to form the controllable gap between adjacent Au electrodes. After reaching to nanometer-scale gap, the secondary Au was deposited again and lift-off both ZEP420A(E-beam resist) and molecular resist, thereby resulting in quantum dot with nano-gap between gold electrodes. Ellipsometry and cyclic voltammetry (CV) were used to analyze the number of self-assembled molecular layer. Also, contact angle and X-ray photoelectron spectroscopy (XPS) were used to analyze chemical properties between gold and self-assembled multilayer. Additionally, Scanning probe microscopy (SPM) and field emission secondary electron microscopy (FE-SEM) were used for characterization on shape of nano-gap and quantum dots.

NS-TuP8 The Efficient Film Growth Method for Active Layer of Polymer Solar Cells, ***K.W. Kim***, *H.J. Kim, B.Y. Hong*, Sungkyunkwan University, Korea

Polymer based organic solar cells have made rapid progress after the advent of bulk-heterojunction concept consisting of an interpenetrating network of electron donor and acceptor material. Since slow growth of active layer allows to improve the cell performance, some approaches have been already used to reduce the film growth rate such as boiling point modification using solvent mixture, slow drying or solvent annealing by reducing spin coating time which controls the solvent annealing time.

In this work, we investigate the role of spin coating frequency combined with solution concentration at fixed active layer thickness on performance of polymer solar cells based on regioregular poly(3-hexylthiophene) (RR-P3HT):[6,6]-phenyl-C61–butyric acid methyl ester(PCBM) system. The thickness of active layer is standardized by controlling the solution viscosity with solution concentration. It is found that the spin coating frequency is associated with solvent evaporation time and highly affects the degree of interpenetration of the crystalline P3HT and the highest power conversion efficiency was obtained with the combination of the possible lowest spin coating frequency and solution concentration under AM 1.5 G spectral illumination of 100 mWcm^{-2}. The structural and optical properties of active layer are characterized by various analysis methods such as X-ray diffraction (XRD), ultraviolet-visible absorption spectroscopy and atomic force microscopy (AFM).

NS-TuP9 Study on Inverted Hybrid Solar Cell with ZnO Thin Film for Stability Improvement, ***J.W. Park***, *Y.S. Park, B.Y. Hong*, Sungkyunkwan University, South Korea

Recently, the organic solar cell has been receiving lots of attention as a clean and safe energy source instead of the fossil fuel due to its lower manufacturing cost and environment-friendly energy conversion capability. Several research groups have claimed the organic solar cells with ~5 % conversion efficiency. However, they still have low efficiency and the unstable because organic materials are easily oxidized by humidity and UV light under the atmosphere environment.

In this work, we propose an inverted-type organic/inorganic hybrid solar cell using ITO/ZnO/P3HT:PCBM/Au (indium tin oxide/zinc oxide/poly(3-hexylthiophene) : [6,6]-phenyl C_{61} butyric acid methyl ester/Au) structure to enhance the efficiency and the stability of the organic solar cell. ZnO thin film is used as buffer layer to prevent the interface of organic layer by UV light from the oxidation and to reduce the energy barrier for easily transferring electron between ITO electrode and the LUMO level of the organic acceptor. Also, ZnO film blocks the injection of the hole from the P3HT to ITO for no charge carrier recombination. It is observed that the power conversion efficiency is significantly dependent on the thickness of ZnO thin film, which is deposited with magnetron sputtering system. The power conversion efficiency of 2.6 % under AM 1.5 G spectral illumination of 100 mWcm^{-2} is obtained when the thickness of ZnO thin film and P3HT:PCBM is optimized. In addition, Au used as back electrode to solve the problem of Al, which is susceptible to reactions with oxygen and water, and to control the work function between HOMO level of P3HT and the energy level of metal electrode. From the periodically testing result for long days, we proved that our solar cell which isn't encapsulated has a longer stability than typical organic solar cell fabricated by the same condition under ambient.

NS-TuP10 Growth of Vertical Si Nanowires Using Square Matrix Anodic Aluminum Oxide Template, ***J.K. Hong***, *K.H. Kim, J.H. Heo, I.S. Jung*, Sungkyunkwan University, Korea

The vertical Si nanowires were grown on Si(100) substrate using a low-pressure chemical vapor deposition(LPCVD) system. The square pattern of AAO was obtained by combining pre-patterning Al thin film surface using focused ion beam (FIB) with anodizing process. The pore size and its period of the square matrix were approximately 50nm and 100nm, respectively. To determine the role of the indent depth on Al surface in AAO formation, FIB doses were varied from 1x10^{17} ions/point to 8x10^{17} ions/points. We found that a minimum indent depth is about 16nm. The minimum indent depth seems to be required to localize electric fields in a downward direction thereby yielding an indented pattern after AAO formation. In addition, we found that the higher voltage in anodizing process yields better uniformity in pore shapes. The Au nanoparticles as the catalyst for epitaxial growth of Si nanowires were deposited at the bottom of the AAO template on Si substrate using a electroless deposition with a mixuture of a solution containing Au ions and 1% HF. The average diameter of Au nanoparticles in each pore was 65nm.

The physical properties were analyzed using secondary electron microscope (SEM), transmission electron microscopy (TEM), and X-ray diffraction. Additionally, the detailed analysis including pore diameter and pore depth were made using scanning probe microscope (SPM).

NS-TuP12 Nanostructuring by Ion Beam: The Role of Surface Active Elements, ***B. Setina Batic***, *M. Jenko*, Institute of Metals and Technology, Slovenia

Ion bombardment has recently attracted much attention as a tool for inducing self-organized patterns on various metal, semiconductor and amorphous surfaces. Depending on the conditions imposed upon the ion beam as well as on the properties of the material, different surface morphologies can form. The most common surface topography that forms under the ion beam influence is ripple-like morphology, which is prevalent in the case of amorphous materials, but in the case of semiconductors and single crystalline metal materials observations of dots, pits, mounds and pyramidal structures have also been documented.

Polycrystalline Fe-3%Si alloy was chosen as a model system for studying sputter induced topography modulations due to its properties: each grain, ranging few µm in size and of different crystalline orientation, behaves as a single-crystal surface that sputters independently of the surrounding grains. Thus, it is possible to experimentally include a large amount of grains of different crystallographic orientations in the same experimental run. Additionally, the samples were doped with a small amount of surface active elements to verify their role on the formation of self-assembled structures.

Samples of Fe-3%Si alloy were polished to achieve a smooth starting surface and subjected to Ar+ ion beam irradiation of different energy, angle and ion dose to obtain a complete set of experimental data on ion induced morphology changes. Results show that the surface exhibits grain-orientation dependent patterns, ranging from well-defined ripple structures to terraces, pits, or pyramidal structures. The characteristic length of these structures is in the order of a few hundred nanometres. Preliminary results show that surface active elements, such as Se or Sn, have a determining role on the formation of ripple-like patterns, causing the ripples to develop facet-like characteristics.

The samples were characterized using a multitechnique approach: Field Emission Scanning Electron Microscope (FE-SEM, Jeol JSM 6500-F) was used for the determination of different structures that formed in individual grains and to visualize a larger area of the sample, while Atomic Force Microscope (AFM, Veeco) gave detailed information on corrugation, individual ripple wavelengths, facet angles, pit depths and other morphological details.

NS-TuP13 Photo-patterning of Nitrophenyl-Terminated Self-Assembled Monolayers by using Localized Surface Plasmon, ***S. Uenishi***, *T. Ichii, K. Murase, H. Sugimura*, Kyoto University, Japan

Patterning of self-assembled monolayers (SAMs) has attracted much attention owing to its potential applications to various microdevices fabrication processes. In particular, photochemical micropatterning of SAMs is of special interest, since it can be adopted into photolithography which has been the most successful microprocessing technology with high productivities. Recently, photoinduced reduction of nitrophenyl-terminated SAMs on silver surfaces has been reported [1], where nitrophenyl groups were converted to phenylamine groups by visible light irradiation. This must be prominently useful technique in the field of biotechnology and photochemistry, because some biomolecules and nanoobjects of noble metals can be adsorbed on amino-terminated surfaces. However, visible light irradiation is difficult to be applied to nanoscale patterning owing to diffraction limit. This can be overcome by using localized surface plasmon with nanoobjects of noble metals. Electromagnetic field relative to the surface plasmon is localized in a few tens of nanometer, which is independent of light wavelength. In this study, we demonstrated photoinduced reduction from nitrophenyl groups to phenylamine groups by using direct light irradiation and localized surface plasmon.

First, 4-nitrobenzenthiol (NBT) SAMs were irradiated with visible light through photomask. The SAMs were formed on gold substrates by immersing the substrate in ethanol solution of NBT (1 mM) at room temperature for 24 hours. Photochemical changes were detected as surface potential shift using Kelvin-probe force microscopy. The surface potential of the irradiated regions was positively shifted by approximately 10 mV. This potential change suggests some photochemical changes induced by the light irradiation on the SAM. Water contact angle measurement and X-ray photoelectron spectroscopy (XPS) were also applied to the SAMs which are irradiated with the light through plain glass plate in these cases. Water contact angle increased from about 45 degrees to about 50 degrees after visible light irradiation. Proof of the photoinduced reduction was not detected by the XPS measurement probably because X-ray irradiation also promoted reduction of the nitrophenyl groups. These results suggest some changes induced on the surfaces by the light irradiation.

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NS-TuP14 Enhanced Thermal Stability and Nanoparticle-mediated Surface Patterning: Pt/TiO$_2$(110), *F. Behafarid, A. Naitabdi, B. Roldan Cuenya*, University of Central Florida

Size-selected Pt nanoparticles were synthesized by inverse micelle encapsulation on PS-PVP diblock copolymers. The thermal stability of these Pt nanoparticles deposited on TiO$_2$(110) has been investigated by scanning tunneling microscopy. Our micelle-based nanoparticles were found to be very stable against agglomeration and they preserved their initial size (~3.2 nm) and hexagonal arrangement up to an annealing temperature of at least 1000°C [1]. Furthermore, the original spherical shape of these particles was found to change upon annealing above 1000°C, leading to the formation of 3D faceted particles. Atomic desorption and cluster coarsening was observed at 1060°C. Our study also revealed that strong nanoparticle/support interactions are present in this system, resulting in the formation of TiO$_2$ nanostripes at high temperature with widths and a 2D spatial arrangement pre-determined by the presence and distribution of the Pt nanoparticles on the substrate.

Further insight into the mechanisms underlying the enhanced thermal stability of our micellar nanoparticles was obtained via a comparative study with UHV-evaporated Pt nanoparticles supported on pristine and polymer-coated TiO$_2$(110) surfaces.

NS-TuP15 STM Measurements at mK Temperatures for Higher Energy Resolution, *Y.J. Song, A.F. Otte*, NIST and University of Maryland, College Park, ***Y. Kuk***, NIST and Seoul National University, Korea, *J.A. Stroscio*, National Institute of Standards and Technology

Since the invention of scanning tunneling microscopy (STM) in early 1980's, STM and STM-based measurement techniques have been used in a variety of fields for their atomic resolution. With the advent of cryogenic microscopes operating around 4K, the high resolution spectroscopic capabilities of the STM have had significant impact. In this poster, we describe our efforts to make STM measurements at even lower temperatures approaching 10 mK to gain further energy resolution in spectroscopic measurements. To realize this enhanced energy resolution, we constructed an ultra high vacuum (UHV) Dilution Refrigerator (DR) based STM system. The DR was constructed very rigidly in order to have a high resonance frequency. Furthermore, it has two independent modes of He3-He4 mixture gas condensation: a traditional 1K pot condenser, and a Joule-Thomson condenser for possible lower noise operation. For STM measurements, we custom-designed and built an STM module suitable for operation at mK temperatures. The whole STM module can be transferred from the upper, room-temperature chamber where the sample and tip can be easily exchanged. The sample holder has five isolated electrical contacts which are also used for kinematic mounting of the sample. This allows four-probe electrical measurements to be performed simultaneously with STM measurements. A cryogenic current amplifier has been constructed and is mounted in the DR for low noise tunneling measurements. We describe the current progress and performance of this new system.

NS-TuP16 A Probe Characterizer for Atomic Force Microscope Fabricated from Si/SiO$_2$ Multilayers, ***H. Itoh***, AIST, Japan

A method to fabricate accurate nanostructures was developed using supperlattices and selective etching technique [1]. A probe shape characterizer for atomic force microscope (AFM) was developed for reliable measurement of AFM image and ISO standardization [2]. Comb-shape lines and spaces (10 nm to 50 nm) were fabricated using Si/SiO$_2$ superlattice. Line width and space distances were determined from the crossectional image of transmission electron microscope. Edge radii of these structures were less than 1.5 nm, and line width and line distance were fabricated in the accuracy less than 1.5 nm. The comb-shape lines and spaces were used to determine the aspect ratios of the AFM probe shape [1]. Aspect ratios of cone-like probe from tip apex to the bottom can be determined from apparent depth in the AFM image obtained from 8 kinds of different space widths. In case of the CNT probe, diameter of cylinder-like probe can be estimated from trajectory of the AFM probe on space structure. Advantage of characterizing probe shape using comb-shape pattern is that uncertainty can be defined from the shape of the reference material. Thus, reconstructed AFM image is reliable and applicable to characterize the precise morphology of nano-materials [3] and nano-structures.

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NS-TuP17 Growth and Optical Properties of ZnO Fern-like Nanoleaves, *H. Ji*, Jilin University, P.R. China, ***H. Gao***, Harbin Normal University, P.R. China, *Y. Zhao*, Northeast Forestry University, P.R. China

Zinc oxide is a very widely studied nanomaterial due to its potential applications in nanoscale optoelectronic and photovoltaic devices. A variety of ZnO quasi-one-dimensional morphologies have been synthesized by different methods. Often applications of the ZnO nanostructures are closed related to their morphology providing motivation to study the relationship between the morphology and growth technique.

Using a mixture of ZnO, Eu$_2$O$_3$ and C powder as source material, ZnO with a novel morphology referred to as nanoleaves was fabricated using thermal evaporation. The structures and morphologies of the as-synthesized samples were characterized by x-ray diffraction, field-emission scanning electron microscopy, high-resolution transmission electron microscopy and energy dispersive x-ray spectroscopy. The ZnO nanoleaves are wurtzite single crystals that have an appearance of fern-like leaves w ith symmetrical paired teeth on opposite sides. For some of the nanoleaves, there are long needles that grow from the end of some of the teeth and forming parallel arrays. The growth mechanism, kinetically driven process and photoluminescence of the ZnO nanoleaves will be discussed.

NS-TuP18 Characteristics of Al-doped ZnO Film and its Application to the Electrode for Inverted Organic Solar Cell, ***D.H. Lee***, *S.U. Lee, B.Y. Hong*, Sungkyunkwan University, Korea

High-quality Al-doped zinc oxide (ZnO:Al; AZO) films are very attractive materials due to relatively low cost, non toxicity and stability at high temperature, and also they are being extensively investigated to apply to various fields such as solar cells, flat panel displays and organic light emitting diodes.

In this work, we investigated the electrical, optical and structural properties of AZO film grown on the glass by RF magnetron sputtering method with zinc oxide target doped Al$_2$O$_3$(2 wt%). AZO films were synthesized at the pressure of 1mTorr with RF power varied from 100 W to 175 W. The optimized AZO film had the transmittance above 85% at visible region and the resistivity of 1.5×10^{-3} ohm-cm at room temperature. The characteristics of AZO film were investigated by X-ray diffraction (XRD), Hall measurement system, UV-visible spectroscopy, and atomic force microscopy (AFM).

In addition, the optimized AZO film in this work was applied to a transparent electrode for an inverted organic solar cells (AZO/P3HT:PCBM/PEDOT:PSS/Au) which was compared with the organic solar cell with the standard structure using indium tin oxide (ITO) as the electrode.

NS-TuP19 Comparison of Oxidation Behaviors of Si$_{1-x}$Ge$_x$ Nanowires, ***S.Y. Kim***, *S.W. Kim, D.-H. Ko*, Yonsei University, Korea

Conventional devices came to have issues as scaling down. One of the methods to overcome the limit of scaling down is semiconductor nanowires and because of their potential application for nano-scale devices they have received considerable attention during the past years. Compared to other semiconductor nanowires, Si & Si$_{1-x}$Ge$_x$ nanowires are more important as for the base-materials of future nano-scale device because of their special merit of being compatible with current silicon device fabrication processes. In addition to this, Si & Si$_{1-x}$Ge$_x$ nanowires are suitable candidates for investigating characteristics associated with quantum size effects. Among the conventional Si-compatible processes, the oxidation properties are of great interests so we investigated the oxidation of Si$_{1-x}$Ge$_x$ nanowires at the point of Ge behaviors during oxidation. Si$_{1-x}$Ge$_x$ nanowires were grown in a LPCVD by VLS method. Source gases of SiH$_4$ and GeH$_4$ were used for growing Si$_{1-x}$Ge$_x$ nanowires on Si (111) substrates. Thin gold layer was deposited as catalyst, and Ge contents of Si$_{1-x}$Ge$_x$ nanowires were controlled to 15% and 30%. Grown nanowires were thermally oxidized in the vertical furnace with the various temperature and time. After oxidation, grown oxide thicknesses were measured by TEM methods and compositions of oxide and remain nanowires were analyzed by TEM and EDS methods. Comparing the oxidation characteristics of the Si$_{1-x}$Ge$_x$ nanowire with those of Si nanowires and (100) Si wafer, it is concluded that Ge plays a significant role in deciding an oxidation characteristics and oxidation characteristics of Si$_{1-x}$Ge$_x$ nanowires can be affected by Ge contents as well as nanowire size.

NS-TuP20 Carbon Nanotube Embedded Three Dimensional (3-D) Carbon Microelectrodes for Rechargeable Microbatteries*, G.H. Kim, E. Kozarsky, H.S. Jee, K.T. Kim, J. Kim, E. Takeuchi, Y.-K. Yoon*, University at Buffalo

Lithium ion rechargeable batteries power a wide range of electronic devices including cell phones, laptop computers, digital cameras, and medical devices because of the high energy density. However, the technological development of the battery has been held back by the limited range of available electrode materials. Desirable battery electrodes are to have a large surface area for high energy density and device compactness, and a fast charging/recharging property for high power demand. Recently, three dimensional (3-D) carbon electrodes have been successfully demonstrated using the polymer carbonization process with lithographically defined high aspect ratio microstructures [1]. The advantages of this approach include the accurate definition of 3-D microstructures using ultraviolet (UV) lithography and converting them into the carbon electrode by pyrolysis, resulting in chemically and mechanically stable, low cost electrodes. However, the carbon electrodes from polymer pyrolysis show relatively high electrical resistivity resulting in slow charging/discharging response. On the other hand, carbon nanotubes (CNT) are known to provide outstanding electrical, mechanical and chemical performance.

In this study, we report carbon nanotube (CNT) embedded 3-D carbon electrodes by using UV lithography on CNT embedded SU8 (photosensitive negative tone epoxy) and subsequent carbonization. Since the final electrodes consist of CNTs embedded in pyrolyzed carbon, they contain high electrical conductivity to contribute to increasing charging/discharging speed and chemical, mechanical stability in the electrolyte environment. Also, the small amount of CNTs in polymer does not interfere much with UV dose in the photolithography process, maintaining the high aspect ratio 3-D micropatterning capability.

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NS-TuP21 Silicidation Behaviors of $Si_{1-x}Ge_x$ Nanowires for Future CMOS Device*, **S.W. Kim**, S.Y. Kim, D.-H. Ko*, Yonsei University, Korea

To overcome the scaling down issues in current semiconductor industry, scientists and engineers have been investigating the alternatives in the last few years. One of the methods is a semiconductor nanowires. They have been received remarkable attentions during the past years due to their potential application for future CMOS devices. Compared to other semiconductor nanowires, Si & $Si_{1-x}Ge_x$ nanowires are more important as for the base-materials of future CMOS devices because of their special merits of being compatible with current silicon device fabrication processes. In addition, Si & $Si_{1-x}Ge_x$ nanowires are suitable candidates for investigating characteristics associated with quantum size effects. For the application to the future nano-scale device process, we investigated the silicidation behavior of $Si_{1-x}Ge_x$ nanowires. $Si_{1-x}Ge_x$ nanowires were grown in a LPCVD by VLS method. SiH_4 and GeH_4 were used as a precursor sources for growing $Si_{1-x}Ge_x$ nanowires on Si (111) substrates. Thin gold layer was deposited as a catalyst, and Ge contents of $Si_{1-x}Ge_x$ nanowires were controlled to 15% and 30%. Ni layer was deposited on the as-grown nanowires by sputtering and RTP process was used for silicidation. The characteristics of Ni germanosilicide films on nanowires were investigated by using TEM and EDS methods. Also, electrical characteristics were measured by using patterned electrodes. Comparing the silicidation characteristics of $Si_{1-x}Ge_x$ nanowires with those of Si nanowires, it is concluded that Ge plays a significant role to determine silicidation characteristics.

NS-TuP22 Electrospun ZnO Nanowire Based Ferroelectric Field-Effect Transistor using a Gate Dielectric Layer of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ Thin Film*, **K.T. Kim**, G.H. Kim, Y.-K. Yoon*, University at Buffalo

Recently, ZnO nanowires (NWs) have been extensively studied for solar cell and field-effect transistor applications because of their intrinsic n-type semiconductor property with a wide band gap of 3.36 eV and a large exciton binding energy of 60 meV[1]. Specially, the nanowire architecture in field-effect transistors provides many advantages against the conventional bulk substrate approach such as device size reduction, isolated channel, reduced leakage current, reduced control voltage, and reduced power consumption even to several nJ[2]. The ZnO nanowire based transistor can be extended to a non-volatile memory device by adopting ferroelectric materials for the gate dielectric layer. While Bi-based perovskite $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) and $Pb(Zr,Ti)O_3$ (PZT) thin films have been extensively investigated for non-volatile ferroelectric random access memory (FRAM) devices, BLT based devices are reported to offer better fatigue resistant characteristic, low processing temperature, and large remnant polarization.

In this study, we show a process to make ZnO nanowires using electrospinning with the polymer ZnO nanocomposite and subsequent sintering in various temperatures and characterize them. Also, BLT is prepared by the metal organic deposition (MOD) process and is spincoated on a Pt(150nm)/Ti(50nm)/SiO_2/Si substrate, followed by sintering in different temperatures (550°C, 600°C, 650°C, and 700°C) to form crystalline perovskite structures [3]. And the ZnO nanowires are formed on the BLT ferroelectric gate and the electrodes for source and drain are defined using a UV lithography followed by metallization. We show non-volatile switching in ZnO NWs with the BLT ferroelectric gate. We also evaluate the field dependent conduction of ZnO NWs with the remnant field of ferroelectric thin films and show fatigue and retention free performance. These devices are useful not only for non-volatile memory devices but also for various biosensors and nanoelectromechanical systems.

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NS-TuP23 Fabrication of n-ZnO Photonic Crystals by Nanosphere Lithography using Inductively-Coupled-Plasma Reactive Ion Etching with $CH_4/H_2/Ar$ Plasma on the n-ZnO/GaN Heterojunction LEDs*, **S.J. Chen***, National Tsing Hua University, Taiwan, *C.-M. Chang, J.S. Kao*, Instrument Technology Research Center, National Applied Research Laboratories, Taiwan, *F.R. Chen, C.H. Tsai*, National Tsing Hua University, Taiwan

Applying photonic crystals with Light Emitting Diodes (LEDs) to improve the light extraction efficiency have been demonstrated successfully. ZnO has been considered as a promising material for the development of next generation UV LEDs with high brightness due to its direct band gap (3.37eV) at room temperature and it has relatively large exciton binding energy. Recently, n-ZnO/p-GaN heterojunction LEDs have been fabricated by several groups. However there has not any experimental evidence yet to integrate photonic crystal with n-ZnO/p-GaN heterojunction LEDs. This paper reports fabrication of n-ZnO photonic crystal/p-GaN LED by nanosphere lithography to further booster the light efficiency.

Usually, electron beam lithography is employed to fabricate the photonic crystals, however, it is a cost process and not suitable for large area production. In our paper, the fabrication of ZnO photonic crystals is carried out by nanosphere lithography (NSL) using inductively-coupled-plasma reactive ion etching (ICP_RIE) with CH4/H2/Ar plasma on the n-ZnO/p-GaN heterojunction LEDs. NSL is a simple and relatively cheaper technique and allows for large-area production. The $CH_4/H_2/Ar$ mixed gas gives high etching rate of n-ZnO film which yields a better surface morphology and results less plasma-induced damages of the n-ZnO film.

The periocity of n-ZnO photonic crystal is designed to fit the spectrum of n-ZnO/p-Gan LED by a Matlab code which suggests an optimum lattice parameter is 200 nm and the air-filling factor of the n-ZnO photonic crystal ranges from 0.35 to 0.65. In our paper we will show our recent result that a ZnO photonic-crystal cylinder has been fabricated by using polystyrene-nanosphere mask with lattice parameter of 200 nm and radius of hole around 80 nm. Experiment results were discussed in detail in terms of surface morphology , photonic-crystal nano-structure and plasma-induced damages which were measured by atomic force microscope, scanning electron microscope and photoluminescence spectrometer respectively.

NS-TuP24 Dielectrophoresis-assisted Deposition and Alignment of Single-Walled Carbon Nanotubes for Electronic Device Fabrication*, Z. Xiao*, Alabama A&M University

Single-walled carbon nanotubes (SWCNTs) have been considered as a promising nanostructured material for the realization of future nanoelectronic devices because of their unique electrical properties such as the ballistic transportation of electrons or holes in SWCNTs. In this paper, we report deposition and alignment of SWCNTs using the dielectrophoresis (DEP) method and fabrication of single-walled carbon nanotube field-effect transistors (CNTFETs) with semiconductor materials as the source and drain materials. Ultra-purified HiPCO-grown single-walled carbon nanotubes (SWCNTs) from Carbon Nanotechnologies, Inc. (CNI) were used for the fabrication of CNTFETs. N-Methyl Pyrrolidone (NMP) was used to disperse SWCNTs in solutions. The dispersion of SWCNTs in the solvent was ultrasonically assisted, and then centrifuged. The degree of dispersion was examined by SEM. Dielectrophoresis (DEP) method was used to deposit, align, and assemble carbon nanotubes (CNTs) across the source and drain of CNTFETs to form the channel. Microfabrication techniques such as UV lithography and e-beam lithography were used to fabricate the CNTFETs. The gap between the source and drain varied from 800 nm to 3 um. Both metals such as gold and semiconductors such as bismuth telluride (Bi_2Te_3) were used as the source and drain materials for the CNTFETs. The drain-source current (I_{DS}) versus drain-source voltage (V_{DS}) and gate voltage (V_G) was characterized for the fabricated CNTFETs. The fabricated devices and measured electrical results will be reported in the Conference.

NS-TuP25 Three-dimensionally Suspended Single-Walled Carbon Nanotubes Inside the Holes of Porous Silicon, ***W. Yi***, *D. Lee, J. Lee*, Hanyang University, Korea

Carbon nanotubes (CNTs) were synthesized inside the holes of the porous silicon substrate by thermal decomposition of C_2H_2. Secondary electron microscopy (SEM) and Raman analysis revealed that single-walled carbon nanotubes (SWNTs) were suspended with three-dimensional networks (3-dim suspended SWNTs). Field emission measurements of those samples showed the enhanced turn-on voltage and emission property compared with pristine SWNT film. We also measured the photoconductivity of 3-dim suspended SWNTs under irradiation of infrared light after making two electrodes on the sample surface. The on/off ratio of resistivity, i.e. the resistance ratio under and without IR irradiation reached up to ~600 enough to be used as commercial IR sensors.

NS-TuP26 System Evaluation and Optimization of the Measurement Uncertainty in the Nanoscale Step-height Inspection by Dynamic Mode Atomic Force Microscopy, ***C.Y. Su***, *Y.H. Lin, S.S. Pai, P.L. Chen, N.N. Chu, C.C. Yang, M.H. Shiao*, Instrument Technology Research Center, National Applied Research Laboratories, Taiwan

Atomic Force Microscopy (AFM) has been extensively adopted in a variety of applications in nanotechnology. Due to the high sensitivity in z-axis, the capability of mapping height distribution from sample topography with the resolution in the sub-angstrom is achieved. In this study, a standard operation process (SOP) has been designed and implemented in order to optimize operational parameters such as scan rate, drive frequency, target amplitude, set-point, integral gain, proportional gain, look-ahead gain and so forth for the AFM dynamic mode inspection. The step-height standards are provided by the national metrology institute Physikalisch-Technische Bundesanstalt (PTB). System evaluation of the measurement uncertainty is accorded to ISO, Guide to the Expression of Uncertainty in Measurement and ISO 4287, Geometrical Product Specifications (GPS) - Surface texture: Profile method – Terms, definitions and surface texture parameters. Repeatability, non-linearity, straightness, noise, probe deformation error, numerical error, system long-term stability and sample uniformity have been included in this evaluation.

NS-TuP29 Surface Structure of Metal-Organic Framework Revealed by High-Resolution AFM, ***P. Cyganik***, *K. Szelagowska-Kunstman, M. Goryl, M. Szymonski*, Jagiellonian University, Poland

Metal-organic frameworks (MOFs) which consist of organic ligands linked together by metal ions belong to a relatively new class of porous materials.[1] Due to their potential applications in storage, separation, and heterogeneous catalysis, MOFs have attracted increasing attention. So far MOF research has been mainly focused on bulk structure of the material prepared in the form of a powder. Only very recently a new, and radically different, approach was undertaken by exploring the possibilities of MOF growth on surfaces in the form of thin films.[2,3] An important issue for further progress in optimizing growth of MOF crystals, and particularly MOF thin films, is control of their surface structure. Therefore, high-resolution imaging of MOF surfaces is of key importance, as has been previously recognized for zeolites which are analogous to MOFs.

The talk focuses on the AFM study of a MOF single crystal surface.[4] By performing analysis both in air and under ultra high vacuum conditions the high-resolution AFM imaging of a MOF surface is demonstrated. The surface structure of a MOF crystal grown directly on the functionalized substrate is revealed and, moreover, this information is further utilized to optimize growth conditions. Finally, our study clearly demonstrates a much higher structural quality of MOF crystals grown on the substrate in comparison to the conventional powder growth method.

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NS-TuP31 Enhanced Photovoltaic Performance of DSSC using Broccoli -Like TiO_2 Film with Surface Modification by Zinc Acetate Solution, ***G. Cai***, *Y. Chen, C. Huang, J. Liang*, National Dong Hwa University, Taiwan

The broccoli-like TiO_2 film as working electrode for dye-sensitized solar cell (DSSC) was fabricated successfully by flat-flame chemical vapor deposition (FF-CVD) method we developed. The cell efficiency approaches 4.2% with the film thickness about 9~ 13 mm if the film was used without further surface modification. As we known, one source of the energy loss in DSSC is charge recombination occurring between electrolyte and working electrode. In order to reduce charge recombination, we supply a thin metal oxide coating on TiO_2 electrode by using surface modification with metal-containing salt solution as precursor. A higher band gap of the metal oxide semiconductor provides energy barrier to prevent electron transfer back to the oxidative species, and then reduce the charge recombination. However, although thicker metal oxide coating may reduces the rate of charge recombination, it may also reduce the rate of electron injection into the conduction band of TiO_2 working electrode and reduce the cell efficiency. Therefore, the thickness of the metal oxide coating needs to be optimized for the DSSC efficiency enhancement. In this research, we choose ZnO as coating oxide, since ZnO has slightly higher band gap (3.37eV) than TiO_2 (3.2eV). We vary the concentration of zinc acetate solution from 0.1 M to 0.001 M for coating different thicknesses of zinc oxide on TiO_2 working electrode. The crystalline quality and morphologies of surface modified TiO_2 electrodes were characterized by using XRD and FESEM. EDS and XPS were used to confirm the presence of zinc on the surface of TiO_2 electrode. The coating thicknesses were determined by high resolution transmission electron microscopy (HRTEM). The DSSCs using these working electrodes were measured under AM 1.5G 100 mW/cm^2 by Keithley 2400 sourcemeter. As a result, as the concentration of zinc oxide precursor solution decreases from 0.1 M to 0.001 M, the cell efficiency increases from 1.9% to 5.6%. The short circuit current density ( ) increases from 3.59 mA/cm^2 to 11.89 mA/cm^2 as the concentration decreases from 0.1 M to 0.001 M . Furthermore, we also found that the excess thickness of zinc oxide coating will block the electron injection, and results in lower efficiency after surface modification. The drop of efficiency from 4.2% to 1.9% is mainly attributed to the decrease of from 10.08 mA/cm^2 to 3.59 mA/cm^2. It reveals that appropriate thin zinc oxide coating is necessary in reducing charge recombination, while maintaining the high rate of electron injection to the conduction band of TiO_2 working electrode.

NS-TuP32 Thickness Dependence of Thin Film Samaria Doped Ceria Oxygen Sensor, ***M. Nandasiri***, Pacific Northwest National Laboratory, *R. Sanghavi*, Arizona State University, *S.V.N.T. Kuchibhatla, P. Nachimuthu, M.H. Engelhard, V. Shutthanandan, W. Jiang, S. Thevuthasan*, Pacific Northwest National Laboratory, *S. Prasad*, Arizona State University, *A. Kayani*, Western Michigan University

Resistive oxygen gas sensors stand out among various types of sensors due to their simplicity, low cost, portability, measurement circuit simplification, and low power consumption. Rare earth materials such as pure and doped ceria are potential candidates for resistive oxygen gas sensors due to their unique ability to lose or gain oxygen in response to ambient oxygen concentration. We have recently observed that 6 atom % Sm doping is optimum for obtaining better conductivity using samaria doped ceria (SDC) films. In order to develop oxygen gas sensors based on SDC thin films, it is important to understand the influence of film thickness on the electrical properties.

In order to achieve this goal, we have grown SDC thin films on sapphire, Al2O3 (0001) substrates by using oxygen plasma-assisted molecular beam epitaxy. The 6 atom% Sm doped SDC films with thickness ranging from 50 – 300nm have been grown and their conductivity was studied. The resistance of these films, obtained by two probe measurement capability under various oxygen pressures (1mTorr-100Torr) and temperatures (473K to 973K) at a fixed voltage of 2V, will be discussed. The differences in the electrical properties, thereby the oxygen ion conductivity, will be explained based on the chemical and structural characteristics of various films. Structural and chemical characteristics of the as grown films were analyzed by various *in situ* and *ex situ,* surface and bulk sensitive techniques.

In this study we observed that, overall conductivity increases with the film thickness at each temperature and oxygen pressure value. We also observed saturation in the conductivity at film thicknesses above 200nm. With the increasing interest for miniaturized oxygen sensors for high temperature uses, the nano-scale thin film doped ceria sensors may have a significant role to play in various future functional applications. In that sense it is vital to undertake fundamentals studies such as this.

Applied Surface Science
Room: C1 - Session AS+NS-WeM

Nanoparticle and Nanoscale Surface Chemistry II
Moderator: D.J. Gaspar, Pacific Northwest National Laboratory

8:00am **AS+NS-WeM1 Size-dependent Properties and Surface Chemistry of Metal Oxide Nanomaterials**, ***V. Grassian***, University of Iowa

Both natural and engineered oxide nanomaterials play important roles in environmental processes. In the case of engineered nanomaterials, the surface properties can be tailored for a number of different environmental applications including deNOx catalysis and carbon dioxide removal and conversion. For naturally occurring oxide nanomaterials, e.g. iron oxides, the size dependent properties and surface chemistry will impact biogeochemical cycles. In this talk, some specific examples of the size-dependent properties and surface chemistry of both natural and engineered metal oxide nanomaterials (e.g. titanium dioxide and iron oxide) in environmental processes will be discussed.

8:20am **AS+NS-WeM2 XPS and SEM/STEM Characterization of Silver Nanoparticles Formed from the X-ray-Induced and Thermal Reduction of Silver Behenate**, ***B.R. Strohmeier***, *K.L. Bunker, C. Lopano, J. Marquis, Jr., J.D. Piasecki, K. Bennethum,* RJ Lee Group, Inc., *R.G. White, T.S. Nunney,* Thermo Fisher Scientific, UK, *R.J. Lee*, RJ Lee Group, Inc.

This study is the first reported use of X-ray photoelectron spectroscopy (XPS) to characterize the organometallic compound silver behenate and its X-ray-induced and thermal reduction. Silver behenate is a long-chain silver carboxylate, $CH_3(CH_2)_{20}COOAg$, that crystallizes as a dimer in a head-to-head configuration. Various silver compounds, including silver behenate, are used as primary components in commercially available photothermographic (PTG) and thermographic (TG) imaging elements. Individual particles of silver behenate powder typically exist as plate-like crystals with surface dimensions of 0.2-2 µm and thicknesses of 100 nm or less. Imaging in PTG and TG devices is based on the formation of silver metal nanoparticles in the 5-30 nm range (and larger aggregates) by the thermal reduction of silver behenate dispersed in a binder incorporated with toner and development chemistry. Silver behenate has also found use as a standard reference material for low-angle calibration of X-ray diffraction instruments because its crystal structure produces a unique multi-peak diffraction pattern.

In this study, the X-ray-induced reduction of silver behenate during exposure to monochromatic Al Kα X-rays in a micro-XPS instrument was investigated as well as its thermal reduction at 100 °C and 250 °C. The X-ray induced decomposition of other silver carboxylates (silver acetate, silver benzoate, and silver trifluoroacetate) was also investigated for comparison to the behavior of silver behenate. In addition, a combined high resolution scanning electron microscope/scanning transmission electron microscope (SEM/STEM) was used in this study to provide complementary morphological information to the XPS results.

Quantitative XPS analysis of silver behenate was consistent with the theoretical C:O:Ag atomic composition. However, brown discoloration of silver behenate powder begins within a few seconds of exposure to Al Kα X-rays and increases significantly with time. Noticeable changes to the XPS spectra and the observed surface composition begin to occur after about 30 minutes of X-ray exposure. Prolonged exposure to Al Kα X-rays resulted in significant changes in the C 1s, O 1s, and Ag 3d peak shapes and positions. Changes in the XPS spectra indicated that exposure to Al Kα X-rays results in the formation of silver metal particles and decomposition of the carboxylic acid potion of the molecule to hydrocarbon species. Thermal reduction of silver behenate powder produced similar changes in the XPS spectra. This study demonstrated that XPS and SEM/STEM are complementary techniques for investigating the chemical composition, morphology, and decomposition of nanomaterials.

8:40am **AS+NS-WeM3 Surface Chemistry of Deuterium Terminated Silicon Nanocrystals and Effect of Surface Passivation on Photoluminescence**, ***N. Salivati***, *J.G. Ekerdt*, University of Texas at Austin

Although silicon nanostructures exhibit size dependent light emission, which can be attributed to quantum confinement, the role of surface passivation has not yet been fully understood. Since the ratio of surface atoms to the total number of atoms is large in nanoscale systems, surface effects play an important role in determining the electronic properties. Uncompensated dangling bonds at the surface establish localized defect states within the forbidden gap of silicon nanocrystals, providing sites for non-radiative recombination of excitons. Defect states are also associated with surface reconstructions that minimize the number of dangling bonds but result in severe distortion of the surface bonds. An effective way of capping the remaining dangling bonds is by using atomic hydrogen or deuterium. Si nanocrystals less than 8 nm in diameter are grown on SiO_2 surfaces in an ultra high vacuum chamber and the as grown surfaces are exposed to atomic deuterium. Desorption spectra are interpreted using analogies to Si (100). TPD spectra show that the nanocrystal surfaces are covered by a mix of monodeuteride, dideuteride and trideuteride species. The manner of filling of the deuteride states on nanocrystals differs from that for extended surfaces as the formation of the dideuteride and trideuteride species is facilitated by the curvature of the nanocrystal. Etching of the nanocrystal surface is observed during TPD, which is a confirmation of the presence of trideuteride species on the nanocrystal surface. No photoluminescence (PL) is observed from the as grown unpassivated nanocrystals. As the deuterium dose is increased, the PL intensity also begins to increase. Strong PL is observed only when the nanocrystals are covered with trideuteride species. The trideuteride species helps in reducing the surface stress and this is expected to enhance PL. When the deuterium dose is increased beyond a point the surface structure breaks down and amorphization of top layer of the nanocrystal takes place. Amorphization reduces the PL intensity. Finally, as the nanocrystal size is varied, the PL peak shifts, which is characteristic of quantum confinement.

9:00am **AS+NS-WeM4 Experimental Characterization of CdSe/ZnS Core/Shell Quantum Dots Encapsulated with Poly(maleic anhydride-*alt*-1-tetradecene)**, ***G. Zorn***, *S.R. Dave, T. Weidner, X. Gao, D.G. Castner*, University of Washington

Semiconductor nanocrystals (Quantum Dots, (QDs)) have started to play a pivotal role in molecular labeling, cancer diagnostics and tumor imaging due to their quantum mechanical and electronic characteristics. These characteristics give them unique optical properties such as size-tunable emission profiles, broad excitation spectra, long fluorescence lifetimes, large Stokes shifts and high quantum yields. The most common QD type is a CdSe/ZnS core - shell structure surrounded by hydrophobic ligands[1]; but for biological applications, QDs have to be transferred into aqueous solutions and require specific techniques for the conjugation of small peptides or antibodies onto their surfaces. In this context, a promising and widely used approach is, to encapsulate the nanocrystals with an amphiphilic polymer[1,2]. Still, there are only few reports regarding characterization of absorbed polymer and theoretical analyses are typically based on simple geometric models.

This work is focused on characterizing the amount of the amphiphilic Poly(maleic anhydride-*alt*-1-tetradecene) (PMAT, Mw~9000) adsorbed onto a TOPO-coated CdSe/ZnS QD, as well as analyzing the polymer structure and the TOPO – PMAT interaction. An insight into the elemental composition of the nanocrystals before and after PMAT encapsulation is provided along with the orientation of the surrounding organic components. EDAX, XPS and ToF-SIMS suggest the QDs are comprised of non-stoichiometric Cd-enriched QDs with a ~0.5 monolayer ZnS shell. SFG C-H stretching of the CdSe/ZnS nanocrystals before PMAT encapsulation shows that there is a significant degree of orientational order in the TOPO film. Moreover, after PMAT encapsulation SFG C-H stretching indicates a certain degree of order in the PMAT polymer layer. Finally, from XPS analysis the number of PMAT molecules per QD is estimated to be ~7 to 1.

Reference:

1. Smith, A. M.; Dave, S.; Nie, S.; True, L.; Gao, X., *Expert Rev. Molec. Diagnos.* **2006,** 6, 231-244.

2. Rhyner, M. N.; Smith, A. M.; Gao, X.; Mao, H.; Yang, L.; Nie, S., *Nanomedicine* **2006,** 1, 209-217.

9:20am **AS+NS-WeM5 2009 AVS Albert Nerken Award Lecture - Reactivity of Nanoparticles and Other Surface Controlled Properties of Materials**, ***D.R. Baer*****, *J.E. Amonette, M.H. Engelhard, J. Liu, P. Nachimuthu, C.M. Wang,* Pacific Northwest National Laboratory, *J.T. Nurmi, P.G. Tratnyek,* Oregon Health and Sciences University, *M. Kaur, Y. Qiang*, University of Idaho **INVITED**

Many materials properties are controlled by surface reactions, including those associated with cracking, dissolution, and corrosion. In each of these cases surface reactions alter the functional properties of the materials.

***** Albert Nerken Award Winner

Detailed analysis of surface reactions in relation to the material environment has been required to understand the mechanisms involved in these processes. Many of the analysis approaches used to understand dissolution, cracking corrosion and other complex material-environment interactions are relevant to the study of some types of nanoparticles. The objective of our current research is to obtain fundamental information about the physical and chemical transformations that occur on and within mineral oxide nanoparticulates due to electron transfer reactions and other interactions with their local environment, including solution contaminants such as chlorinated hydrocarbons. The nature of the reactive surfaces, the accessibility of reactive sites, and the structures of the surface and interface layers often change significantly as particles respond to and react with their local environment (e.g. surface structure alterations, phase changes, passive layer formation …). Although geochemically induced changes occur for bulk materials, the nature and rate of these changes can be more dramatic for nano-sized mineral phases. Our research focuses on obtaining information about these geochemically mediated transformations and how they alter particle reactivity, electron availability and particle mobility. Our research includes 1) synthesis of well-defined nanoparticles (NPs), 2) characterization of their surface and bulk composition as well as physical and electronic structure (prior to and following reaction measurements), and 3) *in situ* real-time and batch measurements of NP properties and reactivity in vacuum and solution. We will report on studies showing the impact of natural organic material (NOM) coatings on the through soil transport and reactivity of iron nanoparticles as well as the role of metal dopants on reactivity and solution aging. We have found that NOM can enhance the transport of iron metal-core oxide-shell nanoparticles through a soil column, decreasing the numbers of particles retained in the soil. We have followed up these observations and examined the impact of NOM coatings on the particle aging. Additional studies are examining the impact of S doping on particle reactivity and aging. These studies involve application of a variety of analysis methods to the particles, including XPS, XRD and TEM as well as batch and in situ measures of chemical reactivity and measurements of particle transport through soil columns.

10:40am **AS+NS-WeM9 Surface Characterization and Simulation of Self-Assembled Monolayer Functionalized Gold Nanoparticles**, ***S.D. Techane***, *L.J. Gamble,* University of Washington, *M.H. Engelhard, D.R. Baer,* Pacific Northwest National Laboratory, *D.G. Castner*, University of Washington

In this research gold nanoparticles (AuNP) are used as model nanoparticles and self-assembled monolayers of alkyl thiols as model organic ligands to create functionalized NP with a variety of surface chemistries. The AuNP size and thiol chain length are varied to study their effects on the properties of the AuNP. Our aim is to create a series of well-defined functionalized AuNP for use in complex biological applications and to use the AuNP-SAMs as standard samples to develop XPS (X-ray photoelectron spectroscopy) data analysis methods for coated NP characterization. We have synthesized and characterized four chain lengths of COOH-SAMs (C6, C8, C11, C16 carboxylic thiols) on various sizes of AuNPs (diameter =14nm, 25nm, 40nm) and flat gold surfaces using the surface sensitive techniques of XPS and ToF-SIMS. Many of the trends expects for increasing SAM thickness are observed. In addition data shows that particle size (surface curvature) had an effect on the XPS and ToF-SIMS measurements. Complementary ATR-FTIR (attenuated total reflectance FTIR) measurements were done to characterize the SAM ordering and crystallinity. As SAMs length increased the CH_2 stretching vibration frequencies (υCH_2) decreased on both AuNPs and flat-Au surfaces. For a given chain length SAMs the υCH_2 also decreased as the AuNPs particle size decreased indicating that longer chain SAMs on the smaller AuNPs (i.e. 14nm-C16 COOH-SAMs) have the most crystalline surface structure. As the XPS C/Au atomic ratio depends on the structure of the SAMs as well as the take-off angles (which range from 0 to 90° for particles) there is a need to develop XPS data analysis methods that accurately account for curved NP surfaces. SESSA (Simulated Electron Spectra for Surface Analysis) and QUASES (Quantitative Analysis of Surfaces by Electron Spectroscopy Software) have been used to simulate the experimental XPS results as a function of take-off angle for COOH-SAMs on flat-Au surfaces. Quantities such as SAM density, thickness, surface roughness and instrumental parameters were tuned in SESSA to optimize agreement between simulated and experimental XPS compositions for SAMs on flat Au surfaces. SESSA results were compared with experimental measurements taken from 3 different XPS instruments: Quantum (EMSL/PNNL), Kratos and S-probe (NESAC/BIO). Approaches are being used to apply SESSA and QUASES to analysis of the particle data.

11:00am **AS+NS-WeM10 Nanocerium Oxide as Antioxidant – Role of Environment and Surface Coating on the Interaction with Reactive Oxygen Species**, ***A.S. Karakoti***, *S. Singh, A. Kumar,* University of Central Florida, *S.V.N.T. Kuchibhatla,* Environmental and Molecular Sciences Laboratory, *W.T. Self, S. Seal*, University of Central Florida

The astounding progress of nanotechnology in numerous areas of science and biotechnology is posed with a significant challenge of overcoming the nanotoxicological properties of these materials. More often than not nanomaterials produce oxidative stress when exposed to cellular environment leading to rapid cell death. While several nanomaterials are linked with oxidative stress; cerium oxide nanoparticles (CNPs) show an inverse behavior by scavenging the reactive oxygen species (ROS) thereby reducing the oxidative stress and acting as antioxidant oxides. The antioxidant properties of nanoceria originate from its redox properties, surface chemistry and nanoparticulate size. It was observed that a critical ratio of Ce^{3+}/Ce^{4+} was required for exhibiting better antioxidant properties. Due to the reversible nature of its redox properties i.e. CNPs can regenerate its active radical scavenging oxidation state upon interaction with ROS such as peroxide and superoxide. To increase the biocompatibility and cell permeability characteristics, CNPs were synthesized in biocompatible mediums such as polyethylene glycol (PEG) and dextran. Cell viability studies showed excellent biocompatibility of the CNPs synthesized in biocompatible mediums. The antioxidant property of CNPs in these medium was compared to the water based CNPs using classical superoxide dismutase (SOD) model and it was found SOD mimetic activity was unaltered by the presence of organic coating on CNPs. Reaction of hydrogen peroxide with CNPs was used to compare the changes in oxidation state of CNPs upon interaction with peroxide species. While both PEG and dextran showed tunable redox property; it was found that the redox property of PEG based CNPs were acutely affected by medium due to change in the polarity and dielectric constant of the medium. A clear indication of formation of charge transfer complex was found with PEG while no such complex was observed with dextran. Additionally CNPs synthesized in PEG (5 – 80 vol% PEG) showed concentration dependent red shift in the formation of CNP-PEG charge transfer complex. Upon dialysis it was found that the polymer formed a stable coating on the surface of CNPs and the surface coating was linked to the observed differences in the regeneration of the oxidation state of nanoparticles. High resolution transmission electron microscopy, Fourier transform infra red spectroscopy and UV-visible spectroscopy were used to characterize the particle size, nature of coating and dynamic oxidation state of nanoceria. X-ray photoelectron spectroscopy used to probe the surface chemistry and oxidation state of CNPs.

11:20am **AS+NS-WeM11 Dynamic Nature of Cerium Oxide Nanoparticles – Influence of Aging and Local Environment**, ***S.V.N.T. Kuchibhatla,*** Pacific Northwest National Laboratory, *A.S. Karakoti,* University of Central Florida, *C.H. Windisch Jr., P. Nachimuthu,* Pacific Northwest National Laboratory, *S. Seal,* University of Central Florida, *S. Thevuthasan, D.R. Baer*, Pacific Northwest National Laboratory

Cerium oxide nanoparticles (CNPs) are a subject of increasing attention in the biomedical field in addition to many traditional applications such as catalysis, sensors and fuel cells. Most of the applications of CNPs are driven by the oxygen buffering capability, which in turn is guided by the ability of cerium to switch between 3+ and 4+ oxidation states. The thermodynamic stability of oxygen vacancies in the particles below 10 nm makes this switching more efficient. Motivated by this fact, the CNPs have been used to study their biological response (cell longevity, toxicity and related aspects) and the preliminary results have shown excellent radical scavenging ability. It has also been noted that the CNPs can effectively regenerate the active redox state. However, an unequivocal mechanism is still not reported.

We have studied, *in situ*, the influence of time (aging) and local environment (chemistry) on the chemistry and structure of CNPs. With the help of UV-Visible and Raman spectroscopy along with microXRD measurements, we have observed that the CNPs are highly dynamic in nature and respond, through changes in chemical state and possibly structure, to the variations in their local environment as a function of time. Raman data with support from XRD and some XPS results suggests that the CNPs undergo the transformation between 3+ and 4+ oxidation state through the formation of a *"peroxide-complex"* in presence of hydrogen peroxide, which as a function of time leads to the formation of cerium oxide nanoparticles, regeneratively. Interaction of CNPs with hydrogen peroxide was used as a model system for explaining the regenerative nature of CNPs in biological applications. Various results from this study, along with the size dependence of the transitions, will be presented while discussing the merits of the findings and their implications to the bio-medical applications.

11:40am **AS+NS-WeM12 Characterizing Environmentally Induced Changes in Nanoparticle Surface Chemistry**, *A.N. Mangham, P. Wiecinski, S.P. Yang, K.M. Louis, R.E. Peterson, W. Heideman,* ***A. Pedersen****, R.J. Hamers*, University of Wisconsin-Madison

The routes of exposure and toxicity of nanoparticles in the environment are expected to be strongly affected by the nature of surface chemical groups exposed on the outside of the particles. We have developed a laboratory-based method that simulates oxidative processes in the environment, and have applied this method to investigate the resulting changes in surface chemistry of “bare” and ligand-functionalized nanoparticles. Using CdSe as a model system, we have compared the behavior of ligands bearing different surface anchor groups including carboxylic acid groups, amines, and phosphonates. Wrapping these ligand-modified nanoparticles with amphiphilic polymers can enhance the particle stability as well as the luminescence efficiency. Surprisingly, the type of surface anchoring group has a strong effect on the stability of even the polymer-wrapped nanoparticles. Using infrared, Raman, and x-ray photoelectron spectroscopies, combined with thermogravimetric analysis, we related the differences in stability of the nanoparticles to the chemical and physical structure of the ligands. Our results show that the most thermally stable groups do not necessarily provide the best protection against degradation. As time permits, the influence of the surface chemistry on the nanoparticle toxicity using a zebrafish model will be presented and discussed.

Nanometer-scale Science and Technology
Room: L - Session NS-WeM

Nanoscale Devices and Sensors and Welch Award
Moderator: R.J. Colton, Naval Research Laboratory

8:00am **NS-WeM1 2009 Medard Welch Award Lecture - Molecular Interfaces to Nanoscale Materials: Making "Dumb" Materials "Smart"**, ***R.J. Hamers******, University of Wisconsin-Madison **INVITED**

Recent years have seen dramatic increases in the ability to synthesize new bulk and nanostructured materials. For many applications, such as sensing and renewable energy, the need for high stability drives a motivation for working with two classes of ‘ultra-stable’ materials: (1) nanoscale carbon, and (2) nanocrystalline metal oxides. While these materials are highly stable they do not provide important properties such as chemical or biological selectivity. Molecular surface chemistry can be used to turn these into “smart” materials by linking molecules that will convey chemical or biological selectivity for sensing or desirable electron-transport properties for applications in renewable energy. We have found that photochemical grafting of alkenes provides a nearly universal method for producing molecular monolayers on a wide range of highly stable materials. Surprisingly, this method works on both wide-bandgap semiconductors such as diamond and TiO_2, as well as metallic materials such as carbon nanofibers. Through a series of studies we have identified the underlying mechanism as an internal photoemission process in which ultraviolet light ejects an electron from the material into an adjacent reactive liquid, leaving behind a reactive (and persistent) hole that serves as a reactive site for molecular grafting. With suitable chemistry, this approach can be used to fabricate (bio)molecular interfaces with a high degree of functionality that can be used (for example) to achieve direct biological-to-electronic signal conversion for sensing. Recent work also shows this to be an excellent approach for novel types of electrocatalytic interfaces of interest for applications in renewable energy. In this talk I will discuss some of our efforts in making and understanding “smart” molecular and biomolecular interfaces to nanocrystalline materials, and some of the resulting applications in sensing and in renewable energy.

8:40am **NS-WeM3 Plasmon Induced Molecular Conductivity in Devices**, *P. Banerjee,* University of Maryland, *D. Conklin, S.U. Nanayakkara,* University of Pennsylvania, *T.-H. Park,* University of Michigan, *M.J. Therien,* Duke University, ***D.A. Bonnell***, University of Pennsylvania

Plasmonics and molecular electronics are two fields that explicitly exploit nanoscale physical phenomena. In the former, optical interactions with nanosized particles induce surface plasmons creating locally intense electric fields. In the latter, two decades of intense research has focused on electrical conduction in organic molecules to enable molecular electronics. The interaction of plasmons and electrical conduction has not been observed. Here we demonstrate the ability of a plasmon to alter the electrical properties of a molecular junction. Arrays of Au nanoparticles with different separations are assembled on an insulating substrate and functionalized with porphyrin compounds. These molecules posses unique optical properties and electron delocalization lengths on the order of 7-8nm. The wavelength and temperature dependence of transport in these hybrid devices reveal differences on photo conduction mechanism with wavelength. Three mechanisms are identified, one that operates in the dark current, one associated with electron-hole generation on absorption and one induced by surface plasmons. This ability of plasmons to directly influence electrical conductivity is a new mechanism of photoconduction that suggests a variety of optoelectronic applications.

9:00am **NS-WeM4 CMOS Compatible Silicon Nanowire Field Effect Transistor as Ultrasensitive Bio-sensor**, *S. Regonda, K. Trivedi, P. Fernandes, R. Tian, O. Seitz, J. Gao, E.M. Vogel, Y. Chabal,* ***W. Hu***, University of Texas at Dallas

Among the emerging devices for the future technology in the nanoscale regime, silicon nanowire (SiNW) devices have received significant attention for applications in logic gates, interconnects, photo detectors and biological and chemical sensors. For biosensing, femtomolar (fM) level detection of protein in solution has been demonstrated using both chemically synthesized nanowires [1] and lithographically defined nanowire field effect transistors (FETs) [2]. This type of sensor offers ultrasensitivity, rapid electronic readout, and does not require bulky sensing apparatus. It has a strong potential to be an ultra-portable and low cost biosensing platform that is badly needed for disease diagnostics and early detection.

In this work, we present our recent work on the similar nanowire FETs defined by e-beam lithography and standard Si processing technologies. This approach provides excellent manufacturability and feasibility of integrating circuitry with the sensor array on a single chip for ultimate system miniaturation and low manufacturing cost. In our process, SiNWs are defined by e-beam lithography in hydrogen silses quioxane resist, followed by a new two-step Si etch process, which is designed to improve the process reliability and controllability. SiNW FETs of 30-100 nm in widths, 10-30 nm in thickness, 5-80 μm in length have been successfully fabricated on Si on insulator (SOI) substrates. Uniform devices with sub threshold slope (SS) of 80 mV/dec and On/off ratio greater than 10^7 have been made reproducibly. We will present various device design and fabrication considerations for using nanoelectronic FETs as biosensors, e.g. source/drain doping effects, oxidation effects, plasma treatment effects, buffer solution effects and stability. These device issues are quite different from conventional use of nanowires in logic gates. We further integrate these SiNW FETs with SU8 microfluidic channels to detect proteins at low abundance in solution. Preliminary results have indicated a sensitivity or detection limit of 2fM. We expect to present controlled sensing results of protein biomarker under controlled flow conditions.

[1] Patolsky, F., Zheng, G and Lieber, C.M, *Nat.Protocols* 1, 1711-1724 (2006)

[2] Eric Stern, et al. *Nature* 445, 519-522 (2007)

9:20am **NS-WeM5 The Role of Surface Chemistry on the Properties of Nanoporous Gold**, ***J. Biener****, M.M. Biener, A.V. Hamza,* Lawrence Livermore National Laboratory, *A. Wittstock, M. Bäumer,* Universität Bremen, Germany, *D. Kramer, R.N. Viswanath, J. Weissmüller*, Forschungszentrum Karlsruhe, Germany

Although surfaces or, more precisely, surface atoms determine the way how materials interact with their environment, the influence of surface chemistry on the bulk of the material is generally considered to be small. However, in the case of high surface area materials such as nanoporous gold the influence of surface properties can no longer be neglected. Therefore, actively controlling surface properties such as diffusion barriers and surface stress by surface chemistry should provide an opportunity to manipulate and fine-tune material properties. Specifically, we will show that surface chemistry is an important factor in determining the stability of nanostructured gold surfaces, and that macroscopic strain can be generated by surface-chemistry induced changes of the surface stress. The latter effect can be used to directly convert chemical energy into a mechanical response without generating heat or electricity first and thus opens the door to surface-chemistry driven actuator and sensor technologies.

Prepared by LLNL under Contract DE-AC52-07NA27344.

9:40am **NS-WeM6 Surface Plasmon Induced Enhancement of Hot Electron Flow Generated by Photons Probed with Metal-Semiconductor Nanodiodes**, ***J.Y. Park****, H.S. Lee, J.R. Renzas, R. Baker, G.A. Somorjai*, University of California, Berkeley and Lawrence Berkeley National Laboratory

We present hot electron generation from photon absorption on metal-semiconductor Schottky diodes and its amplification by localized surface plasmon resonance. Hot electron flow was generated on a gold thin film (<

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* Medard W. Welch Award Winner

10 nm) by photon absorption and directly measured as a form of photocurrent on chemically modified gold thin film metal-semiconductor (TiO_2) Schottky diodes. The short-circuit photocurrent obtained with low energy photons (lower than the 3.1 eV bandgap of TiO_2) is consistent with Fowler's law, which confirms the presence of hot electron flow. The morphology of the metal thin film was modified to a connected gold island structure with a lateral length scale of 50- 100 nm after heating in oxygen. The nanometer scale domains in the gold island structures were electrically connected to the Ohmic pad, ensuring the measurement of the flow of hot electrons. These connected island structures exhibit a localized surface plasmon with peak energy at 550- 570 nm, which was separately characterized with UV-Vis. Hot electron flow (after normalizing photon absorption) was enhanced by a factor of three on the connected gold island structure. This result indicates correlation between the hot electron flow and localized surface plasmon resonance. Possible mechanisms for surface plasmon induced enhancement of hot electron generation are also discussed.

10:40am **NS-WeM9 Gallium Nanoparticles: An Alternative Metal for Surface-Enhanced Raman Scattering**, ***P.C. Wu***, *C.G. Khoury, T.H. Kim, Y. Yang,* Duke University, *M. Losurdo, G. Bruno,* IMIP-CNR, Italy, *T. Vo-Dinh,* Duke University, *H.O. Everitt,* Army AMRDEC, *A.S. Brown*, Duke University

The recent increased use of surface-enhanced Raman spectroscopy (SERS) for chemical and biological sensing is intimately tied to the surging interest in developing plasmonic metallic nanostructures. Typically silver or gold, SERS substrates exploit the plasmon resonance and the associated localized surface fields to enhance Raman scattering from the molecule of interest. We will present an alternative plasmonic metal, gallium, for use as SERS substrates. Gallium's prevalence in optoelectronic device growth also suggests their potential for integrated SERS structures. Our previous work has demonstrated interesting properties of gallium that make it an attractive metal for SERS sensing schemes compared to Ag or Au; these include its thermal and oxidative stability. Also in contrast to the properties of Ag and Au, Ga plasmonic nanoparticles can be tuned for size resulting in a plasmon resonance that varies from the near IR through the visible and into the deep UV.

Gallium nanoparticles (NPs) deposited onto dielectric substrates (glass and sapphire) were grown by molecular beam epitaxy. Nanoparticles were tuned to different plasmon resonances (i.e. mean size) to discern the effect NP geometry (size, distribution, and interparticle spacing) has on the strength of the Raman enhancement. In this work, solutions of the standard Raman dye Cresyl Fast Violet were dropcast onto the NP substrate at varying concentrations to evaluate the linear correlation between SERS intensity and molecular concentration. Direct comparison between bare (unmetallized) surfaces and metallized surfaces were made to quantify the Raman enhancement resulting specifically from the presence of Ga NPs. The enhanced Raman signal in the presence of Ga NPs suggest that Ga NP are effective alternatives to Ag and Au for SERS applications.

11:00am **NS-WeM10 Effect of Functional Substrates on Optoelectronic Properties of Hybrid Nanostructures**, ***D. Conklin***, University of Pennsylvania, *P. Banerjee,* University of Maryland, *S.U. Nanayakkara,* University of Pennsylvania, *T.-H. Park,* University of Michigan, *M.J. Therien,* Duke University, *D.A. Bonnell*, University of Pennsylvania

Functionalized gold nanoparticles are assembled on ferroelectric and non ferroelectric substrates. The assemblies are designed to exhibit photoconductivity by controlling particle size, distribution, density, and by linking with optically active porphyrin complexes. The wavelength and temperature dependence of transport is used to determine the effect of the substrate on the optoelectronic properties. Specifically, the effect of substrate local field due to the domain polarization is determined by comparing the response of similar nanostructures on non ferroelectric (SiOx) substrates. Activation energies of high temperature transport mechanisms and tunneling parameters of low temperature transport mechanisms are compared. The combination of optoelectronic molecular nanostructures and a functional substrate suggests new device strategies.

11:20am **NS-WeM11 Control of Coupled Silicon Atomic Quantum Dots for Nano-Electronic Computing Architectures**, ***J. Pitters,*** National Institute for Nanotechnology, Canada, *B. Haider,* University of Alberta, Canada, *G. Dilabio,* National Institute for Nanotechnology, Canada, *L. Livadaru, J. Mutus, R. Wolkow*, University of Alberta, Canada

Coupled quantum dots form an attractive basis both for fundamental studies of single electron control and as potential building blocks for future nano-electronic devices. One computing scheme, Quantum-dot Cellular Automata (QCA), is based upon "cells" of tunnel coupled quantum dots and electrostatic interactions between adjacent cells to transmit binary information and perform calculations with minuscule power consumption. Efforts to fabricate electrostatic QCA devices have been limited by the need for extreme cryogenic conditions. We have demonstrated a new approach using the scanning tunneling microscope (STM) at room temperature. We show that the silicon atom dangling bond (DB) state, on an otherwise hydrogen terminated surface, serves as a quantum dot. These atomic quantum dots can be assembled into multi-DB ensembles through precise hydrogen atom removal using the STM tip. Assembly at critical distances leads to electron tunnel coupling between DBs and control over the net electron occupation of assembled quantum dot DBs is also demonstrated. Additionally, it is shown that a pair of tunnel-coupled DBs can be switched, using electrostatic control, from a symmetric bi-stable state to one exhibiting an asymmetric electron occupation. Similarly, the setting of an antipodal state in a square assembly of four DBs is achieved, demonstrating at room temperature the essential building block of a quantum cellular automata device.

11:40am **NS-WeM12 Towards Wafer-Scale Fabrication of Room-Temperature Single-Electron Transistors**, *P. Bhadrachalam, V. Ray, R. Subramanian,* ***S.J. Koh***, University of Texas at Arlington

We recently demonstrated CMOS-compatible fabrication of single-electron transistors (SETs) that operate at room temperature (Nature Nanotech. V.3, p.603, 2008). This was realized using a new device architecture in which source and drain electrodes are vertically separated with a Coulomb island placed between the electrodes. Here, we present two important advancements toward wafer-scale fabrication of room-temperature SETs for practical applications. Firstly, we present a technique for placing Coulomb islands between the source and the drain electrodes with nanoscale precision, which significantly improves the yield of device fabrication. This accurate placement was made possible by electrostatically guiding Coulomb islands onto the center of the electrode gap. The electrostatic guiding structures were made on a large scale using self-assembled monolayers (SAMs) of positively- and negatively- charged molecules. Secondly, we present a very small fluctuation of the background charges for our fabricated SETs. The uncontrolled fluctuation of background charges has been one of the major obstacles to the practical implementation of SET devices. The shift of background charges was directly measured from the phase shift of Coulomb oscillations at room temperature and it was found that the charge shift was only ~0.01*e* (*e*: electron charge) over a time span of more than a week. These two advancements show a great promise for realization of integrated systems of room-temperature SETs for practical use. (Supported by NSF CAREER (ECS-0449958), ONR (N00014-05-1-0030), THECB (003656-0014-2006))

Tribology Focus Topic
Room: C4 - Session TR+NS-WeM

Nanomechanics and Nanotribology
Moderator: C.M. Mate, Hitachi San Jose Research Center

8:00am **TR+NS-WeM1 Nonlinear Contact Area Dependence of Sliding Friction for Metallic Nanoparticles**, ***D. Dietzel***, *T. Moenninghoff, A. Schirmeisen*, University of Münster, Germany

The existence of superlow friction under appropriate interface conditions is one of the most intriguing concepts in nanotribology. If an interface between two incommensurate surfaces is atomically clean, a state of virtually frictionless sliding is anticipated, often referred to as 'superlubricity' or 'structural lubricity'. But although superlubricity is a widely accepted theoretical concept, an unambiguous and direct verification has been difficult in the past. Theory predicts that the lattice mismatch at the interface causes a decrease of the potential barrier between stable states with increasing contact size that ultimately leads to vanishing friction. Therefore, analyzing the contact area dependence of superlubric friction might be a straightforward approach to confirm the frictional conditions.

Unfortunately, conventional friction force microscopy (FFM) has limitations inherent to the experimental configuration when it comes to contact area dependent measurements: Apart from the rather limited variety of material combinations, the fixed tip radius makes it especially difficult to analyze effects as a function of the contact area. In order to analyze the contact area dependence of interfacial friction, the friction between two objects in relative motion with a well-defined contact area should be measured instead of the friction between tip and surface. Therefore we have manipulated nanometer scale metallic particles on atomically flat surfaces by contact mode atomic force microscopy techniques and quantitative information on interfacial friction has been extracted from the lateral manipulation of these nanoparticles[1]. In previous experiments[2] we found two distinct frictional states during particle sliding of Sb-particles on HOPG substrate: Some particles show finite friction increasing linearly with interface area, thus reinforcing Amonton's law at the nanoscale, other particles assume a state of frictionless or 'superlubric' sliding.

In this contribution we show new measurements which were concentrated on the particles exhibiting vanishing friction. By optimizing our experimental sensitivity we succeeded for the first time to analyze the contact area dependence of friction force of these low friction particles. In contrast to the 'Amonton'-like particles, interfacial friction of the low friction particles showed strongly nonlinear contact area dependence. The experimental results are compared to theoretical considerations, which predict that the shear stress of sliding superlubric particles should decrease with increasing particle size.

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

[2] Dietzel et al., Phys. Rev. Lett. 101, 125505 (2008).

8:20am **TR+NS-WeM2 Why is Graphite so Slippery? Gathering Clues from Atomically Resolved Three-Dimensional Lateral Force Measurements**, ***M.Z. Baykara**, T.C. Schwendemann, B.J. Albers, N. Pilet, E.I. Altman, U.D. Schwarz*, Yale University

Conventional lateral force experiments give insufficient insight into the fundamental reasons for graphite's outstanding qualities as a solid lubricant due to an averaging effect caused by the finite contact area of the tip with the sample. To overcome this limitation, we used a noncontact atomic force microscopy-based approach that enables use of atomically sharp tips. The new technique [1], performed using a home-built low temperature, ultrahigh vacuum atomic force microscope [2], allows the measurement of normal and lateral surface forces in a dense three-dimensional raster with picometer and piconewton resolution.

In this presentation, we analyze the height and lattice site dependence of lateral forces, their dependence on normal load, and the effect of tip shape in detail. The lateral forces are found to be heavily concentrated in the hollow sites of the graphite lattice, surrounded by a *matrix* of vanishingly small lateral forces. It will be argued that this astonishing localization may be a reason for graphite's excellent lubrication properties. In addition, the distance and load dependence of the lateral forces experienced along possible "escape routes" from the hollow sites, which would be followed by a slider that is dragged out of them, are studied. Surprisingly, the maximum lateral forces along these escape routes, which ultimately determine the static friction, are found to depend linearly on normal load, suggesting the validity of Amontons' law in the noncontact regime.

[1] B. J. Albers *et al.*, Nature Nanotechnology **4**, 307 (2009).

[2] B. J. Albers *et al.*, Rev. Sci Instrum. **79**, 033704 (2008).

8:40am **TR+NS-WeM3 Atomistic Simulations of Friction and Wear of Carbon-Based Materials**, ***I. Szlufarska**, Y. Mo, M. Mishra*, University of Wisconsin, Madison **INVITED**

Controlling tribological properties requires understanding a bewildering array of interrelated mechanisms, including elastic instabilities, plastic deformation, fracture, and chemical reactions. Large scale atomistic simulations have been used to unravel some of these mechanisms. Tribological studies are typically divided into a wearless regime, where deformation is primarily elastic, and a wear regime where permanent deformation occurs. For wearless contacts, I will discuss the breakdown of continuum mechanics at the nanoscale and present our recent discovery of friction laws in dry nanoscale contacts. This discovery lays a foundation for unified friction laws across all length scales. In the wear regime I will focus on the origins of recently observed ductile wear in nominally brittle SiC. Although this ductile wear holds potential for greatly enhancing the ease of machining of high-performance ceramics, its origin is still an open question. I will evaluate potential mechanisms for ductile wear, including the possibility of transformation to more ductile phases, dislocation mediated plasticity, and nanoindentation-induced amorphization.

9:20am **TR+NS-WeM5 MD and AFM Studies of the Adhesion of Diamond, Silicon, and UNCD**, ***J.A. Harrison**, P.L. Piotrowski, G.T. Gao,* United States Naval Academy, *R.J. Cannara,* National Institute of Standards and Technology, *R.W. Carpick*, University of Pennsylvania

For the past several years, we have used molecular dynamics (MD) simulations and classical reactive empirical bond-order (REBO and AIREBO) potentials to elucidate the atomic-scale mechanisms of friction and adhesion in solid lubricants. Recently, we have conducted complementary MD and atomic force microscopy (AFM) examinations of adhesion and atomic-scale friction for diamond, silicon, and nanocrystalline diamond interfaces. These materials are highly relevant to micro- and nano-electromechanical systems (M/NEMS), nanomanufacturing, and a host of other applications. The conditions of the simulations and the experiments were designed to correspond as closely as the methods allow. The effects of variables including diamond (or silicon) crystal orientation, hydrogen termination, temperature, and roughness on adhesion and friction can all be examined. In this talk, we will discuss our most recent results which highlight atomic mechanisms of friction and adhesion as well as the limits of continuum mechanics.

*JAH acknowledges support from The Air Force Office of Scientific Research (AFSOR) as part of the Extreme Friction MURI and from The Office of Naval Research. JAH & RWC also acknowledge support from AFOSR's Aerospace, Chemical, and Material Sciences Directorate.

9:40am **TR+NS-WeM6 Which Fractal Parameter Most Determines Adhesion?**, *D. Liu,* Worcester Polytechnic Institute*, J. Martin,* Analog Devices, Inc.*, **N.A. Burnham***, Worcester Polytechnic Institute

The topography of a surface can be characterized by three fractal parameters: its surface roughness, its roughness exponent, and its lateral correlation length [1]. In 2001, T.S. Chow [2] predicted that a decrease in adhesion by orders of magnitude would follow from increasing the roughness exponent of a surface (i.e. by making it smoother), and that adhesion could also be lowered by decreasing its lateral correlation length (shorter wavelength). In 2007 [3], we published a simple analytical model, together with experimental data, that demonstrated the strong influence of surface roughness on adhesion. This year, using atomic force microscopy, experimental data were collected from MEMS sidewalls of varying topography but with the same chemical treatment in order to untangle which of the three fractal parameters is – or are – most important in determining adhesion. The data are inconsistent with Chow's predictions; his assumption was that only the asperities on the surface contribute to the adhesion. In contrast, our numerical simulations of the tip-sample adhesion for surfaces with varying fractal parameters include both the asperities and the bulk of the sample.

Together with the simulations, the previous and current experimental data support the conclusion that surface roughness is a significant predictor of adhesion, with the adhesion dropping by more than an order of magnitude for a roughness change from 1 to 10 nm. For the roughness exponent, the simulations follow the same trend as Chow's predictions, in that adhesion should decrease with increasing roughness exponent (smoother), but rather than predicting orders of magnitude change, the simulations reveal only a 20% decrease as the roughness exponent changes from 0 to 1. Here, the experimental data were more consistent with the simulation than Chow's predictions, although they were not conclusive. The scatter in the data was large, and the range of the roughness exponent only varied from 0.85 to 0.99, for which the simulations predict a change in adhesion of approximately 10%. For the lateral correlation length, the experiment showed a wide range of adhesion values for smaller correlation lengths and low adhesion for larger correlation lengths (longer wavelengths); we are still investigating the theoretical basis of this observation. We hope to contribute to the understanding of adhesion so as to minimize stiction in MEMS.

References

1. A.-L. Barabasi and H.E. Stanley, Fractal concepts in surface growth (1995)
2. T.S. Chow, Phys. Rev. Lett. 86, 4592 (2001)
3. D. Liu, J. Martin, and N.A. Burnham, Appl. Phys. Lett. 91 043107 (2007)

10:40am **TR+NS-WeM9 Multiscale Modelling of the Indentation and Scratch Damage of Ultrathin Coatings on Architectural Glass**, ***S.J. Bull**, A. Oila*, Newcastle University, UK

Although optical coatings are generally designed for their functional requirements it is often the mechanical properties of the system which limits performance. For instance, the major in-service failure mechanism of modern solar control coatings for architectural glass can be scratch damage. Many of these coatings are multilayer structures made from individual layers of less than 100nm thickness and different coating architectures are possible (i.e. different layer materials, thicknesses and stacking order). To assess their mechanical response, coated samples may be subjected to indentation and scratch tests; however, it is not always possible to predict the failure mechanisms of such coatings and modelling approaches have to be developed to understand the deformation mechanisms. This presentation will focus on the problems of measuring the plasticity and fracture properties of very thin coatings (<100nm) and the use of multi-scale modelling approaches to predict performance for coatings on glass.

11:00am **TR+NS-WeM10 Cognitive Molecular Engineering In Nanotribology - Intrinsic Friction Analysis**, *D.B. Knorr, **R.M. Overney***, University of Washington

In the new *Age of Molecular Engineering*, one of the objectives is to cognitively design molecules that if condensed, provide materials with anticipated properties. In regards of tribological systems, such as lubricants, the objective would be to offer chemists with molecular design parameters based on which molecules could be synthesized that dissipate energy in a targeted fashion. Thereby, the input would come either directly from experimental observations, or indirectly via computer simulations that are based on models that are relevant to the materials.

This is in contrast to the majority of current research efforts in tribology or nanotribology. State-of-the-art molecular models in tribology focus on generic periodic potentials that are thermally and mechanically inert. Experimental methods provide mostly only phenomenological parameters, such as the friction coefficient, or process descriptive parameters, such as the stick-slip phenomena. Such generic “black-box” approaches, fail to address frictional energy dissipation that are linked to material intrinsic molecular or submolecular modes of relaxation, and hence, do not provide the necessary input for a cognitive molecular design strategy for an effective tribological system.

This talk will highlight the importance of material intrinsic relaxation modes for frictional dissipation involving organic systems. Phenomenological friction analysis data, i.e., friction coefficients from friction-load curves, will be contrasted with spectroscopic data from an intrinsic friction analysis (IFA), involving a time-temperature superposition analysis of friction-velocity isotherms. Both data analysis methodologies, involving lateral force microscopy, reveal an astonishing correspondence regarding the dissipated energy and the energy involved in activating intrinsic relaxation modes and cooperative phenomena. Specifically, we will address surface and sub-surface energy relaxations in amorphous macromolecular model system (e.g., polystyrene) and their relevance to frictional energy dissipation within well defined loading regimes. Depending on the coupling strength (cause for cooperativity) between molecular actuators involved (e.g., rotating side chains or translating polymer backbones) the dissipation in energy can carry a significant entropic energy contribution, accounting for up to 80% of the apparent Arrhenius activation energy. The IFA methodology discussed in this paper that provides direct insight into the enthalpic and entropic energy contributions of friction dissipation processes is shown to be well suited as an analysis tool towards cognitive molecular engineering in tribology.

11:20am **TR+NS-WeM11 Optimization of Tailored Multifunctional Nanocomposite Structures**, ***T. Shenk***, *R. Winter*, *K. Benjamin*, South Dakota School of Mines and Technology

Polymer nanocomposites provide unique solutions to industrial and scientific applications where weight must be minimized and functionality maximized. Researchers are interested in improving the ability to tailor a product to meet specific weight, thermal, optical, mechanical and electrical requirements. Historically functional composite structures have been realized through a top-down approach. With the advent of atomic level measurement tools and experimental techniques a bottom-up approach to the creation of multifunctional structures is receiving intense study. We are developing unique multifunctional structures using such a bottom-up approach with the intent of developing molecular simulations to guide such a process. Properties of polymeric nanocomposite structures are tailored and optimized through a fundamental understanding of intermolecular forces. While macroscopic models of bulk properties of polymer nanocomposites have been characterized, much less is known on the dynamics of their interfacial characteristics, which must be fully developed in order to be able to tailor fabrication of multifunctional nanocomposites using the bottom-up approach. Self assembly, targeted functionalization and spin coating are used to provide consistent means of creating multilayer multifunctional thin film composite strictires allowing for the investigation of multifunctional composites. We investigate the affects of sonication, high shear mixing, and surface modification on the ability to control dispersion to create and predict multifunctional layers of epoxy spin coated nanocomposites and control desired mechanical properties such as conductivity, optical transmission and absorption, loss and storage moduli and coefficient of thermal expansion. The Interfacial Force Microscope (IFM), coupled with the Biaxial Loading Instrument, which allows for refined and uncoupled control of mixed-mode characterization of interface adhesion, will be used to determine interfacial characteristics of these multi-functional composites.

Biomaterial Interfaces
Room: K - Session BI+AS+NS-WeA

Quantitative Nanoscale Sensing at Biosurfaces and Interfaces
Moderator: F. Höök, Chalmers University of Technology, P. Kingshott, Aarhus University, Denmark

2:00pm **BI+AS+NS-WeA1 Characterizing Self-Assembled Supported Lipid Membranes for Biosensing**, ***E.O. Reimhult***, ETH Zurich, Switzerland **INVITED**

More than 50% of all drug targets are membrane proteins, which require a lipid membrane environment to retain correct conformation and function. This highlights the need to create sensing tools for analytical profiling of transmembrane protein function subject to e.g. drug binding. Furthermore, it is increasingly realized that the compositionally complex and dynamically rearranging lipid membranes can be important active regulators of biological function in their own right. The complexity of the *in vivo* cell membrane and the need to apply high throughput techniques like arrays and highly surface sensitive analytical techniques make model systems highly desirable. Thus, supported lipid bilayers (SLBs) which combine control of membrane properties with surface analytical techniques receive increasing interest.

Biosensor interfaces can be easily functionalized with an SLB by self-assembly from liposomes. However, design of more native-like SLBs, e.g., having diverse lipid compositions, including glycolipids or mimics thereof, demands further developments of this assembly technique. This in turn prompts for more advanced characterization of the formation and structure of SLBs.

We present advances in instrumentation and interpretation of data from multi-technique studies of liposome adsorption and SLB formation, which enhance the understanding of the assembly process and the sensor response obtained for different membrane conformations. In particular, we demonstrate advances in waveguide spectroscopy which allow for characterization of the rupture kinetics of supported lipid bilayers by liposome fusion, but also to in real time distinguish differences in structure for membranes of different compositions and under various environmental conditions. These advances also open the possibility to study differential binding to and into SLBs and to use rearrangements in the SLB as an amplifier of membrane protein binding events.

As examples, we also present the results of such detailed multi-technique characterization of the self-assembly of new supported lipid membrane mimics, e.g., bacterial membrane mimics containing lipopolysaccharides and poly(ethylene glycol)-lipids, including how the presence of a polymer directly attached to the lipids affects the self-assembly and how the hydrophilic polymer is distributed and rearranged in the membrane under mechanical perturbation. Such self-assembled polymer-membranes have great potential for creation of membrane arrays incorporating membrane proteins thanks to high stability and less perturbation of the membrane components due to the mobile polymer spacer layer.

2:40pm **BI+AS+NS-WeA3 Nanoplasmonic Biosensing: Artificial Cell Membranes, Structural Changes and Quantification of Bound Mass**, ***M. Jonsson***, *A. Dahlin, P. Jönsson, S. Petronis, F. Höök*, Chalmers University of Technology, Sweden

The resonance condition for excitation of plasmons associated with metal nanostructures is highly sensitive to changes in the interfacial refractive index, which has made the phenomenon highly popular as transducer principle for label-free sensing of biomolecular recognition reactions. There is a particular need for sensor concepts that are compatible with studies of the cell membrane, which can be explained from the fact that more than half of the most commonly used drugs are directed towards membrane-associated reactions. This is also relevant with respect to diagnostics of viral diseases, because viruses typically infect host cells via adsorption to the cell membrane. During the past years we have developed nanoplasmonic biosensing platforms that are compatible with studies of artificial cell membranes, such as lipid vesicles and supported lipid bilayers (SLBs).[1-3] In addition to probing specific binding of ligands to membrane receptors, we showed that nanoplasmonic sensors provide a unique means to probe biomolecular structural changes, such as during the formation of a SLB from adsorption and rupture of lipid vesicles.[1]

We have previously used a metal film perforated with nanoholes as an electrode for combined nanoplasmonic and quartz crystal microbalance measurements.[3,4] Besides two independent measures on biomolecular structural changes, the combined sensor setup was shown to provide new information that enabled the quantification of adsorbed mass on the sensor surface with only the density of the molecules as unknown parameter.[3]

In the current work we utilize the continuity of a perforated plasmon active metal film to fabricate nanoplasmonic pores with liquid access to both sides of the nanopores.[5] This structure opens up for a wide range of novel applications. For example, extending our previous work on plasmonics and cell membrane mimics, an appealing possibility is to measure transport of both charged and non-charged molecules through lipid membranes that span the pores. Plasmonic pores can also be used for flow-through sensing, where flowing the target molecules through the pores will facilitate molecules to reach the sensor surface in an efficient way and circumvent limitations due to mass-transport.[6]

References:

1 Jonsson, M. P. et al. *Nano Letters* **2007**, *7*, 3462-3468.

2 Dahlin, A. B.; Jonsson, M. P.; Höök, F. *Advanced Materials* **2008**, *20*, 1436-1442.

3 Jonsson, M. P.; Jönsson, P.; Höök, F. *Analytical Chemistry* **2008**, *80*, 7988-7995.

4 Dahlin, A. B.; et al. *ACS Nano* **2008**, *2*, 2174-2182.

5 Jonsson M. P. et al. Manuscript in preparation

6 Eftekhari F. et al. *Analytical Chemistry* **2009**, ASAP

3:00pm **BI+AS+NS-WeA4 Transfer of Biomolecules between Lipid Membranes**, ***A. Kunze***, *S. Svedhem,* Chalmers University of Technology, Sweden, *P. Sjövall,* SP Technical Research Institute of Sweden, *B.H. Kasemo*, Chalmers University of Technology, Sweden

The study of the interaction between biomembranes is of great interest for both basic research and applications in biosensing technology. In biological systems the interaction between membranes including transfer of biomolecules plays a pivotal role. For instance, it is central in energy supply to and communication between cells and for the function of a large number of drugs. A controlled transfer of lipid molecules, or other biomolecules, between lipid vesicles (liposomes) and solid supported lipid bilayers (SLBs) provides a new platform for modifying and controlling SLBs that can be used in biosensing technology. Mechanistic studies of this process are furthermore important for the understanding of a number of important biomolecule-membrane and inter-membrane events.

We will present how transfer of biomolecules between an SLB and liposomes can be monitored in real-time giving more insight into the complex mechanism of transfer including influence of electrostatic interaction, ionic strength, phase and molecular structure of lipids, as well as time scale of the transfer process. Recent results show that the interaction process consists of an attachment-transfer-detachment (ATD) sequence, where added liposomes first attach to a preformed SLB, then transfer lipid molecules and eventually detach, leaving behind a compositionally modified SLB and ditto vesicles.[1] We will demonstrate how the ATD process can be used for *in situ* modifications, changing the membrane composition, e.g. for the formation of a highly stabilized (SDS-resistant) lipid monolayer on TiO_2, which can then be used for the reassembly of an SLB.[2] We propose this as a promising method for *in situ* preparation of asymmetric SLBs.

The main experimental techniques used to study these processes at these interfaces between two biomembranes are the quartz crystal microbalance with dissipation monitoring (QCM-D), t otal internal reflection fluorescence microscopy (TIRF), fluorescence microscopy and time-of-flight secondary ion mass spectrometry (TOF-SIMS) and optical reflectometry.

[1] Kunze, A.; Svedhem, S.; Kasemo, B. Lipid Transfer between Charged Supported Lipid Bilayers and Oppositely charged Vesicles, Langmuir in press

[2] Kunze, A.; Sjövall, P., Kasemo, B.; Svedhem, S. In situ preparation and modification of supported lipid layers by lipid transfer from vesicles studied by QCM-D and TOF-SIMS, J. Am. Chem. Soc., 131:2450-2451, 2009

4:00pm **BI+AS+NS-WeA7 Nanopores for Sensing Membrane Processes and Enzyme Reactions**, ***M. Mayer***, University of Michigan **INVITED**

This talk demonstrates that pores with diameters below 50 nanometers make it possible to detect enzyme reactions, molecular phases transitions, and nanoscale self-assemblies *in situ* and in real time. For instance, coating the inner walls of nanopores with self-assembled lipid bilayers, afforded controlled shrinkage of this pore to a size that made it possible to detect individual proteins. Remarkably, the extent of pore shrinkage could be controlled with sub-nanometer precision by the chain lengths of the acyl chains on the lipids that were chosen to assemble the bilayer. Due to the extreme sensitivity of single-channel recording of ion currents through nanopores, this approach made it possible to monitor molecular changes and rearrangements of the lipid bilayer. These changes included phase transitions, variations in membrane composition, and enzymatic reactions on membranes. For example, this approach made it possible to monitor the activity of attomolar amounts of phospholipase D (PLD) and phospholipase C (PLC) – two membrane-active enzymes that are critical for cell signaling.

4:40pm **BI+AS+NS-WeA9 Development of Microresonator Arrrays for Mass and Viscoelastic Characterization of Adsorbed Molecular and Biomolecular Thin Films**, ***D.L. Allara***, *S. Tadidagapa, P. Kao*, Pennsylvania State University

A multiple pixel micromachined quartz crystal resonator array with a fundamental resonance frequency in the 60-100 MHz range has been designed, fabricated, and tested for applications to accurate mass and viscoelastic measurements of adsorbed thin molecular and biomolecular films. Operating with high Q-factors in the range of 25000–50000 and appropriately lower in liquids, the high stability and inherent low noise of the quartz crystals allow for an unprecedented resolution of one part in 10 million for density/viscosity variations. Further, multiple pixels, capable of independent functionalization with SAMs, can be tracked in parallel to give large numbers of independent measurements simultaneously. By measuring the frequency decrease at overtone frequencies it also is possible to vary the decay length of the shear wave away from the electrode and thereby identify individual variations in the density and viscosity of the local environment and accurately monitor small changes in the viscoelastic loading of adsorbed films. The performance of the resonator is illustrated with examples such as the adsorbed protein films in which the damping factor undergoes an order of magnitude change in transitioning from monolayer to multilayer adsorption. This aspect is highly desirable for accurate determination of behavior such as conformational changes.

5:00pm **BI+AS+NS-WeA10 Plasmonically Coupled Nanoparticle-Film Molecular Ruler**, ***R.T. Hill***, *J.J. Mock, A. Degiron, S. Zauscher, D.R. Smith, A. Chilkoti*, Duke University

Experimental analysis of the plasmonic scattering properties of gold nanoparticles controllably placed nanometers away from a gold metal film shows that the spectral response of this system results from the interplay between the localized plasmon resonance of the nanoparticle and the surface plasmon polaritons of the gold film, as previously predicted by theoretical studies. In addition, the metal film induces a polarization to the single nanoparticle light scattering resulting in a doughnut-shaped point spread function when imaged in the far-field. Both the spectral response and the polarization effects are highly sensitive to the nanoparticle-film separation distance, and thus, the plasmonically coupled NP-Film system represents a new variant of the previously reported plasmonic molecular rulers. A surface-based molecular ruler shows promise in potential biosensor and diagnostic devices.

5:20pm **BI+AS+NS-WeA11 Label-free Imaging of Cell Adhesion Dynamics using Surface Plasmon Resonance Imaging Ellipsometry**, ***D.W. Moon***, *J. Gil, W. CheGal, H. Cho, S. Kim*, Korea Research Institute of Standards and Science, S. Korea

The interaction between cell and extracellular matrix (ECM) governs multiple cellular functions and contributes to promote inflammation and tumor metastasis. Therefore, cellular behavior needs to be monitored in the ECM interactive circumstance. Most of previous studies on cell adhesion are based on immunofluorescence microscopy. For cell adhesion dynamics studies, label-free optical techniques that can monitor continuously cell-ECM interfaces for living cells are required.

Here we developed surface plasmon resonance imaging ellipsometry (SPRIE) which can simply image cell-ECM interfaces for live cells with high contrast and at real-time. To visualize cell adhesions to ECM, null-type imaging ellipsometry technique with the attenuated total reflection coupler was applied and both of transverse magnetic and electric waves were made use of. These characteristics make it possible to acquire the high contrast image of cell adhesions. Different features and dynamics of cell adhesion patters in ~ 100 nm cell-ECM interfaces were observed for A10, human coronary artery smooth muscle cell hCASMC, and human umbilical vein endothelial cells (HUVEC) on fibronectin and collagen ECM layers with 1 µm spatial resolution and 30 sec time interval upto 3 days. Harmonized changes of entire adhesion proteins were observed during cell division and cell migration through our imaging system without any labeling. SPRIE images were compared with confocal fluorescence microscopic images of cell adhesion proteins for validation of SPRIE images. Preliminary results on SPRIE studies on the effect of shear force on cell adhesion and migration will be also discussed. We expect that SPRIE cell adhesion dynamic imaging methods would be useful for further understanding of cell biology and development of drug screening methodology relevant to cell adhesion and migration.

5:40pm **BI+AS+NS-WeA12 Label-Free Determination of Protein-Ligand Equilibrium in Aqueous Solution using Overlayer Enhanced Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (OE-ATR-FTIR)**, ***T.C. Ruthenburg***, *S.S.N. Park, T.A. Aweda, C.F. Meares, D.P. Land*, University of California, Davis

Protein binding/affinity studies are often performed using Surface Plasmon Resonance techniques that don't produce much spectral information. Measurement of protein binding affinity using FTIR is traditionally performed using high protein concentration or deuterated solvent. By immobilizing a protein near the surface of a gold-coated germanium internal reflection element interactions can be measured between an immobilized protein and small molecules in aqueous solution. Using flow injection analysis the on and off rates of these interactions and dissociation constant for the system can be determined. The dissociation constant for the molecule Yttrium-aminobenzyl-DOTA binding to the antibody 2D12.5 system was determined.

Nanometer-scale Science and Technology
Room: L - Session NS-WeA

Nanotubes - Electronics and Functionalization
Moderator: E.I. Altman, Yale University

2:00pm **NS-WeA1 Chemical and Biological Functionalization of Carbon Nanotubes**, ***S.S. Wong***, SUNY Stony Brook and Brookhaven National Laboratory **INVITED**

In the first part of the talk, we update covalent chemical strategies commonly used for the focused functionalization of single walled carbon nanotube (SWNT) surfaces. In particular, we explore advances in the formation of nanotube derivatives that essentially maintain and even enhance their performance metrics after precise chemical modification. We especially highlight molecular insights (and corresponding correlation with properties) into the binding of functional moieties onto carbon nanotube surfaces. Controllable chemical functionalization suggests that the unique optical, electronic and mechanical properties of SWNTs can be much more readily tuned than ever before with key implications for the generation of truly functional nanoscale working devices.

In the second part of the talk, we investigate the biocompatibility, specificity, and activity of a ligand-receptor-protein system covalently bound to oxidized SWNTs as a model proof-of-concept for employing such SWNTs as biosensors. In the third part of the talk, we describe a novel SWNT-based tumor-targeted drug delivery system (DDS) which has been developed, consisting of a functionalized SWNT linked to tumor-targeting modules as well as prodrug modules. There are three key features of this nanoscale DDS: (a) use of functionalized SWNTs as a biocompatible platform for the delivery of therapeutic drugs or diagnostics, (b) conjugation of prodrug modules of an anticancer agent (taxoid with a cleavable linker) that is activated to its cytotoxic form inside the tumor cells upon internalization and *in situ* drug release, and (c) attachment of tumor-recognition modules (biotin and a spacer) to the nanotube surface.

2:40pm **NS-WeA3 Carbon Nanotube-Based Biosensor for Detection of MicroRNA**, ***V.Z. Poenitzsch***, *T. Booker, A. Clark, N. Nitin*, Southwest Research Institute

Carbon nanotubes (CNT) – field effect transistor (FET) sensors are promising candidates for label-free, sensitive detection of biological molecules. In this study, we have developed a proof-of-concept biosensor for the detection of microRNA (miRNA) in which designer oligonucloetide (ODN) probes covalently attached to CNTs serve as a highly specific molecular recognition function and FET device that translate changes in CNT electric properties serves as a signal transduction function. MicroRNA-21 was selected in this study as a model miRNA molecule. Basic research has shown that over-expression of miRNA-21 is associated with development of leukemia, breast cancer and prostate cancer. CNTs were functionalized with designer oligionucleotide (ODN) probes having conformational structures and sequences that are highly specific for hybridization with target miRNA-21. Conjugation of ODN probes with CNTs was examined using zeta potential surface charge measurements, fluorescent labeling, and atomic force and scanning electron microscopies. Biological activity and hybridization of immobilized ODN probe with miRNA 21 were further monitored using quartz crystal monitor measurements and fluorescent labeling. Subsequently, CNT-ODN network films were deposited using dielectrophoretic technique. Thin and wide metal electrodes that allow for increased Schottky contact areas were fabricated by magnetron sputter deposition of metals for source and drain electrodes using a shadow mask and tilted angle. Electrical impedance spectroscopy and current-gate voltage measurements were used to study the effect of ODN attachment and hybridization event on CNT electronic properties. In this presentation, we will discuss the fabrication and characterization of the developed sensor along with challenges of meeting the required specificity and sensitivity for real-world applications such as in vitro medical diagnostics.

3:00pm **NS-WeA4 Effect of Carboxy-Functionalized Multiwall Carbon Nanotubes on the Conductivity Performance of Tricomponent LBL Films**, ***X. Gu***, *D.B. Knorr,* University of Washington, *G. Wang,* Tongji University, China, *R.M. Overney*, University of Washington

Lithium batteries offer high energy density, a flexible, lightweight design and longer lifespan than competing battery technologies. Poly(ethylene oxide) (PEO) is a polymeric material which has extensively been adopted as an electrolyte component in solid state rechargeable lithium batteries. PEO exhibits good complexation properties and high flexibility and retains good mechanical stability at temperatures up to its melting point. Recently, a layer-by-layer (LBL) technique was introduced to prepare battery thin films. This method offers fine control and tunability of material properties and architecture at the nanometer scale, and is a relatively simple method to implement. Films were fabricated by alternating deposition of PEO and poly(acrylic acid) (PAA) layers from aqueous solutions, However, PEO/PAA layer-by-layer (LBL) films exhibit low ionic conductivity when dry, and thus the inhibition of PEO crystallinity alone is not sufficient to improve the ionic conductivity. To achieve more enhanced conductivity in PEO films, various methods have been introduced. The exceptional electronic properties of carbon nanotubes (CNTs) have prompted intensive studies of PEO/CNTs composites. However, at present, these composites have shown only a moderate conductivity enhancement. LBL assembly has shown for other polymers to allow for excellent control of thickness and composition and diminished phase segregation compared with other methods of construction of CNT composites.

In this work, we demonstrate that fabrication of LBL films with carbon nanotubes is possible in a complex tricomponent film of PEO, PAA, and carboxy-functionalized multiwall carbon nanotubes (MWNT-COOH). Successful incorporation of carbon nanotubes layers and excellent surface coverage was observed by AFM topography images and lateral force microscopy. Our system displayed fast growth of LBL assembled films in the deposition process with film thicknesses reaching 1 mm for films composed of 10 cycles of layers. Rapid growth of the films affords fast preparation of PEO/PAA LBL films with incorporated carbon nanotubes which is essential for battery application. Impedance measurements and electrostatic force microscopy (EFM) were used to analyze the differences in ionic conductivity before and after incorporation of MWNT-COOH in to PEO/PAA assemblies. As expected, conductivity improved with the incorporation of the MWNT-COOH treatment. To this end we also employed thermomechanical characterization techniques including shear-modulation force microscopy (SM-FM) to investigate molecular mobility in the tricomponent systems.

4:00pm **NS-WeA7 Graphene Chemistry**, ***R.C. Haddon***, University of California, Riverside **INVITED**

We have recently demonstrated the high density functionalization of epitaxial graphene wafers with nitrophenyl groups.[Bekyarova, E.; Itkis, M. E.; Ramesh, P.; Berger, C.; Sprinkle, M.; de Heer, W. A.; Haddon, R. C., Chemical Modification of Epitaxial Graphene: Spontaneous Grafting of Aryl Groups. *J. Am. Chem. Soc.* **2009,** 131, 1336-1337] The chemical formation of covalent carbon-carbon bonds involving the basal plane carbon atoms offers a versatile approach to the control of the electronic properties of graphene; the transformation of the carbon centres from sp^2 to sp^3 introduces a barrier to electron flow by saturating the carbon atoms and opening a band gap which allows the generation of insulating and semiconducting regions in graphene wafers. This prototype chemistry when applied to carbon nanotubes allowed both covalent and ionic modification of the electronic structure; covalent attachment of functional groups was shown to transform the metallic single-walled carbon nanotubes into semiconductors.

In this talk I will discuss our recent results on the electronic and magnetic properties of chemically modified graphene and its relationship to single walled carbon nanotubes.

4:40pm **NS-WeA9 Spectroscopic Study of the Electron Transport Suppression Phenomenon in Carbon Nanotubes Field-Effect Transistors**, ***F. Lapointe***, Université de Montréal, Canada, *C.M. Aguirre,* École Polytechnique de Montréal, Canada, *P.L. Lévesque,* Université de Montréal, Canada, *P. Desjardins,* École Polytechnique de Montréal, Canada, *R. Martel*, Université de Montréal, Canada

Carbon nanotubes field-effect transistors (CNFETs) were thought to exhibit exclusive hole transport under ambient atmosphere because of the high potential barrier to electron injection at the electrode-nanotube contact interface. This hypothesis did not hold against a set of new experiments we devised, where ambipolar transport was observed under ambient atmosphere by merely changing the nature of the dielectric used as the substrate. Using controlled atmosphere experiments, we pinpointed the phenomenon responsible for the inhibition of electron transport in CNFETs, and showed it is mainly caused by an electrochemical charge transfer to the aqueous oxygen redox couple. We postulated that intermediates of the redox charge transfer are stabilised at the SiO$_2$ surface as charged oxygen species leaving a net negative charge at the surface and thus screening the applied gate potential. Focusing on a spectroscopic investigation, we tested the existence of these species. Thermodesorption spectroscopy experiments coupled to reflection-absorption infrared spectroscopy under high vacuum conditions were used to probe the dielectric interface of CNFETs operated under ambient atmosphere prior to insertion into the experimental chamber.

5:00pm **NS-WeA10 Direction Control of Carbon Nanotube Growth on Corrugated Patterned SiO$_2$ using Casimir Force and its Application to High Current FET**, ***K. Matsumoto***, *S. Iwasaki, T. Kamimura, K. Inoue, T. Kishimoto, Y. Ohno, K. Mehashi*, Osaka University, Japan

The direction control of the carbon nanotube(CNT) growth on the SiO$_2$/Si substrate was first succeeded in at our will using the attractive force of "Casimir force" which concentrates at the upper edge of the corrugated pattern. By applying the present technique for CNT FET, the drain current was enhanced more than 10 times than the conventional CNT FET because of the effective bridging of CNTs between the source and drain electrodes.

The process for the direction control of CNT growth is as follows; The SiO$_2$/Si substrate was processed to form the corrugated pattern using the electron beam lithography and CF$_4$ plasma etching. The planed width and spacing of the corrugated pattern is 100nm and its depth is 40nm. After the formation of the corrugated pattern, 0.5nm thick Co catalyst is formed at the end of the corrugated pattern by the photolithography. Then the sample was set in the thermal CVD to grow the CNT at 800C. The CNTs which started to grow from the catalyst are attracted to the upper edge of the corrugated pattern and follow the direction of the corrugated pattern. So, the direction of the CNT growth can be controlled at our will only by forming the corrugated pattern on SiO$_2$/Si substrate.

The direction controlled growth of CNT on the corrugated pattern was confirmed by SEM observation. The CNT grew more than 7mm straightforward along with the corrugated pattern. Furthermore, it becomes clear that the CNT follows not on the bottom edge but at the upper edge of the corrugated pattern by the SEM observation from the tilted angle. In order to clarify the reason why CNT is attracted to the upper edge of the corrugated pattern, the Casimir force, which is a kind of van der Waals force, along with the cross section of the corrugated pattern was calculated. In the calculated results, the density of the Casimir force shows the highest peaks near the upper edges of the corrugated pattern. Because of these highest peaks of the Casimir force density, it becomes clear that the carbon nanotube is attracted to the upper edge of the corrugated pattern and grow following the direction of the pattern.

By applying this technology, FET with the direction controlled CNT channel was fabricated and its electrical property was examined. From the SEM observation, it was confirmed 8 CNTs were bridged between the source and drain electrodes. The dependence of the drain current on the gate bias at room temperature was examined, and the drain current reached as high as 2.5mA at V_g = -5V, which is about ten times higher than the conventional CNT FET. This is because a number of CNTs bridged between the source and drain electrodes can work as channels of FET.

5:40pm **NS-WeA12 Field Emission Properties of Wall-Number-Selected Carbon Nanotube Arrays**, ***D.H. Lee***, *S.O. Kim, W.J. Lee*, KAIST, Republic of Korea

The wall-number-selective growth of vertical carbon nanotube (CNT) arrays is achieved by the combination of block copolymer lithography and plasma enhanced chemical vapor deposition of CNTs, and the field emission properties were measured as a function of wall-number, length, density and doping concentration of CNT arrays. Block copolymer lithography is an attractive nanopatterning method for generating a uniform catalyst particle arrays for carbon nanotube growth. In this work, highly uniform nanopatterned iron catalyst arrays were prepared by tilted evaporation through block copolymer nanotemplates, and the sub-nanometer-scale tunability of catalyst particles enabled the excellent controllability of the wall-number and density of the CNT arrays. Moreover, the use of ammonia in the growth of CNT arrays ensured that the CNTs were nitrogen doped, and the doping concentration of nitrogen can be adjusted by controlling the flow rate of ammonia gas. Substitution of a carbon in a CNT wall with a more electron-rich nitrogen atom provided additional electrons and enhanced the conductivity of the nanotubes. With the excellent controllability of CNT arrays, we investigated the field emission properties of the grown CNT arrays. Wall-number, length, density and the doping concentration of CNT arrays were changed independently to investigate their effect on the field emission properties. Therefore, superior field emission performance of CNT arrays was acquired by controlling the physical and chemical parameters of CNT arrays.

Nanometer-scale Science and Technology
Room: L - Session NS-ThM

Characterization and Imaging at the Nanoscale
Moderator: C. Nakakura, Sandia National Laboratories

8:00am **NS-ThM1 Depth Resolved Luminescence from ZnO Nanowires**, ***R.A. Rosenberg****, S. Vijayalakshmi, M. Abu Haija,* Argonne National Laboratory*, J. Zhou, J. Liu, S. Xu, Z.L. Wang*, Georgia Institute of Technology

Nanodevices based on wide bandgap semiconductors have great potential in applications running from photon detectors to gas sensors. Critical to their successful implementation is knowledge of the surface and interfacial properties. In the present work we have utilized the limited penetration depth of soft x-rays (550-1000 eV) to study the near surface properties of vertically aligned ZnO nanowires. For a grazing angle of 5 degrees the penetration depth of these x-rays varies between 11 and 65 nm. Thus by obtaining optical luminescence spectra as a function of energy it is possible to probe the near surface region with nm-scale resolution. We will present energy dependent optical luminescence data from ZnO nanowire samples with diameters of 350 nm, 390 nm and 720 nm. In each case the ratio of the oxygen vacancy luminescence to the near band edge luminescence intensity peaks at an energy corresponding to ~17 nm x-ray penetration. This shows that the nanowires of three different diameters have a near surface defect region with a width of ~20 nm, which agrees with the conclusions from previous photoluminescence and cathodoluminescence studies [1-3]. Applications of this technique to other systems will also be discussed.

This work was performed at the Advanced Photon Source and was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-06CH11357.

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8:20am **NS-ThM2 Scanning Chemical Microscopy of Nanoscale Roughness Formation in Photoresist Materials**, ***R. Ramos****, I. Riisness, M. Gordon*, University of California Santa Barbara

Developing a molecular-level understanding of surface chemistry is of critical importance for advancements in the fields of surface science, materials research and catalysis. In particular, the ability to characterize, interrogate and image the chemical composition of surfaces at high spatial resolution would provide greater insight into surface reaction mechanisms and dynamics. For this purpose, optical spectroscopy, when combined with scanning probe microscopy, is a powerful tool for simultaneous chemical identification and imaging of surfaces at the nanoscale. Over the past few years, enhancement of optical fields through plasmonic coupling of light with metal nanostructures has been used for near-field vibrational spectroscopy (e.g., surface- and tip-enhanced Raman spectroscopy – SERS/TERS). However, these techniques have not seen widespread use for surface nanocharacterization because of poor quality field enhancers (i.e., reproducible tips) and difficulties in interpreting spectroscopic data.

In this work, we will show how careful design of the plasmonic properties of the tip and scanning configuration can turn TERS into a robust chemical analysis technique. Our experimental setup combines a tuning fork/cantilever-based scanning probe microscope with in-situ Raman and reflectance spectroscopy; the system also allows simultaneous mechanical and electrical surface interrogation at the nanoscale. In this talk, we will demonstrate that spatially correlating topography with chemical fingerprinting can provide insight into mechanisms of photoresist roughening. This issue is critical in the microelectronics industry as the size of device structures is reduced; specifically, roughness generated during the lithography and plasma etching steps in device fabrication is ultimately transferred into the active parts of the device, leading to lower performance. By combining near-field optical and chemical interrogation with traditional far-field vibrational spectroscopy and X-ray photoelectron spectroscopy, we will highlight the chemical processes involved in roughness formation in advanced photoresist polymers and investigate how they are affected by plasma exposure.

8:40am **NS-ThM3 In Situ Nanoscale Characterization of Gas Fluxes of Organic Membranes by Flux-Lateral Force Microscopy***, **L.S. Kocherlakota**, D.B. Knorr, R.M. Overney*, University of Washington

Characterization studies of polymeric membranes for enhancing the gas transport rates are highly significant in current separation technologies. However transport property analyses like gas permeability measurements are bulk scale methods with limited access to local transport properties in multiphase systems such as nanocomposites membranes. In this context our group has developed a flux-lateral force microscopy (F-LFM) technique[1] for the in situ nanoscale characterization of the membranes, by monitoring the gas fluxes through them on a nanoscale. This technique, which is based on atomic force microscopy (AFM) utilizes the lubricating effect and the mechanical property changes in the membrane to determine fluxes. It was demonstrated by this technique that lateral force *vs.* pressure curves offered a direct measure of local gas permeabilities. In this paper we present the nanoflux analysis in Poly(trimethyl silyl propyne) (PTMSP), a glassy polymer with highest gas permeability of all known synthetic polymeric systems as well as high organic vapor/permanent-gas selectivity. The local fluxes in PTMSP films measured by F-LFM are compared to global fluxes obtained from conventional integrated methods. The sensitivity of F-LFM technique is demonstrated by presenting the reverse selective transport rates of He and CO_2 in PTMSP membranes as detected by the technique. The paper will also address the impact of aging, and flux dependence on film thickness.

Reference:

[1] J.H. Wei, M. He, and R.M. Overney**,** *Direct measurement of Nanofluxes and Structural Relaxations of Perflourinated Ionomer Membranes by Scanning Probe Microscopy,* J.Membrane Sci. **279,** 608-14 (2006)

9:00am **NS-ThM4 Nanoscale Electrodes by Conducting Atomic Force Microscopy at Elevated Temperatures**, ***M. Louie****,* California Institute of Technology*, A. Hightower,* Occidental College*, S. Haile*, California Institute of Technology

The combination of conducting atomic force microscopy (AFM) and electrical measurements (AC impedance spectroscopy and cyclic voltammetry) offers many advantages for measuring fuel cell electrode kinetics. The use of a conducting AFM probe as a nanoelectrode enables isolation and characterization of a single electrode-electrolyte interface without the need for a reference electrode. Furthermore, this technique permits studies of the spatial dependence of mechanistic phenomena while providing controllable electrode-electrolyte contact areas. The feasibility of using a nanoscale probe as a fuel cell electrode has been examined for the polymer electrolyte membrane system at room temperature (1-2). Higher temperature capabilities would make this technique useful for a wide variety of material systems, including low-to-intermediate temperature solid electrolytes.

Here, we demonstrate the viability of conducting AFM under controlled environments and at temperatures relevant to proton conducting solid acid compounds. Solid acid compounds have been demonstrated as viable proton conducting electrolytes for fuel cells (3-4), with peak power densities of ~ 400 mW/cm^2 at ~ 240 ºC (5). Such fuel cells provide several advantages over polymer membrane fuel cells, including improved kinetics due to higher operating temperatures, impermeability of the membrane to fuels, and elimination of the need for complex water management systems. However, activation overpotential losses, particularly at the cathode, limit the performance (6), and electrode kinetics are not yet well understood.

We select cesium hydrogen sulfate, $CsHSO_4$, as a representative solid acid electrolyte for the study of oxygen electroreduction. Experiments are performed with a platinum-coated probe in contact with $CsHSO_4$. The Pt-based counter electrode, which covers the entire opposing area of the electrolyte, is effectively reversible and contributes negligible overpotential to the measurements. We discuss the experimental challenges associated with high impedance systems and mitigation strategies to extract meaningful information. We also present impedance spectra and cyclic voltammograms for Pt|$CsHSO_4$.

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6. S. M. Haile, C. R. I. Chisholm, K. Sasaki, D. A. Boysen, T. Uda, *Faraday Discussions* **134**, 17-39 (2007)

9:20am **NS-ThM5 Unraveling Atomic Structures on CeO_2(111) by Dynamic Force Microscopy***, **M. Reichling***, Universität Osnabrück, Germany **INVITED**

Cerium dioxide (ceria) is a material that is widely used for catalytic applications. It is, for instance, an essential part of the 3-way catalytic converter known from automotive technology and holds substantial promise in other diverse research areas like solid-fuel cell technology for the production of hydrogen. In this context, ceria acts as an oxygen buffer as well as promoting noble-metal catalytic activity. The capability for storing and releasing oxygen is believed to be the result of the rapid formation and elimination of oxygen vacancy defects. Therefore, defects at slightly and strongly reduced CeO_2, specifically on the thermodynamically most stable (111) surfaces are of great interest as they may be the key to understanding surface chemistry on ceria.

To reveal and identify surface and sub-surface defects on CeO_2(111), we apply dynamic scanning force microscopy (NC-AFM) providing highest resolution images of the surface structure and its irregularities. For the identification of defects, the detailed atomic structures of features found in experiments is related to predictions from DFT calculations on relevant surface defects. In this way, we are able to identify surface and sub-surface vacancies, surface hydroxide and Ce^{3+} ions. Furthermore, we demonstrate that water readily adsorbs at the surface at room temperature but may diffuse and cluster on terraces as well as step edges. Individual water molecules can also be laterally manipulated by the tip of the force microscope with atomic precision.

10:40am **NS-ThM9 High-Resolution Atomic Force Microscopy in Three Dimensions***, **U.D. Schwarz**, M.Z. Baykara, T.C. Schwendemann, B.J. Albers, N. Pilet, E.I. Altman*, Yale University

With the recent introduction of three-dimensional atomic force microscopy (3D-AFM), the recording of dense three-dimensional surface force and energy fields with atomic resolution have become possible for the first time [1]. The main obstacles for producing high-quality 3D force maps are long acquisition times that lead to data sets distorted by drift, and tip changes. Both problems are reduced but not eliminated by low-temperature operation.

As we will show, key for the successful realization of 3D-AFM is the application of novel data acquisition and analysis procedures. In particular, an image-by-image data acquisition scheme cuts measurement times by avoiding repeated recording of redundant information, while allowing post-acquisition drift correction. All steps are illustrated with measurements performed on highly oriented pyrolytic graphite in ultrahigh vacuum at a temperature of 6 K. The area covered spans several unit cells laterally and vertically from the attractive region to where no force could be measured. The resulting fine data mesh maps piconewton forces with 6.8 pm lateral and 2 pm vertical resolution. From this 3D data set, two-dimensional cuts along any plane can be plotted. Cuts in a plane parallel to the sample surface show atomic resolution, while cuts along the surface normal visualize how the attractive atomic force fields extend into vacuum. At the same time, maps of the tip-sample potential energy, the lateral tip-sample forces, as well as the energy dissipated during cantilever oscillation can be produced with identical resolution (pN resolution for forces, meV for energies, pm for x, y, and z). Room temperature operation might be possible due to the unique post-acquisition drift correction ability. Applications in the areas of chemical imaging, surface catalysis, nanotribology, thin film growth, and device fabrication are envisioned.

[1] B. J. Albers *et al.*, Nature Nanotechnology **4**, 307 (2009).

11:00am **NS-ThM10 Looking Deeper: Multifunctional Scanning Probe Microscopy***, I. Riisness, R. Ramos, C. Carach,* ***M. Gordon***, University of California Santa Barbara

Scanning probe microscopy (SPM) has truly revolutionized the morphological and electrical characterization of surfaces at the nanoscale; however, it is still impossible to identify and image the chemical functionality of a surface at similar resolutions. For the latter, one desires a hybrid probe system which combines traditional SPM functionality with spatially-correlated spectroscopic (chemical) data at length scales <10 nm.

To this end, we will highlight multifunctional surface imaging of chemistry, morphology, and elastic/electrical properties for several material systems using our hybrid SPM instrument. In this system, a plasmonically-active metallic tip is used to locally enhance EM fields in the tip-surface gap, enabling near-field chemical imaging via Raman spectroscopy. In this talk, we will discuss instrument design, tip preparation/characterization, and initial imaging results on polythiophene-based photovoltaic films, phase-segregated diblock co-polymers, and adsorbates on metallic nanoparticles.

Biomaterial Interfaces
Room: K - Session BI+AS+NS-ThA

Micro and Nanoengineering of Biointerfaces I
Moderator: G.J. Leggett, University of Sheffield

2:00pm **BI+AS+NS-ThA1 Spatial Organization and the Mechanics of Signal Transduction in Cell Membranes**, ***J.T. Groves***, University of California, Berkeley **INVITED**

Signal transduction in living cells is carried out through cascades of chemical reactions, which generally begin on the cell membrane surface.

In recent years, there has been growing realization that the large-scale spatial arrangement of cell surface receptors can regulate the outcome of ensuing signal transduction process. Signaling through the T cell receptor (TCR) in the context of the immunological synapse provides a case in point. Spatial reorganization of TCRs occurs on multiple length-scales, and apparently with multiple purposes, during antigen recognition by T cells. The cell membrane and cytoskeleton, working as an inseparable unit in this case, create the mechanical framework within which TCR signaling processes occur. To better study these phenomena, a new experimental strategy, in which the spatial positions of cell membrane receptors are directly manipulated through mechanical means, has emerged. By physically inducing a 'spatial mutation' of the signali ng apparatus, the role of spatial organization in signal transduction as well as the mechanisms by which it arises can be illuminated. Specific applications of this strategy to TCR signaling and other cell-cell signaling systems will be discussed.

2:40pm **BI+AS+NS-ThA3 Investigation of Array Spotting of Polymer Supported Lipid Bilayers**, ***S. Kaufmann***, *M. Homenuke,* ETH Zurich, Switzerland, *J. Sobek,* University of Zurich, Switzerland, *E.O. Reimhult, M. Textor*, ETH Zurich, Switzerland

Supported lipid bilayers (SLB) constitute a simple model of cell membranes and are of particular interest as components of future generations of biosensors based on transmembrane proteins. Techniques which are able to produce arrays with small micrometer-sized sensor areas in a cheap and fast way are beneficial. A major challenge producing such arrays of SLBs is their need for an aqueous environment during formation and operation, which has so far prevented the wide-spread use of common techniques to produce arrays such as spotting.

Poly(ethylene glycol) (PEG) can be incorporated into the membrane of liposomes through lipid molecules end-functionalized with a PEG chain and these liposomes were shown to spontaneously fuse to PEG-SLB on glass surfaces with a highly hydrated PEG cushion on each side of the membrane allowing ample space and protection for incorporation of membrane proteins[1,2]. Since Cremer and coworkers [3] also showed that with increasing PEG concentration the air-stability of PEG-SLBs increases it is a very promising SLB system to use for spotting where membrane air exposure during processing is a severe constraint.

We present an investigation of the limits to spontaneous PEG-SLB in terms of PEG-lipid density, demonstrating that crossing the mushroom-to-brush regime of polymer concentration prevents the PEG-SLB formation due to steric effects and shielding of the interactions[2]. Furthermore, we present conditions under which formation of PEG-SLBs is facilitated and can proceed by liposome fusion also in the brush regime as well as characterization of the kinetics of formation and the structure of these PEG-SLBs. The use of such buffers and liposomes for production of membrane arrays on glass using a non-contact piezo-spotter was then explored in detail in order to find optimal conditions of buffer composition and PEG concentration.

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3:00pm **BI+AS+NS-ThA4 Direct Laser Patterning of Soft Matter: Photothermal Processing of Supported Phospholipid Multilayers with Nanoscale Precision**, ***M. Mathieu***, *D. Schunk, S. Franzka, C. Mayer, E. Hasselbrink, N.O. Hartmann*, University of Duisburg-Essen, Germany

Supported phospholipid bilayers and multilayers are widely recognized as model systems of biological membranes. Recently, these coatings have also gained significant attention as flexible biomolecular matrixes in various micro- and nanofabrication schemes [1]. Here, we report on direct laser patterning of supported phospholipid bilayer stacks. Direct laser patterning techniques are widely recognized as powerful tools in rapid prototyping and small volume fabrication. They offer a high flexibility in fabrication of complex 2D structures and patterning can be carried out at fast writing speeds over macroscopic length scales at ambient pressures or even in liquids [2]. For patterning multi-layered dioleyl-phosphatidic acid (DOPA) films were deposited on native silicon samples via spin coating. Then photothermal processing with a focused laser beam at $\lambda = 514$ nm is used for removal of the coating at predefined positions without causing any significant change in adjacent areas. Moreover, processing with nanoscale precision is feasible despite the soft and fluid nature of phospholipid films. In particular, holes with diameters from 1.8 µm down to 300 nm and below are fabricated using a laser spot diameter of about 2.5 µm [3]. Furthermore, partial removal can be carried out at incremental steps leaving a distinct number of bilayers behind. The underlying nonlinear dependence of the patterning process on the laser intensity is traced back to the interplay between the laser-induced transient local temperature rise and the thermally activated desorption of the phospholipid molecules. Generally, the lateral resolution in photothermal processing depends on the thermal and chemical stability of the coating. Phospholipid films, of course, are soft supramolecular assemblies. Despite their soft nature, however, the collective interactions are quite strong. This gives rise to a strong nonlinearity as observed here. Considering these features, photothermal laser processing constitutes a powerful tool for micro- and nanopatterning of phospholipid films.

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3. M. Mathieu, D. Schunk, S. Franzka, C. Mayer, E. Hasselbrink, N. Hartmann, Small, accepted.

3:40pm **BI+AS+NS-ThA6 The Role of Liposomes in Fluorescent Based Microarrays: From Surface Immobilization of Membrane Proteins to Highly Fluorescent Labels**, ***M. Bally***, ETH and University Zurich, Switzerland, *K. Bailey,* CSIRO, Australia, *S. Syed, S. Buergel, J. Voeroes*, ETH and University Zurich, Switzerland

Technologies utilizing arrays of immobilized biomolecules on planar surfaces are emerging as powerful high throughput tools for bioanalytical measurements. Nowadays, optical sensors based on fluorescence detection are the most widespread. However, many applications especially in the area of protein sensing, rely on the availability of optimized sensing interfaces and signal amplification strategies. Liposomes, due to their hollow particle-like structure and their unique chemical and physical properties, have greatly contributed to the development of sensitive and accurate biological assays.

In this presentation, we highlight with results obtained recently, the contributions of phospholipid vesicles to the development of high performance fluorescence based biosensors.

First, liposomes are an optimal platform for the surface immobilization of membrane proteins since they provide the natural environment required for the functional surface immobilization of these fragile molecules. We demonstrate the creation of a functional, heterogeneous array of G-protein coupled receptors. Vesicles obtained from cellular membrane extracts containing either the H1R-histamine receptor or the M2R-muscarinic receptors were immobilized on a conventional oligonucleotide microarray via complementary tags. Fluorescent ligand binding assays were then performed illustrating that the receptors kept their native conformation. As an alternative platform, we introduce a novel approach for the creation of vesicle multilayers using zirconium phosphate chemistry. As demonstrated in a model biomolecular binding assay, such three dimensional constructs increase the protein loading capacity of a sensor surface.

Liposomes are also excellent candidates as labels for biological assays: phosphocholine-based vesicles are non-fouling and biomolecules or marker molecules (e.g. fluorophores or enzymes) can be easily attached to their surface or encapsulated in their inner cavity. We show that fluorescently labeled phospholipid vesicles provide simple and cheap means for signal amplification and sensitive protein detection on a microarray format. Using vesicles, up to 100 fold increase in sensitivity was observed in a model protein microarray with confocal read-out, compared to a conventional assay performed with fluorophore labeled antibodies.

The various approaches presented here will contribute to the development of sensitive and high performance microarrays for a variety of applications including the investigation of membrane proteins.

4:00pm **BI+AS+NS-ThA7 Fusion of Biomimetic 'Stealth' Probes into Lipid Bilayer Cores**, ***B. Almquist***, *N. Melosh*, Stanford University

The ability to specifically and non-destructively incorporate inorganic structures into or through biological membranes is essential to realizing full bio-inorganic integration, such as arrayed on-chip patch-clamps, drug delivery, and biosensors. However, molecular delivery and interfaces to inorganic objects, such as patch-clamp pipettes, generally rely upon destructive formation of membrane holes and serendipitous adhesion, rather than selective penetration and attachment to the bilayer. In fact, materials greater than a few nanometers in size have not been shown to penetrate lipid bilayers without disrupting the continuity of the membrane. In this talk, I will discuss the development of nanofabricated probes that spontaneously insert into the hydrophobic membrane core by mimicking the hydrophobic banding of transmembrane proteins, forming a well-defined bio-inorganic lateral junction. These biomimetic 'stealth' probes consist of hydrophilic posts with 2-10 nm hydrophobic bands formed by molecular self-assembly, and are easily fabricated onto a variety of substrates including silicon wafers, nanoparticles, and atomic force microscope (AFM) tips.

By fabricating this architecture onto AFM probes, we have directly measured the penetration behavior and adhesion force of different molecular functionalities within the bilayer. It has been found that following insertion, the stealth probes remain anchored in the center of the bilayer, while purely hydrophilic probes have no preferred location. The strength of the stealth probe adhesion varies greatly between short and long chain alkane functionalizations, indicating that chain mobility, orientation, and hydrophobicity all contribute to molecular stability within the bilayer. In addition, the consequences of geometric factors such as band thickness and the presence of multiple bands on interface stability have been established. By selectively choosing the desired properties of the hydrophobic band, it will be shown that it is possible to tune the failure tension of the interface from values comparable to that of pristine lipid vesicles to only a fraction of the strength. Finally, the ability to transfer the stealth probe behavior to other platforms (e.g. nanoparticles for drug delivery) will be discussed.

4:20pm **BI+AS+NS-ThA8 Seeing Nanopore-spanning Supported Lipid Bilayers**, ***K. Kumar***, *S. Kaufmann, M. Textor, E.O. Reimhult*, ETH Zurich, Switzerland

Supported lipid bilayers (SLBs) present a highly interesting cell-membrane-like format to study sensitive ion channels or other membrane proteins. If formed by the rupture of liposomes, they then have the major advantage over other planar membrane architectures for biosensing in that they can be formed completely bereft of organic solvents by self-assembly, enabling the further incorporation of the aforementioned sensitive membrane proteins.[1] Porous structures allow the use of fusogenic surfaces which enhance the formation of SLBs from liposomes, while accommodating the incorporation of larger membrane proteins by decoupling them from the surface. We have developed a particle lithography process to produce high aspect ratio pores with a diameter tunable between 40 nm and 200 nm into silicon nitride, silicon oxide or titanium oxide to take advantage of a range of different surface chemistries. SLBs were formed on these porous substrates and characterized by fluorescence and force microscopy. These results suggest that the underlying nanotopography of the substrate plays a major role in both the formation and characterisation of nanopore-SLBs. The outcome of liposome adsorption is strongly influenced by roughness features in the same size range as the liposomes, which has important implications for the reproducible formation and characterization of nanopore-spanning planar lipid membranes necessary for future applications in integrated membrane-based sensing.

1. Reimhult, E. and K. Kumar, Trends in Biotechnology, 2008. 26(2): p. 82-89.

4:40pm **BI+AS+NS-ThA9 Formation of Protein Surface Patterns by Ligand Self-Selection *from Mixed Protein Solutions***, *M. Dubey*, University of Washington, *K. Emoto*, Great Basin Scientific, *H. Takahashi, D.W. Grainger*, University of Utah, ***D.G. Castner***, University of Washington

Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has been shown to be very sensitive for surface analysis and has been very useful for trace element detection. With the advent of improved analyzers, imaging ToF-SIMS provides spatial distribution of different species and helps in plotting the surface reactivity maps. Use of multivariate analysis, especially Principal Component Analysis (PCA) makes this technique even more powerful by differentiating regions with different chemistries. ToF-SIMS and PCA has been used in this work to study a very important two component patterned chemistry, which can have applications in bio-chips and cell-based biosensors. The chemistry is based on n-hydroxysuccinimide (NHS) esters; these molecules are widely used as leaving groups to activate covalent coupling of amine-containing biomolecules onto surfaces. The present work utilizes our knowledge of a previously studied model system, where NHS molecules were self-assembled on a gold substrate, and XPS and ToF-SIMS was used to characterize and understand the effect of hydrolysis and regeneration. We have demonstrated the extension of this chemistry to a commercial poly(ethylene glycol) (PEG)-based polymer films coated on glass slides. NHS and methoxy-capped regions were co-patterned onto these slides using photolithographic methods; then imaged with ToF-SIMS/PCA. NHS surface reactive zones are clearly resolved at high sensitivity despite the complexity of the matrix chemistry. Surface-specific protein coupling was observed by surface-selective reaction of streptavidin with the NHS patterns. The next step involved the preparation of photolithographic patterns of two affinity ligands (biotin and chloroalkane) for the specific immobilization of two different proteins (Streptavidin and HaloTag®). Spontaneous formation of high-fidelity surface patterns of the two proteins from their mixed solution was observed and characterized. In addition to Streptavidin and HaloTag®, ToF-SIMS detected the presence of non-specific BSA adsorption, a masking protein present in excess in the protein solutions, onto the patterned surfaces. ToF-SIMS amino acid-derived ion fragment yields summed to produce surface images can reliably determine which patterned surface regions contain bound proteins, but do not readily discriminate between different co-planar protein regions. However PCA of the ToF-SIMS data, improves discrimination of ions specific to each protein, facilitating surface pattern discrimination based on protein type. Also, ToF-SIMS imaging detected regions where residue from incompletely removed UV-exposed photoresist was present and its influence on protein adsorption.

5:00pm **BI+AS+NS-ThA10 Fabrication of Protein Patterns by Direct Electron-Beam Writing in a Protein-Repelling Template**, *N. Ballav*, Universität Heidelberg, Germany, *H. Thomas, T. Winkler, A. Terfort*, Goethe-Universität Frankfurt, Germany, ***M. Zharnikov***, Universität Heidelberg, Germany

One of the challenges of modern nanotechnology is the development of reliable, efficient, and flexible methods for the fabrication of ordered and complex patterns comprised of different proteins. An essential element of almost all available approaches is a protein-repelling "background" matrix, surrounding the active protein-adsorbing areas – the matrix prevents adsorption of proteins beyond these areas. Such a matrix is usually comprised of oligo- or poly(ethylene glycol)-based materials and is generally prepared by a backfilling procedure after the fabrication of the protein-attracting patterns. We present an alternative approach, showing that the protein-repelling matrix, both SAM- and polymer-like, can be used as a primary template for *direct* electron-beam writing of both *non-specific* and *specific* protein patterns of *any desirable shape*, including gradient ones, on a flexible length scale. The above factors make the approach quite versatile, which is additionally strengthened by intrinsic flexibility of electron-beam lithography, a wide range of suitable electron energies, broad availability of commercial oligoethylene glycol compounds, variable substrate material, and flexible choice of the target proteins. Complex gradient patterns fabricated by the suggested approach can become an important tool for mimicking natural biological interfaces which frequently possess gradient character – a typical way of encoding and displaying directional biological information.

Nanometer-scale Science and Technology
Room: L - Session NS-ThA

Characterization & Imaging at the Nanoscale II
Moderator: U. Schwartz, Yale University

2:00pm **NS-ThA1 Nanoelectrical Probing with Multiprobe SPM Systems Compatible with Scanning Electron Microscopes**, *J. Ernstoff*, Nanonics Imaging Ltd., Israel, ***A. Lewis***, Hebrew University of Jerusalem, Israel, *A. Ignatov, H. Taha, O. Zhinoviev, A. Komissar, S. Krol, D. Lewis*, Nanonics Imaging Ltd., Israel

A scanning electron microscope compatible platform that permits multiprobe atomic force microscopy based nanoelectrical characterization will be described. To achieve such multiple parameter nanocharacterization with scanning electron microscope compatibility involves a number of innovations both in instrument and probe design. This presentation will focus on how these advances were achieved and the results obtained with such instrumentation on electrical nano-characterization and electrical nano-manipulation. The advances include: 1. Specialized scanners; 2. An ultrasensitive feedback mechanism based on tuning forks with no optical feedback interference that can induce carriers in semiconductor devices; and 3. Unique probes compatible with multiprobe geometries in which the probe tips can be brought into physical contact with one another. Experiments will be described with such systems that will include multiprobe electrical measurements with metal and glass coated coaxial nanowires of platinum. This combination of scanning electron microscopes integrated with multiprobe instrumentation allows for important applications not available today in the field of semiconductor processing technology.

2:20pm **NS-ThA2 Nanocone Chemical Analysis with High Resolution Scanning Auger Microscopy**, ***S.N. Raman***, *J.S. Hammond, D.F. Paul, D.G. Watson, P.E. Larson, R.E. Negri*, Physical Electronics

The recent dramatic increase in nanotechnology research has pushed the development of analytical techniques to elucidate the growth mechanisms of nanostructures. Scanning electron beam techniques, including Scanning Auger Microscopy, have provided valuable imaging and elemental characterization tools for these structures with a spatial resolution better than 10 nm. To enhance the Auger analysis for nanocones, high energy resolution chemical state spectroscopy and imaging has been combined with the imaging capabilities of a CMA based Scanning Auger. Using a combination of these Auger analytical capabilities, the analysis of nanocones grown by plasma enhanced chemical vapor deposition reveals a non-uniform chemical composition between several different nanocones. The quantitative elemental analysis as well as the imaging of different chemical states has been obtained without imaging artifacts induced by the shapes of the vertically oriented nanocone structures. These results provide further insights into the nanocone growth mechanisms.

2:40pm **NS-ThA3 Epitaxial Growth of Al on Sapphire for Qubit Applications**, ***F. da Silva***, University of Colorado, Denver, *B.P. Gorman, M. Kaufman*, Colorado School of Mines, *J.S. Kline, D.A. Braje, D.S. Wisbey, D.P. Pappas*, National Institute of Standards and Technology

The pursuit of new low loss materials and epitaxial structures to enhance the performance of superconducting quantum bits (qubits) has heightened in recent years. The small number of defects observed in epitaxially grown structures, compared with polycrystalline and amorphous materials, accounts for several improvements reported in qubit operation such as the reduction in the density of two-level fluctuators and longer coherence times **[1]**. Qubit structures of interest are superconductor-insulator-superconductor (SIS) tri-layers deposited on an insulating substrate. Two candidates for the substrate and superconductor metal are sapphire (α-Al_2O_3) and Al respectively **[2]**. Complete defect removal requires a study of each layer and its corresponding interfaces. In this work we focus our attention on the interface between the substrate and the first superconductor layer. We used transmission electron microscopy (TEM) techniques to analyze the growth of Al (111) films on sapphire (0001) substrates. While the sapphire substrate induces the growth of epitaxial Al along a <111> direction as desired, the subsequent [111[planes grow with either ABC or ACB stacking resulting in twin-related "grains" within the epitaxial film. In addition, slight (1-5°) in-plane misorientations are observed in adjacent, twin-related Al grains and appear to correspond to the slight rotations between the oxygen atoms along the c-axis of the sapphire. In other words, because the Al orients itself with the oxygen atoms on the sapphire basal planes, any miscuts of the sapphire substrate to within ±1/6 of the unit cell c-axis will slightly misorient the Al due to the slight rotation of the oxygen atoms with respect to the c-axis of the sapphire cell **[3]**. Finally, these twinning and misorientation effects appear to induce other growth defects in the subsequent layers used in the qubit circuit. Based on these results, we propose the use of a chemically compatible oxide buffer layer which does not have rotations between successive O layers within its unit cell.

[1] S. Oh, K. Cicak, J. S. Kline, M.A. Sillanpää, K.D. Osborn, J.D. Whittaker, R.W. Simmonds, and D.P. Pappas, Phys. Rev. B **74**, 100502R (2006).

[2] J. Martinis, Quantum Information Process **8**, 81 (2009).

[3] D.L. Medlin, K.F. McCarty, R.Q. Hwang, S.E. Guthrie, and M.I. Baskes, Thin Solid Films **299**, 110 (1997).

3:00pm **NS-ThA4 Real Time Scatterometry for Profile Control during Resist Trimming Process in a HBr/O_2 Plasma**, ***M. El Kodadi***, LTM-CNRS, France, *S. Soulan, P. Schiavone*, Georgia Institute of Technology, *M. Besacier*, LTM-CNRS, France

In situ , real time control of the different process steps in semiconductor device manufacturing becomes a very important challenge, especially for the lithography and plasma etching processes. We have developed a specific software and hardware tools to perform dynamic scatterometry, using in situ spectroscopic multi-wavelength ellipsometry. This technique is non-invasive, non-destructive optical metrology technique. It uses the analysis of the signature of the light scattered by periodic structure to infer the shape of a feature.

In this study the authors show that dynamic scatterometry can be used for real time monitoring during the resist trimming process of two different resist materials, the M78Y resist from JSR, exposed at 248nm wavelength using an ASML/300 scanner, and the 193 nm resist "JSR 1682" . The etch gases used in this study are HBr and O_2.with two different bias power conditions "0 and 50" WBias power. Then we discuss about the influence of chemistries and bias power on the etched profile. We report how the plasma conditions can induce some chemical modifications of the resist films, and we explain how this issue can be addressed in the scatterometric real time control of the resist trimming process. A Jobin-Yvon ellipsometer, capable of real time acquisition of sixteen wavelengths, is plugged onto chamber of a Decoupled Plasma Source (DPS) from Applied Materials. The measurements are made in real time in the etch chamber during the process.

For validation purposes, the same process has been interrupted at several different times and the trimmed feature profiles have been measured using a 3D AFM from Veeco Instruments. The comparison between scatterometry and AFM measurement shows an excellent match for both CD and height parameters with a difference less than 2% .

This proves that dynamic scatterometry provides reliable results and shows a great potential as a real time monitoring technique for etch process control. This characterization technique can be viewed as an invaluable tool for the accurate control of the patterning of current and next generations of semiconductor devices.

3:40pm **NS-ThA6 Advancing QPlus AFM Performance at 5K Towards Lower Oscillation Amplitudes and Higher Frequencies**, *A. Bettac, J. Koeble,* ***K. Winkler****, B. Uder, M. Maier, A. Felz*, Omicron NanoTechnology GmbH, Germany

The QPlus sensor with its high spring constant and an optimized quality factor allows operation at very small oscillation amplitudes and is therefore ideal for atomically resolved imaging on all types of surfaces, i.e. for insulators, semiconductors and also for metallic surfaces. We have integrated the QPlus technology into an established low temperature STM platform. The extremely low signal of the QPlus sensor due to small oscillation amplitudes requires the first amplification stage to be very close to the sensor, i.e. it has to be compatible with low temperatures.

We present atomic resolution imaging on single crystal NaCl(100) with oscillation amplitudes below 100 pm_{pp} (peak to peak) and operation at higher flexural modes at frequencies of up to 318 kHz in constant df imaging feedback at 5K. We also present atomic resolution measurements on metallic Au(111) and Ag(111) surfaces with an extremely high stability at 5 K [1]. On a reconstructed Si(111) 7x7 surface further investigations in a temperature range between 50 K and 1070 K demonstrate the capability of the QPlus sensor for ultimate resolution in pure NC-AFM and dynamic STM measurements. At low temperatures, atomically resolved images of the rest atom layer will be presented. High temperature measurements close to the phase transition between the (1x1) and (7x7) show dynamics in the formation of step edges and kinks.

[1] A. Bettac, J. Koeble, K. Winkler, B. Uder, M. Maier, and A. Feltz, Nanotechnology, in print

4:00pm **NS-ThA7 Monatomic In Adatom Chains Assembled on the InAs(111)A Surface by Low-Temperature Scanning Tunneling Microscopy**, ***J. Yang***, Paul Drude Institute for Solid State Electronics, Germany, *K. Kanisawa*, NTT Corporation, Japan, *Ch. Nacci, S. Fölsch*, Paul Drude Institute for Solid State Electronics, Germany

Atom manipulation by scanning tunneling microscopy (STM) at cryogenic temperatures has proven to be a powerful experimental tool to study the physics of assembled nanostructures at surfaces. Since its implementation in the early 1990s [1], STM-based manipulation has been applied mainly to atoms and molecules adsorbed on metal surfaces. Here we demonstrate the extension of this technique to III-V semiconductor materials and report the fully reversible repositioning of In adatoms on a InAs (111)A surface by vertical manipulation at 5 K, i.e., by transferring individual atoms from the surface to the STM tip and vice versa. This allows us to assemble compact structures with the In atoms added one by one and occupying nearest-neighbor vacancy sites of the (2x2)-reconstructed surface (separation of the vacancy sites $a_0\sqrt{2}$=8.57 Å, a_0: cubic InAs lattice constant). Combining this approach with scanning tunneling spectroscopy (STS), we studied the electronic properties of monatomic adatom chains representing a model case of a one-dimensional electron system. The STS data reveal substantial electronic coupling between the In chain atoms leading to the formation of an unoccupied quantum state delocalized along the chain. Regarding the substantial interatomic spacing of 8.57 Å present here it appears that substrate-mediated coupling is essential for the along-chain linking rather than direct interatomic coupling reported previously in metal-on-metal adatom chains [2,3]. Our results demonstrate that the combined approach of atom manipulation and local spectroscopy is applicable to explore atomic-scale quantum structures in a semiconductor-based system.

[1] J. A. Stroscio and D. M. Eigler, Science 254, 1319 (1991).

[2] N. Nilius, T. M. Wallis, and W. Ho, Science 297, 1853 (2002).

[3] S. Fölsch, P. Hyldgaard, R. Koch, and K. H. Ploog, Phys. Rev. Lett. 92, 56803 (2004).

Support by the Japanese Agency of Science &Technology (JST) and the German Research Foundation (DFG) is gratefully acknowledged.

4:20pm **NS-ThA8 Making Mn Substitutional Impurities in InAs using a Scanning Tunneling Microscope**, ***Y.J. Song**,* NIST and University of Maryland, College Park*, S.C. Erwin,* Naval Research Laboratory*, G.M. Rutter,* National Institute of Standards and Technology*, P.N. First,* Georgia Institute of Technology*, N.B. Zhitenev,* National Institute of Standards and Technology*, Y. Kuk,* NIST and Seoul National University, Korea*, J.A. Stroscio*, National Institute of Standards and Technology

The ability to manipulate single atoms has been demonstrated for both lateral and vertical manipulation using a tunable chemical-bond interaction between the scanning tunneling microscope (STM) probe tip and adsorbed atom [1]. More recently a new form of atom manipulation involving the exchange of two different surface atoms has been observed with Mn atoms on III-V surfaces; the motivation being the understanding magnetic interactions in these dilute magnetic semiconductors [2]. In this presentation we discuss detailed measurements and theoretical calculations of the STM induced exchange of Mn and In atoms on the InAs(110) surface. Mn was deposited onto the InAs(110) surface at 7K and were observed as single adatoms. We used the STM to artificially substitute the single Mn adatoms with In atoms in the top-most surface layer. This process involves raising the sample tunneling voltage beyond a certain threshold voltage of approximately -0.6 eV. We determined the statistical analysis of the threshold voltages for different offset tunneling currents and measured high resolution STM images of the initial and final Mn states as a function of tunneling voltage. We calculated the pathway and energetics for this atomic exchange with density functional calculations and compare with the STM measurements.

[1] J. A. Stroscio and D. M. Eigler, Science **254**, 1319 (1991).

[2] Dale Kitchen *et al*, Nature **442**, 436 (2006).

Biomaterial Interfaces
Room: K - Session BI+AS+NS-FrM

Micro and Nanoengineering of Biointerfaces II
Moderator: E.O. Reimhult, ETH Zurich, Switzerland

8:20am **BI+AS+NS-FrM1 Colloid Crystal Surface Patterning for Studying Biointerface Phenomena**, ***P. Kingshott***, Aarhus University, Denmark **INVITED**

Patterning of many types of biomolecules over length scales ranging from micrometers to nanometers is of great interest for biosensors, cell culture dishes, medical implants and tissue engineering. Ideally these devices require attachment of biomolecules at specific locations on solid substrates with precisely controlled chemistry, but to function fully the non-specific adsorption in surrounding regions must be prevented. Currently, the most widely used techniques for patterning are photolithography, soft lithography and electron beam lithography, all of which involve multi-step surface modification directly onto substrates, and are time consuming and expensive. We have shown recently that highly ordered binary colloid patterns, with controllable dimensions, can be generated from simple self-assembly of large and small particles onto surfaces, where single layers of large particles are surrounded by crystals of smaller particles. In addition, when the particles are pre-coated with proteins (e.g. albumin, lysozyme and antibodies) the assembly process also takes place. This opens up the possibility of patterning many proteins on one substrate with controllable dimensions and high order. The crystals are also used to generate chemical patterns since the large particles act as a mask during, for example sputtering of Au, since the region in contact with the substrate remains uncoated. The thickness of gold features can be controlled by the sputtering time. We demonstrate that the resultant Au layer can be coated with a protein resistant mercapto-oligo(ethylene glycol) layer ((1-mercapto-11-undecyl)-tri(ethylene glycol)) that allows selective adsorption of fluorescently labelled proteins, such as FITC-labelled antibodies or rhodamine-labelled albumin, only onto the Si regions of the pattern. In another approach, binary patterns made from silica and amine polystyrene particles are heated at 100 ºC (above glass transition temperature of polystyrene) followed by etching with HF to remove the silica particles creating highly ordered 2- and 3D porous substrates. In summary, we introduce a novel method for generating highly-ordered patterns from colloid crystals that is very fast, inexpensive, and allows patterns of multiple biomolecules over large areas in 2- and 3D.

9:00am **BI+AS+NS-FrM3 Biological Nanoarrays: from Protein-DNA Interaction Studies to Cell Adhesion Investigations**, ***M. Palma****, J. Abramson, M. Schvartzmann, A. Gorodetsky, C. Nuckolls, M.P. Sheetz, J. Hone, S.J. Wind*, Columbia University

Nanopatterned arrays of biomolecules are a powerful tool to address fundamental issues in many areas of biology.

Combining nanolithography and biomolecular self-assembly strategies, we report on the fabrication of nanopatterned biomimetic surfaces and their use in a variety of biological studies.

We have fabricated arrays of Au/Pd nano-dots of dimensions down to the sub-10nm regime using electron-beam and nanoimprint lithography. Different chemical strategies at surfaces have been pursued to organize biological relevant nanoarchitectures into hierarchical arrays in which structural parameters, such as the spacing and nature of specific functional groups, could be systematically varied and controlled.

The generation of DNA nano-dot arrays allowed us to follow the activity (at surfaces) of a restriction enzyme in real time and at the nanoscale: fluorescence microscopy enabled the monitoring of the kinetics of such protein-DNA interaction.

Furthermore we will show how our nanopatterned biomimetic surfaces can be used to probe the importance of both the geometric arrangement (i.e. spatial ordering of transmembrane proteins, integrins) as well as the role played by peptide sequences as cell binding domains in the formation of cell focal adhesions.

Finally, we will highlight the broader utility and application of such functional nanopatterned surfaces for nanoscopic control and studies: biochemical specificity can be used to selectively place individual nanocomponents with a high degree of control over both position and orientation, as well as to organize functional nanostructures into dense arrays with very fine pitch.

9:20am **BI+AS+NS-FrM4 Arbitrary Topographical Patterns Fabrication by using Two-Photon Photopolymerization**, ***H.J. Jeon***, University of California, Berkeley, *H. Hidai*, Tokyo Institute of Technology, Japan, *D.J. Hwang, K.E. Healy, C.P. Grigoropoulos*, University of California, Berkeley

Two photon photopolymerization (TPP) is a direct laser writing technique, which is known as a powerful tool to make arbitrary 3D structures. Here we demonstrate a method for fabricating high aspect ratio (~10) patterns of varying height by using TPP process in order to study contact guidance of cells. Ridge patterns of various heights and widths were fabricated through single laser scanning steps by low numerical aperture optics, hence at much higher processing throughput. Fibroblast cells were seeded on parallel line patterns of different height (~1.5-µm, ~0.8-µm, and ~0.5-µm) and orthogonal mesh patterns (~8-µm and ~4-µm height, ~5-µm and ~5.5-µm height, and ~5-µm and ~6-µm height). Cells experienced different strength of contact guidance depending on the ridge height. Furthermore, cell morphology and motility on microscale anisotropic cross patterns and parallel line patterns in different aspect ratio (1:2, 1:4, and 1:∞), size of grid (12-, 16-, and 24-µm distance neighboring longer side ridges) was also studied quantitatively. The significant effect of the cross patterns on cell alignment and directionality of migration, and motility was observed on 1:4 cross patterns and parallel line patterns, even though all cross patterns could have an effect on cell attachment and morphology. Overall, it is noted that cell morphology and motility can be influenced by the height of ridges, the aspect ratio of cross pattern and the size of grid.

9:40am **BI+AS+NS-FrM5 2D & 3D Nanoarrayed Chemical Contrasts for Better Biorecognition Kinetics**, ***G.R. Marchesini****, P. Lisboa, A. Valsesia, C. Pascual, P. Colpo, F. Rossi*, Joint Research Centre, European Commission, Italy

Monitoring biomolecular recognition events with Surface Plasmon Resonance (SPR) heavily relies on the right surface chemistry. Uniform self assembled monolayers with carboxylic functional groups are widely used but might show steric hindrance, thus limiting the interpretation of the biorecognition kinetics. Furthermore, such negatively charged surface needs to be passivated upon immobilization of the ligand to prevent nonspecific electrostatic-driven binding of components from the analyte matrix.

In the present study we evaluate alternatives based on a 2D and 3D array of carboxylic nanodomains on a chemically contrasting matrix. By means of plasma-based colloidal lithography and e-beam lithography we were able to array ≈ 200 nm wide carboxylic motifs having a hexagonal 2-D crystalline structure on a gold surface. The interstitial gold was further modified with contrasting thiol chemistries or vapour enhanced deposition of nonadhesive material like poly ethylene oxide (PEO). The two 2D nanoarrayed chemical contrasts evaluated were carboxylic nanodomains on either a methyl-based or PEO-based matrix.

In addition, the 3D nanoarray based on a carboxylated dextran hydrogel matrix was evaluated for effects on the mass transport. In these cases, mass transport is one of the major challenges when measuring binding kinetics of biointeractants on a surface using a surface plasmon resonance (SPR) biosensor. The presence of a hydrogel on the surface increases the interactant density improving the sensitivity. Nevertheless, this is done at the expense of aggravating the mass transport phenomena.

The influence of the nanoarrayed chemical contrasts combined with the sensitivity improvement due to the band-gap effect on the kinetics of model biomolecular interactants was evaluated using an imaging SPR system and correlated with surface characterization techniques as atomic force microscopy, ellipsometry, and contact angle measurements.

10:00am **BI+AS+NS-FrM6 Spatially Selective Deposition of a Zwitterion with Alkyl Pendant Groups on Periodically Poled Lithium Niobate**, ***Z.Z. Zhang****, J. Xiao,* University of Nebraska-Lincoln, *D. Wu,* North Carolina State University, *A. Gruverman*, University of Nebraska-Lincoln, *L. Routaboul, P. Braunstein, B. Doudin,* Université Louis Pasteur Strasbourg, France, *O. Kizilkaya,* Louisiana State University, *C. Borca,* Paul Scherrer Institute, Switzerland, *P.A. Dowben*, University of Nebraska-Lincoln

We have spatially selectively deposited a zwitterion compound from the class of N-alkyldiaminoresorcinones (or 4,6-bis-dialkylaminobenzene-1,3-diones, $C_6H_2(NHR)_2(O)_2$), compounds, where $R = C_5H_{11}$. These molecules have very strong local dipoles as the delocalized benzene π molecule of the zwitterion "core" loses aromatic character due to the large charge separation. This charge separation provides this type of zwitterion molecule with a large electric dipole moment across the "benzene" like plane. Unlike the ferroelectric materials, the electric dipole of this class of zwitterions when adsorbed on metal surface (and most substrates) is not switchable, which makes these zwitterion compounds more like an electret. We have been able to demonstrate that at least one of this class of zwitterion compound will selective adsorb from solution on periodically poled lithium niobate substrates using infra-red spectra-microscopy. The spatial localization zwitterion on lithium niobate suggests that the ferroelectric poling of lithium niobate either alters the surface chemistry of lithium niobate or that there is some dipole-dipole interaction between the substrate and the zwitterion. We believe the interaction is an interface effect as no alteration in the bulk properties has been observed from spatially resolved near edge X-ray adsorption fine structure (NEXAFS) of the bulk properties. The spatial zwitterion structure is consistent with the periodically poled lithium niobate structure. Crystals of periodically poled lithium niobate (PPLN) with congruent composition (Crystal Technologies) were used as deposition templates. A periodic domain structure (period of ~28 μm) was fabricated by depositing a photoresist mask on the +c sample face and by applying a voltage of 10 kV through a fixture with an electrolyte solution. The mask was removed after poling by means of chemical-mechanical polishing leaving behind a bare ferroelectric surface, prior to the exposure to the zwitterion molecular solution.

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