Nanometer Structures
Room: C-207 - Session NS-MoM

Nanomechanics
Moderator: N.A. Burnham, Worcester Polytechnic Institute

9:00am **NS-MoM3 Structural Properties of Polymeric Nanostructures**, ***J.J. de Pablo***, University of Wisconsin-Madison **INVITED**

9:40am **NS-MoM5 Dynamics and Mechanics of Nanoscale Adhesive Contacts**, ***K.J. Wahl***, U.S. Naval Research Laboratory, *S.A.S. Asif*, Hysitron, Inc. **INVITED**

Recent advances in atomic force microscopy (AFM) and nanoindentation enable examination of surface mechanical properties of ultrathin films and compliant materials with far greater resolution and accuracy than ever before. In our laboratory, we have implemented dynamic mechanical analyses of nanoscale adhesive contacts using a 'hybrid' nanoindenter, coupling depth-sensing nanoindentation with AFM positioning capabilities. This combination allows surface sensitive, quantitative mechanical properties measurements of nanostructures and thin films, at a single point as well as while scanning. We illustrate these expanded capabilities with several examples: 1) a dynamic nanoscale Johnson-Kendall-Roberts (nano-JKR) adhesion test, and 2) scanning nanomechanics. The nano-JKR test allows study of processes that occur during the formation and breaking of adhesive contacts with diameters smaller than the optical limit, and can be used to measure dynamic visco-elastic properties including loss and storage moduli, adhesion energy, and strain energy release rate. Scanning nanomechanics provides a means of directly imaging mechanical response and properties with sub-micron spatial resolution. We will discuss how these new capabilities can be used to test the models and limits of continuum contact mechanics.

10:20am **NS-MoM7 Creep Compliance and Stress Intensity in Small Viscoelastic Contacts**, ***W.N. Unertl***, University of Maine, *M. Giri*, Hewlett-Packard - Corvallis

Adhesive contacts to viscoelastic materials with dimensions smaller than a few microns are difficult to analyze. This is due, in part, to the inability to measure the contact size directly. One consequence is the lack of a quantitative method to measure time-dependent mechanical properties. We demonstrate a method to overcome these difficulties. First, we extend a theory of viscoelastic contact[1] to show how the contact radius, the stress intensity at the contact edge, and the creep compliance function can be extracted directly from load vs. deformation data. Then, we apply this analysis to load controlled indentation data for a paraboloidal diamond probe on a styrene-butyl acrylate substrate with 27 C glass transition temperature. The probe is brought into contact, the load is increased linearly to a predetermined maximum, and then decreased until the contact ruptures. Loads up to 3 mN result in deformations up to 2 mm in depth depending on the loading rate and contact time. Viscoelastic effects, indicated by the occurrence of maximum penetration after maximum load, were largest for contact times near 20 s. Calculated contact radii are up to 6 mm. The creep compliance for this material is described by a power law in time with exponent near 0.8. In contrast to predictions of simple fracture mechanics models, the stress intensity is not a unique function of the speed of the contact edge. This suggests either an interaction potential between the probe and polymer that is rate dependent or a polymer response that is non-linear under the conditions that occur at the contact periphery in these experiments. These results bring into question all previously reported nanoscale measurements of the mechanical properties of viscoelastic materials.

[1] C.Y Hui, J.M. Baney, and E.J. Kramer, Langmuir 14, 6570 (1998).

10:40am **NS-MoM8 Mechanical and Electrical Properties of Mo_3Se_3-Nanowires and Nanowire-networks**, ***A. Heidelberg***, *G. Staikov*, *J.W. Schultze*, Heinrich-Heine-Universität Düsseldorf, Germany, *J.J. Boland*, University of North Carolina at Chapel Hill

Nanowires and nanotubes have attracted enormous interest as potential building blocks for nanotechnology.[1] This interest can be traced to the novel structural, mechanical and electronic properties of these nanomaterials. Here we describe a study that measures these properties in the case of the $(Mo_3Se_3)^-$-nanowire system.[2] The mechanical properties of single nanowires or bundles were studied using an SPM-nanomanipulator. This instrument allows us to controllably apply forces (µN-nN range) to supported Mo_3Se_3-nanowires to effect nanoscale manipulations. Using the lateral force data of the manipulations, the mechanical properties like Youngs modulus and tensile strength of the nanowires can be calculated. The electrical properties of bare $LiMo_3Se_3$-nanowires have previously been shown to have metallic behaviour.[3] Exchanging the Li-counterion to alkylammonium, alkylpyridinium or alkylpiperazinium counterions produces network structures of the nanowires with a defined interwire spacing. Conductivity measurements at different temperature and oxidation times show that these networks act as percolation networks and have semiconducting behaviour. In addition the corrosion rate of the Mo_3Se_3-nanowires is slowed down in the wire networks, demonstrating that the organic coating forms partially insulating layers.

[1] J. Hu, T. W. Odom, C. M. Lieber; Acc. Chem. Res. 32 (1999) 435
[2] J. M. Tarascon, F. J. DiSalvo, Solid State Commun. 52 (1984) 227
[3] J. H. Golden, F. J. DiSalvo, J. M. J. Fréchet, Chem. Mater. 7 (1995) 232.

11:00am **NS-MoM9 Towards the Sensing of Atomic Interactions by Nanoindentation with Extremely Sharp Tips**, ***J. Fraxedas***, ICMAB-CSIC, Spain, *S. Garcia-Manyes*, CBEN and University of Barcelona, Spain, *P. Gorostiza*, University of California, Berkeley, *F. Sanz*, CBEN and University of Barcelona, Spain

A force F applied to a surface acts directly on the surface atoms and is transmitted to the bulk atoms via the crystal lattice. The bonds play thus a crucial role in the mechanical response because of their strength and spatial distribution. For a point force only few atoms are involved. In this case the elastic deformation of the surface critically depends on in-plane interactions. In order to demonstrate the relevance of such interactions we have done nanoindentation experiments on 2D materials and ionic single crystals with an AFM. The stiffness k of the crystal and an estimated radius d_s of the elastically perturbed surface can be evaluated from expression $F(\delta)=k\delta(1-d_s/\sqrt{(\delta^2+d_s^2)})$,[1] where δ stands for the surface deformation. k is related to the Debye frequency ω_D ($k_D=m\omega_D^2$), where m represents the mean atomic mass. The calculated values of k_D are very close to the experimentally derived values of k (i. e., $k=84\pm13$ Nm^{-1} and $k_D=86$ Nm^{-1} for NaCl). Nanoindentation thus reveals the collective behavior of nanoscale volumes since many atoms are involved in the process (ca. 140 ion pairs for the alkali halides). We observe that $k/d_s=c_{11}$, where c_{11} represents the (1,1) component of the elastic tensor. Feynman developed a simple model relating the anion-cation interatomic interaction k_{ac} to elastic constants for small strains for NaCl-type crystals assuming central forces.[2] Within this approximation we obtain $k_{ac}<13$ Nm^{-1}, in good agreement with $k_{ac}=10\text{-}12$ Nm^{-1}, obtained in the harmonic limit from long wavelength TO phonon frequencies.

[1] J. Fraxedas, S. Garcia-Manyes, P. Gorostiza, F. Sanz, Proc. Natl. Acad. Sci. USA 99, 5228 (2002)
[2] R. P. Feynman, R. B. Leighton, M. Sands in The Feynman Lectures on Physics (Addison-Wesley, 1964), pp. 10.

11:20am **NS-MoM10 Playing Nano-squeeze with Fluids**, ***M. Heuberger***, ETH Zuerich, Switzerland **INVITED**

It was found, over two decades ago, that some fluids exhibit a remarkable spectrum of new properties when confined between two atomically smooth and nearly parallel mica sheets in the surface forces apparatus. Oscillatory or structural forces, as well as a dynamic solidification of such thin fluid films were reported. What do these fluids have in common and what can we learn from their behavior? Well-established thermodynamic measurements of fluids adsorbed into porous materials suggest a shift of critical points, transition temperatures and enthalpies, which are more pronounced the smaller the pore radius. Recently, unexpected density and film-thickness fluctuations were discovered in these confined fluid films. Can a shift of thermodynamic quantities in small volumes account for the observed fluctuations? Recent results reveal a relationship between the thickness of the mica sheets and the amplitude of the fluctuations in the eSFA. I will present new details of the contact mechanics at sub-Angstrom resolution and discuss the role of nano-particles in SFA measurements. A comparison of measurements obtained with conventionally prepared and particle-free surfaces is shown. A mechanical model involving nano-particles is invoked to explain the observed effects.

Magnetic Interfaces and Nanostructures
Room: C-205 - Session MI+NS-MoA

Self-Assembly and Nanomagnetism
Moderator: D. P. Pappas, DOC/NIST/EEEL/Magnetic Technology Division

2:00pm **MI+NS-MoA1 Self-assembly and Magnetism in Novel Core-shell Microspheres**, ***E.L. Bizdoaca***, *M. Spasova*, *M. Farle*, Halbleiterphysik und Optik, TU Braunschweig, Germany

We report on the fabrication and characterization of new composite core-shell particles with a defined shape, composition and multilayer shell thickness. These colloids can be produced by the layer-by-layer technique.[1] They consist of a core of a polystyrene (PS) microsphere (640 nm diameter) coated with consecutive shells of Fe_3O_4 nanoparticles (12 nm diameter) / polyelectrolytes /Au nanoparticles (15 nm). For the formation of the gold shell Au nanoparticles encapsulated in a very thin layer of silica (2 nm) were used. Composite core-shell particles were self-assembled into 1D periodic long-chain structure (up to 600 µm) by magnetophoretic deposition.[2] The length and separation of the chains were found to depend on the magnitude of the magnetic field and on the concentration of the water-based colloidal solution. The self-organization and the homogeneity of the colloidal coating were characterized by transmission electron and atomic force microscopy. Magnetic properties were determined by angular dependent ferromagnetic resonance (FMR) and SQUID-magnetometry between 5 and 300 K. FMR reveals long-range magnetic order at 300 K due to the dipolar coupling and an easy axis in plane, along the chains. We report a reduced magnetic moment in comparison with the magnetite bulk value. The remanence magnetization and the coercivity field (240 Oe) are not temperature dependent between 5 and 300 K. Supported by Deutsche Forschungsgemeinschaft. .

[1] F. Caruso et al, Chem.Mater.13 (2001) 109.

[2] E. L. Bizdoaca et al, J. Magn. Magn. Mater. 240 (2002) 44.

2:20pm **MI+NS-MoA2 Magnetic Resonance and X-ray Magnetic Circular Dichroism of Monodisperse Co Nanoparticles**, ***U. Wiedwald***, *M. Spasova*, Technical University Braunschweig, Germany, *M. Hilgendorff*, Hahn-Meitner-Institut, Germany, *M. Ulmeanu*, *E.L. Bizdoaca*, Technical University Braunschweig, Germany, *M. Giersig*, Hahn-Meitner-Institut, Germany, *M. Farle*, Technical University Braunschweig, Germany

Monodisperse Co nanoparticles with an medium diameter of 12 nm (σ < 5%) are prepared by the thermolysis of $Co_2(CO)_8$.[1] After using a size-selective separation technique they are redispersed in toluene. For structural and magnetic investigations the samples are prepared by controlled evaporation of the solvent on various substrates. Detailed TEM analysis of the structure of Co nanoparticles shows that they consist of a 8-9 nm metallic Co core and a 1-2 nm thick CoO shell, both crystallized in fcc structure.[2] Angular dependent ferromagnetic resonance (FMR) of these arrays of Co nanoparticles reveals a remanent magnetization at 300 K that is due to long-range dipolar coupling between the nanoparticles.[3,4] A preliminary g-factor analysis yields a value of $g = 2.15 \pm 0.02$ that is close to bulk fcc value and in good agreement with the structural analysis. X-ray absorption fine structure (XAFS) shows a multiplet structure in the Co L_3 edge that is due to a superposition of metallic Co and Co in an oxidic environment. No evidence for x-ray magnetic circular dichroism (XMCD) at the $L_{2,3}$ edges is found for as prepared ex-situ samples for temperatures between 20 K and 300 K. After slight Ar^+ ion etching a well resolved XMCD signal with a strongly enhanced orbital-to-spin-moment ratio is observed. The results of the FMR and XMCD analysis will be compared and discussed in terms of the contributions from the antiferromagnetic CoO shell. This project is supported by the European Community, contract no. HPRN-CT-1999-00150 and the Access to Research Infrastructure action of the Improving Human Potential Programme. M. H. thanks the Deutsche Forschungsgemeinschaft, Az.: II C 10 - SPP 1072 for support.

[1] M. Hilgendorff et al., Aust. J. Chem. 54 (2001)

[2] M. Spasova et al., Proc. Spring MRS Meeting, San Francisco (2002), submitted

[3] U. Wiedwald et al., J. Vac. Sci. Technol. A 19 (2001)

[4] M. Spasova et al., J. Magn. Magn. Mat. 240 (2002)

2:40pm **MI+NS-MoA3 Surfactant-mediated Shape Control, Magnetism and Self-assembly of Cobalt Nanocrystals**, ***K.M. Krishnan***, *Y.P. Bao*, *M. Beerman*, University of Washington **INVITED**

Magnetic nanocrystals, monodisperse in size, shape and surface structure are now routinely synthesized by the rapid injection of an organometallic precursor into a hot coordinating solvent containing appropriate surfactants. The success of this method depends on temporally separating the nucleation and growth of the nanocrystals in solution and to control the precursor concentration to achieve size distribution focusing. In addition, careful choice of surfactant pairs that preferentially bond to different crystallographic planes of the growing nanocrystal can also be used to control the shape of the nanocrystals, including the preparation of high-aspect ratio particles or nanorods. For practical applications these nanocrystals must be organized into ordered arrays with well-defined inter-particle distances. In such nanocrystals, with a weak (van der Waals) attractive interaction between the metallic cores and a weak steric repulsion arising from the surfactant chains, entropy-driven self-assembly processes dominate. If particles of two different sizes are allowed to self-assemble, entropy driven wetting arising from depletion forces can be used to control the final organization. Use of solvent-nonsolvent pairs can be used to gently precipitate the nanocrystals into large scale ordered arrays. Details of the growth of Co nanocrystals with controlled size and shape, their subsequent self-assembly into ordered arrays, their characterization by a range of electron microscopy measurements and their isolated and collective magnetic behavior will be discussed.

3:20pm **MI+NS-MoA5 Structure and Magnetism of Colloidal Composite AgCo Nanoparticles**, ***M. Spasova***, Technishe Universität Braunschweig, Germany, *T. Radetic*, Lawrence Berkeley Laboratory, *N.S. Sobal*, Hahn-Meitner-Institut Berlin, Germany, *C. Raeder*, Technishe Universität Braunschweig, Germany, *M. Hilgendorff*, Hahn-Meitner-Institut Berlin, Germany, *U. Dahmen*, Lawrence Berkeley Laboratory, *M. Giersig*, Hahn-Meitner-Institut Berlin, Germany, *M. Farle*, Technishe Universität Braunschweig, Germany

Monodisperse, air-stable $Ag_{100-x}Co_x$ composite nanoparticles with a mean diameter of 12 nm have been synthesized by methods of colloidal chemistry.[1] The composition x was varied between 20 and 73 at.% Co. High resolution Transmission Electron Microscopy (TEM) and selected area electron diffraction have showed that the nanoparticles consist of precipitates of fcc Co and fcc Ag grains. No evidence for alloy formation was observed. Element-specific TEM images obtained by electron energy-loss spectroscopy and X-ray microanalysis indicate that Co is predominantly found in the surface region of the particles and the particles have an $Ag_{core}Co_{shell}$ structure. No Co oxide formation was observed in spite of Co being located at the particle surface. Magnetic properties of arrays of the nanoparticles on Si substrates were investigated by angular dependent ferromagnetic resonance and SQUID magnetometry between 5 and 300 K. The blocking temperature is found to depend on the particle composition. It increases with increasing Co content. At room temperature the nanoparticles containing 73 at.% Co are below and the $Ag_{55}Co_{45}$ nanoparticles are above their respective blocking temperatures. At lower temperatures contributions from additional magnetic phases are observed. The magnetization curves were analyzed as a function of temperature taking into account both paramagnetic and ferromagnetic contributions. The results are discussed in context to contributions from the Co/Ag interfacial and surface magnetism. The work has been supported through EC contract no. HPRN-CT-1999-00150.

[1] N.S. Sobal at el., Nano Letters, in press.

3:40pm **MI+NS-MoA6 Study of the Magnetic Cluster/Superconductiviting Matrix Interface: the Co/Nb System**, ***V. Dupuis***, *L. Favre*, *M. Jamet*, *J. Tuaillon-Combes*, *P. Melinon*, *A. Perez*, DPM Lyon - France

Thin films consisting on pure Co nanoparticles embedded in a Nb superconducting matrix have been prepared from clusters preformed in the gas phase using the Low Energy Cluster Beam Deposition (LECBD) technique.[1] Such films are subsequently e-beam lithographied in view to prepare ultrahigh sensitivity Micro-SQUID magnetometer devices and to study the magnetization reversal mechanism of an individual nanocluster.[2] X-ray characterization experiments and Transmission Electron Microscopy performed on an assembly of cobalt clusters embedded in a niobium matrix have shown that such nanogranular films consist on crystallized fcc Co-grains in the form of 3 nm-diameter tuncated octahedron (~ 1000 Co-atoms) randomly distributed in the polycrystalline niobium matrix. Sites of Co-atoms in the cluster core and at the cluster-matrix interface have been evidenced showing an alloyed Co-Nb interface concerned by almost one monolayer. On another hand, VSM magnetization measurements performed in the superparamagnetic regime evidenced a magnetic size of the Co-clusters lower than the one as deduced from TEM observations. So, in-situ complementary measurements under synchrotron radiation performed on Co/Nb bilayers grown in UHV confirm the presence of an alloyed Co_6Nb_7 interface which acts as a magnetically dead layer. Finally, from micro-SQUID measurements performed at 35 mK on one individual Co-cluster, we obtained a 3D-astroid shape corresponding to second order bi-axial anisotropy terms which can be attributed to surface anisotropy contributions ("Néel" model) underlying the main interfacial contribution in such nano-object.

[1] A. Perez et al. Materials Transactions, Special Issue on Nano-Metals 1, 42,1460 (2001).

[2] M. Jamet et al. Phys. Rev. Lett., 86, 4676 (2001).

4:00pm **MI+NS-MoA7 Magnetic Nanowires for Media and Devices Fabricated Using Copolymer Templates**, ***M.T. Tuominen***, *M. Bal, A. Ursache, Q. Xiao, J.T. Goldbach, T.P. Russell*, University of Massachusetts **INVITED**

Arrays of magnetic nanowires and nanowire devices were fabricated using nanoporous templates derived from self-assembling diblock copolymer films. Poly(styrene-methacrylate) (PS-PMMA) diblock copolymers as porous templates that were used to fabricate hexagonal arrays of vertical nanowires with densities of exceeding 1x10^12 per square inch. Electrodeposition within the template produces 10nm-scale magnetic cobalt nanowire arrays that exhibit large perpendicular coercivity and remanance making them potential candidates for ultrahigh-density perpendicular magnetic storage media. The internal crystal morphology of the nanowires, and consequently magnetic properties, can be manipulated and tuned by electrodeposition process parameters. The copolymer templates have been patterned laterally using conventional lithographic exposure to fabricate novel 3D magnetic nanowire devices. This includes current-in-plane magnetoresitive devices and current-through-wire switching field devices. Anisotropic magnetoresistance measurements show a sharp and complete magnetization reversal, indicating single-domain nanowire switching behavior. Such properties offer promising potential for new magnetic nanodevices built upon on single-domain elements. This work is supported by US National Science Foundation Nanoscale Interdisciplinary Research Team grant DMI-0103024 and Materials Research Science and Engineering Center grant DMR-9809365.

4:40pm **MI+NS-MoA9 Evolution of Fe Nanocluster Magnetism Grown on Pt(111)**, ***P. Bencok***, *S.S. Dhesi*, European Synchrotron Radiation Facility, France, *P. Ohresser*, Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, France, *N. Brookes*, European Synchrotron Radiation Facility, France

The magnetic structure of nanoparticles is a fascinating research area with many new and unexpected results. For the preparation of nanostructures one may use a well chosen system with appropriate growth modes. Room temperature deposition of submonolayer Fe ultrathin films on Pt(111) results in the formation of single layer clusters whose size increases with the amount of Fe. The structure of the stable pseudomorphic fcc clusters was studied using scanning tunnelling microscopy. The clusters were grown and measured in-situ by x-ray magnetic circular dichroism of Fe $L_{2,3}$ edge at beamline ID8 of the European Synchrotron Radiation Facility in Grenoble. Sum rule analysis was used to extract the magnetic spin and orbital moments with changing cluster size. The clusters show superparamagnetic behaviour with blocking temperature in the range 10-250 K increasing with cluster size. The easy axis of magnetization is perpendicular to the surface for all the range of cluster sizes studied. The orbital moment of the clusters as well as its angular anisotropy (related to the magnetic anisotropy energy) is enhanced in comparison with the bulk value and increases with decreasing cluster size. This enhancement is given by the increase in the number of perimeter atoms as the cluster radius diminishes. The perimeter atoms have reduced atomic coordination leading to the higher orbital moment. The magnetic spin moment per atom is lower than for bulk Fe. This behaviour can be explained by changes in the local atomic structure that is very sensitive to the atomic volume.

Nanometer Structures
Room: C-207 - Session NS+BI-MoA

Nanobiology
Moderator: V. Vogel, University of Washington

2:20pm **NS+BI-MoA2 Molecular Shuttles Based on Motor Proteins: Transporters for Nanotechnology**, ***H. Hess***, *J. Clemmens*, University of Washington, *C.M. Matzke, G.D. Bachand, B.C. Bunker*, Sandia National Laboratories, *J. Howard*, Max-Planck-Institute of Molecular Cell Biology and Genetics, Germany, *V. Vogel*, University of Washington

Active transport in cells, utilizing molecular motors like kinesin and myosin, provides the inspiration for the integration of active transport into synthetic devices. Hybrid devices, employing motor proteins in a synthetic environment, are the first prototypes of molecular shuttles - an active nanoscale transport system. The key problems for the construction of a molecular shuttle are guiding the direction of the motion, controlling the speed, and loading and unloading of cargo. Various techniques, relying on surface topography and chemistry as well as flow fields and electric fields, have been developed by us[1] and others[2] to guide the movement of molecular shuttles on surfaces. The control of ATP concentration, acting as fuel supply, can serve as a means to control the speed of movement. The loading process requires the coupling of cargo to the shuttle, ideally by a strong and specific link. Applications of molecular shuttles can be envisioned e.g. in the field of Nano-Electro-Mechanical-Systems (NEMS), where scaling laws favor active transport over fluid flow, and in the bottom-up assembly of novel materials. Recently, we demonstrated that the shuttles can be employed as self-propelled nanoscale probes to image surface topography.[3] The construction of an image relies on the tracking of the random movement of a large number of independent probes, a concept which is fundamentally different from e.g. the deterministic movement of a single tip in scanning probe microscopy. An aspect of our research is that devices using molecular shuttles can be based on mechanisms which are unique to the microscopic world. An example of this is the possible application of a Brownian ratchet for directional sorting.[4]

[1] Hess, H., et al., Nano Letters, 2001. 1(5): p. 235.

[2] Hess, H. and Vogel, V., Rev. Mol. Biotechn., 2001. 82: p. 67.

[3] Hess, H., et al, Nano Letters, 2002. 2(2): p. 113.

[4] Hess, H., et al., Appl. Phys. A, 2002. 75: p. 309.

2:40pm **NS+BI-MoA3 Nanomechanics of an Intrinsically Unstructured Protein**, *R. Mukhopadhyay*, ***J.H. Hoh***, Johns Hopkins School of Medicine **INVITED**

Microtubule-associated proteins (MAPs) are a class of proteins that bind to the surface of microtubules. These proteins are known to stabilize microtubules against depolymerization, and there evidence to suggest that MAPs play a role in maintaining spacing between adjacent microtubules and may play a role in cellular mechanics. MAPs are composed of two domains: the microtubule binding domain and the projection domains. Biophysical studies of the projection domain suggest that it is highly unstructured. We have recently developed a system to study the molecular mechanics of the projection domain of MAPs. In this system MAPs are end-grafted by their positively charged microtubule binding domains to a negatively charged surface. The properties of the projection domain are then probed by direct atomic force microscope (AFM) force measurements. These measurements show a long-range repulsive force that extends more than 100 nm from the surface, and is consistent with a polymer brush like interaction. A unique thrombin cleavage site at the boundary between the microtubule binding domain and the projection domain allows the projection domain to be proteolytically removed. This results in a total loss of the long-range repulsive force. The force is also sensitive to ionic strength, suggesting that, consistent with its sequence, the projection domain behaves as a polyelectrolyte. The polyelectrolyte nature of the projection domain and the large number of phosphorylation sites suggests a mechanism for regulating the mechanical properties of the protein. This notion is supported force measurements on phosphorylated and dephosphorylated MAPs. Thus phosphorylation of the MAP projection domain offers a biochemical mechanism for modulating the molecular mechanics of MAPS and the intermolecular forces between microtubules.

3:20pm **NS+BI-MoA5 Nanostructures for Analysis of individual Biomolecules**, ***H.G. Craighead***, *S.W. Turner, M. Foquet, J. Korlach, W. Zipfel, M. Levene, W.W. Webb*, Cornell University

We have used nanofabrication methods to create fine-scale fluid channels and optical devices for nano-scale spatial confinement of optical excitation for use in the analysis of individual biomolecules. Functional fluid systems with dimensions down to ~35 nm have been etched and created by use of sacrificial layer techniques. Narrow fluid channels have been used for DNA fragment sizing by single molecule analysis and used for fluorescence correlation spectroscopy with improved signal-to-noise ratios. Related lithographic approaches have been used to create regions of optical excitation, confined in all 3 dimensions, using metallic nano-constrictions or "zero mode waveguides" in which electromagnetic waves are exponentially attenuated. These devices enable practical studies of dynamic biochemical processes at the single molecule level. An example of such a process is the observation of the activity of a single DNA polymerase molecule during the replication of a DNA molecule. We have been able to optically observe the incorporation of individual bases in the DNA replication process. With optically differentiated base types, this could lead to high speed sequencing of single DNA molecules. These approaches may allow highly parallel observation and analysis of biochemical activity at the single molecule level. This work has been supported by The National Institutes of Health, the National Science Foundation through the NBTC and the Department of Energy. Fabrication of devices was done at the Cornell Nanofabrication Facility.

3:40pm **NS+BI-MoA6 Polyelectrolyte Multilayer Self Assembled Nanoparticles for Delivery of Transforming Growth Factor Beta**, ***C. Catuogno***, *M. Tabrizian*, McGill University, Canada

Biocompatible and biodegradable nanoparticles with additional high drug encapsulation efficiency and controllable targeting would form an ideal drug delivery system. Investigation of the possibility of making such vehicles is presented in this work. Such devices could be used in combination with polymeric bone scaffolds for delivery of transforming growth factor beta (TGF-b) in order to accelerate bone cell differentiation and bone formation in vitro. The particle shell is made of natural carbohydrate polymers namely chitosan or hyaluronic acid that are commonly used in tissue engineering. Chitosan is insoluble in water or in alkaline solutions but dissolves readily in dilute solutions of most organic acids. Chitosan has gel-forming ability at low pH and swells in acidic medium or in water. These proprieties added to those of hyaluronic acid have motivated the use of both materials to control TGF-b adsorption and release from the nanoparticles. Additionally, composite materials have been shown to improve mechanical properties of scaffolds. The nanoparticles are built from a succession of polyelectrolytes using the layer-by-layer method. Colloidal iron oxide particles are adsorbed on the polymer layers and encapsulated into the nanoparticles. This aims at inducing the guidance of nanoparticles using an external magnetic field to desired site of delivery when such device is used for in situ bone generation.

4:00pm **NS+BI-MoA7 Resolving Scanning Tunneling Microscopy Features of Oligomers Adsorbed on Si(100)**, ***B. Grandidier***, *Mathieu Dubois, C. Delerue, J.P. Nys, D. Stievenard,* IEMN, France, *J. Roncali*, IMMO, France

Scanning tunneling microscopy (STM) gives the possibility to observe complex organic molecules on silicon surfaces in ultra-high vacuum. Although the reactivity of the silicon surfaces often leads to the modification of the molecular electronic states, a clever synthesis of the molecules can keep their structures intact after adsorption. As a result, the molecules are imaged in their integrity and the contrast variation observed along the molecules is usually associated with the highest occupied and lowest unoccupied electronic states of the molecules. Here, we have investigated the STM imaging of conjugated oligomers on Si(100) by tight binding simulations. The molecules are physisorbed on the surface and extend over a few dimers rows. Due to coupling of the molecular states with the electronic states of the silicon surfaces, we show that the off-resonance tunneling process is the major contribution to the tunneling current in usual tunneling conditions. As a result, the potential barrier is lowered when the tip scans above a molecule and the contrast variation gives an enhancement of the Si dimer rows. Experimental STM images of conjugated oligomers confirm this theoretical prediction.

4:20pm **NS+BI-MoA8 Q-dots Patterned Surfaces for Cell Adhesion**, *A. Szucs*, ***J.P. Spatz***, University of Heidelberg, Germany

Highly luminescent semiconductor quantum nanodots (Q-dots) regularly patterned on different substrates, were synthesized and applied as binding sites for single cell receptors in order to study cell adhesion. CdS, CdSe and CdTe/ Q-dots in the size range of 2-8 nm in diameter were generated in Poly (styrene-b-2-vinyl-pyridine) (PS-P2VP)/inorganic hybrid reverse micellar system (RM). Solid Cd salts loaded polymer cores, constructed by the 2-vinyl-pyridine, were used as nanocompartments for preparation of uniform semiconductor nanoparticles. Particle size could be controlled by varying the diameter of the RM core, via the length of the core constructing polymer, and by changing the precursor salt loading in the polymer core. Different kinetics and structures were observed inside the RM core during the particle formation by using different precursor salts (Cd(ClO4)2, Cd(OAc)2). Photo luminescent properties of semiconductor nanoparticles were investigated by different methods (UV-VIS spectrophotometry, steady-state fluorescence, color luminescence imaging). "In situ" surface patterning on different substrates (Glass, Si-wafer etc.) by self-organization of the diblock copolymer micelles on the surfaces was monitored by AFM measurements.

4:40pm **NS+BI-MoA9 Cell Adhesion to Nanostructured Interfaces**, ***J.P. Spatz***, University of Heidelberg, Germany **INVITED**

Nanostructures with micrometer or nanometer spacings have been prepared through pure self-assembly of diblock copolymer micelles (formation and compartmental localization of metallic nanodots within block copolymer micelles) or in combination with a top-down approach (electron beam lithography). Within these structures, 7 nm Au particles can be positioned with a precision of < 10 nm and large freedom in pattern choice (periodic, aperiodic, dotes, lines). Specifically, this is obtained by casting a solution of HAuCl4 loaded block copolymer micelles onto the prestructured resist film. Due to capillary effects and steric hindering, the particles are centered within the prepatterned holes and at the edges of prestructured lines. Subsequent lift-off of the resist allows the removal of all micelles with the exception of those that are in direct contact to the underlying substrate. The block copolymer is then removed by plasma etching, which strips the polymer micelle and reduces the gold salt to gold thereby leaving behind nanoscopic dots or lines of gold in a defined array. These nanostructured interfaces are used as platform for biofunctionalisation of solid interfaces. The surfaces are used as a tool to investigate cluster formation of focal adhesion associated proteins of fibroblasts. Cultured human melanocytes allowed to study the regulation of cell shape through contact with interfaces offering different topography and biochemical pattern. The cellular morphology of melanocytes is a measurable indicator for cell reaction to the cellular environment. The characteristic cellular shape of different cell cultures was quantified by different shape parameters like the number and length of dendrites. A decreased signal-to-noise ratio was found for melanocyte cells concerning the number of dendrites and orientation of dendrites if cultured on biochemically and topographically structured substrates.

Surface Engineering
Room: C-111 - Session SE+NS-MoA

Nanoparticle and Nanofiber Surface Technologies

Moderator: A.A. Voevodin, Air Force Research Laboratory

2:00pm **SE+NS-MoA1 Investigation of Erbium Dispersion in Electrospun Nanofiber Matrices**, *W. Kataphinan*, ***R.D. Ramsier***, *E.A. Evans, D.H. Reneker*, University of Akron

Thermally stable nanofibers can be doped with molecular and atomic species. As an example, electrospun nanofibers made from polydiphenoxyphosphazene (PDPP) have been doped with erbium (Er) using Er(III) nitrate hydrate dissolved in ethanol. The Er/PDPP matrices are thermally stable up to 150 C in air for extended periods of time. Nanofibers electrospun from ceramic precursors are stable up to much higher temperatures. Infrared spectroscopy, electron microscopy and other techniques are used to quantify the influence of the electrospinning parameters (voltage, solvent, concentration, etc.) on the structural and spectral properties of the nanofibers and the dispersion of the Er-based dopants. Differences between methods for doping the fibers will be described based on these results. These results expand the useful operating temperature range of polymer nanofiber systems as well as the use of nanofiber matrices as a support for the dispersion of molecular and atomic scale dopants.

2:20pm **SE+NS-MoA2 Grafting of Poly (N-isopropylacrylamide) in Surfactant Templated Mesoporous Silica Films and Particles**, *Q. Fu*, ***G.V. Rama Rao***, *J. Huang, G.P. Lopez*, The University of New Mexico

Surface-initiated atom transfer radical polymerization (ATRP) is an effective and versatile method used to generate grafted polymers on surfaces. We report grafting of a poly (N-isopropylacrylamide) (PNIPAAM), a thermally responsive polymer, into a mesoporous silica matrix using the ATRP technique. PNIPAAM exhibits a lower critical solution temperature (LCST) at 32°C in water, below which it is in an expanded conformation and soluble in water. Above the LCST, PNIPAAM is in compacted state and insoluble in water. Synthesis of mesoporous films and monodisperse microparticles was carried out through an acid catalyzed sol-gel process using a surfactant template approach. We used a non-ionic surfactant (Pluronic-P123) and a cationic surfactant (cetyltrimethyl ammonium bromide) for the present study. The LCST of the hybrid films was established by static contact angle measurements. These hybrid materials exhibited thermo responsive behavior by changing from hydrophilic to hydrophobic state with change in temperature. X- ray diffraction and transmission electron microscopic studies on the films and particles confirmed the presence of an ordered porous structure before and after ATRP. The grafting of the polymer onto the pore surface was confirmed by drastic decrease in pore volume of the particles after ATRP. Pore opening and closing due to contraction and expansion of PNIPAAM was studied by fluorescent dye uptake behavior of particles by monitoring the fluorescence intensity in flow cytometry experiments. It was found that the uptake of the dye into the pores was obstructed below LCST, and above LCST, the polymer was collapsed and facilitated the passage of dye into the mesopores. The dye in the pores was entrapped by cooling the particles to below LCST and subsequently the dye was released by washing with water above LCST. These materials have potential application in controlled release, chemical separation and control of fluidic transport.

2:40pm **SE+NS-MoA3 Structural, Optical and Photocatalytic Properties of Nd^{3+} Doped TiO_2 Nanoparticles**, ***W. Li***, *S.I. Shah, C.-P. Huang*, University of Delaware, *O. Jung*, Chosun University, Korea

TiO_2 nanoparticles, with Nd^{3+} dopant concentration ranging from 0 to 1.5 at.%, were synthesized using metallorganic chemical vapor deposition. The dopant concentration and TiO_2 stoichiometry were verified by x-ray photoelectron spectroscopy and energy dispersive x-ray spectroscopy. Particle size and crystal structure were obtained by x-ray diffraction and high-resolution transmission electron microscopy which showed the nanoparticles are polycrystalline anatase with 22 nm average particle size. Red shifts of TiO_2 absorption edge with the increase of Nd^{3+} concentration were observed by spectrophotometery. 1.5 at.% Nd^{3+} shows ~0.15 eV red shift. The photoreactivities of Nd^{3+} doped and undoped TiO_2 were measured by studying the degradation of 2-chlorophenol solutions under ultra violet radiation. Nd^{3+} position in TiO_2 lattice critically affects the photocatalytic activity of TiO_2 nanoparticles. Nd^{3+} position in TiO_2 lattice was studied by using XRD peak shifts. The results of these studies will be presented.

3:00pm **SE+NS-MoA4 Computational Studies of Gas-Phase Growth of Soot Nanoparticles Using Fully-Integrated Integrated Molecular Dynamics and Kinetic Monte Carlo Methods**, ***A. Kubota***, *W.J. Pitz, C.K. Westbrook*, Lawrence Livermore National Laboratory

Combustion under fuel-rich gas conditions leads to the formation of soot nanoparticles. We study this process of carbon nanoparticle formation through the use of fully-integrated kinetic Monte Carlo and molecular dynamics methods. Rule-based polymerization and gas-surface kinetics are used in the chemical kinetic mechanism. This mechanism includes competitive H-abstraction and H-addition, as well as carbon-species addition, termination and cyclodehydrogenation and ring-closure reactions. We demonstrate that nanoparticle structure, morphology and rates are strongly coupled to the chemical kinetics as well as the gas-phase conditions. We compare modeling results with available experimental measurements.

3:20pm **SE+NS-MoA5 Enhancement of High Temperature Oxidation Resistance of Fe-Cr-Ni Alloys Using Nanocrystalline CeO2 Coating Synthesized by Microemulsion Technique**, ***S. Seal***, *S. Patil, S. Kuiry*, University of Central Florida

Fe-Cr-Ni alloys are usually subjected to high temperature oxidation during their various processing stages like rolling, forging and heat treatment. Extensive scaling losses are found to occur in these components in such aggressive environments at elevated temperatures. Therefore, development of coating that imparts oxidation resistance to Fe-Cr-Ni alloys is important not only for applications of these alloys at elevated temperatures but also to protect the oxidation losses during high temperature processing. The present study investigates the effectiveness of nano-sized CeO2 coating to enhance high temperature oxidation resistance of Fe-Cr-Ni alloys. Nanocrystalline CeO2 particles were synthesized with micro-emulsion technique using AOT [sodium bis(2-ethylhexyl) sulphosuccinate] as a surfactant. Kinetics of high temperature oxidation was studied on both bare and coated rectangular specimens in dry air. The scale cross section and surface morphology were characterized by using SEM, EDS, XPS and HRTEM studies.

4:00pm **SE+NS-MoA7 Formation and Optical Properties of Peridically Arranged Silver Nanoparticles by Irradiation with Linear Polarized Ultrashort Laser Pulses**, *A. Heilmann, A. Kiesow,* ***D. Katzer***, Fraunhofer-Institute for Mechanics of Materials Halle, Germany, *A. Podlipensky, G. Seifert, H. Graener*, Martin-Luther-University Halle, Germany

We report on a new and simple method to generate periodically ordered metallic, wire-like structures in an organic polymer-like matrix by irradiating thin films with series of ultrashort laser pulses. The films, which were deposited by alternating plasma polymerization and metal evaporation, are characterized by a two-dimensional particle size and shape distribution, i.e. all silver particles are arranged on one plane within the plasma polymer matrix. After laser irradiation with linearly polarized ultrashort (pulse duration < 150 fs), the nanostructure of the film changes from a relatively uniform particle distribution to a formation of an ensemble with metal particle nanowires. This was demonstrated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Material ablation during laser irradiation was not observed. The individual nanowires are between 100 to 250 nm wide with equal line space ratio. The obtainable structure size is not a function of the focusability of the laser and is significantly smaller than the laser wavelength used. The orientation of these wire-like structures is correlated to the linear polarization of the laser pulses, and is independent on the write direction of the laser beam. This dependence on laser polarization results in anisotropic optical properties. The optical extinction spectra were measured by locally resolved optical spectroscopy and by using linearly polarized light. The shift of the extinction peak depending on different steps of nanowire formation was analyzed. The optical spectra were correlated with the different nanostructures and various models were discussed to explain the material transport in the film.

Nanometer Structures
Room: C-207 - Session NS+SE+SS+MM-TuM

Nanotribology
Moderator: K.J. Wahl, Naval Research Laboratory

8:20am **NS+SE+SS+MM-TuM1 Ultralow Friction Coatings and Surfaces**, ***J.M. Martin***, Ecole Centrale de Lyon, France **INVITED**

From a technological point of view, very low friction in solid lubrication may be interesting in micromechanisms requiring neither friction noise nor instabilities, together with low power consumption. Theoretical approaches at the atomic scale coupled with experimental approaches using proximal probe techniques have been developed to study atomic scale friction behaviors and energy dissipation modes. The two limiting factors for friction reduction at the macro-scale are S0 (shear strength of the interface film) and a (pressure coefficient).[1] Approaching very low friction requires the reduction of both S0 and a below the MPa range. Thus lowering to zero friction would require the vanishing of both the adhesive and the external pressure. However these conditions are unlikely to be perfectly achieved in practice. Thus zero friction may not be possible. However, friction values in the 10-3 range or even less (near-frictionless sliding) have been experimentally reached in some practical situations. Here we examine ultralow friction by using a macro-scale sphere/plane contact configuration (maximum pressure of 1 GPa). Friction in the 0.001 range is associated with a shear strength of 1 MPa. We report experimental evidence of superlow friction with different coatings: pure molybdenum disulfide MoS2,[2] molybdenum dithiophosphate (Modtp) tribofilms and hydrogenated diamondlike carbon a-CH.[3]

[1] I. Singer, J. Vac. Sci. Technol., A12(5), (1994) 2605.

[2] J.M. Martin, C. Donnet, Th Le Mogne and Th Epicier, Physical Review B 48, No 14, (1993) 10583.

[3] C. Donnet et al, Surface and Coating Technology, 94, (1997) 456.

9:00am **NS+SE+SS+MM-TuM3 Frictional Properties of Small Model Lubricant Molecules Adsorbed on VC(100)**, ***L.C. Fernandez-Torres***, *S.S. Perry*, University of Houston, *B.-I. Kim*, Sandia National Laboratories

The frictional modification of the non polar (100) of vanadium carbide (VC) surface through small molecule adsorption at room temperature has been investigated from a fundamental perspective. These molecules represent the functionalities incorporated into lubricants and used to appropriately tailor the lubricant's properties and enhance its performance. Ultrahigh vacuum atomic force microscopy (AFM) has been employed to determine the changes in frictional response and interfacial adhesion. Scanning tunneling microscopy (STM) has been used to elucidate surface morphology. X-ray photoelectron spectroscopy (XPS) has been utilized to determine the composition of the species formed by the interaction of these adsorbates with the VC surface. This successful methodology has been developed during a recent investigation of ethanol, and in this study has been extended to other low molecular weight alcohols as well as an ester. The results will be rationalized in terms of chemical reactivity, adsorbate layer composition, extent of coverage, and changes in the interfacial shear strength and discussed in terms possible lubrication schemes.

9:20am **NS+SE+SS+MM-TuM4 Adhesion and Deformation in Nanoscale Contacts between W(110) and Au(110) in Ultra High Vacuum**, ***S.A. Smallwood***, *R.J. Lad*, *W.N. Unertl*, University of Maine

Tribological phenomena change as the contact area decreases from macroscopic to atomic dimensions, but these changes are not well understood. We report studies of the force versus deformation behavior of contacts with diameters up to about 50 nm using well-characterized metal surfaces in ultra-high vacuum. These contact sizes are intermediate between those previously studied. The contacting bodies were a Au(110) single crystal and sharp tips of W wires. The W probes were cleaned by field evaporation and their atomic structure determined using field ion microscopy (FIM). All were terminated by (110) planes and radii varied between 12 nm and 24 nm. The probes were mounted in double cross-hair force sensors. After cleaning by sputtering and annealing cycles, the Au was transferred to a piezoelectric tube scanner and moved into tunneling contact with the probe. Deflection of the force sensor and electrical current were measured as the Au crystal was brought into mechanical contact to a predetermined maximum displacement and then withdrawn. Prior to the first yielding event, the data is well described by elastic contact mechanics theory. The reduced modulus of 61 Â± 26 GPa agrees with the value calculated assuming bulk properties. The work of adhesion has an upper bound of about 0.3 J/m2. The first observable yielding events occur at a mean normal stress of 12 Â± 2 GPa, comparable to the values reported for larger probes, but half that reported for smaller contacts on Au(111). Hardness is about 6 GPa near the surface and decreases by about fifty percent at 8 nm indentation depth. Prior to first yield, contact conductance remains far below one quantum. Deformation is confined to the Au. FIM demonstrates that the W probe is not deformed for penetrations as deep as its radius. Scanning tunneling microscopy shows that the indentation holes are asymmetric and that pile-up extends about one indentation diameter beyond the indent.

9:40am **NS+SE+SS+MM-TuM5 Chemical Force Microscopy of Aluminium Oxide Surfaces**, ***T.T. Foster***, *M.R. Alexander*, UMIST, UK, *E. McAlpine*, Alcan International, UK, *G.J. Leggett*, University of Sheffield, UK

The combination of wettability, chemical force microscopy (CFM) and friction force microscopy (FFM) has been used to analyse changes at the oxide-covered surface of aluminium after magnetron sputter deposition. A model self-assembled monolayer (SAM) system was first developed to enable comparisons to be made with the more complex aluminium system. The monolayers were produced by self-assembly on Au (111) and Ag (111) substrates. The gold-coated AFM tips were modified with SAMs of alkanethiols terminated in a methyl or carboxylic acid group. Friction coefficients were measured for SAMs varying in chain length and terminal group chemistry. Using carboxylic acid modified tips; measurements were performed on the surface of aluminium. Adhesion forces were found to decrease with storage time in a desiccated environment, attributed to the adsorption of contaminant molecules from the atmosphere. In contrast the friction coefficient showed no significant change with storage time, presumably because the sliding tip, under loading, is able to displace contaminant molecules. Contact angle goniometry was used to study changes in surface wettability on the aluminium surface. The water contact angle increased linearly with the log of storage time, supporting the hypothesis that adsorption of hydrophobic contaminants modifies the aluminium surface. Contact mode characterisation of the aluminium oxide surface provided clear images of the oxide surface. A nitric acid-based cleaning procedure was developed that was capable of removing adventitious contamination and returning the aluminium oxide surface to condition that appears similar to the freshly deposited surface. This study clearly demonstrates the capability of CFM for characterising complex aluminium surfaces and studying changes in surface chemistry.

10:00am **NS+SE+SS+MM-TuM6 Nanotribology and Related Structural Changes During Wear of Diamond-like Carbon Films**, ***J. Goldsmith***, *E.A. Sutter*, *J. Moore*, *B Mishra*, Colorado School of Mines, *M. Crowder*, Maxtor Corporation

Diamond-like carbon (DLC) thin films are used for wear and corrosion protection of magnetic disks, micro-electro-mechanical systems (MEMS), and tool bits. Magnetic information storage density increases when the read-write head gets closer to the disk. The magnetic layers degrade very quickly without a good protective interface. The use of DLC thin films becomes increasingly popular as they can provide a protective surface due to their excellent tribological properties as low friction and high hardness. In both magnetic disks and MEMS applications, the DLC films are in the thickness range of 2 - 5 nm and in most cases are amorphous in structure. Characterizing the tribological and structural properties and identifying the wear mechanisms of DLC films on the nanoscale is a challenge. Here we present results on the nanotribology of the DLC films performed using both an atomic force microscope and a nanoindenter. We investigate the wear behavior of the DLC films and the role of transfer film. We find that the formation of transfer film plays an important role in providing low-friction. The nanotribological investigations are correlated with the structural changes that occur in the DLC film as well as in the transfer film detected using Raman spectroscopy and cross-sectional transmission electron microscopy.

10:20am **NS+SE+SS+MM-TuM7 Tribology and Surface Forces in MEMS**, ***J.S. Zabinski***, Air Force Research Laboratory, *S.T. Patton*, *K.C. Eapen*, UDRI, *S.A. Smallwood*, Systran, Inc. **INVITED**

Microelectromechanical systems (MEMS) offer the potential to provide new capabilities and products for commercial and military applications. Simple devices are already common in the marketplace, but friction, stiction, and wear prevent reliable operation of more sophisticated types of MEMS devices that have contacting surfaces in relative motion. These tribological problems are fundamentally difficult to solve and are magnified because MEMS are expected to operate in very harsh environments, such as at elevated temperature and in space. The performance and reliability of MEMS are strongly dependent on the environment in which they operate.

For example, moisture can cause device failure by stiction or it can provide excellent lubrication, depending on the device and the relative concentration of water vapor (i.e., relative humidity). Operation in vacuum is particularly severe and the wear mechanisms are different than in dry or moist environments. Methods to control system tribology include lubricant coatings, monolayers, and new materials. The tribological mechanisms operating in moist air through vacuum will be discussed along with strategies to control friction, stiction, and wear that have significantly improved MEMS reliability. In addition, the effects of storage on device performance will be presented.

11:00am **NS+SE+SS+MM-TuM9 Tribological Measurement on MEMS Platforms**[1], ***M.T. Dugger***, *S.V. Prasad*, Sandia National Laboratories **INVITED**

Microelectromechanical systems (MEMS) fabricated using surface micromachining (SMM) and other lithographic techniques such as LIGA have resulted in actuators, counter-meshing gears and other moving mechanisms having complex tribological interfaces that are rough on the nanometer scale and have unusual surface morphologies. Meaningful friction and wear measurements of microsystems must be made at loads and speeds relevant to MEMS operation. Since friction and wear are properties of systems, measurements must also involve interactions of surfaces having the morphology and chemistry present in real devices. Experimental techniques for acquiring friction data during sub-micron displacement and under nanoNewton forces are critical for the fundamental understanding of energy dissipation and wear mechanisms in MEMS. However, experimental investigation of surface interactions in MEMS under relevant contact conditions requires techniques beyond those that are currently available. MEMS friction measurement platforms which bring real MEMS surfaces into contact are needed to define the design space, to investigate aging and failure mechanisms, and to validate models of friction and wear derived from fundamental studies. We have therefore developed both SMM and LIGA devices containing isolated tribological contacts from which quantitative friction forces can be extracted. These structures are used to investigate interface performance, degradation and failure mechanisms. Methods of quantifying static and dynamic friction in SMM and LIGA micromachined contacts will be presented. Examples will be shown of how these structures are being used to investigate degradation of monolayer lubricants and hard coatings for SMM devices, as well as the tribological behavior of metallic contacts in LIGA.

[1] Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

Surface Engineering
Room: C-111 - Session SE+NS-TuM

Nanocomposite and Nanolayered Coatings
Moderator: Y.-W. Chung, Northwestern University

8:20am **SE+NS-TuM1 The Effect of Columnar Growth in the Hardness of TiN/NbN Superlattices**, ***J.M. Molina-Aldareguia***, *T. Joelsson, M. Oden,* Linkoping University, Sweden, *W.J. Clegg,* Cambridge University, UK*, L. Hultman,* Linkoping University, Sweden

Nitride superlattices can be much harder than the individual component materials of which they are made, for a comparable defect and residual stress state. However, there appears to be considerable variation in the observed magnitude of this effect. The aim of this work was to investigate the origin of this variation by comparing two series of epitaxial TiN/NbN superlattices grown by reactive magnetron sputtering on MgO(001) single crystals: one that displayed superlattice hardening and another that did not. According to X-Ray Diffraction and X-Ray Reflectivity studies, the composition modulation was strong and the composition change at the interfaces abrupt in both series, indicating that the hardening is strongly influenced by some other microstructural parameter besides the layering. To investigate this, the deformation mechanisms were studied using a focused ion beam workstation to prepare cross-sectional transmission electron microscopy specimens under nanoindentations. These studies show that the superlattices with no hardening possess a columnar structure with voided boundaries, which act as preferential sites for shear to take place. This implies that the incorporation of porosity at the columnar boundaries, which is dependent on the growth conditions, is responsible for the variation observed in the magnitude of the hardening effect in TiN/NbN superlattices.

8:40am **SE+NS-TuM2 Optical Behavior of Zirconia-Titania Nanolaminate Films**, ***C.R. Aita***, University of Wisconsin-Milwaukee, *J.D. DeLoach*, Texas Instruments

Nanolaminate films of wide band gap semiconductors have bilayer periodicity much less than the wavelength of optical photons. These films are excellent candidates for high refractive index coatings througout the visible spectrum, coupled with optical band gap tailorability in the near-ultraviolet region. Here, we demonstrate this concept using ZrO_2-TiO_2 nanolaminates. Multilayer films were grown at room temperature by sequential reactive sputter deposition from metal targets using O_2-bearing discharges. Bilayer periodicity ranged from several to tens of nanometers. Total film thickness was in the 200 to 500 nm range. Optical transmission and reflection measurements were carried out in the 190 to 1100 nm wavelength range. Optical parameters were determined from these measurements. The results show that the refractive index throughout the region of high transmission was constant, equal to 2.2, and independent of nanolaminate architecture. On the other hand, the onset of fundamental optical absorption was strongly dependent upon bilayer architecture. A blue shift of the optical absorption edge was observed as the bilayer ZrO_2 increased. Optical band gap values spanned a range of 2 eV, from appproximately 3 eV for TiO_2 to 5 eV for ZrO_2, giving the system tailorability. The results are discussed in terms of the primacy of the coordination of a central cation (Zr or Ti) with its nearest neignbor O atoms in determining the features of the fundamental optical absorption edge. We show that the model developed to explain the results for the ZrO_2-TiO_2 system can be applied to other nanolaminates or nanocomposites in which the spatial extent of the wavefunctions describing near edge optical transitions is comparable to the short-range order in the film.

9:00am **SE+NS-TuM3 Nanocomposite and Nanolayered Hard Coatings**, ***J. Patscheider***, *T. Zehnder*, *J.C. Cancio*, EMPA, Switzerland **INVITED**

Nanostructuring of hard coatings, which is achieved by combining two phases with atomically sharp interfaces, opens up new possibilities to improve conventional coatings with respect to their hardness, limited temperature stability and their frictional behavior. The best known combinations of well-separated phases for increased hardness are multilayered superlattices as well as nanocomposite coatings. Nanocomposite coatings proved successful in promoting hardness, oxidation resistance, improved wear behavior and other properties relevant for protective coatings. Such coatings are composed of nano-crystalline grains of transition metal nitrides or carbides, which are surrounded by amorphous hard matrices. Most nanocomposite hard coatings show typically a maximum of the hardness, which can range from 30 GPa to reported values above 60 GPa, as the composition is changed from the pure crystalline phase (no amorphous component) to compositions dominated by the amorphous phase. At the hardness maximum the domain size of the nanocrystalline phase is below 10 nm and the amorphous layer separating the nanocrystals, is only a few atomic bond lengths thin. A comparison to hadness-enhanced superlattices show that the critical dimensions necessary to obtain this effect are of the same order, i.e. the domain size in hard nanocomposites and the single layer thickness in superlattices are both below 10 nm. Due to the absence of dislocation activity, deformation of nanocomposites will be only due to grain boundary sliding. This process requires more energy than deformation by dislocation movement, which is synonymous to increased hardness. In some cases the amorphous phase can act as a solid lubricant (a-C or a-C:H) or as diffusion barriers (Si_3N_4) for improved thermal stability. The amorphous phases in nanocomposites thus cause, apart from the enhanced hardness, additional effects that are beneficial for the performance of these new wear-protective coatings.

9:40am **SE+NS-TuM5 Characterization of TiCrN Nanocomposite Protective Coatings for Biomedical Applications**, ***S.M. Aouadi***, Southern Illinois University*, K.-C. Wong, K.A.R. Mitchell,* University of British Columbia, Canada*, F. Namavar, E. Tobin,* Spire Corp.*, D.M. Mihut, S.L. Rohde*, University of Nebraska, Lincoln

The structural, chemical, optical, and mechanical properties of TiCrN nanocrystalline multiphase films deposited by ion beam assisted deposition (IBAD) were studied by means of X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), spectroscopic ellipsometry (SE), and nanoindentation. The primary phases in the films, their volume fractions, and the elemental compositions were determined from XRD and XPS measurements. The TiCrN films consisted of two phases, namely Ti-N and Cr, for nitrogen concentrations lower than titanium concentrations. For larger nitrogen concentrations, an additional phase (Cr2N) was identified. The topography of the various films was measured using AFM. The optical constants were measured using spectroscopic ellipsometry. A correlation between the elemental/phase composition and optical constants was established. The usefulness and limitations of effective medium theories (EMA) to model the optical constants of these nanocrystalline composite materials will be discussed. The mechanical properties of the coatings were evaluated using nanohardness testing. The hardness and elastic modulii were found to depend on the constituting phases and were measured to be 22-32 GPa and 180-260 GPa, respectively.

10:00am **SE+NS-TuM6 Preparation and Characterization of Chemically Bonded Si_3N_4 and TiN Nanocomposites Prepared by Mechanical Alloying and Sintering**, ***S.W. Deore***, *M. Kesmez, M.A. Hossain,* Lamar University, *J.R. Parga,* Instituto Technologico de Saltillo, Mexico, *D.L. Cocke*, Lamar University

Mechanical alloying using high-energy ball milling is a promising materials processing technique to synthesize nanocomposites for superior mechanical and chemical properties. However, the need to sinter, the application of heat to a powder or a powder body, to increase interparticle bonding, and usually density, tends to result in the destruction of the nanosized components. We have been examining the use of chemical binders that can be pyrolyzed to ceramic binding components at lower temperatures. The heating regime for the sintering process has been determined from the DSC analysis of the binders. Silicon nitride and titanium nitride nanocomposite powders have been prepared using high energy SPEX milling in a nitrogen atmosphere. The composites have been characterized using XRD, XPS, FTIR and SEM. Although both solid phase and liquid phase binders have been examined for their binding properties and hence, the properties of the obtained nanocomposites. The preferred characteristics of the binder precursors will be discussed and a major problem of wetting of the binder to the nanoparticles encountered will be delineated.

10:20am **SE+NS-TuM7 Comparison Studies of Titanium Silicon Carbide Hard Coatings Deposited by Pulsed Laser Deposition and Magentron Sputtering Assisted Pulsed Laser Deposition**, ***A.R.P. Ayalasomayajula***, *J.E.R. Krzanowski*, University of New Hampshire

Titanium silicon carbide films have been grown by Pulsed Laser Deposition (PLD) as well as Magnetron Sputtering Assisted Pulsed Laser Deposition (MSAPLD) on Si (111) and 440C steel substrates at different substrate temperatures and at different substrate bias at 400°C. Experiments are also conducted with different laser powers for C ablation and sputtering powers for $TiSi_2$ content in the deposited films to investigate the effect of C and $TiSi_2$ mechanical and tribological properties. X-ray Diffraction has been employed to find the crystal structure and orientation of the deposited films. Film morphology and roughness are measured by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) techniques, respectively. The film hardness was measured by nano-indentation, while x-ray photoelectron spectroscopy (XPS) was used to estimate the film composition using depth profiling. The residual stress of the deposited was measured by 2D-area General Area Detector Diffraction System. TiSiC films deposited by PLD have shown reasonably high hardness values (37GPa) compared to $TiSi_2C$ films by MSAPLD which have shown hardness values 30GPa at 400°C. The hardness is correlated with residual stress of the deposited films, where we have observed high tensile stress for MSAPLD films leading to decrease in hardness values. Tribological studies have also been conducted to evaluate the friction and wear properties of these films. The mechanisms of hardness enhancement and its relation to tribological properties has also been explained.

10:40am **SE+NS-TuM8 Response of Nanocrystalline Materials to Ion and Neutron Irradiation**, *A. Kubota,* ***M.-J. Caturla***, *T. Diaz de la Rubia, B.D. Wirth,* Lawrence Livermore National Laboratory

Plasma-facing materials are generally exposed to a harsh radiation environment. Radio-frequency excited plasmas under biased conditions produce energetic ion radiation which can lead to material damage and erosion at the surface. In fusion plasma applications however, materials face significant bulk defect production and damage due to deeply penetrating 14 MeV neutrons and Helium nuclear reaction products, leading to embrittlement and void swelling. We discuss results of computational simulations to assess the feasibility of high grain-boundary-density nanocrystalline materials in fusion environments. The performance of the nanocrystalline metals is discussed in terms of defect migration to and annihilation at the grain boundaries, as well as Helium migration along the grain boundary network.

11:00am **SE+NS-TuM9 Novel Properties and Potential Applications of CrBN Films Produced via Unbalanced Magnetron Sputtering**, ***D.M. Mihut***, *T.Z. Gorishnyy, D.M. Schultze,* University of Nebraska, *S.M. Aouadi*, Southern Illinois University, *S.L. Rohde*, University of Nebraska

CrBN nanocrystalline and amorphous materials produced using ion-assisted unbalanced magnetron sputtering were deposited on to a variety of substrates, to investigate the potential of these coating in several applications ranging from coatings on AFM tips to very smooth films for tribological coatings. Coatings were deposited over a range of temperatures from ambient (<200°C) to nearly 900°C, and their thermal stability investigated. Selected films were studied both in-situ and ex-situ using spectroscopic ellipsometry to determine their optical properties and provide correlation between the optical properties and chemical/structural changes in the films, providing a valuable resource for work in these new, but complex multi-phase materials. In addition, these films were characterized post-deposition using X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), infrared spectroscopic ellipsometry (IR-SE), transmission electron microscopy (TEM), nanoindentation, and microwear. XPS, AES, and IR-SE were used in tandem to reveal the crystal structure of the BN phase in these ternary compounds. The amorphous to nanocrystalline nature of the coatings were deduced using AFM and TEM. The mechanical properties (wear rate, hardness, elastic modulii) of the coatings were evaluated using a nanohardness/microwear analyses. Several interesting applications, are currently under investigation as CrBN films have been found to provide a unique combination of very low roughness (rms < 0.2 nm) and high surface hardness (> 22 GPa) under certain growth conditions.

11:20am **SE+NS-TuM10 Preparation, Structure, and Properties of Composite Fullerene-Like CNx Films Produced by Pulsed Laser Ablation**, ***A.A. Voevodin***, *J.G. Jones, J.S. Zabinski,* Air Force Research Laboratory, *Zs. Czigany, L. Hultman*, Linkoping University, Sweden

Production of composite CNx films made of fullerene-like structures in an amorphous matrix using laser ablation of graphite in nitrogen is reported. Deposition was optimized based on investigations of chemistry, excitation stage, kinetic energy, temperature, and spatial distributions of molecular (CN and C2) and atomic (C and N) species, using element specific imaging, time-of-flight experiments, fluorescence spectroscopy, and molecular vibration sequence analyses. Studies showed the importance of plume / substrate interaction in generating excited CN and C2 molecules with high vibrational energy at the condenasation surface for low deposition pressures. Films were characterized with x-ray photoelectron spectroscopy, Raman spectroscopy, high-resolution transmission electron microscopy, nanoindentation, and stress analyses. Nitrogen content directly depended on the concentration of CN radicals at the condensation surface. Formation of fullerene-like structures required a high vibrational temperature of these radicals, which was maximized at about 4 eV for depositions at 10 mTorr N2 and laser fluences of ~7 J/cm2. The presence of C2 had only a minor effect on film composition and structure. Optimization of plasma characteristics and a substrate temperature of 300 C helped to produce about 1000 nm thick solid films of CNx (N/C ratio 0.2 - 0.3) and pure carbon consisting of fullerene-like fragments and packages. Films exhibited elastic recovery of about 80%, elastic modulus of 160-250 GPa and hardness of up to 30 GPa, which was twice that of fullerene-like carbon films. The unusual combination of high elasticity and hardness was explained by cross-linking of fullerene fragments induced by the incorporated nitrogen. Correlations between plasma composition, film structure and properties are established. Results of film mechanical testing demonstrate benefits of the film application as a hard protective coating to resist brittle fracture at high contact loads.

11:40am **SE+NS-TuM11 Tribological Analysis of Nano-composite Diamond-like Carbon Films Deposited by Unbalanced Magnetron Sputtering**, ***D.-Y. Wang***, Mingdao University, Taiwan, *Y.-Y. Chang*, National Chung-Hsing University, Taiwan

Ti contained nano-composite DLC coatings have been developed with improved tribological characteristics. These coatings were synthesized using an unbalanced magnetron sputtering (UBMS) process with a combination of graphite and metal targets. A 100 kHz pulsed d.c. power supply was applied to the substrates to control the substrate arcing and radical excitation during the DLC formation. The microstructure of the nano-composite DLC film was investigated by using cross-section TEM/SAD, x-ray diffraction, Raman and XPS. Tribological properties such as wear mechanism, transfer phenomenon, friction coefficient, and wear life were evaluated and compared with commercial Ti-C:H DLC coatings by using pin-on-disk wear test analyses. The optimized Ti/C multi-layered DLC coatings give satisfied friction performance in the pin-on-disk test with lower wear rate of 1-3 x 10^{-17} m^3/Nm and lower friction coefficient of 0.09-0.1 sliding against 100Cr6 and WC materials. The easily transferred oxide- free graphite-like sp^2 phases form a lubricious layer, which posses low shear strengths under applied stresses. The low friction coefficients and wear rates during the tribological action are anticipated.

Nanometer Structures
Room: C-207 - Session NS+EL-TuA

Quantum Dots
Moderator: J. Nogami, Michigan State University

2:00pm **NS+EL-TuA1 Peter Mark Memorial Award Address: Mechanisms of Semiconductor Nanostructure Formation**, ***R.S. Goldman****, University of Michigan **INVITED**

Recently, semiconductor nanostructures have shown significant promise for a wide range of electronic, optoelectronic, and magnetic applications. In this talk, I will discuss the formation mechanisms of a variety of semiconductor nanostructures, including phase separation-induced alloy nanostructures and strain-induced self-assembled quantum dots. I will show how we have used data from cross-sectional scanning tunneling microscopy, in conjunction with x-ray reciprocal space maps, to develop new models for self-ordering of InAs/GaAs quantum dot superlattices[1] and spontaneous lateral phase separation in InAlAs alloys.[2] I will also describe our recent investigations of the role of elastic anisotropy in semiconductor nanopatterning, towards the formation of three-dimensional quantum dot crystals. These mechanisms are likely to be applicable to a wide range of heteroepitaxial semiconductor nanostructures.

This work was supported in part by the National Science Foundation (CAREER Award and Nanoscale Exploratory Research Program) and the Army Research Office (MURI Program)

[1] B. Lita, R.S. Goldman, et al, Appl. Phys. Lett. 75, 2797 (1999); Surface Review and Letters 7, 539 (2000).

[2] B. Shin, A. Lin, K. Lappo, R.S. Goldman, et al Appl. Phys. Lett . 80, 3292 (2002).

2:40pm **NS+EL-TuA3 Strain Effects and Inter-Dot Coupling in Self-Assembled Quantum Dot Arrays**, ***H.T. Johnson***, *R. Bose,* University of Illinois at Urbana-Champaign, *B.B. Goldberg,* Boston University, *H.D. Robinson*, University of California at Los Angeles **INVITED**

A computational model is used to simulate optical properties of self-assembled InAlAs/AlGaAs quantum dot arrays. Array sections containing up to 30 dots of varying size, shape, and spacing are considered. Comparisons are made to experimental results for arrays characterized using near-field scanning optical microscopy (NSOM). The experimental and computational studies both measure emission/absorption spectra with energy resolution that shows the effects of individual dots in the array. In the computational approach, the optical properties are computed from the spectrum of electron and hole states found for the ensemble. The energies and wave functions in the spectrum are first computed using a strain-modified k-p Hamiltonian approach; the spectrum includes confined electron and hole states associated with individual dots in addition to some delocalized states associated with coupled dots as well as the wetting layer. By modeling the entire ensemble of dots simultaneously, it is possible to consider effects related to long range field interactions between dots, such as linear elastic fields and extended quantum mechanical states. Two key results are of interest. First, it is found that even minor contact between the optical fiber tip and the sample surface leads to indentation strain large enough to substantially shift emission wavelengths of individual dots in the array. Second, extended states in groups of neighboring quantum dots lead to sharp, well-defined resonances in the emission spectra for the arrays. Results of the simulations clearly show these effects that are also observed in the experimental data.

3:20pm **NS+EL-TuA5 Growth of Ge Quantum Dots on Si(100) Without a Wetting Layer** [1], *K. Yoo,* Oak Ridge National Laboratory, *F. Flack,* University of Wisconsin - Madison, *H.H. Weitering,* Oak Ridge National Laboratory, *M.G. Lagally,* University of Wisconsin - Madison, *Z. Zhang,* ***J.F. Wendelken***, Oak Ridge National Laboratory

When Ge atoms are deposited directly onto a Si(100) substrate, the growth follows the Stranski-Krastanov growth mode in which three-dimensional Ge islands, or quantum dots (QDs), are formed on top of three monolayer thick wetting layers. For many optical and electronic device applications, Ge QDs without the wetting layer may be highly preferred. Using a buffer-layer assisted growth approach,[2] we have achieved the formation of Ge QDs on Si(l00) without a wetting layer. These QDs are shown to possess a narrow size distribution and are also substantially smaller than the QD hut clusters that are formed with the normal SK growth mode. Using the buffer layer approach, Ge QDs have been grown in a single layer and in multiple layers with silicon spacer layers as has been done with multilayers of conventionally grown Ge hut clusters. Due to the fact that growth in the buffer layer approach is well isolated from any stress effects associated with a preceding layer of QDs, it is not expected that the QDs in separate layers will exhibit any layer to layer alignment effects as observed for SK growth. However, the smaller size of the QDs obtained with the buffer layer approach may be expected to exhibit stronger quantum size effects. Initial tests with samples prepared by this approach show a strong photoluminescence signals in the IR that exhibit striking differences from PL results[3] obtained from Ge QDs grown by conventional means with a wetting layer.

[1] Work supported in part by the U. S. DOE at Oak Ridge National Laboratory, managed by UT-Battelle, LLC under Contract DE-AC05-00OR22725, and in part by the NSF at the University of Wisconsin through the MRSEC program.

[2] J. H. Weaver and G.D. Waddill, Science 251, 1444 (1991).

[3] M.W. Dashiell, U. Denker, and O.G. Schmidt, Appl. Phys. Lett. 79, 2262 (2001).

3:40pm **NS+EL-TuA6 Spontaneous Generation of Free-Standing Ge Quantum Dots on Silicon-on-Insulator**, ***E.A. Sutter***, *P.W. Sutter, P. Zahl,* Colorado School of Mines

The growth of heteroepitaxial materials on engineered composite substrates such as silicon-on-insulator (SOI) opens a new route for controlling the structural and electronic properties of materials at the nanoscale. Local lattice strain induced by Ge quantum dots grown coherently on SOI - a composite of an ultrathin monocrystalline Si template supported by amorphous SiO_2 on a conventional Si wafer, causes significant local distortion in the Si template and can be used as a tool for nanoscale band structure engineering of the Si substrate. The Ge islands themselves form on SOI initially as huts and then transform into domes, similar to the sequence of epitaxially constrained shapes they assume on bulk Si (100). While the shape sequence of epitaxial Ge islands on bulk Si ends here, we observe further dramatic morphological changes on ultrathin SOI: a spontaneous transformation to free-standing Ge islands accompanied by a breakup of the thin Si slab. We use a combination of atomic force microscopy (AFM) and transmission electron microscopy (TEM) to document the sequence of shape transformations of Ge islands on SOI. We investigate in detail the island shape evolution and redistribution of the substrate material between the islands both before and after the breakup of the ultrathin Si slab of the SOI substrate.

4:00pm **NS+EL-TuA7 Production and Structure of Gas-phase Prepared Germanium Nanocrystals**, ***C. Bostedt***, *T. van Buuren, T.M. Willey, J. Plitzko,* Lawrence Livermore National Laboratory, *T. Moller,* Hasylab at DESY, Germany, *L.J. Terminello,* Lawrence Livermore National Laboratory

Clusters and nanocrystals represent a new class of materials, which exhibits promising novel properties. Germanium nanoparticles are particularly interesting, as the cubic as well as the tetragonal crystal phases have been reported for particle sizes below 5 nm, depending on the production method. We have developed a gas-aggregation based production method for germanium nanoclusters, with which nanocrystals in the bulk-like cubic phase from 1 to 10 nm in size can be produced. The clusters are condensed out of supersaturated Germanium-vapor, which is cooled down in a He-atmosphere and are subsequently deposited on a variety of substrates. The particle sizes and phases have been well characterized by transmission electron microscopy (TEM), x-ray diffraction (XRD) and atomic force microscopy (AFM). The crystal phase - production method relationship is discussed. Only little is know about the surface structure of nanocrystals. Information about the surface structure is difficult to obtain. No distinct particle boundaries can be imaged with TEM. Photoemission spectroscopy (PES) has been shown to be a powerful tool to investigate bulk-crystal semiconductor surfaces. PES experiments have been performed on Ge nanocrystal films and a disordered surface shell around a crystalline core is deduced for the nanoparticles. .

C. Bostedt acknowledges a fellowship from the German Academic Exchange Service DAAD in the HSP-III program, N. Franco from the Spanish Education and Culture Office. The work is supported by the US-DOE, BES Material Sciences under contract W-7405-ENG-48, LLNL.

4:20pm **NS+EL-TuA8 Surface Passivation Effects of Deposited Ge-Nanocrystal Films Probed with Synchrotron Radiation**, *C. Bostedt,* ***T. van Buuren***, *T.M. Willey,* Lawrence Livermore National Laboratory, *T. Moller,* Hasylab at DESY, Germany, *L.J. Terminello,* Lawrence Livermore National Laboratory

Clusters and nanocrystals represent a new class of materials that exhibit promising novel properties. The production of these nanostructures in the gas phase gives control over not only the size of the nanoparticles, but also over surface passivation - often not possible in other growth modes. The clusters are condensed out of supersaturated Germanium-vapor which is

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***** Peter Mark Memorial Award Winner

cooled down in a He-atmosphere and are subsequently deposited on a variety of substrates. Their surfaces can be subsequently passivated with different materials evaporated into the vacuum chamber. This approach allows us to probe in a controlled and dynamic fashion the effect of surface passivation on nanocluster properties. X-ray absorption spectroscopy (XAS) and photoemission (PES) were performed on thin films of Germanium (Ge) clusters. Clean Ge nanocrystal films are found to exhibit much stronger quantum confinement effects at the band edges than similar Si particle films. These findings are compared to recent electronic structure calculations. For passivated nanocluster films we find that the passivating agent strongly alters the electronic structure of the clusters. In general the absorption edge shifts to significantly higher energies compared to cluster films without surface passivation. These results will be discussed in terms of a reduction of the cluster-cluster interactions.

C. Bostedt acknowledges a fellowship from the German Academic Exchange Service DAAD in the HSP-III program. The work is supported by the US-DOE, BES Material Sciences under contract W-7405-ENG-48, LLNL.

4:40pm **NS+EL-TuA9 Growth and Properties of Si Compatible Nanostructures: Si Quantum Dots Grown on CaF_2/Si Films**, ***A. Klust***, *A.A. Bostwick, T. Ohta, Q. Yu, M.A. Olmstead*, University of Washington

Si/CaF_2 is a promising candidate for epitaxial semiconductor/insulator heterostructures for optoelectronic applications because of the low lattice mismatch (0.5%) and large band gap difference (12.4 eV for CaF_2 vs. 1.1 eV for Si). In addition, the strongly dissimilar ionic/covalent bonding character in the system CaF_2/Si allows it to serves as a model system both to study heteroepitaxy of two dissimilar materials and to study the influence of bonding character and electronic structure on scanning probe microscopy. Here, we present an investigation of ultra-thin (1-3 molecular layers) CaF_2 films and Si quantum dots grown on these films using both non-contact atomic force microscopy (ncAFM) and scanning tunneling microscopy (STM). On the one hand, the extremely large band-gap of CaF_2 makes STM measurements difficult; stable imaging is not possible for films thicker than 3-4 molecular layers. On the other hand, STM gives complementary information to that obtained with ncAFM. For instance, scanning tunneling spectroscopy is used to characterize the electronic properties of single Si QD. Furthermore, the contrast during STM imaging of the CaF_2 films depends strongly on the polarity of the bias voltage and the film thickness. Non-contact AFM is used to clarify this behavior to separate electronic and topographic contributions to the STM images. Atomically-resolved ncAFM images of the CaF/Si interface layer will be shown and compared with similar published data obtained from bulk CaF_2(111) crystals.[1] The atomic structure of the CaF/Si interface layer is practically identical to the surface structure of bulk CaF_2(111), while the electronic structure differs. We discuss the influence of the different electronic structure on atomic resolution ncAFM.

[1] A. S. Foster, C. Barth, A. L. Shluger, and M. Reichling, Phys. Rev. Lett. 86 (2001) 2373.

5:00pm **NS+EL-TuA10 Formation of Self-Assembled Copper-Oxide Nano-Dots on SrTiO3(100)**, ***I. Lyubinetsky***, Pacific Northwest National Laboratory

In addition to offering a wide range electrical, optical and magnetic properties, oxide nanostructures can be stable in a range of environments without needing to add protective layers. In this work, we have observed the formation of self-assembled oxidized-copper nanodots on the SrTiO3(100) substrate using oxygen plasma assisted molecular beam epitaxy. The composition and structure were examined by x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy, x-ray diffraction, and scanning probe microscopy in a wide range of growth parameters (temperature, oxygen pressure, and Cu flux). Under different growth conditions different shapes and/or composition have been found: truncated dots, square pyramids, and multifaceted domes with composition to be Cu2O or containing Cu metal also. Since nanostructure composition changes with temperature, observation made by interrupting growth and cooling may not be adequate. Thus, in addition to scanning probe measurements in ambient conditions, XPS spectra have been acquired at elevated temperatures in step-by-step mode at different stages of nanodots formation. Observed correlations between structural and composition changes will be discussed. Understanding of the evolution of the dot shape, size and composition would allow us to optimize formation conditions to synthesize cooper oxide nanodots with desirable parameters.[1]

[1] This work has been conducted as part of the PNNL Nanoscience and Nanotechnology Initiative supported by the Office of Biological and Environmental Research, U. S. Department of Energy.

Nanometer Structures
Room: Exhibit Hall B2 - Session NS-TuP

Nanometer Structures A

NS-TuP1 Calibration Methods for Displacement and Cantilever Stiffness in AFM, *G.A. Matei, E.J. Thoreson,* ***N.A. Burnham***, Worcester Polytechnic Institute, *X. Chen,* University of Nottingham, *C.H. Hodges*, University of Leeds

The laser beam in our AFM was placed half on and half off a cantilever that was hanging freely above a reflective surface. The resulting two beams interfered and the interference could be detected at the photodiode, yielding a simple and accurate means of calibrating the scanner displacement. This approach will be extended to the calibration of the amplitude of oscillating cantilevers. Also, we compared the experimentally determined values of stiffness for ten cantilever probes using four different methods[1]. For rectangular silicon cantilever beams of well-defined geometry, the approaches all yield values within seventeen percent of the manufacturer's nominal stiffness. One of the methods is new, based on the acquisition and analysis of thermal distribution functions of the oscillator's amplitude fluctuations. We evaluate this method in comparison to the three others and recommend it for its ease of use and broad applicability.

[1] N.A. Burnham, X. Chen, C.S. Hodges, et al., submitted to Review of Scientific Instruments.

NS-TuP2 Atomic Force Microscope Assisted Oxidation of Zirconium Surfaces, ***N. Farkas***, *G. Zhang, S.F. Lyuksyutov, E.A. Evans, R.D. Ramsier*, The University of Akron, *J.A. Dagata*, National Institute of Standards and Technology

We present results from scanning probe oxidation of zirconium (Zr) surfaces using atomic force microscope tips in air. For both single-crystal and sputter deposited thin-films of zirconium, rapid oxide growth kinetics are replaced by much slower processes as a function of oxidation time (0 - 300 s). We track these kinetics vs. Zr film thickness (10 - 50 nm), relative humidity (25 - 60 %), and applied voltage (0 - 20 V). In addition, we are able to modify the nanolithographic process by incorporating nitrogen into the top 10 nm of the sputtered films. Our results contribute to a more comprehensive description of the nanolithographic process and complement efforts to model and control the oxidation of Zr surfaces.

NS-TuP3 Molecular Dynamics Simulations of Nanofluidics, ***K. Lee***, *S.B. Sinnott*, University of Florida

The design of ultrafiltration membranes using carbon nanotubes to allow gases to selectively pass through the membrane depends on the understanding of the diffusion and adsorption of the gases within the carbon nanotubes. The nanofluidics of hydrocarbons, oxygen, and carbon dioxide has been studied with molecular dynamics simulations in our research. These macroscopic behaviors can be simulated with multiple integrations of the interactions among the atoms in a system. The interatomic forces in the simulations are calculated using a classical reactive empirical bond-order hydrocarbon potential coupled to Lennard-Jones and Coulombic potentials. For a shorter time period, the location, the trace, and the orientation of the gas molecules in the nanotubes are affected by the diameters of the nanotubes, and the structures of the carbon nanotubes. The transport of gas molecules for a longer time period is described by nonequilibrium followed by equilibrium states. Until reaching the equilibrium state, the gas density in a carbon nanotubes increases on and levels off. During the nonequilibrium state, the gas molecules move back and forth through the nanotube. This behavior and the time for the level-off are affected by the concentration of gas molecules both in and outside of the carbon nanotube. It is found that the molecular volumes of the gas molecules and the composition of the gas mixtures also have an important effect on the separation behavior.

NS-TuP4 STM and STS Characterization of Silicon Phthalocyanines for the Molecular Quantum Dot Cellular Automata Implementationn, ***M. Manimaran***, *G.L. Snider, V. Sarveswaran, M. Lieberman*, University of Notre Dame

The surface characterization of organic molecules adsorbed on solid surfaces has been investigated intensively in recent years. In particular, the adsorption of long-chain substituted hydrocarbons (CH3(CH2)2X, X= CH3, OH, SH,S,SS, NH2, Cl, Br, I, etc on highly oriented pyrolytic graphite (HOPG) and Au surfaces was well studied because of their importance in wide range of applications in biology and molecular devices such as Quantum-dot cellular automata (QCA). QCA is a computation paradigm based on the Coulomb interactions between the neighboring cells. The prime idea is to represent binary information, not by the state of a current switch, but rather by the configuration of charge in a bistable cell. In its molecular realization the QCA cell can be a single molecule. Si-phthalocyanine (SiPc) is one of the promising candidates for the QCA. In this study, SiPc molecules, which are double-dot-like entities, are deposited on Au and Si(111) substrates initially. These molecules are then observed under UHV-STM to determine if the molecules would self assemble, and also to determine their electronic properties via voltage vs. current (I/V) measurements. In addition to the STM and STS studies, XPS, PL and ellipsometric results will be presented in this paper.

NS-TuP5 Substrate Temperature Dependence of Electrical Conduction in Nanocrystalline CdTe:TiO$_2$ Sputtered Films, ***S.N. Sharma***, National Physical Laboratory, India, *S. Kohli,* Colorado State University, *S.M Shivaprasad,* National Physical Laboratory, India, *A.C. Rastogi*, University of Massachusetts

TiO$_2$ thin films with high volume fraction (~ 50-60 %) of CdTe nanoparticles were prepared by rf magnetron sputtering from a composite TiO$_2$:CdTe target. Variations in the substrate temperature, T$_S$ (room temperature-RT and 373 K), produces two distinct structural regimes with different electrical properties in thermally treated TiO$_2$ thin films: (i) a metallic regime for low T$_S$ films where the CdTe/Cd grains touch each other and form a metallic continuum. Here, homogeneous, ordered and electrically-continuous structure was obtained. Here, due to the presence of large-scale coalescent islands of CdTe/Cd, three-dimensional network of crystallites could be realized. Such films exhibited positive temperature coefficient of resistance. For metallic regime films, electrical conduction is essentially due to electrical percolation through CdTe/Cd crystallites embedded in an amorphous TiO$_2$ matrix. XPS studies indicated the segregation of metallic Cd upon thermal treatment which were responsible for metallic-type of conduction exhibited by these films. (ii) a non-metallic regime for high Ts films in which small isolated particles of CdTe/Cd are dispersed in an amorphous matrix. Here, highly disordered and electrically-discontinuous structure was obtained and thus formation of CdTe network could not be realized. The formation of oxides on the surface of the CdTe/Cd crystallites acts as an electrical insulation and thus, the conduction is thermally activated. The electrical conduction in high T$_S$ films is essentially by hopping mechanism thus indicating transfer of charge carriers via thermally activated tunneling. Such films exhibited negative temperature coefficient of resistance.

NS-TuP6 Nanolithography and Biofunctionalisation for Cell Adhesion Studies, *A. Szucs,* ***M. Arnold***, *Ch. Geierhaas, J.P. Spatz*, University of Heidelberg, Germany

Periodic and artificial lateral nanostructures with micrometer or nanometer spacings have been prepared through the combination of a top-down approach (electron beam lithography) with a bottom-up approach (formation and compartmental localization of metallic and semiconductor nanodots within block copolymer micelles). E-beam lithography was used to construct patterned templates with characteristic spacings greater than 200 nm of coarse prestructures. Within these structures, Au nanoparticles and/or quantum dots (Q-dots) (CdS, CdSe and CdTe) in the size range of 2-8 nm could be positioned with a precision of approx. 10 nm by means of a self-assembling polymer micelle. The particle size was controlled by the length of the reverse micellar core constructing polymer and the salt loading inside the core. Specifically, it was obtained by casting a solution of HAuCl4 and/or Cd salt loaded block copolymer micelles onto the prestructured resist film. Due to capillary effects and steric hindering, the particles are centered within the prepatterned holes and at the edges of prestructured lines. Subsequent lift-off of the resist allows the removal of all micelles with the exception of those that are in direct contact to the underlying substrate. The block copolymer is then removed by plasma etching, which strips the polymer micelle and reduces the gold salt to gold thereby leaving behind nanoscopic dots or lines of gold in a defined array. These nanostructured interfaces are used as platform for biofunctionalisation of solid interfaces. The surfaces are used as a tool to investigate cluster formation of focal adhesion associated proteins of fibroblasts.

NS-TuP7 In situ STM Study on Electrochemical Formation and Desorption of Self-assembled Monolayer in Ethanol Solution Containing KOH and Alkylthiol, ***K. Uosaki***, *H. Wano*, Hokkaido University, Japan

Oxidative formation and reductive desorption of self-assembled monolayer (SAM) of alkylthiol in ethanol solution containing KOH and various concentration of alkylthiol was investigated by in situ STM. Cyclic voltammograms show the formation process is slower than the desorption process. When the concentration of the thiol was very low (~ micro M), no vacancy island (VI) was observed even in positive potential region where SAM formation is expected. As more thiol was added at the positive potential region, the growth of VIs, i.e., SAM, was observed. The VIs disappeared and herringbone structure appeared on the surface as potential became more negative than the certain value, showing the restoration of the reconstructed, i.e., clean, surface. The herringbone structure became clearer with time. When the potential was scanned positively, disappearance of the herringbone structure and the growth of the VIs were observed. Drastic change of step lines reflecting the higher mobility of gold atoms was also observed during the formation and desorption of the SAM.

Microelectromechanical Systems (MEMS)
Room: C-210 - Session MM+NS-WeM

Nanotechnology and Nanofabrication in NEMS
Moderator: H.G. Craighead, Cornell University

8:20am **MM+NS-WeM1 Probing Nanomechanical Systems with Electron Tunneling Devices**, ***A.N. Cleland***, University of California, Santa Barbara **INVITED**

We have been integrating active electronic devices with nanomechanical systems, in order to probe both the mechanical and thermodynamical behavior of the integrated system. I will discuss experiments in which we have developed fabrication approaches allowing the integration of superconductor-normal metal tunnel junctions with suspended mechanical structures to develop an ultrasensitive bolometer and calorimeter, with which we have been able to confirm the observation of the quantum of thermal conductance, the integration of single-electron transistors with mechanical resonators, displacement sensing using an integrated quantum point contact, and the development of a double quantum dot integrated with an L-band mechanical resonator. I will briefly discuss the potential application of these types of integrated probes for quantum-limited measurements.

9:00am **MM+NS-WeM3 Fabrication and Characterization of a Carbon Nanotube Torsional Oscillator**, ***P.W. Williams***, *A.M. Patel, S.J. Papadakis, M.R. Falvo, S. Washburn, R. Superfine*, University of North Carolina

Carbon nanotubes have extraordinary mechanical properties and have been demonstrated to show atomic scale effects in the frictional[1] and electronic properties[2] of their contacts. We are exploring the applications of these properties in nanoelectromechanical Systems (NEMS). Torsional oscillators represent a device geometry for the measurement of fundamental properties of nanotubes as well as high frequency oscillators and sensors.[3] Using individual multi-wall carbon nanotubes as torsional springs, we have fabricated NEMS paddle oscillators. We will report on the fabrication of these structures as well as measurements of their torsional compliance using atomic-force-microscope force-distance curves. The measured shear modulus will be compared with existing theoretical expectations, and unexpected hysteresis effects will be discussed. Along with compliance measurements, progress toward characterization of resonant behavior including measurements of quality factor and resonant frequencies will be presented. This work is supported by the National Science Foundation and the Office of Naval Research.

[1] M. R. Falvo, J. Steele, R. M. Taylor, et al., Physical Review B 62, R10665 (2000).

[2] S. Paulson, A. Helser, M. B. Nardelli, et al., Science 290, 1742 (2000).

[3] S. Evoy, D. W. Carr, L. Sekaric, et al., Journal of Applied Physics 86, 6072 (1999).

9:20am **MM+NS-WeM4 Femtogram Detection using Nanoelectromechanical Oscillators**, ***B. Ilic***, *D. Czaplewski, H.G. Craighead*, Cornell University, *P. Neuzil*, Institute of Microelectronics, Singapore

Micro and nanoelectromechanical systems (MEMS and NEMS) represent an emerging sensor technology that provides a closely coupled link between the physical, chemical and biological worlds. Nanomechanical systems can be used as mass based sensors with sensitivity several orders of magnitude better than conventional quartz crystal oscillators. Here we present a resonant frequency-based NEMS mass sensor, comprised of surface micromachined low-stress polycrystalline silicon cantilever beams for the detection of self assembled monolayers. In our experiment, we demonstrate a method for detecting the mass of Aminopropyltriethoxysilane (APTS), Hexamethyldisilazane (HMDS) and Octadecyltrichlorosilane (OTS) self assembled monolayers (SAM) using a resonant frequency-based detection sensor. The highly sensitive balance considered here is a resonating cantilever beam fabricated using electron beam lithography. For this experiment, devices with dimensions of varying length (l) from 3µm to 15µm, width (w) of 500nm to 2µm and thickness (t) of 150nm and 320nm, were used. Devices were coated with various monolayers and resonant frequency was measured before and after the addition of SAM. Signal transduction was accomplished in vacuum by employing an optical interferrometric system to measure the frequency shift due to the additional mass loading. The measured frequency shift was correlated to the mass of the SAM and was found to be in good agreement with the analytical results. For the smallest device geometry, we observed a resonant frequency shift due to the presence of 4 femtograms of HMDS. By further tailoring cantilever dimensions, the sensitivity of our devices can be greatly improved, thus extending their application to DNA, viruses and other analytes with mass on the order of attograms.

9:40am **MM+NS-WeM5 IR Imaging Using Uncooled Nanostructured Microcantilever Thermal Detectors[1]**, ***P.G. Datskos***, Oak Ridge National Laboratory and University of Tennessee, *S. Rajic, L.R. Senesac, J. Corbeil, N.V. Lavrik*, Oak Ridge National Laboratory

Bimaterial microcantilevers have been shown to detect infrared (IR) radiation and can operate as uncooled thermal detectors. The transduction mechanism is the bending of the bimaterial microcantilever due to thermally-induced stress. Therefore, it is important to minimize cantilever deflections caused by factors other than IR radiation (e.g. intrinsic mechanical stresses and ambient temperature fluctuations) while increasing photon absorption in the desired spectral region. In this paper we report on IR imaging using optimized microcantilever designs that are immune to ambient temperature changes and other sources of interfering mechanical stresses. In addition, we achieved increased absorption of IR photons using resonant nanostructured detector surfaces. We modeled and experimentally measured responses of such devices to IR radiation as well as to ambient temperature changes. We will present and discuss our latest results.

[1] We like to acknowledge support from the Defense Advanced Research Projects Agency, the National Science Foundation and DOE. This work was partially supported by the Laboratory Director's Research and Development Program of Oak Ridge National Laboratory. Oak Ridge National Laboratory is operated for the U.S. Department of Energy by UT-Battelle under contract DE-AC05-96OR22464.

10:00am **MM+NS-WeM6 Frequency and Phase Entrainment in MEMS Oscillators**, *M. Zalalutdinov*, ***K.L. Aubin***, *A.T. Zehnder, B. Ilic, D. Czaplewski, L. Sekaric, J.M. Parpria, H.G. Craighead*, Cornell University

Synchronization of light-induced self-sustained vibration of MEMS resonators by external parametric perturbation was demonstrated. Self-oscillation of disc-type MEMS resonators induced by CW laser light has been described earlier.[1] In the work presented here, partial modulation of the laser power was used to provide additional parametric excitation through the laser beam induced stress as a physical mechanism to control the parameter - the effective spring constant of the resonator. Modulation depth as low as 5% of CW laser power at frequencies near n times (n=1,2,3...) the natural resonant frequency of the oscillator was shown to cause the frequency and phase of the mechanical motion to become entrained to the modulation frequency (over n). The range of frequencies over which entrainment was possible was shown to vary with modulation amplitude. Once entrainment of the mechanical vibrations is achieved, one can tune the mechanical frequency of vibration by about 10% by changing the modulation frequency. During that tuning, the phase difference between the modulation signal and the mechanical motion was shown to vary as much as 130°. In a synchronized state, stability of the vibrations appears to be limited only by that of the modulation source, allowing us to demonstrate better than 10^{-9} stability for the frequency of the mechanical motion. Integration of entrained MEMS and NEMS oscillators into a phase-locked loop (PLL) circuit in order to build a high stability reference oscillator is currently under study.

[1] M. Zalalutdinov, A. Zehnder, A. Olkhovets, S. Turner, L. Sekaric, B. Ilic, D. Czaplewski, J. M. Parpia and H. G. Craighead, "Auto-Parametric Optical Drive For Micromechanical Oscillators" Appl. Phys. Lett., Vol. 79, pp 695 (2001).

10:20am **MM+NS-WeM7 Fabrication of Submicron-Scale Metallic Comb-Drive Actuators**, ***S.W. Park***, *N.A. Kumar, J.B. Lee*, The University of Texas at Dallas

Comb-drive actuators have been widely used for more than a decade in many applications including resonators, accelerometers, and tunable capacitors with the advance of micromachining technologies. While single crystal or poly Si have been preferred materials for comb-drive actuators, metallic high aspect ratio comb-drive actuators were also of interest due to its electrical property such as lower resistivity in some applications. In this paper, we report the development of fabrication of a sub-micron scale (sub-micron gap and width) all metallic comb-drive actuator with small overall foot-print. All metallic comb-drive actuators with sub-micron gap/width and small foot-print have many advantages over traditional silicon-based micron scale comb-drive actuators. Such advantages include large increase of capacitance per unit area (good for sensing applications) and higher quality factor due to low equivalent series resistance of the metallic comb-finger structures (good for tunable capacitor application). The comb-drive actuator was designed as a tunable capacitor and intensive modeling of such tunable capacitor was carried out. Fabrication of such comb-drive actuators was started with a multiple spin-coatings of polymethyl methacrylate (PMMA) or SU-8 on an oxidized silicon substrate. PMMA was investigated for low aspect ratio and SU-8 was investigated as a potential electron beam photoresist for high aspect ratio comb-drive actuator fabrication. Numerous experimental runs were performed to find optimum exposure doses, developing conditions, etc. Different metals such as Cu, Cr, Ti/Cu, and Cr/Cu were investigated as candidate materials for comb-drive actuators. Optimum fabrication process based on PMMA was developed for 1:1 aspect ratio all metallic 500-nm width/gap comb-drive actuator. Preliminary results on negative tone SU-8 resist based comb-drive actuator with a goal of achieving high aspect ratio (up to 5:1 aspect ratio) structure will also be reported.

10:40am **MM+NS-WeM8 Controlling Energy Losses in Nanoscale Structures with Surface Chemistry**, ***J.A. Henry***, *Y. Wang, M.A. Hines*, Cornell University

Why are we unable to predict the dynamic properties of nanoscale devices from the well-known behavior of bulk materials? For example, the quality (or Q) of nanoscale resonators is often orders of magnitude lower than similar macroscopic devices. Here, we show that simple changes in the surface chemistry of MHz silicon resonators can lead to large changes in Q, indicating that surface loss mechanisms become very important at this length scale. For example, the oxidation of H-terminated silicon resonators causes the Q to plummet by as much as 50% while inducing only a minuscule change in frequency of approximately 0.05%. The scaling of both the energy losses and the frequency shifts with oscillator size and thickness are consistent with a surface-driven process. Infrared absorption measurements confirm that chemical changes are limited to a few monolayers of the surface. Possible mechanisms for these losses will be discussed.

Nanometer Structures
Room: C-207 - Session NS-WeM

Nanostructured Materials
Moderator: W.N. Unertl, University of Maine

8:20am **NS-WeM1 Electronic Structure of Nitrogen Doped Ultrananocrystalline Diamond**, ***J. Birrell***, University of Illinois at Urbana-Champaign, *O. Auciello, J.A. Carlisle, J.E. Gerbi, J.M. Gibson, D.M. Gruen*, Argonne National Laboratory

The local bonding structure of ultrananocrystalline diamond (UNCD) thin films synthesized using $Ar/CH_4/N_2$ microwave plasmas has been investigated using near-edge x-ray absorption fine structure (NEXAFS). These films exhibit a dramatic increase is electrical conductivity (up to 150 Ω^{-1} cm^{-1}) as nitrogen gas is added to the plasma. Theoretical models predict that this is due to an increase in band gap states due to the presence of nitrogen at the grain boundaries. C 1s NEXAFS experiments have been performed to ascertain the ratio of sp^2/sp^3 bonded carbon in these films. It was found that, as nitrogen is added, the amount of sp^2-bonded carbon increases by roughly %50 compared to the undoped films, but overall the films remain largely sp^3-bonded. The sp^3 σ^* exciton, located at ~289 eV, diminishes in intensity, however, in spite of an observed increase in grain size with nitrogen content in the plasma. These results, as well as previous experiments using high resolution transmission electron microscopy, are used to explain the observed changes in the materials properties of nitrogen doped UNCD.

8:40am **NS-WeM2 Growth, Microstructure and Properties of Fullerene-Like Carbon Nitride Thin Solid Films Deposited by DC Magnetron Sputtering**, ***Zs. Czigány***, *J. Neidhardt, I.F. Brunell, L. Hultman*, Linköping University, Sweden

Fullerene-like CN_x ($x \leq 0.2$), as an inherently nanostructured material, were deposited as thin solid films by reactive magnetron sputtering of graphite in a nitrogen and argon discharge. The films were characterized by HRTEM, EELS, XPS and nanoindentation. Most fullerene allotrope synthesis is completed in the gas phase at high temperatures and the resulting material does not form a dense solid film. In comparison, the route to fullerene-like material presented here is by continuous surface nucleation and growth of curved basal planes at relatively low temperature. Plasma characterization revealed low flux of low energy species in the deposition flux with high portion of reactive complexes (e.g., CN, C_2N, C_2N_2). In the fullerene-like structures N substitutes for C and reduces the energy barrier to form pentagons in graphite sheets, thus inducing curvature of the basal planes. N also increases the reactivity of the neighboring C atoms, thus promoting sp^3 cross-linking between C atoms in neighboring fullerene domains and provides solid CN_x films with high elasticity. TEM imaging of fullerene-like structures in a thin solid film form gives rise to difficulties compared to isolated fullerene features. Sample preparation methods for artefact-free specimens with thickness compatible with the characteristic feature size of fullerene-like domains will be discussed.

9:00am **NS-WeM3 Selective Oxidation of Faulted Halves of Si(111):(7x7) with Ozone**, ***K. Miki***, NRI-AIST and NIMS, Japan, *T. Narushima*, NRI-AIST, Japan, *M. Kitajima*, NIMS, Japan

For nano-scale devices, an electronic isolation technique is desired since the working current is very small and therefore leakage through the substrate should be suppressed. In this paper we demonstrate a nano-scale selective reaction to realize this isolation technique. For this model case, we used an ozone radical to selectively oxidize one subunit of Si(111)-7x7. This surface has two different subunits; the faulted and unfaulted halves. Due to whether or not a stacking fault exists, the electronic states of the two halves differ, especially around 0.5 eV below Ef. This state is the backbond state of the adatoms. Therefore we could expect selective oxidation with some radicals on either the faulted or the unfaulted half. In conventional thermal oxidation, this possibility has already been denied, while ozone remains a possibility. We introduced highly concentrated ozone gas onto 7x7 reconstructed Si(111) surface in a UHV chamber in a split second. At room temperature, by means of scanning tunneling microscopy, it is found that the faulted sites are imaged as depressions at the sample bias of 0.8 V, but the other sites are mostly unchanged. This depression could be due to back bond oxidation. The reactive site of the oxygen changed with temperature, up to 873 K. As the substrate temperature increased, the chemical reaction selectivity disappeared. This may be due to diffusion of backbond oxygen atoms, which has a barrier height around 1eV. We intend to make 2.7 nm-size nano structure (unit size of 7x7) with atomic scale isolation of backbond oxidation state. It is very useful because it does not involve processing at high temperature, which could induce damage, or disappearance, of nano structures.

9:20am **NS-WeM4 Dynamics of Br-Si(100)-(2x1): Surface Modification in the Absence of Desorption**, ***E. Graugnard***, *G. Xu, V. Petrova, K.S. Nakayama, J.H. Weaver*, University of Illinois at Urbana-Champaign

The dynamics of surface modification of Si(100)-(2x1) with Br has been studied using variable temperature scanning tunneling microscopy (STM). A clean surface was saturated with Br at room temperature and then heated on the STM stage to 700 K, where no surface modification was expected. To our surprise, we found that the surface was, in fact, modified after heating for several hours. From sequential images of the same area, we were able to observe the formation and growth of novel defect structures, which consist of parallel atom vacancy lines separated by a single dimer row and could grow to be 120 nm in length. The formation of these vacancy lines was accompanied by Si adatom transfer onto the terrace, where regrowth dimers could form. The vacancy lines were often terminated at regrowth chains or dimer vacancy pits. We observed diffusion of regrowth features, but diffusion was limited to regions of the terrace where there were no vacancy structures. Thus, regrowth islands formed on defect-free areas of the terrace, and these islands limited the growth of the defect lines. As the surface roughened, the dynamics of the features became increasingly complicated with the atom vacancy lines converting into dimer vacancy lines and vice versa. The formation mechanisms and dynamics of these surface structures will be discussed.

9:40am **NS-WeM5 Surface, Bulk and Interfacial Analysis of Self-assembled NAno-phase Particle (SNAP) Films**, *L.S. Kasten*, AFRL/MLBT (UDRI), Wright-Patterson AFB, *V.N. Balbyshev*, AFRL/MLBT (UTC), Wright-Patterson AFB, *D.J. Gaspar*, Pacific Northwest National Laboratory, ***M.S. Donley***, AFRL/MLBT, Wright-Patterson AFB

The chemistry, structure, and morphology of Self-assembled NAnophase Particle (SNAP) coatings were investigated using a variety of surface analysis methods. A new method of forming functionalized silica nanoparticles in-situ in an aqueous sol-gel process, and then crosslinking the nanoparticles to form a thin film, is an excellent example of a nanoscience approach to coatings. Results will be presented on the surface morphology, structure, surface chemistry, and chemical structure of SNAP films. The surface chemistry of the films was investigated using X-ray photoelectron spectroscopy (XPS), grazing angle XPS, and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). The surface morphology of films was examined using Atomic Force Microscopy (AFM), while X-ray Diffraction (XRD) was used to investigate film structure. The chemical structure and adhesion mechanism of SNAP coatings were also investigated via TOF-SIMS. Very little chemical difference between the outermost surface and bulk regions is seen, while the adhesion mechanism is related to the nature of the cross-linking agent. The results of these analyses will be discussed in detail and a model of the proposed chemical structure will be presented.

10:20am **NS-WeM7 Electronic Structure of Ag/Cu Striped Nanostructures**, *J. Lobo*, ***E.G. Michel***, Universidad Autonoma de Madrid, Spain, *A. Bachmann,* Universitaet Osnabrueck, Germany, *S. Speller,* Katholieke Universiteit Nijmegen, The Netherlands, *L. Roca,* LURE-CNRS, France, *J. Kuntze, J.E. Ortega*, Donostia International Physics Center and Centro Mixto CSIC/UPV, Spain

The deposition of Ag on a stepped Cu surface gives rise to a periodic faceting of the surface.[1] The superstructure obtained is a very regular distribution of Cu and Ag stripes, with a lateral width in the range of 50-100 Å. The electronic band structure of this nanostructure has been studied using angle-resolved photoemission, for a range of Ag coverages between 0 and 1.2 ML. The photoemission experiments have been performed at the SU8 undulator beam line at LURE (Orsay, France). Surface states at Ag/Cu one-dimensional striped nanostructures are decoupled into Ag- and Cu-like stripe states. A model potential scaled from the infinite system explains the results. As a consequence, both Cu-like and Ag-like states display the characteristic periodicities of the corresponding facet plane. Furthermore, Cu-like stripe states exhibit the same terrace quantum-size effects observed in the infinite Cu(111) vicinal crystals.

[1] A. R. Bachmann, A. Mugarza, J. E. Ortega, and S. Speller, Phys. Rev. B 64, 153409 (2001).

10:40am **NS-WeM8 Patterned Anodization on Aluminum Surfaces**, ***J. Yan***, *V. Goparaju, P. Atanasov, G. López*, The University of New Mexico

Nanoporous aluminum oxide (AAO), highly ordered arrays of uniform and straight pores with tunable features, can be formed through anodization of aluminum in an acid solution. Through-hole AAO membranes have recently been explored as an alternative to conventional lithographic techniques to achieve high resolution, to fabricate fine patterns over a large area, and to minimize costs. The inherent fragility of AAO membranes, however, limits their integration into established microfabrication process. To address this issue, we pre-patterned bulk aluminum sheets and vacuum-evaporated thin aluminum films on glass with silica through a sol-gel process or chemical vapor deposition. After a two-step anodization, we observed highly ordered, uniform and straight nanopores on uncovered areas, and no pores were observed for the covered areas after silica had been removed, thus providing intermittent aluminum supports to the fragile nanoporous AAO. This work allows facile incorporation of AAO in a robust form into microdevices for microelectronics, microfluidics and integrated optics.

Nanometer Structures
Room: Exhibit Hall B2 - Session NS-WeP

Nanometer Structures B

NS-WeP1 Electrostatic Force Spectroscopy of Pure InP and Self-assembled InAs/InP Quantum Dots Studied by Non-contact Atomic Force Microscopy, ***R.-P. Stomp***, McGill University, Canada, *S. Studenikin, P. Poole, A. Sachrajda,* National Research Council, Canada, *P. Grutter*, McGill University, Canada

The purpose of this work is to develop a low-temperature, non-contact Electric Force Microscope (EFM) technique to image semiconductor dots embedded in a dielectric matrix. Non-contact Atomic Force Microscope (nc-AFM) is a very versatile tool to study conductive as well as non-conductive surfaces without damaging them. Our microscope operates at 4.5K with a built-in heater and the possibility of applying a magnetic field up to 8T.[1] In this study we use samples of self-assembled InAs quantum dots embedded in InP grown by chemical beam epitaxy.[2] In the present study, we are investigating the change in resonance frequency of the AFM tip as function of tip-sample bias voltage, or electrostatic force spectroscopy, of bare InP and InAs/InP quantum dot. In case of bare InP an asymmetric frequency-voltage dependence was observed that enabled us to determine the charge sign of the carrier and to deduce the work function potential of the material. This is an on going work, and results on the quantum dot samples will be presented and discussed. It has been previously demonstrated that quantum dot spectra can be measured by EFM, where we can observe the filling of energy levels at low temperature.[3]

[1] M. Roseman., P.Gruetter, Rev. Sci. Instr. 71, 3782 (2000)
[2] J. Lefebvre, P.J. Poole et al., J. Cryst. Growth, 234, 391 (2002)
[3] D. Aykutlu, Y. Yamamoto, cond-mat/0103125 (2001) .

NS-WeP2 Defects in Cylindrical Multi-shell Copper Nanowires, ***J.W. Kang***, *J.J. Seo, H.J. Hwang*, Chung-Ang University, Korea

We have performed atomistic simulations for cylindrical multi-shell (CMS)-type Cu nanowires containing defects. Our investigation has revealed some physical properties that have not been detected in previous studies that have considered defect-free nanowires. Since the vacancy formation energy is lowest in the core of a CMS-type nanowire, a vacancy formed in the outer shell of a CMS-type nanowire naturally migrates toward the core. The maximum of the formation energy of an adhered atom on the surface of a CMS-type nanowire was modeled using a 16-11-6-1 nanowire. The formation energy of an adhered atom decreased when the diameter of the CMS-type nanowire was either above or below the diameter of the peak energy maximum. This investigation found three recombination mechanisms for the vacancy-adhered atom pairs: (i) by direct recombination, (ii) by a kick-in recombination, and (iii) by a ring recombination. Vacancy formation energy calculations show that an onion-like cluster with a hollow was formed, and molecular dynamics simulations for various CMS-type nanowires found that vacancies migrated towards the core. From these, we obtained basic information on the formation of hollow CMS-type metal nanowires (metal nanotubes).

NS-WeP3 Dispersion Relation of the Electromagnetic Waves in the Strong-coupling Superconductive Nano-disk, *V.Z. Lozovski,* ***D.V. Reznik***, Institute of Semiconductor Physics NAS of Ukraine

The investigated system consists of the superconductor disk on the surface a dielectric substrat. We study the dispersion relations of the electromagnetc waves which can be excitated in the system. The dimensions of the disk is order of 100-1000 Å. We take into account the strong coupling of the superconductor in the framework of the enhanced u-v- transformations method which was developed in.[none 1] The dispersion relation are determine by the pole part of the effective susceptibility. The susceptibility is calculated by solution of Lipman-Shwinger self-consistent equation. This equation is solved by exact summation of iteration procedure series proposed in.[2] The initial receptivity was written in terms of u-v-coefficients. One takes into consideration strong-coupling. We take into account the despersion of the phonon energy and perturbation of the electron energy spectrum at Fermi level by electron-phonon interaction. The proposed approach allows us to calculate the effective nonlocal susceptibility for the both weak and strong coupling superconductors. As it is shown in[2] the effective susceptibility can be rewritten as the tensor product of the initial susceptibility and inverse mass operator. Then the electromagnetic waves dispersion relations are determined by the roots of the real part of the determinant of the effective susceptibility inverse matrix. The dispersion curves depend on the electromagnetic properties of the substrate and disk material, the strength of the coupling in superconductor and the geometry of the system (thickness and radius of the disk). Moreover, dispersion depends on coordinate in which electromagnetic field is investigated.

[1] B.I. Khudik, V.Z. Lozovski, A.B. Nazarenko, Phys. Stat. Sol.(b) 148, 297-303 (1988).
[2] V.Z. Lozovski, Physica E, 9, 642-651 (2001).

NS-WeP4 Zinc Sulfide Coating on Carbon Nanotubes, ***H.S. Kim***, University of Florida

Mophological study on zinc sulfide (ZnS) synthesized by a solid state reaction on the outermost shells of multiwalled nanotubes (MWNT) is presented. It was found that ZnS coats the surface of CNTs in the forms of ultrathin films, quantum dots, and nanorods. ZnS nanorods were grown on the surface of MWNTs without the presence of catalyst suggesting the vapor-liquid-solid (VLS) mechanism is not applicable for the here shown growth process. The average diameter of nanorods on MWNTs is about 140 nm and the length is around 250 nm.

Zinc Sulfide Coating on Carbon Nanotubes.

NS-WeP5 Gas Sensor Based on Metal and Metal Oxide Individual Nanowires and Nanowire Arrays, ***Y. Zhang***, *A. Kolmakov, G. Cheng, M. Moskovits*, University of California, Santa Barbara

We report on the approach, which can constitute a novel versatile platform for micro- and nanosensor application. Arrays of nanowires with tunable diameters and length in the range of 10-100 nm and 5-200 micrometers, respectively, were fabricated from the catalyticaly active materials inside close-packed nanochannel alumina templates. Electrodes deposited on the surfaces of these nanostructures provides electrical contacts which with the incorporated heaters determines the device architecture. In particular, metal (Cu, Ag, Pb, Pd) and metal oxide (SnO_2) individual nanowires and their arrays were tested using HRTEM, XPS and Auger spectroscopy. Chemical reactivity and gas sensitivity toward hydrogen and carbon monoxide of individual and assemblies of Pd and SnO_2 nanowires were assessed using conductivity measurements and TPD analysis. These structures based on single nanowires and nanowire arrays offer full range of options useful to gas sensing, including robustness, high surface-to-volume ratio, small size if required, functionalization via doping, integrability into other devices.

NS-WeP6 Switching Behavior of Plasma Polymer Thin Films Containing Metal Nanoparticles, ***A. Kiesow***, Fraunhofer-Institute for Mechanics of Materials Halle, Germany, *J.E. Morris,* Portland State University, *C. Radehaus,* Technical University Chemnitz, Germany, *D. Katzer, A. Heilmann*, Fraunhofer-Institute for Mechanics of Materials Halle, Germany

The nanostructures of plasma polymer thin films containing silver-particles are characterized by particle size and particle shape distribution and have been investigated by means of transmission electron microscopy (TEM). The electrical properties have been determined and correlated with the nanostructures. Three different nanostructural types could be observed: metallic, percolation, and dielectric region. While for the metallic and dielectric regions, respectively, metallic conduction and thermally activated tunneling can be identified as the dominant conduction mechanisms, a switching effect was observed for the region near percolation. These drastic abrupt changes in the current (I) -voltage (V) behavior (of up to 6 orders of current magnitude) are reversible, and can be defined as threshold bistable switching. The threshold voltage is dependent on the switching frequency.

NS-WeP7 Frequency Dependence of Local Electronic Properties: Nanoimpedance Spectroscopy, *S.V. Kalinin,* ***R. Shao***, *D.A. Bonnell*, University of Pennsylvania

Progress in nanoelectronics necessitates an understanding of the structure and properties of materials on the local level. While substantial advances have been made in local property measurement particularly based on scanning probes, they have accessed either dc properties or ac properties at a single frequency. The ability to probe the frequency dependence of local electronic properties would lead directly to mechanistic considerations of trap states at defects, scattering at interfaces, etc., in nano or molecular electronics. We have developed a local spectroscopy that determines tip-surface impedance directly over a wide frequency range (40 Hz - 110 MHz) with nanometer spatial resolution. This approach is generalized to spatially resolved nanoimpedance spectroscopy and imaging. The technique will be illustrated on 2-D structures, an atomically abrupt interface and a nano wire; and a 3-D structure, a nano particle on a substrate.

Nanometer Structures
Room: C-207 - Session NS+EL-WeA

Nanolithography & Self Assembly
Moderator: P.S. Weiss, The Pennsylvania State University

2:00pm **NS+EL-WeA1 Recent Development in Nanoimprinting Lithography**, ***L.J. Guo***, University of Michigan **INVITED**

Nanoimprinting lithography is an emerging technology that promises ultra-high resolution, high throughput and low cost. Unlike soft contact printing that uses an elastomer stamp, nanoimprinting uses a hard mold to create nanoscale features by directly imprinting into the polymer film at a temperature higher than its glass transition temperature (T_g). Sub-10 nm resolution and large area patterning have already been demonstrated in the past. This talk will present some recent development in nanoimprinting lithography, including imprinting at reduced temperature by using low T_g polymer materials; a reversed imprinting technique that enables "inking" of polymer materials onto a substrate, and patterning on non-flat surfaces without planarization, as well as the creation of simple 3D structures. This reversal nanoimprinting method also offers a unique advantage by allowing imprinting onto a flexible substrate that is otherwise difficult to spin-coat with polymer film, and we have demonstrated this by imprinting on a 50 mm thick flexible polyimide film. Nanoimprinting not only has the ability to pattern nanoscale features, but also it is compatible with polymer material processing. Based on these characteristics, we have applied it to two new applications. The first one is polymer micro-ring resonator photonic device fabricated by nanoimprinting, which is in the form of a micro-ring closely coupled to a waveguide, and offers unique properties such as narrow bandwidth filtering, high quality factor, compactness, and could find important applications in integrated photonic circuits. The second application is in organic polymer light emitting diodes (OP-LEDs), where we have developed a simple method based on nanoimprinting to define the OP-LEDs with pixel size ranging from nano- to micron-scale. The demonstration of those small size OP-LEDs indicates the possibility of fabricating ultra-high resolution OP-LEDs for applications such as micro-displays.

3:00pm **NS+EL-WeA4 Fabrication of Molecular Nanostructures by Scanning Near-Field Optical Lithography**, ***K.S.L. Chong***, *S. Sun, G.J. Leggett*, University of Sheffield, UK

Nanoscale patterns of self-assembled monolayers (SAMs) on gold and silver can be fabricated by a new technique called scanning near-field photolithography (SNP).[1] In SNP, a 244 nm laser coupled to a scanning near-field optical microscope is used to carry out nanometre scale photopatterning of SAMs. The photooxidised SAMs can be dipped into a solution of a different thiol, which displaces the oxidised material and adsorbs at the surface. Chemical patterns with linewidths of 40 nm were routinely obtained though patterns as small as 25 nm have been observed by friction force microscopy. The oxidised pattern can also be transferred to the underlying substrate by wet etching where linewidths of 80 nm have been obtained on gold substrates. Because of the ease by which SAMs can be patterned by this method, SNP can be routinely used to create nanoscale molecular patterns. Nanoscale patterns in SAMs can be used as templates for the attachment of biomolecules offering another approach to the miniaturisation of biological devices. Preliminary data have shown that proteins may be successfully immobilised to micron-scale patterned monolayers created using similar photochemistry. These methods are currently being combined with SNP in order to create biological nanostructures.

[1] Shuqing Sun, Karen S.L. Chong and Graham J.Leggett, J.Am.Chem.Soc, 2002, 124, 2414.

3:20pm **NS+EL-WeA5 Photoinduced Anisotropy of Second-Harmonic Generation from Azobenzene-Modified Alkylsiloxane Monolayers**, *Y.W. Yi*, ***T.E. Furtak***, Colorado School of Mines, *M.J. Farrow, D.M. Walba*, University of Colorado

Non-contact alignment of substrates in liquid crystal displays offers the advantage of reduced contamination and minimal surface charging. This approach also provides a means of reversible alignment after a device has been assembled. With this objective we have synthesized self-assembled monolayers based on dimethylaminoazobenzene units covalently attached to a glass surface by means of a short alkylsiloxane anchor (azo-SAM). The resulting architecture favors an orientation in which the axis of the azobenzene group should be nearly parallel to the surface with an isotropic azimuthal distribution. Under illumination with polarized UV light the trans-cis isomerization and subsequent relaxation serves to wiggle the molecule into an orientation perpendicular to the UV optical field. We have tested this scenario using optical second harmonic generation. We are able to identify a surface order parameter that characterizes the photoalignment of the azobenzene group. These data correlate with the recently reported behavior of nematic liquid crystal cells containing one substrate treated with the same azo-SAM.[1] This work is supported by NSF MRSEC grant DMR-9809555.

[1] "Liquid Crystal Alignment by Photo-Buffing Azo-SAMs", G. Fang, N. A. Clark, J. E. Mcclennan, M. Farrow, D. Walba, March Meeting of the American Physical Society, Indianapolis (3/20/20002).

3:40pm **NS+EL-WeA6 Nanostructuring of Hydrogenated Silicon Surfaces by Electron Beam Irradiation of Self-assembled Hydroxybiphenyl Monolayers**, *A. Küller, W. Geyer, V. Stadler*, Universität Heidelberg, Germany, *T. Weimann*, Physikalisch Technische Bundesanstalt, Germany, *W. Eck*, ***A. Gölzhäuser***, Universität Heidelberg, Germany

A new species of aromatic self assembled monolayers, hydroxy biphenyl, are formed on hydrogen terminated silicon and used as a negative tone electron beam resist. The formation of the monolayer and the electron induced modifications are observed by X-ray photoelectron spectroscopy. Nanometer patterns in the molecular layer were defined by low energy electron proximity printing as well as via conventional e-beam lithography. The patterns are transferred into silicon by a wet chemical etching process in KOH. The fabrication of patterns with lateral dimensions below 20 nm is demonstrated.

4:00pm **NS+EL-WeA7 Electrode Modification by Electron-induced Patterning of Self-assembled Monolayers**, ***B. Völkel***, *G. Kaltenpoth, T. Felgenhauer, W. Geyer, H.T. Rong*, Universität Heidelberg, Germany, *M. Buck*, University of St Andrews, UK, *A. Gölzhäuser*, Universität Heidelberg, Germany

Nanopatterns on electrode surfaces control the electrochemical deposition. An example is the formation of nanoscale dots or wires via the preferred nucleation at defects and step edges.[1] We present a method to artificially fabricate such electrochemical templates via coating of electrodes with self-assembled monolayers (SAMs) and subsequent patterning by electron beams. SAMs provide a flexible route to modify electrode surface properties via their molecular structure, ranging from inert alkane chains, which exhibit a blocking behavior, to redox active moieties. The e-beam patterning offers perspectives to generate arrays of microelectrodes with specific functionality. We coated gold electrodes with SAMs of w-(4'-methyl-biphenyl-4-yl)-dodecylthiol (BP12) and hexadecanethiol (HDT) and patterned them by electron beam lithography. The subsequent copper deposition in an electrochemical cell revealed that the e-beam patterned alkanethiol behaves opposite than e-beam patterned biphenyl. Similar to the behavior of these materials as resists,[2] HDT acts as a "positive template" leading to copper deposition only on the irradiated parts. BP12 acts as a "negative template", where the irradiated biphenyl layer is cross linked and exhibits a blocking behavior,[3] hence copper is only deposited on the non-irradiated parts. By using these effects well defined Cu nanostructures could be generated.

[1] M. P. Zach, K.H. Ng, R.G.Penner, Science 290, 2120 (2000).

[2] A. Gölzhäuser, W. Geyer, V. Stadler, W. Eck, M. Grunze, K. Edinger, T. Weimann, P. Hinze, J. Vac. Sci. Technol B 18, 3414 (2000).

[3] T. Felgenhauer, C. Yan, H.T. Rong, A. Gölzhäuser, M. Buck, Appl. Phys. Lett. 79, 3323 (2001).

4:20pm **NS+EL-WeA8 Electrochemically Controlled Film Formation of Self-assembled Monolayers of Biphenyl-based Thiols**, *I. Thom, B.J. Livesay*, StAndrews University, UK, ***P. Cyganik***, Jagiellonian University, Poland, *M. Buck*, StAndrews University, UK

Usually self-assembled monolayers (SAMs) of thiols are prepared by mere immersion of the substrate in a solution containing the respective thiol. Whereas a number of preparation parameters such as the thiol concentration, temperature, immersion time, or solvent type have been investigated in some detail, no systematic studies have been performed on how the substrate potential affects the kinetics of film formation and the resulting SAM structure. Since the potential controls the bonding of a thiol to the substrate, i.e. its stability, the rate of adsorption/desorption and the mobility of the thiols are affected and, consequently, a pronounced influence of the potential can be expected. Using thiols which are characterized by a biphenyl unit and an alkane spacer chain between the aromatic moiety and the SH group we have studied the kinetics of film formation using nonlinear optical spectroscopies and scanning tunneling microscopy. Both the kinetics of film formation and the final film structure undergo significant changes ranging the potential from values near the reductive desorption of thiols to values around zero volts.

4:40pm **NS+EL-WeA9 Modification of Self-assembled Monolayers by Free Radical-dominant Plasma: The Effect of the Chain Length and the Substrate**, *M. Zharnikov*, *S. Frey*, ***M. Grunze***, Universität Heidelberg, Germany, *M.-C. Wang*, *J.-D. Liao*, *C.-C. Weng*, Chung Yuan Christian University, Taiwan (ROC), *R. Klauser*, Synchrotron Radiation Research Center, Taiwan (ROC)

Synchrotron-based high-resolution photoelectron spectroscopy was applied to study the modification of aliphatic and aromatic thiol-derived self-assembled monolayers (SAMs) on (111) gold and silver substrates by a nitrogen-oxygen downstream microwave plasma. It was found that the plasma treatment does not result in a "soft" modification of SAMs, but in their massive damage and disordering. Contrary to the electron beam treatment, both the aliphatic and aromatic films became modified and damaged in a similar way, with the extent of the changes depending on the length of the molecular chains and, above all, on the substrate. For SAMs on Au a profound desorption of the entire SAM constituents and a complete fragmentation of the residual hydrocarbons is observed. For the SAMs on Ag only partial desorption and oxidation took place and, for short treatment times, the films remained practically intact. The desorption of molecular species was preceded by the oxidation of the pristine thiolates to weakly-bonded sulfones, which occurred after the penetration of chemically active oxygen species into the S/substrate interface via defect sites. Such a mechanism clearly explains the observed dependence of damage extent on the SAM thickness and emphasizes the importance of the strength of the thiolate-substrate bond. Thus, a stronger thiolate-substrate bond can be suggested for Ag as compared to the Au substrate. In addition, considering the similarity of the plasma-induced processes and UV-photooxidation, one can extend the major conclusions obtained for the plasma treatment to UV-photooxidation.

Nanometer Structures
Room: C-207 - Session NS-ThM

Single Molecule Devices
Moderator: T. Michalske, Sandia National Laboratories

9:40am **NS-ThM5 Toward the DNA Electronics**, *T. Kawai*, ***H. Tabata***, Osaka University, Japan **INVITED**

DNA is one of the most promising molecules as the scaffold for molecular nanotechnology toward nanoelectronics. DNA has the special double helix structure with p-electron cores of well-stacking bases for one-dimensional charge transport. The investigations of DNA on the nanostructure, electrical conductivity and electronic states have significant implications for the application of DNA in electronic devices and in DNA-based electrochemical biosensors. It is worthily noted that divergent and controversial conclusions were reported in DNA-mediated charge transport. The direct measurements of the intrinsic electrical characteristics of polynucleotides using a conducting probe atomic force microscope have been performed using self-assembled two dimensional DNA networks. It has been revealed that DNA without carrier doping is a wide-gap semiconductor. Upon carrier doping, poly(dG)?poly(dC) show the p-type behaviors, presumably due to the shallow ionization potentials of DNA bases. The conductivity of these molecules has been successfully controlled by chemical doping, electric field doping and photo-doping. It is found that the poly(dG)?poly(dC) has the best conductivity and can act as a conducting nanowire. The conductive mechanism is discussed by the charge hopping model based on the SPM observation of DNA nanostructure. For the advanced construction of DNA based molecular memories and circuits, gold and cobalt particles have been assembled within the two-dimensional DNA networks. Gold particles are arranged artificially with DNA molecular template as an average separation distance of 260nm. The pattern of the complex is controlled by changing the concentration of the DNA solution, suggesting that this method is effective in achieving the positional control of nano-scale molecular memories and circuits.

T.Kawai et al; Appl.Phys.Lett.,77,3848(2000), Appl.Phys.Lett., 77,3105(2000), Surf.Sci.Lett,432,L611(1999), J.Vac.Sci.Technol.B17,1313(1999), Jpn.J.Appl.Phys. 39, 581(2000), 38,L606(1999), 38,L1211(1999)

10:20am **NS-ThM7 Lander Molecules Acting as Nanomolds on Cu(110)**, ***F. Rosei***, *Y. Naitoh*, *P. Thostrup*, *M. Schunack*, University of Aarhus, Denmark, *P. Jiang*, *A. Gourdon*, CEMES-CNRS, France, *E. Laegsgaard, I. Stensgaard,* University of Aarhus, Denmark, *C. Joachim,* CEMES-CNRS, France, *F. Besenbacher*, University of Aarhus, Denmark

The adsorption of a large organic $C_{90}H_{98}$ molecule, known as the Lander molecule, is studied by Scanning Tunneling Microscopy (STM) on a Cu(110)surface.[1] Manipulation experiments on isolated Landers anchored at step edges at low temperatures, reveal a restructuring of the Cu steps. Surprisingly, when the molecule is removed from the step, a tooth-like structure appears (two atomic rows in width), corresponding to the distance between the spacer legs within the molecule. Scanning Tunneling Spectroscopy measurements are in progress to investigate the electronic states of the Lander on Cu(110). This is the first prototype of more complex molecular machines able to selffabricate nanostructures with the prospect of developing planar and atomically precise interconnections of molecular nanodevices. Furthermore, by nanopatterning the substrate via O_2 chemisorption and using this template for Lander adsorption, we show that it is possible to self-assemble long 1D molecular wires. This type of assembly opens new possibilities for ordering organic molecules on surfaces.

[1] F. Rosei et al., Science 296, 328 (2002).

10:40am **NS-ThM8 Electronic Properties of Individual Defects in Molecular Circuit Elements**, ***S.V. Kalinin***, *M. Freitag, A.T. Johnson, D.A. Bonnell*, University of Pennsylvania

The local property variations of nanowires, nanotubes, and functional molecules dictate the behavior of nanoelectronic devices. Scanning Gate Microscopy (SGM) provides information regarding individual defects during dc transport. To determine local properties of defects during ac transport, we have developed Scanning Impedance Microscopy (SIM). In combination these measurements quantify the electronic structures of individual defects in nanocircuits. A circuit is configured with a molecule or nanotube on an oxidized Si wafer with metal contacts at each end and a back electrode. In the case of a semiconducting single walled carbon nanotube the defects become depleted at a gate voltage that is related to the local electronic structure of the defect. The depletion voltage for each individual defect can be accessed in several ways. In SGM the current through the circuit is measured and the scanning probe tip provides a local gate voltage. In SIM an ac signal is applied across the circuit while the tip measures the local potential amplitude. The gate voltage in this case can be applied both from the back electrode (back gate) and the tip (tip gate). In both SGM and SIM the defects are manifest as sharp discontinuities in the image when they are depleted. The gate voltage dependence of the image contrast is a direct measure of the difference in Fermi energies at these defects. A comparison of results from nanotube circuits and molecular circuits will be presented and implications to local electronic structure and transport mechanisms will be discussed.

11:00am **NS-ThM9 Single Molecular Switches**, ***P.S. Weiss***, The Pennsylvania State University **INVITED**

We use intermolecular interactions to direct molecules into desired positions to create nanostructures, to connect functional molecules to the outside world, and to serve as test structures for measurements on single or bundled molecules. We use and develop scanning probe microscopes to determine both local structures and the electronic and other local properties. We have applied these to isolate molecules with electronic function to determine the mechanisms of function, and the relationships between molecular structure, environment, connection, coupling, and function. We have been able to demonstrate that single molecules can function as multistate switches, and have determined important aspects of the mechanism, function, and persistence of switching. We will discuss the origins of switching and the relevant aspects of the molecular structure and environment required.

11:40am **NS-ThM11 High-bias Conductance in Single-atom Contacts of Au Alloys**, *J. Mizobata, A. Fujii, S. Kurokawa,* ***A. Sakai***, Kyoto University, Japan

Single-atom contacts of Au have a strong tendency to exhibit a conductance quite close to 1G0, one quantum unit of conductance, as long as a bias voltage is less than 1 V. They show a well-defined peak at 1G0 when their conductance data are plotted in a histogram. With increasing the bias, however, the 1G0 peak decreases in height and disappears at 1.9 V at room temperature. This result suggests that a single-atom 1G0 contact of Au becomes unstable under high biases, perhaps due to an extremely high current density in the contact, which may cause electromigration or current-induced bond weakening. In an effort to improve the stability of single-atom contacts of Au, we have recently carried out experiments on Au alloy contacts, containing Ag and Pt as solute atoms, and compared their high-bias conductance with that of pure Au. All measurements were performed at room temperature with varying the bias from 0.2 V to 2.0 V. In the case of an Au20wt%Ag alloy, we found that the 1G0 peak is systematically higher than that of pure Au for 0.2-1.2 V. The Ag alloying is thus effective for improving the stability of Au single-atom contacts against high contact current. However, the 1G0 peak height difference between AuAg and pure Au disappears for higher biases, and the positive effect of Ag alloying is somehow limited for biases lower than 1.4 V. On the other hand, an alloying with 20wt%Pt yields no enhancement in the 1G0 peak height, and the peak disappears at 1.0 V. Therefore the effect of alloying on the high-bias 1G0 conductance of Au depends on an alloying element.

Magnetic Interfaces and Nanostructures
Room: C-205 - Session MI+NS-ThA

Magnetic Imaging
Moderator: G.D. Waddill, University of Missouri-Rolla

2:00pm **MI+NS-ThA1 Atomic-scale Surface Magnetic Structures of Mn_3N_2 Observed by Spin-polarized Scanning Tunneling Microscopy**, ***H. Yang***, *A. Smith,* Ohio University

The development of spin-polarized scanning tunneling microscopy (SP-STM) has made possible the imaging of surface magnetic structures in real space down to the atomic scale.[1] In this talk, we will discuss the magnetic structure of Mn_3N_2 (010) surface investigated using SP-STM with antiferromagnetic (AFM)-coated tungsten (W) tips. The Mn_3N_2 film was grown by molecular beam epitaxy. The surface structure of the film was studied in-situ. Normal STM images of Mn_3N_2 (010) obtained using W tips reveal row structures, corresponding to Mn atoms at the intersection of surface and N vacancy planes which occur every third atomic layer.[2] By using AFM-coated W tips, we observed a modulation in the height of the rows, which is attributed to the spin-polarized effect in which the tunneling current has a component which depends on the angle between the surface and tip magnetic moments. The row modulation implies that the Mn moments are ferromagnetic within a row but AFM from row to row. We show, using a new method, that it is possible to extract the magnetic component, which is proportional to the integrated local magnetization density of states.[3] The extracted magnetic component is compared with various surface spin models, which will be discussed. This work is supported by NSF under Grant No.9983816.

[1] S. Heinze, M. Bode, A. Kubetzka, O. Pietzsch, X. Nie, S. Blugel, and R. Wiesendanger, Science, 288, 1805 (2000).
[2] H. Yang, Hamad Al-Brithen, Arthur R. Smith, J. A. Borchers, R. L. Cappelletti, and M. D. Vaudin, Appl. Phys. Lett., 78, 3860 (2001).
[3] D. Wortmann, S. Heinze, Ph. Kurz, G. Bihlmayer, and S. Blugel. Phys. Rev. Lett., 86, 4132 (2001).

2:20pm **MI+NS-ThA2 Spin-Orbit Effects on Fe/W(110) Revealed by Scanning Tunneling Spectroscopy**, ***M. Bode***, University of Hamburg, Germany, *S. Heinze,* IBM Research Division, *A. Kubetzka, O. Pietzsch,* University of Hamburg, Germany, *X. Nie, G. Bihlmayer,* Forschungszentrum Jülich, Germany, *S. Blügel,* Universität Osnabrück, Germany, *R. Wiesendanger*, University of Hamburg, Germany

We have studied the dependence of the spin-averaged tunneling current on the direction of the magnetization experimentally on the well-defined model system Fe/W(110) with its well-known magnetic structure at the nanometer scale.[1,2] We found by scanning tunneling spectroscopy (STS) and first-principles calculations that the surface electronic structure of an Fe double layer on W(110) depends on the orientation of the magnetization. From a detailed analysis of the electronic structure we deduce how the signature of the magnetization direction is imprinted via the spin-orbit interaction. Our analysis reveals that it is not the splitting of bands but changes of the orbital character of certain bands which affects the tunneling current. As an important implication of this effect the magnetic nanostructure of surfaces can be investigated with a conventional nonmagnetic tip, similar to an earlier proposal by Bruno et al.[3] The underlying physics of the spin-orbit dependent differential conductivity can be considered as the static limit of the magnetic linear x-ray dichroism or the ballistic or tunneling analogon of the anisotropic magnetic resistance of ferromagnets.

[1] O. Pietzsch et al., Phys. Rev. Lett. 84, 5212 (2000).
[2] M. Bode et al., Phys. Rev. Lett. 86, 2142 (2001).
[3] P. Bruno, Phys. Rev. Lett. 79, 4593 (1997).

2:40pm **MI+NS-ThA3 Magnetic Imaging and Spectroscopy of $Fe_xNi_{(1-x)}$ Thin Films on Cu(111)**, ***Y. Sato***, *T.F. Johnson, S. Chiang,* University of California, Davis, *M. Hochstrasser, J.G. Tobin,* Lawrence Livermore National Laboratory, *A. Scholl,* Lawrence Berkeley National Laboratory, *J.A. Giacomo, D.B. Hoffman,* University of California, Davis

We are studying the system of FeNi/Cu(111) to understand the surface/interface magnetism relevant to the application of the giant magnetoresistive effect to magnetic recording heads. We have used X-ray Magnetic Linear Dichroism (XMLD) and Photoemission Electron Microscopy (PEEM) at the Advanced Light Source, and Low Energy Electron Microscopy (LEEM). Using XMLD, the dichroism signals from both the Fe and Ni peaks were measured, and the asymmetries were calculated. Both the Fe and Ni asymmetries as a function of temperature have been fit to the theoretical curve to extract the critical exponent β. Preliminary analysis indicates that for thicker films, the values are consistent with 3D mean-field magnetic models. As a function of Fe concentration x, the total weighted asymmetry, $A_T= xA_{Fe}+(1-x)A_{Ni}$, where A_{Fe} and A_{Ni} are the respective elemental asymmetries, shows a monotonic increase from 2% to a maximum of 8.5% for x~65%, near the bulk Invar concentration. For higher x, the asymmetry is quenched, indicating a magnetic transition taking place in the film system. This magnetic instability for high x agrees with the trends in Curie temperature as a function of x, as measured from XMLD spectra, PEEM data, and previous work on FeNi/Cu(100).[1] The PEEM images show a change in the domain structure of the films for x~42-55%. The domain structures are defined well by 180° domain walls, and their size is much bigger than for other concentrations. The magnetization appears to align along one of the crystal axes. Low Energy Electron Microscopy images of the growth of the films will also be shown.

[1] F.O.Schumann, S.Z.Wu, G.J.Mankey, R.F.Willis Phys.Rev.B 56, 2668 (1997).

3:00pm **MI+NS-ThA4 Falicov Award Presentation**

3:20pm **MI+NS-ThA5 Magnetic Resonance Force Microscopy at Millikelvin Temperatures**, ***H.J. Mamin***, *R. Budakian, D. Rugar,* IBM Almaden Research Center **INVITED**

Magnetic resonance force microscopy (MRFM) offers the promise of combining the spectral resolving power and three-dimensional imaging capabilities of magnetic resonance with the high resolution of scanning probe techniques. The greatest payoffs are expected once it is possible to detect and manipulate individual spins. There is now evidence that one of the greatest obstacles to reaching this goal is that of thermally-driven fluctuations in the magnetic tip, which interfere with the quantum state of the spins. For this reason, we have begun an effort to perform MRFM at millikelvin temperatures in a dilution refrigerator. Some essential technical improvements have been incorporated, included detection of the cantilever displacement with ultralow optical powers, and ultra-efficient generation of microwave fields using a superconducting resonator. Using this newly developed apparatus, we have successfully demonstrated MRFM on an ensemble of electron spins at millikelvin temperatures. We are investigating various nonequilibirum effects, including spin relaxation times, which will have important implications for the feasibility of single spin detection.

4:00pm **MI+NS-ThA7 Magnetic Force Microscopy Study of Various Lithography Patterned Magnet Arrays**, ***X. Zhu***, *P. Grutter,* McGill University, Canada, *V. Metlushko,* University of Illinois at Chicago, *B. Ilic,* Cornell University, *Y. Hao, F. Castano, S. Haratani, C.A. Ross, B. Vogeli, H.I. Smith*, Massachusetts Institute of Technology

Magnetic force microscopy (MFM) with in-situ magnetic field has been used to study lithography pattered magnet arrays: elongated elements, rings, disks, empty squares and sub 100 nm pseudo spin valve structures (PSV) (NiFe/Cu/Co). Great care has been taken to reduce the MFM tip stray field induced irreversible distortion by choosing a constant height mode, using small magnetic moment tips, operating in vacuum, and using a digital PLL.[1]This allows us to study the details of magnetic structures. For example, the nature of the head-to-head domain wall in a permalloy ring can be revealed, and the vortex structure with a core singularity in a permalloy disk can be found by high resolution imaging. In the PSV structures, the parallel and two different antiparallel configurations for both magnetic layers (NiFe and Co) in an element can be distinguishable. A local hysteresis loop technique has been developed to study the switching behavior of individual elements.[2] In a permalloy disk, the abrupt switching due to a nucleation or annihilation process has been revealed by monitoring cantilever frequency shift at a fixed location above the disk while sweeping the external magnetic field. In a PSV structure, the abrupt switching for both individual layers is clearly distinguishable. The hysteresis loop of patterned arrays can be obtained by MFM in the presence of an external magnetic field. The anisotropy induced by interdot coupling can be found in a closely packed square lattice disk array which shows a much smaller nucleation field along the (100) direction than the (110) direction. In the PSV structures, the layer coupling and the broad switching field distribution have been investigated through major and minor hysteresis loop obtained by MFM.

[1] X. Zhu, et al., J. Appl. Phys., May (2002).
[2] X. Zhu, et al., to be published in Appl. Phys. Lett.

4:20pm **MI+NS-ThA8 Magnetic Dipoles in Patterned Magnetic Metal Dot Arrays**, ***T.-H. Kim***, *J.H. Choi, Y. Kuk*, Seoul National University, South Korea

Magnetic dipole arrangement was studied with scanning tunneling microscope and magnetic force microscope (MFM) in patterned magnetic metal dot arrays. Magnetic dot arrays on silicon substrate were made by following procedures: (1) electron beam lithography, (2) shadow mask deposition, (3) electro-chemical anodizing of aluminum layer and successive deposition of magnetic metals. MFM image reveals individual magnetic dipole with small dot-dot interaction. The correlation between the shape anisotropy with the direction of magnetization will be discussed.

Nanometer Structures
Room: C-207 - Session NS-ThA

Nanowires
Moderator: D.A. Bonnell, University of Pennsylvania

2:00pm **NS-ThA1 Biofunctionalized Nanowires for Biosensing and Assembly**, ***C.D. Keating***, The Pennsylvania State University **INVITED**

This presentation will focus on the characterization, derivatization, and some applications of segmented metallic nanowires having stripes of different metals along their length. These particles are prepared by sequential electrodeposition of metals (e.g. Au, Ag, Pd, Pt, Co) within the pores of alumina or polycarbonate templates, and typically range from 30-300 microns in diameter and up to 10 microns in length. They can be released from the template and derivatized with proteins or nucleic acids for use in sensing or assembly. The metal segments can be used as an optical barcode to enable multiplexed bioanalysis or as a chemical pattern to spatially control (bio)chemical derivatization along the length of the particle. Both multiplexed bioanalytical applications and DNA-directed nanowire assembly will be discussed.

2:40pm **NS-ThA3 Aligned Dielectrophoretic and Electrophoretic Deposition of Single Wall Carbon Nanotubes**, ***P.E. Pehrsson***, Naval Research Laboratory, *J.W. Baldwin*, NRC/NRL Postdoctoral Fellow, Naval Research Laboratory

Carbon nanotubes offer real promise for a variety of nanotechnology applications such as resonator arrays for RF electronics, sensors, and other devices. We use dielectrophoresis (DEP) and electrophoresis (EP) to position nanotubes on surfaces and then measure their electrical conductivity. We vary the solution concentration and sonication procedures to control tube aggregation. We also use functionalized single-wall nanotubes (SWNTs), e.g. fluorinated, oxidized or with attached organosilanes. Functionalization can introduce potentially charged species such as carboxylic acid and may also change the nanotube's conductivity and permittivity, both of which may enhance its susceptibility to dielectrophoresis. The resistance across a gap spanned by a few tubes is typically above a $M\Omega$, but resistance across the gap drops sharply (to 10-20 $k\Omega$) at higher tube densities, possibly due to formation of a continuous percolation network. Tube purity is critical for good deposition. Contaminant particles in the suspension alter the deposition under specific deposition conditions. Some particles are unassociated with nanotubes and respond to the electric fields like other dielectric particles. Other particles (possibly leftover Ni nanocatalyst or amorphous carbon) are attached to the tubes and may pull them along in response to the fields. We are evaluating the interplay between surface chemistry on the nanotubes and at the electrode/liquid interface and the forces governing DEP and EP. DEP makes particles move in the direction of higher or lower electric field depending on the relative frequency-dependent conductivity and permittivity of the solvent and particle, and the particle size, shape, and surface chemistry. It could ultimately solve two of the biggest problems impeding the exploitation of carbon nanotubes; 1) separation of metallic and semiconducting nanotubes; and 2) removal of non-nanotube contaminants without the need for aggressive acid cleaning.

3:00pm **NS-ThA4 Functionalizing Molecular Lines on H-Si(100)**, ***P. Kruse***, *D.D.M. Wayner*, *R.A. Wolkow*, National Research Council of Canada

SPM-based lithography on H-terminated Si(100) and Si(111) surfaces has received considerable attention in recent years. It is based on stepwise controlled removal of H-atoms and subsequent reaction of molecules with the resulting Si-radicals (dangling bonds). Previously, we have reported the remarkable capacity of styrene to induce a chain reaction on these surfaces, resulting in self-directed line growth along dimer rows in the case of the Si(100) surface.[1] We have now examined a number of avenues for creating lines with built-in functionality. The incorporation of heteroatoms such as nitrogen in vinyl pyridine would be desirable, but the facile interaction of the lone electron pair of the nitrogen atom with the silicon dangling bonds prevents line growth. Aldehydes such as benzaldehyde are shown to undergo the same line growing mechanism as their vinyl compound analogues such as styrene. This offers the unique opportunity to create functionalized molecular lines by exposing the surface to dialdehydes. It is shown that in a rigid molecule such as terephthaldicarboxyaldehyde only one aldehyde group per molecule reacts with the surface whereas the other group is available for further reactions. This study seeks to open avenues for customizing molecular lines from self-directed growth for a wide variety of applications. Lines with preserved reactive groups or metal-complexing abilities can serve as devices or conducting wires on the surface and become building blocks of molecular electronics.

[1] G.P. Lopinski, D.D.M. Wayner, and R.A. Wolkow, Nature 406, 48 (2000).

3:20pm **NS-ThA5 Growth, Properties and Applications of Semiconductor Nanowires[1]**, ***L. Samuelson***, Lund University, Sweden **INVITED**

One-dimensional (1D) semiconductors, or nanowires, have interesting physical properties and may offer possibilities to realize ultra-small electronic and photonic devices[2] as well as new kinds of circuitry.[3] Well defined nanowires (or nanowhiskers) can be formed using size selected catalytic nanoparticles to induce growth. By locating individual nanoparticles on predefined locations on a substrate also the position of the nucleation of individual nanowires may be controlled.[4] It was recently shown that not only homogeneous nanowires, but also multi-heterostructures with good electronic properties may be formed within a nanowire, even for combinations of materials having large differences in their lattice constants.[5] I will describe results from our studies of the electronic properties of heterostructures and will present examples of 1D heterostructure nanoelectronic devices created in nanowire systems.

@super 1@ I want to ackhowledge contributions from a number of students and colleagues (see author lists in refs. 5 and 6), especially Jonas Ohlsson on whisker growth, Mikael Bj@um o@rk on physics investigations and Prof. Reine Wallenberg on transmission electron microscopy.

@super 2@ K. Hiruma et al., "GaAs p-n junction formed in quantum wire crystals", Appl. Phys. Lett. 60, 745 (1992)

@super 3@ Y. Huang et al., "Directed assembly of one-dimensional nanostructures into functional networks", Science 291, 630 (2001)

@super 4@ B. J. Ohlsson et al., "Size-, shape-, and position-controlled GaAs nano-whiskers", Appl. Phys. Lett. 79, 3335 (2001)

@super 5@ M. T. Bj@um o@rk et al., "One-dimensional steeplechase for electrons realized", Nano Lett. 2, 87 (2002).

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4:00pm **NS-ThA7 Metal-Catalyzed Nanowires for Integrated Devices and Interconnections**, ***T.I. Kamins***, *X. Li*, *T. Ha*, *R.S. Williams*, Hewlett-Packard Laboratories

As integrated-circuit technology progresses, interconnections between active devices become more important in determining overall circuit and system density and performance. Without special circuit techniques, interconnection delays can degrade circuit performance even if the device speed improves. Defining multiple levels of fine wires by conventional lithography becomes increasingly difficult as dimensions decrease, and defining wires by advanced techniques becomes attractive. Wires can be formed at the nanoscale by nanoimprint lithography or by self-assembly techniques such as anisotropic lattice-mismatched epitaxy or metal-catalyzed nanowire growth. The latter is especially attractive because the surfaces are formed by growth, rather than by etching, which can cause crystal damage. The catalyzing nanoparticles can be in the liquid phase or possibly in the solid phase during growth. Nanowires formed by self assembly can be used as interconnections between devices, and devices can also be formed within the nanowires, allowing close integration of the nanowires and devices. If the nanowire is uniformly doped, tradeoffs must be made between the series resistance in the interconnection and the ability to deplete the wire in the device region, limiting performance. Requiring the maximum depletion region to be at least half the wire diameter limits the conductance of the interconnection, and therefore the charging time of the device, to possibly unacceptable values. If portions of the wire can be selectively doped, the interconnecting region and the device can be separately optimized.

4:20pm **NS-ThA8 Gadolinium Silicide on Si(100)**, ***B.C. Harrison***, *J.J. Boland*, University of North Carolina at Chapel Hill

The fabrication and characterization of nanoscale structures is motivated by the desire to produce materials and devices with novel optical, structural, and electronic properties. A large part of this effort involves discovering ways to replace current microelectronic technology with faster and cheaper nanostructures. One system of current interest is lanthanide silicide nanowires that spontaneously self-assemble on the Si(100) surface.[1,2,3] The high aspect ratio, large mechanical strength, micrometer length scales, and metallic character[3] suggest applications as nanoscale interconnects. However, these wires cannot be successfully used in electronic circuits until the morphology and placement is controlled and their electrical properties are well characterized. This study focuses on the morphology and electrical properties of Gadolinium silicide since this silicide has the smallest lattice constant mismatch in the wire growth direction of any of the available lanthanide silicides. Scanning Tunneling Microscopy (STM) is used to study the atomic structure of the nanowires and the wetting layer that grows by a Stranski-Krastanov mechanism while the local electrical properties of these structures are probed by STS.

[1] Chen, Y.; Ohlberg, D. A. A.; Williams, S. J. Appl. Phys. 2002, 91, 3213.

[2] Chen, Y.; Ohlberg, D. A. A.; Medeiros-Riberio, G.; Chang, Y. A.; Williams, S. Appl. Phys. Lett. 2000, 76, 4004.

[3] Nogami, J.; Liu, B. Z.; Katkov, M. V.; Ohbuchi, C.; Birge, N. O. Phys. Rev. B 2001, 63, 233305-1. .

4:40pm **NS-ThA9 Atomic Structure and Electronic Properties of Rare Earth Silicide Epitaxial Nanowires on Si(001)**, ***J. Nogami***, Michigan State University

Several groups have recently reported growing nanowires of rare earth (RE) metal silicides on the Si(001) surface.[1,2,3] These nanowires grow by self assembly during the deposition of the RE metal on the Si(001) surface. They have many desirable properties such as crystalline structure, metallic conduction, and micron scale length. Recent STM and STS results on Dy and Ho silicide nanowires will be shown. Metal coverage, growth temperature, substrate step density, and post growth annealing duration all have strong effects on the nanowire morphology and surface density. Macroscopic transport measurements on nanowire networks will also be discussed.

[1] C. Preisenberger et al, J. Phys. D 31,L43 (1998)

[2] Y. Chen et al, Appl. Phys. Lett. 76, 4004 (2000)

[3] J. Nogami et al, Phys. Rev. B 63, 233305 (2001).

5:00pm **NS-ThA10 Fabrication of Low-dimensional Nanostructured Substrates**, ***M. Yoshimura***, Toyota Technological Institute, Japan, *K. Ojima*, NIMS, Japan, *K. Ueda*, Toyota Technological Institute, Japan

A clean Si(110) surface is reconstructed into so-called "16x2" superstructure, where pentagonal silicon clusters (hereafter, "pentagons") form one-dimensional up-and-down terrace structure with monatomic layer (0.2 nm) in height and about 5 nm in periodicity. This structure is expected to be a novel template for low-dimensional nanostructures. Since high step-density in this surface is due to relaxation of surface stress caused by formation of pentagons, it is possible to control the terrace width by modifying surface stress intentionally. Recently we succeeded in increasing terrace width by about 50% in Sn/Si(110) system. In this surface, Sn atoms form trimers, which are inserted into the pentagons. Then the spacing between pentagons is increased, giving lower surface stress and lower density of steps. Thus the arrangement of pentagons dominates surface structure in Si(110). However, the atomistic processes of rearrangement have not yet been clear. Here we first demonstrate the control of dimensionality of Si(110)-16x2 surface, namely, single or double domain, by using tilted wafers. We found that the epitaxial growth of metals on these surfaces was completely different from each other. Secondly, we examined adsorption of other metals on Si(110) to see how the pentagons change their positions and how the surface stress is relaxed. In contrast to Sn/Si(110), the up-and-down terraces immediately annihilate on Ag/Si(110) system. Lastly we compare the case of Ge(110), which forms a similar 16x2 structure, and discuss the mechanism of stress relaxation in (110) surface based on above results.

Nanometer Structures
Room: C-207 - Session NS-FrM

Novel Surface Nanoprobes
Moderator: S.A. Smallwood, Wright Patterson Air Force Base

8:20am **NS-FrM1 Correlated Spectroscopic and Scanning Probe Microscopy Approaches to Studying Molecular Assemblies at Interfaces**, ***C. Yip***, University of Toronto, Canada **INVITED**

The rational design of protein-based supramolecular architectures requires careful consideration of not only intramolecular structure but also the intermolecular interactions that control their self-association into higher order structures. We are particularly interested in the role of interfacial structure and chemistry in defining the nucleation and growth of these systems and specifically the synthesis of extended two-dimensional protein arrays. While scanning probe microscopy provides an excellent tool for studying these processes in real-time, there is an obvious need for integrated instrumentation that provides correlated analytical capabilities. We report here on the development and implementation of a multi-modal coaxial instrumentation platform that enabled the simultaneous acquisition of spectral, optical, and probe microscopy data. Examples will be drawn from studies of lipid phase transitions and protein assembly into two and three-dimensional architectures.

9:00am **NS-FrM3 ATR Vibrational Spectroscopy Towards Single Molecule Sensitivity and Molecular Level Spatial Resolution**, ***M. Futamata***, National Institute of Advanced Industrial Science and Technology (AIST), Japan **INVITED**

Recent developments in SPM (Scanning Probe Microscopy) or SXS (Surface X-ray Scattering) provide us atomic level information on structural changes at solid/liquid interfaces. However, it is in principle difficult to identify adspecies or to characterize interaction between adspecies and substrates even with these techniques. Vibrational spectroscopy gives valuable information on this point, if inherently low sensitivity is overcome. We have studied highly sensitive ATR (Attenuated Total Reflection)-IR and Raman spectroscopy utilizing surface plasmon polariton (SPP) with higher spatial resolution beyond diffraction limit by combining with SNOM (Scanning Near-field Optical Microscopy). Recently, ATR-IR spectroscopy allowed us to elucidate water molecules at hydrophobic SAM (Self-assembled monolayer)/solution interfaces, whose hydrogen-bond network are completely broken to give a sharp O-H stretching band at quite high-frequency region. In addition, amphiphilic organic nanotubes in solution substituting the water result in multilayer formation of the monomers. On single molecule characterization with micro-SERS (Surface Enhanced Raman Scattering) on Ag nanoparticles, we found the blinking (drastic intensity fluctuation with time) for adenine molecules without using electronic resonance effect. Raman image from aggregated Ag particles shows the parallel polarization to connecting axes gives significantly larger enhancement than perpendicular direction. These results are in good agreement with the theoretical evaluation of the local electric field using FDTD (Finite Difference Time Domain) method. (3) ATR-SNOM Raman spectroscopy utilizing SPP yields the enhancement of Raman signal up to 300 times and enables us to obtain the SNOM-Raman image with ca. 50 nm of spatial resolution.

9:40am **NS-FrM5 Accurate Real-Space Measurements of Surface Lattice Parameters**, ***J.A. Kramar***, *G.M. Witzgall, V.P. Scheuerman*, National Institute of Standards and Technology

At the National Institute of Standards and Technology (NIST), we have built a metrology instrument called the Molecular Measuring Machine (M^3) with the goal of performing nanometer-accuracy two-dimensional feature placement measurements over a 50 mm by 50 mm area. The instrument uses a scanning tunneling microscope to probe the surface topography, and a Michelson interferometer system to measure the lateral probe movement, both having sub-nanometer resolution. The lateral position is servo controlled, based on the interferometer readings, using a digital signal processor. The instrument environment includes temperature control, a vacuum system with a base pressure below 10^{-5} Pa, and seismic and acoustic vibration isolation. Several artifacts have been measured to validate the instrument performance. Initially, an average pitch measurement was made on a grating that was produced by laser-focused atomic deposition of Cr.[1] The average line pitch for this grating was measured to be 212.69 nm, with an estimated fractional standard uncertainty of 25 x 10^{-6}. This estimate was derived from a consideration of the sources of uncertainty for a 1 mm point-to-point measurement, including the effects of interferometer and sample alignments, Abbé errors, motion cross-coupling, and temperature variations. Most recently, M^3 measurements were made of the surface lattice parameters of a conducting organic crystal and compared to the bulk lattice constants as determined by x-ray crystallography. In initial small-area measurements, the lattice constants of nominally 1.02 nm and 750 pm were in agreement to within 70 pm. These data represent a major achievement in performing a direct, real-space measurement of crystal lattice parameters using ultra-high accuracy interferometry.

[1] J.J. McClelland, R.E. Scholten, E.C. Palm, and R.J. Celotta, "Laser Focused Atomic Deposition," Science, Vol. 262, pp. 877-880, 1993.

10:00am **NS-FrM6 Microwave Evanescent Microscope with Coupled Shear-field Topography Measurement**, ***S.W. Robey***, *S.J. Stranick*, National Institute of Standards and Technology

Near-field probes are being developed to combat the diffraction limit in a wide spectral range from the visible through the IR and into the microwave regime. We are developing evanescent capabilities at GHz frequencies for a variety of applications. Two design criteria are broadband capability and the ability to independently measure sample topography. A system based on a coaxial transmission line resonant structure evanescently coupled to the sample via a scanning tunneling microscope tip will be described. Standing wave resonances in the structure provide high sensitivity with quasi-broadband coverage from ~ 1 GHz to 20 GHz. While previous designs have used soft contact or employed the capacitive feedback to provide height control, we have successfully implemented shear-force measurement to provide the necessary independent topographic information on either conducting and insulating materials. A variable single stub mechanism allows tuning to critical coupling at a selected resonance once near-contact is achieved. The design and implementation of the microscope will be discussed, with comparison to other microwave evanescent systems. Measurements on compositionally graded thin films of $Ba_xSr_{1-x}TiO_3$, buried metallic lines on IC's, and investigation of correlations in topographic and dielectric contrast will illustrate capabilities.

10:20am **NS-FrM7 Factors Influencing the Capacitance-Voltage Characteristics Measured by the Scanning Capacitance Microscope**, ***G.H. Buh***, National Institute of Standards and Technology and Seoul Nat'l Univ., Korea, *J.J. Kopanski, J.F. Marchiando, A.G. Birdwell,* National Institute of Standards and Technology, *Y. Kuk*, Seoul National University, Korea

The scanning capacitance microscope (SCM) can be used to measure two-dimensional dopant profiles in semiconductors with nanometer scale resolution. Dopant concentration information is extracted from the local capacitance-voltage (C-V) characteristics measured between the SCM tip and the semiconductor sample. Two important artifact effects on C-V curves measured via SCM are discussed. It is found that the stray light from the laser of the atomic force microscope (AFM) dramatically affects the measured C-V curve. The difference between the usual SCM C-V curves measured under this high stray light condition and SCM C-V curves measured in a true dark condition will be shown and discussed. The distortion of C-V curves caused by the lock-in modulation voltage will also be discussed. After reducing these effects, SCM C-V curves are obtained that show markedly different behavior from that of conventional one-dimensional C-V curves. These measured C-V curves have a much stretched-out shape and non-zero dC/dV signals in the depletion and inversion region. Measured C-V curves are compared with three-dimensional calculations of the capacitance between the tip and sample. Determination of the dopant density directly from SCM C-V curves will be discussed. Finally, we will discuss optimal SCM imaging conditions, which overcome effects from surface charge and work function variation, and produce more accurate dopant profile measurements.

10:40am **NS-FrM8 Two-Dimensional Dopant Profiling by Novel Scanning Capacitance Force Microscopy**, ***K. Kobayashi***, *K. Kimura, H. Yamada, K. Matsushige*, Kyoto University, Japan

We have newly developed scanning capacitance force microscopy (SCFM), which is capable of mapping local differential capacitance (dC/dV) without external capacitance sensors, based on electrical force detection. While an electric field alternating at a fixed frequency (f) is applied between a tip and a sample, an induced electrostatic force (ESF) oscillating at its third harmonic frequency (3f) is detected using a lock-in amplifier (LIA). Because the magnitude of the induced ESF is proportional to the product of the square of the applied electric field and the capacitance of the sample (C) which can be modulated at f by the applied electric field especially in semiconductors, the amplitude and the phase of the induced ESF alternating at (3f) contain information on the differential capacitance (dC/dV) of the sample. SCFM works both in contact mode and dynamic mode. Since the sensitivity of SCFM is inherently high owing to the extremely high force sensitivity in scanning force microscopy (SFM), SCFM can be a high-resolution dopant-profiling technique for semiconducting samples. For demonstration of SCFM, a silicon test sample having several microfabricated patterns of p-type, n-type and heavily-doped n-type regions was imaged. Moreover, we demonstrated that SCFM could be also an important analytical tool for high-resolution characterization of ferroelectric domains in ferroelectric material such as a ferroelectric copolymer thin film.

11:00am **NS-FrM9 Imaging Subsurface Reflection Phase with Quantized Electrons**, *I.B. Altfeder, V. Narayanamurti*, ***D. Chen***, Harvard University

Lead quantum wells (QW) epitaxially grown on annealed Pb/Si(111) interface form a model system for the study of interactions between quantized electrons and adiabatically modulated boundaries. Tunnel spectra of this system reveal a previously unknown adiabatic shift of QW resonances due to lateral variations of the electronic reflection phase at the buried interface. With this effect, lateral distribution of the subsurface reflection phase can be probed, using scanning tunneling microscopy.

I. B. Altfeder, V. Narayanamurti, and D. M. Chen, Phys. Rev. Lett. 88, 206801 (2002).

11:20am **NS-FrM10 Spectroscopic Scanning Tunneling Microscopy Using Semiconductor Tips with Engineered Electronic Structure**, ***P.W. Sutter***, *J.S. Palmer, P. Zahl, E.A. Sutter*, Colorado School of Mines

III-V semiconductors and heterostructures are proposed as a new class of materials for use as probe tips for scanning tunneling microscopy (STM). Compared to the metal tips used conventionally, semiconductors with carefully tuned electronic properties have the potential to significantly increase energy resolution and contrast in spectroscopic STM, particularly in emerging applications such as single molecule vibrational microscopy and spectroscopy.[1] We are exploring InAs as a candidate probe material for spectroscopic STM with ultrahigh energy resolution. Using cleaved InAs probes, we demonstrate atomic-resolution STM imaging on highly oriented pyrolithic graphite (HOPG) and on clean semiconductor surfaces, such as Si(111) 7x7. Tunneling spectroscopy with InAs probes on these materials shows clear signatures of the band structure of the semiconductor tips in local conductance spectra. Routes are studied to adjust the Fermi-level in semiconductor tip materials, thus creating a tunneling distribution that is tunable and significantly narrower than that obtainable with a conventional metal tip.

[1] B.C. Stipe, M.A. Rezaei, and W. Ho, Science 280, 1732 (1998).

11:40am **NS-FrM11 First SEM, SAM and Combined SEM/STM Results of a Novel UHV Compatible Electron Column with Sub 3 nm Resolution**, ***J. Westermann***, *M. Maier, G. Schaefer*, OMICRON NanoTechnology GmbH, Germany, *J. Bihr*, LEO Elektronenmikroskopie GmbH, Germany, *J. Zach*, CEOS GmbH, Germany, *T. Berghaus*, OMICRON NanoTechnology GmbH, Germany

Scanning Electron Microscopy has been a proven tool for a huge variety of scientific applications for decades. Recently, new challenging applications are emerging from the fields of Semiconductor- and Nanotechnology. A key issue for these applications is the non-destructive imaging of the typically very sensitive, small and thin structures with nanoscale dimensions, as well as the characterisation of their chemical composition and electrical properties. Here, we present electron optical concepts and first results of a true UHV compatible version of an SEM column designed to meet the new requirements of ultra low outgassing, low beam voltages, and high resolution with high beam currents. Performance checks on nanostructured samples prove an ultimate lateral resolution below 3 nm at 15 keV beam energy and still below 5 nm at 3 keV at a working distance being compatible with electron energy analysers, and sample currents being suitable for Auger electron analysis. Beam currents in the nA range can be achieved with spot sizes below 10 nm at 1kV beam energy, thus enabling to use this column as an excitation source for chemical characterisation with ultimate spatial resolution in Scanning Auger Microscopy. First static Auger and SAM results demonstrating the outstanding spatial resolution will be shown. Furthermore, we report on the combination of this SEM column with simultaneous Scanning Probe Microscopy (SPM). This combination allows a continuous zoom from mm scale down to the atomic level on the same sample position, precise positioning of the SPM probe, as well as electrical contacting of nanosized structures (e.g. nanotubes or semiconductor devices).

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