Surface Engineering
Room 132 - Session SE-MoM

Nanocomposites, Multilayers, & Nanostructured Materials

Moderator: G.J. Exarhos, Pacific Northwest National Laboratory

9:40am **SE-MoM1 Magnetron Sputtered W/C Films with C@sub 60@ as Carbon Source***, **J.-P. Palmquist,*** Uppsala University, Sweden*; M. Oden, Zs. Czigany, J. Neidhart, L. Hultman,* Linköping University, Sweden*; U. Jansson,* Uppsala University, Sweden

Thin films in the W-C system have been prepared by magnetron sputtering of W with co-evaporated C@sub 60@ as carbon source. We have previously demonstrated epitaxial growth of several binary and ternary metal carbides as well as superlattice structures and gradient films at very low deposition temperatures (100-500 oC). In this study, we present the first results of epitaxial deposition of several phases in the W-C system. In addition, nanocrystalline tungsten carbide films can be deposited. At low C@sub 60@/W ratios, epitaxial growth of @alpha@-W with a solid solution of carbon was obtained on MgO(001) and Al@sub 2@O@sub 3@(0001) at 400 oC. The carbon content in these films (10-20 at%) was at least an order of magnitude higher than maximum equilibrium solubility and gives rise to an extreme hardening effect. Nanoindentation measurements showed that the hardness of these films increased with the carbon content and values as high as 35 GPa were observed. At high C@sub 60@ /W ratios, films of the cubic @beta@-WC@sub 1-x@ (x = 0-0.6) phase was deposited. This phase is not thermodynamically stable at T< 2500 oC but is frequently observed in thin film deposition. The microstructure of the @beta@-WC@sub 1-x@ films was dependent on the deposition conditions. At high deposition rates, nanocrystalline films with a grain size <30 Å were obtained in the temperature range 100-800 oC. The hardness of these films varied from 14 to 24 GPa. Also, for the first time, we have demonstrated epitaxial growth of single-crystalline @beta@-WC@sub 1-x@ films on MgO(001) at very low deposition rates, ~5 Å/min. Finally, at intermediate C@sub 60@/W ratios, epitaxial films of hexagonal W@sub 2@C was deposited on MgO(111), while polycrystalline phase mixtures was obtained on other substrates.

10:20am **SE-MoM3 Synthesis and Characterization of Thermally Stable TiB@sub 2@/TiC Nanolayered Superlattice Coatings for Dry Machining Applications***, **K.W. Lee,*** Northwestern University, US*; Y.H. Chen, Y.-W. Chung, K. Ehmann, L.M. Keer,* Northwestern University

It was demonstrated from previous studies that nanolayered superlattice coatings with the correct choice of components and layer thicknesses have enhanced hardness, due to interfaces providing barriers against dislocation motion and multiplication. We expect superlattice coatings made of two immiscible components to be stable against interdiffusion. Therefore, the layer structure and reasonable hardness for such superlattice coatings should be preserved at high temperatures. These thermally stable coatings are desirable for protection of cutting tools in dry machining applications, which may operate at temperatures in the 800 â€“ 1000 C regime or higher. For this reason, TiB@sub 2@ and TiC were chosen for this investigation. Nanolayered coatings made of these two immiscible components were synthesized by dc dual-cathode magnetron sputtering. Substrate rotation was used to enhance uniformity of the coating. Substrates included silicon, M2 steel and WC cutting inserts. Superlattice coatings with TiB@sub 2@ (001) and TiC (111) preferred orientations on Si (001) were synthesized. Transmission electron microscopy studies showed that the layer structure of the coating was preserved after annealing in vacuum at 1000 C for one hour. Room-temperature hardness of these coatings approaches 50 GPa, far exceeding the rule-of-mixture value. Coatings synthesized using the substrate rotation system have improved surface smoothness and reduced internal stress. Wear and durability tests on coated M2 steel and WC cutting inserts demonstrated the improved tribological performance of these coatings under unlubricated conditions compared with other standard coatings such as TiN.

10:40am **SE-MoM4 Chemical Vapor Deposition and Characterization of TiO@sub 2@ Nanoparticles***, **W. Li**, S.I. Shah, C.P. Huang,* University of Delaware*; O.J. Jung,* Chosun University, South Korea

Chemical vapor deposition (CVD) was used to deposit TiO@sub 2@ nanoparticles with and without metal ion dopants. X-ray photoelectron spectroscopy (XPS) and X-ray energy dispersive spectroscopy (EDS) experiments confirmed the TiO@sub 2@ chemical composition. X-ray diffraction (XRD) patterns showed the polycrystalline anatase structure of TiO@sub 2@. Transmission electron microscopy (TEM) revealed that these particles are nanosized with an average diameter of approximately 20-30 nm. The nanosized particles can provide a large surface to volume ratio and large number of free surface charge carries which are crucial for the enhancement of photocatalytic activity. In order to improve the photocatalysis efficiency, Pd@super 2+@, Pt@super 2+@, Nd@super 3+@ and Fe@super 3+@ transition metal ion were also incorporated as dopants. The effects of dopants on photocatalytic kinetics were investigated by studying the degradation of 2-chlorophenol (2CP) with an ultraviolet light source. The results showed that doped TiO@sub 2@ nanoparticles have higher photocatalytic efficiency than those without dopants with Nd3+ showing the highest efficiency. Time of 90% destruction of 2CP was reduced by one half with Nd3+ doping when compared with undoped TiO@sub 2@.

11:00am **SE-MoM5 Nanocomposite Tribological Coatings with "Chameleon" Surface Adaptation***, **A.A. Voevodin**, J.S. Zabinski,* Air Force Research Laboratory **INVITED**

Composite coatings where hard nanocrystalline grains are embedded in an amorphous matrix provide considerable improvement in hardness, toughness, wear resistance, and friction reduction. A review of their design concepts is provided with a focus on: (1) improvement in toughness characteristics; and (2) adaptive tribological behavior. Embedding small 5-20 nm hard nanocrystalline grains in an amorphous matrix helps to arrest crack development and introduces ductility through grain boundary sliding. Matrix materials may be selected to provide adaptation of the surface chemistry and/or microstructure to variations in environment and loading conditions to mantain tribological properties. Such materials have been coined chameleon coatings. A combination of nanocrystalline TiC and WC embedded into an amorphous diamond-like carbon (DLC) matrix enabled the coatings to adjust their mechanical response from hard to ductile and significantly reduced the danger of brittle failure. A similar concept was used to improve toughness of composite coatings made of nanocrystalline yttria-stabilized zirconia (YSZ) embedded in an amorphous YSZ/Au matrix. In another example, a combination of nanocrystalline WC and WS2 in an amorphous DLC matrix exhibited surface chemical and microstructural self-adjustment in sliding contact when test environment was cycled from humid to dry. This coating could repeatedly adjust its surface from hexagonal WS2 for sliding in dry nitrogen or vacuum environments to graphitic carbon for sliding in humid air, maintaining a low friction coefficient in both environments. The YSZ/Au nanocomposite developed a gold rich surface layer during heating at 500 °C in air, which considerably improved YSZ tribology in temperature cycling. This coating was further doped with MoS2 and carbon to obtain an environmental adaptation similar to that in the WC/DLC/WS2 system. Chameleon coating designs and applications for advanced tribological coatings are discussed.

11:40am **SE-MoM7 Nanometer-size Monolayer and Multilayer Molecule Corrals on HOPG: A TOF-SIMS, XPS and STM Study***, **Y.J. Zhu**, T.A. Hansen, S. Ammermann, J.D. McBride, T.P. Beebe, Jr.,* University of Utah

The surface chemistry of highly oriented pyrolytic graphite (HOPG) bombarded with energetic Cs@super +@ ions was studied using the combined surface analysis techniques of TOF-SIMS, (time-of-flight secondary ion mass spectrometry), XPS (x-ray photoelectron spectroscopy) and STM (scanning tunneling microscopy). Controlled surface modification and defect production were achieved by bombardment of HOPG with Cs@super +@ ions at various energies and at various dose densities. XPS shows cesium implanted into HOPG exists in an oxidized state. The Cs@super +@ bombardment of HOPG enhances oxygen adsorption due to both the dissociative adsorption of oxygen at defect sites produced by Cs@super +@ ions, and by the formation of cesium oxide. The surface coverage of cesium on HOPG increases linearly with increasing Cs@super +@ dose density at low bombardment energies, and decreases rapidly with increasing Cs@super +@ bombardment energy due to cesium implantation below the surface. The thermal stability of cesium in HOPG has a complex behavior at elevated temperatures. Defects created by Cs@super +@ ion bombardment in HOPG were subsequently oxidized at 650 @super o@C in air to controllably produce nanometer-size monolayer and multilayer molecule corrals (etch pits). Multilayer pits can be produced using higher energy Cs@super +@ ion bombardment, and monolayer pits can be produced using lower energy Cs@super +@ ion bombardment. The pit density, pit yield, pit diameter and pit depth can be controlled by varying experimental conditions, and they were studied systematically by STM. The measured depth-resolved growth rates for multilayer pits are in good agreement with the model of the growth rate acceleration by adjacent layers. The results obtained lead to a better understanding of the kinetics and mechanism of the graphite oxidation reaction, and more importantly to the accurate production and control of nanometer-size monolayer and multilayer molecule corrals on HOPG.

Magnetic Interfaces and Nanostructures
Room 110 - Session MI+NS-MoA

Nano Magnetics

Moderator: P.N. First, Georgia Institute of Technology

2:00pm **MI+NS-MoA1 Preparation and Magnetic Studies of Mass-Selcted Iron Clusters***, **V. Senz**, R.-P. Methling, A. Kleibert, J. Bansmann, K.E.H. Meiwes-Broer,* Universitaet Rostock, Germany

We have investigated the magnetic properties of mass-selected iron clusters using the magneto-optical Kerr effect (MOKE) in the visible and soft x-ray energy range. Using a continuously working cluster source (Arc Cluster Ion source - ACIS) we codeposited mass-selected iron clusters into a matrix of evaporated silver atoms on a silicon substrate. The source is based on cathodic arc erosion in inert gas environment and supersonic expansion. Its intensity and stability allows an enhanced mass-separation which is achieved by means of an electrostatic quadrupole deflector. Magnetization curves were measured for cluster sizes of 8.1nm and 11.7nm. The hysteresis curves reveal the transition from the ferromagnetic to the superparamagnetic state in dependence on the cluster size and temperature. Recently, element-specific reflectivity measurements have been carried out in the energy range of the Fe 2p core levels using linearly polarized light (X-MOKE). The observed MOKE effect at the 2p levels is much larger than the respective value at the Fe 3d valence band due to the enhanced spin-orbit interaction.

2:20pm **MI+NS-MoA2 Fabrication of Nanomagnet Arrays using Anodic Porous Alumina***, **J.H. Choi**, H.-Y. Kang, W.-G. Park,* Seoul National University, Korea*; Y. Kuk,* Seoul National University, Korea, South Korea

Anodic porous alumina has attracted increasing attention because of its naturally self-ordered porous structure and the capability for the fabrication of dots in nanometer scale. We present two fabrication processes of nanomagent arrays using anodic porous alumina. Electrochemically polished aluminum sheet is anodized in oxalic and sulfuric acid under constant voltage condition and porous alumina is used as a template. Co is electrodeposited in the pore of alumina and the deposition is stopped before Co fills the pore completely. Finally, ion milling is used to remove the upper side of alumina and get smooth surface. In the second process, we use anodic porous alumina as a mold for imprint lithography. Anodic porous alumina is placed on the PMMA/SiO@sub 2@/Co multilayer for the imprint. Hexagonal dot arrays are generated on PMMA and pattern-transferred to lower Co layer using reactive ion etching and ion milling. In both processes, nanomagnet arrays with the size of 40 ~ 100nm are successfully fabricated. The magnetic properties of the particles and their interactions have been investigated by spin polarized scanning tunneling microscopy, magnetic force microscopy and spin polarized scanning electron microscopy.

2:40pm **MI+NS-MoA3 Torques and Tunneling in Nanomagnets***, **D.C. Ralph**, E.B. Myers, M.M. Deshmukh, E. Bonet, F.J. Albert, R.A. Buhrman,* Cornell University **INVITED**

When the size scale of magnetic devices is shrunk to nanometer dimensions, qualitatively new properties can emerge. I will discuss two recent examples. First, I will review investigations of a new mechanism -- spin-transfer -- by which applied currents can be used to manipulate the orientation of ferromagnetic moments. Unlike traditional schemes which utilize a magnetic field to control magnetic reorientation, spin-transfer is based on the exchange interaction. It is a torque that results when a spin-polarized current scatters from a magnetic element, and in the process transfers spin-angular momentum to the magnet. Depending on device geometry and the magnitude of the applied magnetic field, this torque can cause either controlled magnetic reversal or the excitation of high-frequency precession driven by a dc current. Another property that emerges only in devices containing metal grains smaller than about 10 nm in diameter is that the electronic states involved in electron transport can be resolved individually. I will discuss spectroscopic measurements of the electronic states which contribute to electron tunneling in cobalt nanomagnets containing about 1000 atoms, and how these states are influenced by exchange interactions, anisotropy forces, and applied magnetic fields. We find that each electronic state in given magnetic nanoparticle is described by a slightly different anisotropy energy, with fluctuations of order 1 to 3 percent. Individual states are not purely spin-up or spin-down, but have a mixed character. Spin-waves and non-equilibrium excitations play a central role in shaping the tunneling spectrum, even at low energies.

3:20pm **MI+NS-MoA5 Self-assembled Magnetic Dots / Antidots and Dot Chains: Epitaxial Co/Ru(0001)@footnote *@***, **D. Li**, C. Yu, J. Pearson, S.D. Bader,* Argonne National Laboratory

We have grown ~ 0-420 nm thick epitaxial Co wedges on flat and grooved Ru(0001) with molecular beam epitaxy at 350 °C to investigate self-assembly in metals and their magnetic properties utilizing ex-situ atomic force microscopy and magnetic force microscope. Three-dimensional islands (dots) or a flat film network with deep holes (antidots) in well-defined truncated pyramidal shapes appear below or above ~ 20 nm, respectively.@footnote 1@ The lateral sizes of these dots/antidots, as well as their spatial distribution on the flat substrates, tend to be uniform at a lengthscale of ~ 10@super 2@ nm in diameter and ~ 10@super 0@ nm in height. This growth mode is mainly driven by strain as a result of an 8% lateral mismatch between the basil plane lattice constants of bulk Co and Ru. On grooved Ru substrates, these self-assembled Co dots align into linear chains along the top and bottom of the grooves. The average dot-to-dot distance within a chain changes from ~ 500 nm to connecting into uniform stripes as a function of coverage. Magnetically, the dots are single domain with in-plane anisotropy. The dot chains have uniaxial anisotropy along the grooves and exhibit dipolar ferromagnetic inter-dot interaction. @FootnoteText@ @footnote *@ Supported by DOE BES-MS #W-31-109-ENG-38. @footnote 1@ Chentao Yu, Dongqi Li, J. Pearson, and S.D. Bader, Appl. Phys. Lett. 78, 1228 (2001).

3:40pm **MI+NS-MoA6 Greatly Enhanced Magnetic Anisotropies in Pure and Bimetallic Co Nanostructures on Pt(111)***, **T. Cren**, S. Rusponi, N. Weiss, M. Epple, H. Brune,* Ecole Polytechnique Federale de Lausanne, Switzerland

We report on the enhancement of the magneto-crystalline anisotropy energy K in low dimensional Co islands induced by firm electronic coupling with the underlying Pt(111) substrate. The Co islands were created on Pt(111) using kinetically controlled MBE growth. The correlation between structure and magnetism has been studied by STM and in-situ Surface Magnetic Optical Kerr Effect (SMOKE). We generally observe that the magnetism of the islands is governed by the out-of-plane anisotropy and the M(H)-loops are well described by a two-state Ising model. For pure Co islands, of roughly 1000 atoms size, the shape has only little influence on magnetism (µ=2.2µ@sub B@/atom for ramified and µ=1.9µ@sub B@/atom for compact islands; bulk value 1,7µ@sub B@). From the blocking temperature we deduce an anisotropy energy of K=0.37meV/atom which is greatly enhanced as compared to the Co bulk value of K=0.7µmeV/atom. For double layers islands K is reduced by a factor of two (K=0.16meV/atom) which clearly demonstrates the role of the Co/Pt interface. Finally, we show that the anisotropy can further be enhanced by decoration with Pd or Pt and by bimetallic alloy islands.

4:00pm **MI+NS-MoA7 Invited Paper***, **A.D. Kent**,* New York University **INVITED**

5:00pm **MI+NS-MoA10 Collective Behavior in Patterned Nanomagnetic Dot Array - A Promising Route to Magnetic Data Processing at Room Temperature***, **A.J. Bennett**, J.M. Xu,* Brown University

It is well known that nanomagnetics could greatly improve data storage. In this work, through theory and experiment, we show that nanomagnetic patterned arrays are equally promising for data processing. Such arrays offer many potential advantages over CMOS circuits of the same scale: power dissipation drops through magnetostatic signal transport replacing resistive and radiative transmission lines; noise resistance is increased by low environmental coupling; interconnection problems are mitigated by signal transfer via "wireless" interactions. Magnetic interaction simulations using typical parameters suggest that room temperature operation is feasible. Experimental evidence and first-principles analysis will be presented to support this finding. We demonstrate specific nanomagnetic arrays which exhibit basic logic functions. We also show that the implementation of these arrays is within the reach of a hybrid strategy of e-beam lithography and a new non-lithographic nanofabrication technique our lab has developed (to be described in a separate report). Modeling collective behavior and designing nanomagnetic array logic represent new challenges which are met by a full-interaction-matrix Monte Carlo technique we developed. This approach enables simulation of nanodisk lattices as well as engineered branched arrays and gates for general logic. Unlike a nearest-neighbor model, our approach includes all interactions; thus, we may predict and compensate for problems arising from long-range interactions which arise in large circuits. In conclusion, magnetic nanostructures and nano-array gates show significant promise for nanoscale, room-temperature information processing.

Thin Films
Room 123 - Session TF+NS+SE+VST-MoA
Nanophase & Multilayered Thin Films

Moderator: E. Majkova, Institute of Physics SAS

2:40pm **TF+NS+SE+VST-MoA3 Precision Multilayered Thin Films for Manufacturing of the Next Generation of Computer Chips***, **E Spiller,*** Lawrence Livermore National Laboratory **INVITED**

Lithographic cameras for the fabrication of circuits below 70 nm line width can not use lenses because no transparent material exists for the required short wavelengths in the ultraviolet. Extreme Ultraviolet (EUV) lithography with wavelengths around 13 nm using multilayer coated mirrors is a main contender for chips with line widths between 30 and 70 nm. Meeting the one Angstrom tolerances on the figure and smoothness of the optical surfaces before and after the multilayer deposition and controlling the profile of the multilayer period to better than 0.1 Angstrom has been a major challenge. The talk will give an update on the status of EUV lithography with emphasis on the fabrication, characterization and understanding of the required film deposition processes.

3:20pm **TF+NS+SE+VST-MoA5 Ion Beam Growth and Properties of SiN/TiN Multilayer Thin Films for Phase-shift Masks in Optical Lithography***, **P.F. Carcia**, M.H. Reilly,* DuPont Central Research and Development*; L.J. Pilione, R.F. Messier,* Pennsylvania State University*; L. Dieu,* DuPont Photomask*; R.S. McLean,* DuPont Central Research and Development

Today's high speed microprocessors and dense memory chips are the result of modern optical lithography that allows printing smaller and smaller circuit features on a Si wafer. In 2002, optical lithographic tools with imaging radiation of 193 nm will produce leading edge devices with sub 100 nm critical dimensions. The continued success of optical lithography, which has delayed the introduction of next generation technologies with X-rays, ions, or electrons, can be attributed to the innovative application of optical resolution enhancement techniques that improve feature resolution and increase process latitude. One of these, the attenuating phase-shift mask (attPSM) improves image contrast with destructive optical interference by transmitting (6-17%) and simultaneously phase-shifting 180 degrees imaging radiation through the mask. In this paper we describe a systematic approach for designing wavelength tunable (248nm to 157 nm) attPSMs with SiN/TiN multilayers. We grew these multilayers by dual ion beam deposition (IBD) because it is potentially a cleaner process than magnetron sputtering. Compared to SiN/TiN multilayers grown by magnetron sputtering, IBD produced films with smaller surface roughness (AFM), less chemical contamination (XPS), and flatter interfaces (XRD, TEM). However, IBD films had higher stress, which can cause distortion of the mask and consequent image placement errors. We have therefore investigated strategies, which will also be discussed, to reduce stress in ion beam sputtered SiN/TiN multilayers.

3:40pm **TF+NS+SE+VST-MoA6 Gold Nanoparticle Films via Inert Gas Deposition: Biased Percolation and Current Induced Organization During and after Deposition***, **L.B. Kish**, P. Chaoguang, J. Ederth,* Uppsala University, Sweden*; W.H. Marlow,* Texas A&M University*; C.G. Granqvist,* Uppsala University, Sweden **INVITED**

Gold nanoparticle films made by inert gas deposition have been attracting attention due to their super hardness and thermal stability, which make the films promising objects for future microelectronics applications. The exact origin of the superior proper ties is unknown and to learn the conditions for optimal properties, strong efforts have been made. The published investigations have been made after the films were deposited. This talk reports a different way of study: measuring the electrical conductivit y during deposition. During the measurement, various electrical fields have been applied in order to test the possible influence of the measuring current on the film formation. The time dependence of the conductivity showed various rich patterns including local maximums/minimums. The exact interpretation of the whole process is yet to be make, however, it is possible to make a phenomenological picture of the origin of the observed current-induced-organization phenomena, which include elements of: - Biased percolation: conductor-insulator transition; - Biased percolation: bad conductor - good conductor transition; - Annealing; - Sintering; - Electromigration. A possible technological application of the observed phenomena is the fabrication of nanoparticle films with controlled disorder, such as, fine tuning of chemical sensors.

4:20pm **TF+NS+SE+VST-MoA8 Deposition of Metallic Nanoclusters by Galvanic Displacement***, **L. Magagnin,*** Politecnico di Milano, Italy*; C. Carraro, R. Maboudian,* University of California at Berkeley

Wet processes for the deposition of metallic films on silicon from fluoride containing solution are currently under investigation,@footnote 1,2@ for applications in microelectronics and in micromechanical systems technology. This work presents a novel method for depositing nanostructured films of noble and platinum-group metals by galvanic displacement from water-in-oil microemulsions. One possible application of this process is coating of the interior walls of microchemical reactors@footnote 3@ for enhanced catalytic activity. The water-in-oil system investigated comprises an organic phase (n-heptane), a surfactant (AOT), and an aqueous solution of hydrofluoric acid and metallic ions. Metallic nanoclusters are deposited by galvanic displacement at the silicon substrate in contact with the fluoride containing water droplets. Nanoclusters with controlled size and distribution are obtained on silicon by regulating the micellar radius and deposition time. Scanning probe microscopy is employed to characterize the deposited films. Microscopic observations are correlated with X-ray diffraction and SEM/EDS analyses to investigate the nucleation and growth of the nanoclusters. @FootnoteText@ @footnote 1@M.K. Lee, J.J. Wang, H.D. Wang, J. Electrochem. Soc. 144, 5 (1997): p. 1777. @footnote 2@L. Magagnin, R. Maboudian, C. Carraro, Electrochemical and Solid-State Letters 4, 1 (2001): p. C5. @footnote 3@K.F. Jensen, "The impact of MEMS on the chemical and pharmaceutical industries", Solid-State Sensor and Actuator Workshop, Hilton Head Island, South Caroline, June 4-8 (2000): p. 105.

4:40pm **TF+NS+SE+VST-MoA9 Cross-Linked Nano-Onions of Carbon Nitride in Thin Solid Films***, **L. Hultman**, S. Stafstrom, Zs. Czigany, J. Neidhardt,* Linköping University, Sweden*; N. Hellgren,* University of Illinois at Urbana-Champaign*; I.F. Brunell,* Linköping University, Sweden*; K. Suenaga,* Meijo University, Japan*; C. Colliex,* Universite Paris-Sud, France

We report on cross-linked carbon nitride nano-onions forming thin solid films by reactive unbalanced magnetron sputtering of graphite in an argon-nitrogen discharge. The onion shells, which contain up to 20 at% N, nucleate and grow atom-by-atom on substrates at temperatures as low as 200 °C. Nanoindentation studies reveals a highly resilient material that is relevant for wear-protective applications. Total energy calculations show the relative stability of C@sub 60-2n@N@sub 2n@ aza-fullerenes and suggests the existence of a novel C@sub 48@N@sub 12@ molecule with the unusual S@sub 6@ point group.

Biomaterials
Room 102 - Session BI+MM-TuM
Biomems & Microdevices

Moderator: W. Knoll, Max-Planck-Institut für Polymerforschung, Germany

8:20am **BI+MM-TuM1 Amplification of Biomolecular Interactions into Optical Signals using Liquid Crystals on Nanostructured Surfaces*, N.L. Abbott*,** *J. Brake,* University of Wisconsin **INVITED**

Anisotropic interactions between thermotropic liquid crystals and surfaces typically cause liquid crystals to be "anchored" in one or more orientations near surfaces. In this talk, we report the use of surface anchoring phenomena involving liquid crystals for the imaging of biomolecular recognition events on surfaces. The approach is based on the observation that anisotropic forces acting between a liquid crystal and an appropriately designed surface can be perturbed by the formation of biological complexes on the surface. The change in structure of the liquid crystal near the surface is communicated deep into the bulk liquid crystal because the orientational correlation lengths of liquid crystals are typically large (micrometers). We report the design of surfaces with nanometer-scale topography and patterned surface chemistry such that protein molecules, upon binding to ligands hosted on these surfaces, trigger changes in the orientations of 1-20 micrometer-thick films of supported liquid crystals, thus corresponding to a reorientation of ~100,000-1,000,000 mesogens per protein. Binding-induced changes in the intensity of light transmitted through the liquid crystal are easily seen with the naked eye and can be further amplified by using surfaces designed so that protein-ligand recognition causes twisted nematic liquid crystals to untwist. We also use the average gray-scale brightness of the optical appearance of the supported liquid crystal to construct an optical response curve as a function of the amount of bound protein. This approach to detection of ligand-receptor binding does not require labeling of the analyte, does not require the use of a complex apparatus, provides a spatial resolution of micrometers, and is sufficiently simple that it may find use in rapid, direct-read assays performed away from centralized laboratories.

9:00am **BI+MM-TuM3 Micropatterns of Biomolecules on Silicon Hydride Surfaces***, J. Pipper, U. Fritz, R. Dahint,* ***M. Grunze,*** University of Heidelberg, Germany

Biochips yield a high potential for technological progress in the fields of diagnostics, drug discovery and nanotechnology. They are usually fabricated by photo- and softlithographic methods, various printing techniques or the use of micro electrodes. Common substrate materials are glass-, silicon oxide- and gold surfaces. A powerful alternative to these approaches is the photochemically initiated attachment of terminally functionalized 1-alkenes onto silicon hydride surfaces accompanied by Si-C single bond formation. Although the high potential use of silicon microstructures for biosensing applications has been postulated for years, it has not been exploited yet due to a lack of functional groups suitable for the coupling of biological species. Problems in surface derivatization occur as a result of unwanted parallel chemical reactions and a possible fragmentation of the organic compounds during illumination. This dilemma has now been overcome by temporarily masking the chemical functionalities with non-photolabile protective groups. The paper reports on the spatially resolved, photochemical modification of planar and porous silicon hydride surfaces for the immobilization of DNA, proteins and cells. In combination with photoactive compounds, the method of light induced surface derivatization can also be transferred to organic materials.

9:40am **BI+MM-TuM5 Nano-Scale Effects on the Interfacial Fluidity of Organic Films***,* ***R.C. Bell,*** *M.J. Iedema, K. Wu, J.P. Cowin,* Pacific Northwest National Laboratory

Interfaces cause fluids in nano-scale spaces to behave very differently than in bulk. We are able to spatially resolve this fluidity with 0.1 nm resolution and show how nanometer films of glassy 3-methylpentane (3MP) are much less viscous at the vacuum-interface than at the 3MP-metal interface using ion mobility to probe the spatially varying flow properties. The amorphous 3MP films are constructed using molecular beam epitaxy on a Pt(111) substrate at low temperatures (<30 K). A 1 eV hydronium (D@sub 3@O @super +@) ion beam gently deposits ions on or into the films (the latter by depositing more 3MP on top of the ions). The ion motion is monitored electrostatically as the film is heated at a rate of 0.2 K/s above the bulk glass transition temperature of 3 MP (77 K). However, the ions begin to move at temperatures as low as 40 K near the vacuum interface, well below the bulk glass transition temperature. The viscosity near the vacuum-interface at 80 K is found to be 12 orders of magnitude lower than that expected of a bulk film. Furthermore, the fluidity perturbations were found to persist over 2.5 nm, which was determined by precisely placing the ions at increasing distances from the interfaces and monitoring the effect on the ion's mobility. Computer modeling is employed to further extract information about the nature of these films.

10:00am **BI+MM-TuM6 Interfacial BioMEMS: Bridging the Micro to the Macro***,* ***T. Desai,*** University of Illinois at Chicago **INVITED**

A great deal of consideration has been given in recent years to the biological uses of micro-electro-mechanical systems (MEMS). However, such devices are not yet found in many clinical settings due to lack of appropriate interfacing between these devices and the biological world. This talk will describe approaches to engineer interfaces that enhance the biocompatibility and functionality of implantable MEMS based devices. First, the surface modification of silicon-based devices on the nanometer and micron scale to ensure device functionality and integration will be described. Such chemical modifications must be incorporated onto silicon substrates to modulate the interfacial response, while at the same time ensuring compatibility with microfabrication and micromachining processing. Secondly, microfabrication techniques that can be used to selectively attach and spatially localize chemical species in order to control interfacial reactions with the body will be discussed. By integrating surface modification protocols with MEMS processing, one can create device surfaces that interact appropriately with multiple populations of cells and the surrounding tissue. The identification of principles for engineering microdevice surfaces will aid in developing therapeutic bioMEMS, lab on a chip platforms, and drug delivery systems that can more effectively interface with the biological world.

10:40am **BI+MM-TuM8 Dynamics of Biomolecular Recognition on Calibrated Beads in Microfluidic Channels***,* ***G.P. Lopez,*** *T. Buranda, J. Huang,* The University of New Mexico*; V.H. Perez-Luna,* Illinois Institute of Technology*; L.S. Sklar,* The University of New Mexico

We have developed a new approach for the analysis of biomolecular recognition in microfluidic systems. The method is based on real-time detection of biomolecular binding to receptor-bearing microspheres comprising affinity microcolumns. The microcolumn format ensures efficient analyte contact with receptors and rapid mixing. Molecular assemblies on microspheres can be characterized and calibrated using flow cytometric techniques prior to packing. Model assays demonstrated include direct fluorescence methods of quantitatively detecting recognition of model analytes by protein receptors and ligands displayed in well-characterized affinity matrices. We establish a model system for detection of recognition between a monoclonal antibody and the FLAG@super TM@ epitope tag. The assay can detect sub-femtomole quantities of antibody with good signal-to-noise ratio and a large dynamic range spanning nearly four orders of magnitude in analyte concentration. Kinetic and equilibrium constants for the reaction of this receptor-ligand pair are obtained through modeling of kinetic responses of the microcolumn and are consistent with those obtained by flow cytometry. Because of the correlation between kinetic and equilibrium data obtained for the microcolumns, quantitative analysis can be done in minutes, prior to the steady state endpoint of the recognition reaction. The approach has the potential to be generalized to a host of bioaffinity assay methods including analysis of small molecule analytes, protein and nucleic acid complexes, and microsystem-based multi-analyte determinations.

11:00am **BI+MM-TuM9 Microfluidic Patterning of Biopolymer Matrices for Cellular Pattern Integrity***,* ***W. Tan,*** *T. Desai,* University of Illinois at Chicago

The ability to design and create biologically relevant patterns via microfluidic patterning on surfaces provides new capabilities for cell biology, the production of biosensors and tissue engineering. However, cellular patterns, defined by microfluidic methods, often lose integrity over time due to cell growth and migration immediately upon removal of the PDMS stamp. In this study, biopolymer matrices were used in conjunction with cellular micropatterning to control cell attachment, growth, and long-term maintenance of these patterns. The incorporation of appropriate matrix materials with microfluidic cell patterning methods results in highly compliant patterns of adherent human endothelial cells (HUVECs) and fibroblasts after several day in vitro. Furthermore, cell type and chemical components in these biopolymer matrices influence the ability of the biopolymer matrices to control cell growth, proliferation and compliance to the patterns. Cell growth and migration in micropatterned biopolymers such as agarose, collagen, collagen-GAG mimics, and collagen-fibronectin are quantitatively measured and compared, and cell-matrix interactions are also examined over time. Results suggest that the use of an appropriate biopolymer matrix helps to control cell growth and maintain pattern integrity for long periods of time. This is essential for conducting stable biological experiments, as well as achieving control over tissue engineering constructs with multiple cell types.

11:20am **BI+MM-TuM10 High Throughput Techniques for Non Invasive Cancer Cell Detection**, *W.C. Wilson, L.F. Pardo, X.Z. Yu,* ***T. Boland***, Clemson University

The usefulness of patterned surfaces, which specifically bind antagonists has been recognized for a wide variety of biomedical applications ranging from drug screening to tissue engineering. Current technologies for creating patterned surfaces suffer from many drawbacks. For optimized results, technologies that are flexible, use a large number of different proteins, high-throughput and inexpensive are warranted. Ink jet technology has shown promise in meeting these criteria and commercial systems are being developed. High throughput and quantitative assaying of the patterns is equally challenging. For example, in early cancer detection, it is desirable to detect a few abnormal cells within millions of normal cells. It is unlikely that PCR based techniques or gene chips will be economically feasible tools for early detection since most of the cost will be associated with analyzing normal DNA. Economical high-throughput screening and concentration technologies may be able to discriminate and select abnormal cells for further analysis. We developed a piezo driven protein and cell printer in our laboratory, able to simultaneously deposit picoliter drops of cell or protein solutions out of nine nozzles. The printer can deliver a single cell per drop to a surface with submicron resolution. Furthermore, it is equipped with a robotic arm and conveyer belt allowing for truly high-throughput printing. Examples of its use including for anti angiogenesis drug screening will be presented. Quantitative assaying is done using a cell scanner. The cell scanner has a resolution of less than 2 Âµ, is fully computer controlled, high-throughput and an economically attractive when compared to epifluorescent microscopes. Results will be presented with fluorescently labeled cells demonstrating the potential of the cell scanner for high-throughput discrimination and selection of prostate cancer cells.

11:40am **BI+MM-TuM11 Electrochemically-Activated Switching of Surface Chemistry Using Tethered Molecular Machines**, ***B.C. Bunker***, *D.L. Huber, J.G. Kushmerick, M. Kelly, C.M. Matzke,* Sandia National Laboratories; *J.F. Stoddart, J. Cao, J.O. Jeppesen, J. Perkins,* University of California, Los Angeles

Sandia National Laboratories is integrating "smart" coatings into microanalytical systems for transporting, separating, and detecting species such as proteins. This paper describes the first demonstration of the use of electrochemically-activated molecular machines to switch surface chemistries. The "motor" for the machines being studied consists of an open aromatic ring system (cyclobis(paraquat-p-phenylene)) referred to as the "blue-box" due to its strong optical absorption properties. Reversible oxidation or reduction of the blue box makes it attract or repel aromatic threads such as functionalized naphthalenes or tetrathiafulvalene (TTF). Researchers at UCLA have succeeded in attaching a disulfide-terminated tail to the blue box which is used to tether the blue box to gold surfaces. Ellipsometry and atomic force microscopy measurements indicate that monolayer films of the blue box are produced. Electrochemical measurements indicate that while the voltages required to reduce the blue box are similar to voltages known to induce switching of the box in solution, adsorption of naphthalene threads is irreversible. Reversible switching is only seen for TTF threads that can themselves be oxidized. Contact angle measurements show that reversible changes in surface chemistry can be induced using appropriate threads. A simple microelectronic device has been constructed to demonstrate how the molecular machines can be used to move liquids or dissolved species within microfluidic systems.

Nanotubes: Science and Applications Topical Conference
Room 133 - Session NT+EL+NS-TuM

Nanotubes: Growth and Characterization

Moderator: S.B. Sinnott, The University of Florida

8:20am **NT+EL+NS-TuM1 Modification of Single wall Carbon Nanotubes**, ***S. Iijima***, NEC Corporation, JST-ICORP and Meijo University, Japan **INVITED**

This talk will discuss hybrid structures of SWNTS with other materials such as various types of fullerenes and other molecules which are incorporated into the interior spaces of nanotubes. It will also cover discussion on chemical modification of SWNTs with organic materials.

9:00am **NT+EL+NS-TuM3 Patterned Growth of Vertically Aligned Carbon Nanofibers by High Density Plasma Enhanced Chemical Vapor Deposition**, ***J.B.O. Caughman***, *V.I. Merkulov, D.H. Lowndes, E.D. Ellis, L.R. Baylor, M.A. Guillorn,* Oak Ridge National Laboratory

Vertically aligned carbon nanofibers (VACNFs) are being studied for use as field emitters. The VACNFs have been grown on a nickel catalyst layer using a high density inductively coupled plasma source. The source operates at 13.56 MHz and couples power to the plasma via a flat spiral coil. A hydrogen and acetylene plasma is used to produce the precursors needed for growth. The aligned VACNFs are grown on a heated substrate located downstream from the ionization zone. The energy of the ions impacting the growth surface is controlled with radio frequency bias. Self-bias voltages are typically in the range of -50 to -300 V. Operating pressures are in the range of 50 to 200 mTorr and growth temperature is typically around 700 degrees C. Results show that the diameter of the VACNFs depends on the size of the nickel catalyst particle and are typically 25-100 nm in diameter. The height of the VACNFs depends on the growth time and bias conditions, with typical lengths of around 1 micron. The VACNFs have been grown on nickel patterns on silicon to form arrays of isolated emitters. The relationship between growth conditions and field emission will be presented.@footnote 1@ @FootnoteText@ @footnote 1@ Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under contract DE-AC05-00OR22725.

9:20am **NT+EL+NS-TuM4 Large-Area Growth of Well-Aligned Carbon Nanotubes by Hot-Filament-Assisted DC Plasma Chemical Vapor Deposition**, ***T. Negishi***, *Y. Hayashi, S. Nishino,* Kyoto Institute of Technology, Japan

For the realization of field emission displays (FED) using carbon nanotubes (CNT), the efficient production method of CNT suitable for them should be developed. In order to obtain aligned CNT perpendicular to substrates for the application, direct growth on catalyst metal plates is desirable. It was reported that well-aligned carbon nanotubes were grown by plasma chemical vapor deposition (CVD). However the growth area was less than 1 inch in diameter. We have succeeded in carrying out the growth of well-aligned CNT with high density on a 5 cm x 5 cm nickel plate by hot-filament-assisted DC plasma (HF-DCP) CVD in the gas of CH@sub 4@/H@sub 2@. The growth method and conditions were as follow. DC voltage of -500V was impressed on the substrate with hot-filaments grounded. The filaments not only raise the temperature of a substrate, but stabilize a DC plasma. A luminous region was observed just above the substrate. By the optical emission spectroscopy, it was confirmed that the luminescence was derived from exited hydrogen and hydrocarbon radicals. Therefore the process is called HF-DCP CVD. Nickel substrates were heated by the filaments to 450-600 °C. The substrates were pretreated in pure hydrogen plasma before the growth of carbon nanotubes. Well-algined CNT about 50 nm in diameter and about 10 microns in length were observed by scanning electron microscopy in the density of about 10@super 9@ cm@super -2@ on the surface of the treated substrate. Field-emission properties of CNT were evaluated and a current density of 1.2 mA/cm@super 2@ was obtained for -1500V bias between the substrate and the counter electrode with a distance of 300 um. By this method, the growth of well-aligned CNT in an even larger area is expected.

9:40am **NT+EL+NS-TuM5 Tailoring Growth and Properties of Nanotube Networks for Applications**, ***B.-Q. Wei***, *Y.-P. Zhao, P.M. Ajayan, G. Ramanath,* Rensselaer Polytechnic Institute

We present strategies for obtaining aligned nanotube architectures, and locally modifying their nanotube properties, to enable their use for applications such as interconnects in future devices. We demonstrate various methodologies such as substrate templating, using gas-phase catalysts delivery, and interfacial reactions, to obtain substrate-selective growth, vertical as well as horizontal alignment, and metal-nanotube-substrate connection formation by chemical vapor deposition (CVD). We describe the use of focused ion beam (FIB) to modify the nanotube structure after deposition. We show that by controlling ion energy and dose, one can either tailor the electrical properties of nanotubes and/or micromachine them. We also report, for the first time, a nanotube-length-independent piezoelectric-like resonance in the impedance spectrum at ~ 37.6 kHz during AC probing of single-walled nanotubes. These will be relevant from the viewpoint of building devices such as ultrasonic nanotransducers, quantum well devices and nano-electromechanical actuators.

10:00am **NT+EL+NS-TuM6 Growth of Carbon Nanotubes and Applications in Microscopy***, **L. Delzeit**, C. Nguyen, R. Stevens, B. Chen, J. Han, M. Meyyappan,* NASA Ames Research Center **INVITED**

11:20am **NT+EL+NS-TuM10 The Effect of Photon Energy, Average Power, and Repetition Rate on Nanotube Synthesis Using a Free Electron Laser***, **B.C. Holloway**, A.D. Friedman,* College of William & Mary*; M.W. Smith,* NASA Langley Research Center*; C.K.W. Adu, A.L. Loper, B.K. Pradham, G. Chen, S. Bhattacharyya, P.C. Eklund,* Pennsylvania State University*; J.E. Fisher,* University of Pennsylvania

The free electron laser (FEL) located at Thomas Jefferson National Accelerator Facility (Jlab) was used to produce single-walled carbon nanotubes (SWNTs) by laser vaporization of a catalyzed carbon target. The Jlab FEL offers the advantage of a high power (~1000 Watts maximum average power), tunable (~2-7 micron), high repetition rate (MHz) photon source where parameters can be varied rather easily compared to tabletop systems. Initial experiments with the FEL show that, under the appropriate conditions, large soot generation rates (>10 mg/min) with high SWNT yield are possible . In addition raman scattering and high resolution transmission electron microscopy (HRTEM) of the FEL-produced material shows novel properties such as larger tube diameters, smaller bundle sizes, and interesting variations with carbon target catalyst composition. While the FEL operating conditions and synthesis system design have not yet been optimized, the potential for large scale production of SWNTS and/or "diameter tuning" using an FEL will also be discussed. Work supported by DARPA, ARO, NSF, and NASA.

11:40am **NT+EL+NS-TuM11 Energy-Filtered Reflection High-Energy Electron Diffraction from Carbon Nanotubes***, **J.T. Drotar**, B.-Q. Wei, Y.-P. Zhao, G. Ramanath, P.M. Ajayan, T.-M. Lu, G.-C. Wang,* Rensselaer Polytechnic Institute

Using reflection high-energy electron diffraction (RHEED), we have observed energy-filtered diffraction patterns from both vertically aligned and randomly oriented multi-walled carbon nanotube samples. The diffraction patterns show a ring structure that roughly corresponds to powder diffraction from graphite. Using a simple kinematic treatment, we were able to obtain information on the crystal structure of the individual nanotubes from the radial profiles of the rings. The interlayer spacing is significantly higher than in graphite, and there is almost no evidence of interlayer correlation. This is consistent with previous x-ray diffraction studies of multi-walled carbon nanotubes. We were also able to obtain information on the alignment and spacing of nanotubes. For the vertically aligned sample, the center to center spacing of the nanotubes was found, from reflection electron energy-loss spectra (REELS), to be 52 ± 12 nm. To the best of our knowledge, this study constitutes the first observation of RHEED patterns from multi-walled nanotubes. @FootnoteText@ This work was supported by NSF and the Interconnects Focus Center New York.

Magnetic Interfaces and Nanostructures
Room 110 - Session MI+EL-TuA

Spintronics II: Spin Injection & Transport

Moderator: B.T. Jonker, Naval Research Laboratory

2:00pm **MI+EL-TuA1 III-V Based Epitaxial Magnetic Heterostructures: Large Tunneling Magneto-Resistance***, **M. Tanaka**,* University of Tokyo, Japan **INVITED**

Tunneling magnetoresistance (TMR) is one of the most important phenomena for future spin-electronics devices. Here, we present very large TMR (>70%) in all-semiconductor magnetic tunnel junctions (MTJs), having (GaMn)As ferromagnetic electrodes separated by an ultrathin AlAs tunnel barrier.@footnote 1@ Trilayer heterostructures, (Ga@sub 1-x@Mn@sub x@)As(x=0.04, 50nm)/AlAs(d nm)/(Ga@sub 1-x@Mn@sub x@)As (x=0.033, 50nm), were grown on p@super +@GaAs substrates by low-temperature MBE. Mesa etched MTJs with the barrier thickness d ranging from 1.3nm to 3.0nm were fabricated, and showed clear TMR due to the change from parallel to anti-parallel magnetization of the two ferromagnetic (GaMn)As layers. Very high TMR ratios up to 75 % were observed at 8K for the junction with d=1.5nm. For d@>=@1.6nm, the TMR ratio was found to decrease with the barrier thickness. This behavior can be explained by calculations assuming that the wavevector k// of carriers is conserved in tunneling. This means that conventional Julliere's model is not valid in such epitaxial MTJs. Also, we have found that the TMR behavior strongly depends on the applied magnetic field direction, which is well explained by the cubic magneto-crystalline anisotropy of GaMnAs.@footnote 2@ Unlike the conventional MTJs made of polycrystalline ferromagnetic metals and an amorphous tunnel barrier, the present MTJs are all-epitaxial monocrystalline semiconductor-based junctions, which have the following advantages: (1) MTJs made of all-semiconductor heterostructures can be integrated with semiconductor circuitry. (2) Many parameters, such as the barrier height, barrier thickness, and Fermi energy of the electrodes, are controllable. (3) Introduction of quantum heterostructures, such as resonant tunneling structures, will be easier than any other material system. @FootnoteText@ @footnote 1@ Y. Higo and M. Tanaka, Physica E (2001), in press. @footnote 2@ Y. Higo and M. Tanaka, J. Appl. Phys. (2001), in press.

2:40pm **MI+EL-TuA3 Spin Filtering and Tunneling Magnetoresistance in Double Barrier Magnetic Heterostructures***, **A.G. Petukhov**, D.O. Demchenko, A.N. Chantis,* South Dakota School of Mines and Technology

We report the results of our theoretical studies of spin-dependent resonant tunneling of holes in GaMnAs-based double-barrier magnetic heterostructures. Our approach is based on the k.p Hamiltonian with exchange-field parameters obtained from first-principle calculations and on multi-band transfer matrix technique. Zeeman splittings of the light hole (LH1) and heavy hole (HH2) resonant peaks are the most striking features of the calculated I-V characteristics of the structures with magnetic emitters. This finding is in good agreement with experimental data by H. Ohno et al.@footnote 1@ The splittings of other resonant channels are smeared due to various bandstructure effects. The resonant tunneling through magnetic quantum wells in GaAs/AlAs/GaMnAs/AlAs/GaAs resonant tunneling diodes displays even more pronounced Zeeman splittings of the resonant channels. These splittings strongly depend on the orientation of the magnetization. The spin polarization of the transmitted current is also quite significant and can be controlled by an external bias. This spin-filtering effect also leads to tremendous enhancement of tunneling magnetoresistance at small biases. @FootnoteText@ @footnote 1@H. Ohno et al., Appl. Phys. Lett. 73, 363 (1998).

3:00pm **MI+EL-TuA4 Magnetotransport in Digital Ferromagnetic Heterostructures***, **T.C. Kreutz**, G. Zanelatto, R. Kawakami, E. Johnston-Halperin, E.G. Gwinn, A.C. Gossard, D.D. Awschalom,* University of California, Santa Barbara

Recent studies of digital ferromagnetic heterostructures (DFH), in which fractional monolayers (ML) of MnAs alternate with interlayers of low temperature (LT) GaAs, have shown that the Curie temperature, Tc, is sensitive to the separation between MnAs sheets.@footnote 1@ We report studies of in-plane magnetotransport in these structures, for Be-doped and nominally undoped LT GaAs interlayers with thicknesses from 10 to 40 ML. For undoped DFH grown at 260 C, structures with 10 ML interlayers show an anom alous Hall effect, while structures with 20 and 40 ML interlayers show only the ordinary Hall effect. The decrease in Tc with increasing interlayer thickness is accompanied by a decrease in the Hall carrier density and mobility. The magnetoresistance of the 10 ML sample has a similar field dependence to bulk GaMnAs. The 20 and 40 ML magnetoresistances are qualitatively different. Effects of Be doping are also considered for DFH samples.. @FootnoteText@ @footnote 1@ R.K. Kawakami, et al APL 2379 (2000).

3:20pm **MI+EL-TuA5 Theoretical Band Offsets in Magnetic Semiconductor Heterostructures: CdCr@sub 2@Se@sub 4@ on Si and GaAs***, **J.M. Sullivan**, S.C. Erwin,* Naval Research Laboratory

Ferromagnetic semiconductors grown on semiconductor substrates are being widely investigated as spin injection sources for spintronics applications. Of the many issues critical to the injection efficiency, the band offset plays a central role. In particular, band offsets provide a direct link between microscopic parameters which can be determined theoretically, and macroscopic properties which can be measured experimentally. Moreover, magnetic band offsets can be tuned by methods well known from traditional band-offset engineering, and thus will be important for efforts to optimize injection efficiencies. Here we present first-principles results for the magnetic band offsets in heterostructures consisting of CdCr@sub 2@Se@sub 4@, an n-type ferromagnetic semiconductor with a Curie temperature of 130 K, grown on Si and GaAs substrates. We first use density-functional total-energy methods to explore and identify stable and metastable interface structures, taking into consideration different interface terminations, intermixing, and polar vs. non-polar interfaces. For the thermodynamically favorable interfaces we then apply standard first-principles methods@footnote 1@ for calculating the band offsets. Finally, we present detailed comparisons to recent experiments@footnote 2@ for these heterojunctions. @FootnoteText@ @footnote 1@ A. Franciosi and C. G. Van de Walle, Surf. Sci. Rep. 25, 1 (1996). @footnote 2@ D. Park et al., unpublished. .

3:40pm **MI+EL-TuA6 Effects of Interface Structure and Chemistry on Spin Injection Efficiency in Spin-LEDs***, **R.M. Stroud**, Y.D. Park, A.T. Hanbicki, B.R. Bennet, B.T. Jonker,* Naval Research Laboratory*; G. Itskos, M. Furis, G. Kioseoglou, A. Petrou,* SUNY Buffalo

The efficiency of spin injection across a heterointerface can be strongly affected by the structure and chemistry of that interface. To quantify the relationship between interface quality and spin injection efficiency, spin-LEDs make an ideal test system. In a spin-LED, carriers with a net spin polarization are injected into a LED, where radiative recombination results in circularly polarized light emission. The optical circular polarization directly reflects the degree of the spin polarization of the injected current. By varying the growth conditions to vary the quality of the interface for ZnMnSe/AlGaAs/GaAs/AlGaAs spin-LEDs, injection efficiencies of 0 to 65% have been achieved. In this system, the primary structural defect, identified by cross sectional transmission electron microscopy, is a stacking fault that nucleates at the ZnMnSe/AlGaAs interface. Stacking fault densities ranged from 10@super 10@ cm@super -2@ for the lowest efficiency samples to < 10@super 8@ cm@super -2@ for the 65% efficiency sample., The optical polarization scales with the stacking fault density, which indicates that the spin injection efficiency is affected by the ZnMnSe/AlGaAs interface structure and chemistry. We compare results for growth on As- and Ga-terminated AlGaAs surfaces, and for structures grown with a Zn- and Se-initiated growth of the ZnMnSe polarized contact layer. These results demonstrate that although the spin injection efficiency is sensitive to interface quality, the spin injection effect is robust enough in all-semicondutor spin-LEDS to withstand moderately high defect densities, and can be produced using pre-grown LEDs. @FootnoteText@ @footnote 1@ This work supported by ONR and the DARPA SpinS program.

4:00pm **MI+EL-TuA7 Recent Developments in Spin Electronics***, **A. Fert**,* Université Paris-Sud, France **INVITED**

My talk reviews recent developments of the research in spin electronics at Unité Mixte de Physique in Orsay. I will focus on the three following topics: 1)Magnetization reversal by injection of a spin-polarized current: After an introduction on the effect predicted by Slonczewski (and also Berger), I will present experimental results obtained on pillar-shaped trilayers (collaboration with LPN-CNRS and University of Brest) and I will describe the pending problems in the understanding of the spin transfer mechanisms generating the reversal. Current-induced reversal could lead to general applications for the switching of spin electronic devices and I will present the perspective in this direction. 2)Magnetic tunnel junction (MTJ): Although applications of the magnetoresistance (TMR) of MTJ are already around the corner, physics of spin-polarized tunneling is still far from being clearly understood. I will present experimental results on epitaxial (single crystal) MTJ which shed light on the physical mechanisms of TMR. 3)Spin injection into semiconductors: the development of devices combining ferromagnets and semiconductors is an important challenge in spin electronics. I will present a model clearing up the conditions for efficient spin injection from a ferromagnetic metal into a semiconductor.

4:40pm **MI+EL-TuA9 Structural and Optical Characterization during Growth of Co on Ga@sub 1-x@In@sub x@As(001)**, ***K. L@um u@dge***[1], Technische Universität Berlin, Germany & University of Minnesota*; P. Vogt,* Technische Universität Berlin, Germany*; B.D. Schultz,* University of Minnesota*; C.J. Palmstrom,* University of Minnesota, United States*; W. Braun,* BESSY*; N. Esser, W. Richter,* Technische Universität Berlin, Germany

The growth of magnetic overlayers on semiconductors has received considerable interest due to their potential use in spintronic devices. The interface between the ferromagnet and semiconductor is critical to spin polarized transport across the interface. Thus, it is important to determine dependence of the interfacial structure and the crystalline quality of the ferromagnetic film on the substrate temperature and surface reconstruction. The initial growth of Co on GaAs(001) has been studied using STM, PES and reflectance anisotropy spectroscopy (RAS). The Co tends to be disordered when grown at room temperature. However, crystalline islands are observed at a substrate temperature of 430 K. STM-images taken during Co deposition show, that the substrate surface morphology does not change during deposition despite the change in surface reconstruction. The initial growth on the As-rich c(4x4) surface is different from the growth on the c(8x2) Ga-rich reconstruction. For growth on the c(8x2) surface two different growth modes can be distinguished. At first Co-atoms are adsorbed into rows to form one-dimensional chains. Further deposition results in epitaxial cubic islands. The PES data indicate two metallic components in the Ga3d core level. One is interpreted as resulting from CoxGay and the other from metallic Ga. The As3d core level contains two different components leading to the conclusion of As-Co bonds at the interface and access As on top. The influence of lattice mismatch on the structural and magnetic properties of the epitaxial Co-layer will be studied by Co growth on Ga@sub 1-x@In@sub x@As(001).

5:00pm **MI+EL-TuA10 Structural and Magnetic Characterization of the Fe@sub x@Co@sub 1-x@ / GaAs(100) Interface**, ***B.D. Schultz***[2]*, L.C. Chen, A. Isakovic, J. Strand, P.A. Crowell,* University of Minnesota*; M.M.R. Evans,* University of Wisconsin-Eau Claire*; C.J. Palmstrom,* University of Minnesota

Two distinct surface contributions to the magnetic anisotropy can be used to control the magnetic properties of thin films of bcc Fe@sub x@Co@sub 1-x@ grown on GaAs (100). On bare GaAs (100), the sp@sup 3@ bonding in the zincblende structure results in a two-fold surface symmetry of the gallium and arsenic bonding and a (2x4)/c(2x8) surface reconstruction for an arsenic surface coverage ~0.75 monolayers. This two-fold surface symmetry reduces the expected cubic four-fold magnetic anisotropy for Fe@sub 1-x@Co@sub x@ films to a strong uniaxial magnetic anisotropy. However, four-fold symmetry is restored in films grown with an interlayer of Sc@sub 1-y@Er@sub y@As(100), in which the rock-salt structure provides an unreconstructed surface. Initial STM images of 0.10 monolayer deposited Fe@sub x@Co@sub 1-x@ on GaAs(100) (2x4)/c(2x8) surface grown by MBE at 95°C indicate isolated clusters of atomic dimensions with preferential attachment along the arsenic dimer rows. The images also indicate that the (2x4)/c(2x8) reconstruction remains relatively undisturbed by the initial nucleation and growth at this coverage. The deposition of bcc Fe@sub x@Co@sub 1-x@ on Sc@sub y@Er@sub 1-y@As(100) indicates there is no preferred nucleation site for the Fe@sub x@Co@sub 1-x@ atoms on the unreconstructed surface. Control of the interfacial properties of ferromagnetic metals and semiconductors is important for optimizing spin dependent transport across these interfaces. Spin dependent ejection of photo generated carriers from GaAs(100) into Fe@sub x@Co@sub 1-x@ ferromagnetic metal contacts has recently been observed. This paper will emphasize the correlation between the structure and chemistry of the Fe@sub x@Co@sub 1-x@/GaAs and Fe@sub x@Co@sub 1-x@/Sc@sub 1-x@Er@sub x@As/GaAs interfaces, determined by STM, RHEED, LEED, XPS, RBS, XRD and TEM, and the magnetic and transport properties. Supported by: ONR-N/N00014-1-0233, DARPA N/N00014-99-1-1005, and NSF-MRSEC NSF/DMR-9809364.

Nanometer Structures
Room 133 - Session NS-TuA
Novel Surface Nanoprobes

Moderator: M. Tsukada, University of Tokyo, Japan

2:00pm **NS-TuA1 Nano-scale Science by Means of UHV Electron Microscopy**, ***K. Takayanagi***[3], Tokyo Institute of Technology, Japan **INVITED**

Nano-scale materials attract interest in fundamental science and technology. Because nano-meter scale materials behave as a new matter, differently from the condenced matter or liquid. As seen from magic number of clusters and carbon nanotubes, nano-scale matter presents degitized and/or quatized characteristics. These characteristics relate with nature of their surface characteristics. We developed an UHV high-resolution electron microscope combined with a miniaturized STM , which enabled us to study nanowires extending our previous analysis on Si(111)7x7 reconstruction. The gold nanowires were found to have multi-tube structure, like carbon nanotubes. In gold tube, each tube consits of gold atomic rows which coil the axis of the tube. The number of atomic rows in the outer tube increases by seven from that of the inner tube, so that the shell closing number is seven. The present STM combined UHV-TEM allow us to open new sciece of the nano-scale matter.

2:40pm **NS-TuA3 Tunneling Spectroscopy of Superconducting Quasiparticles by Scanning Tunneling Microscope with a Bulk NbN Tip***, **H. Bando**, Y. Aiura, K. Mitsugi,* National Institute of Advanced Industrial Science and Technology, Japan*; K. Oguchi, Y. Nishihara,* Ibaraki University, Japan*; Y. Kumashiro,* Yokohama National University, Japan

Use of superconducting tip is expected to extend the capability of scanning tunneling microsopy by allowing detection of superconducting quasiparticles in the atomic resolution. A few groups have succeeded in the measurements with supercunducting tips made of Nb or Ag/Pb coated PtIr, however, technically there remain challenges as for the cleaning of tip apex etc. We employed bulk NbN crystals, whose surface is chemically stable, and prepared tips by fracuture. Results of topographic measurements, SIN tunneling on Au, and SIS' tunneling on NbN films with the tunneling resistance varied for orders of magnitute are presented.

3:00pm **NS-TuA4 Demonstration of a Tunable Bistable Tunnel Device with a Low Temperature STM and a Self-organized Ga Array on Si(111)@footnote 1@***, **I.B. Altfeder**,* Harvard University*; D. Chen,* Rowland Institute for Science

Self-organized nano-structures on Si substrates have drawn much current research effort. The usefulness of these structures critically depends on physical properties they can offer for potential nanoscale device applications. We report here an unusual bistable transport behavior of a tunnel junction form between an STM tip and a two dimensional (2D) Ga array self-assembled on a Si(111) substrate. At 77K, large hysteresis loops appear in the I-V spectra when electrons are injected from the tip to the 2D Ga array, characteristic of the switching between ON - OFF conductance states. The turn-on bias varies from -3.1 V to -4.0 V and shows an inverse dependence on the tip-sample distance, indicating a strong field effect. The turn-off bias, however, is essentially pinned at a conductance threshold of -2.7 V. These observations demonstrate the basis of a nanoscale tunable bistable tunnel device with the potential for digital and storage applications. @FootnoteText@ @footnote 1@I. B. Altfeder and D. M. Chen, Phys. Rev. Lett. 84, 1284 (2000).

3:20pm **NS-TuA5 Theory and Perspective of the Spin-Polarized STM***, **S. Blügel**,* Forschungszentrum Jülich, Germany **INVITED**

In the frontier field of nano-magnetism understanding complex magnetic structures is crucial. We demonstrate that the spin-polarized scanning tunneling microscope (SP-STM) offers a great potential to unravel complex magnetic superstructures on different length scales. Different operating modes of a SP-STM@footnote 1@ will be discussed: It is shown that the spectroscopy mode (SP-STS) and the modulating tip-magnetization mode (SP-STMTM) are ideal to analyze complex magnetic structures on a mesoscopic length scale as created by atomic-scale ferromagnetism. Further we propose the application of the constant-current mode of a SP-STM for the investigation of surfaces of complex atomic-scale magnetic structures of otherwise chemically equivalent atoms. A recent application@footnote 2@ gave evidence of the capabilities of the SP-STM in terms of the first unambigious proof of two-dimensional antiferromagnetism in magnetic monolayer films on non-magnetic

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[1] **Falicov Student Award Finalist**

[2] **Falicov Student Award Finalist**

[3] **IUVSTA Award Winner**

substrates predicted already in 1988.@footnote 3@ We argue, that in general any magnetic superstructure leads to an SP-STM image characteristic of the superstructure and is not superimposed on the image of the chemical lattice. This opens the door to study even more complex magnetic structures such as non-collinear spin-structures or spin-density waves. We present calculated SP-STM images of frustrated antiferromagnets on triangular lattices: a coplanar non-collinear periodic Néel state for Cr/Ag(111) and a multiple spin-density wave state of a Mn-monolayer on Cu(111), which we determined in Ref.@footnote 4@ to be the magnetic ground states of these systems. All calculations are based on the vector-spindensity formulation of the density functional theory. @FootnoteText@ @footnote 1@ D. Wortmann et al., Phys. Rev. Lett. 86, accepted (2001). @footnote 2@ S. Heinze et al., Science 288, 1805 (2000). @footnote 3@ S. Blügel et al., Phys. Rev. Lett. 60, 1077 (1988). @footnote 4@ Ph. Kurz et al., Phys. Rev. Lett. 86, 1106 (2001).

4:00pm **NS-TuA7 Charge Imaging of Electrons and Holes Trapped in Gate Oxides and at the Oxide-silicon Interface***, **R. Ludeke**, E. Cartier,* IBM T.J. Watson Research Center

We have observed individual electrons and positive charge both in bulk SiO@sub 2@ and Al@sub 2@O@sub 3@ gate oxides, and trapped on dangling-bond derived states (P@sub b@ centers) at the SiO@sub 2@-Si(111) interface. The charge is observed as sharp virtual holes in the surface topography measured with an Atomic Force Microscope operating in the non-contact mode in ultra high vacuum (UHV). The polarity of the charge was ascertained from contrast differences in Kelvin images that were simultaneously acquired with the topographs. The trapped charges in the bulk of the oxides exhibited a tendency to cluster. The P@sub b@ centers were created by the removal of H from the H-Si interfacial bonds by annealing the Si(111) samples to 600°C. Their densities in the mid 10@super 12@ cm@super -2@ range were measured with the AFM and confirmed by capacitance-voltage experiments. The distributions of the negatively and positively charged (holes) traps are peaked, respectively, in the upper and lower halves of the band gap. This allows the selective capture of electrons or holes that depends on the position of the local Fermi level E@sub F@. E@sub F@ is controlled by the bias applied to the metallic AFM tip. We have modeled the band bending beneath the tip, which, depending on the bias and the binding energy of the trap state, can lead to temporary filling of the trap that leads to unusually sharp features in the images. Thus the trap's physical location and, less directly, the trap level relative to the band edges can be ascertained from these experiments.

4:20pm **NS-TuA8 'Artifact-free' Electrostatic Force Measurement using Noncontact Atomic Force Microscopy***, **K. Okamoto**, Y. Sugawara, S. Morita,* Osaka University, Japan

Noncontact atomic force microscopes (NC-AFM) using frequency modulation (FM) method have the potential ability to obtain surface structure of any materials, such as metals, semiconductors and insulators with atomic resolution. NC-AFMs simultaneously detect several kinds of forces acting between the tip and the sample surface; the van der Waals force, the chemical bonding force and the electrostatic force (ESF) et al. Each of the forces contains the different physical information about the surface. Although each of them is desirable to be separately detected, no method to completely separate them has not been realized. This lack results in the deviation of the NC-AFM images, namely the 'artifacts.' In this presentation, we propose the novel method to completely separate the ESF from other forces. The Kelvin probe force microscopy (KPFM) is often used to measure and separate the ESF with AFM. However, the KPFMs still involve an extra deviation, which is due to an AC electric field applied for KPFM measurement. Our new method proposed here can completely eliminate the influences due to the ESF on the topography with keeping all merits of KPFM by introducing the artifact eliminator circuit, which adjust the signal for height regulation of the tip. Our method can measure the topography and the spatial distribution of the ESF, which reflects the spatial distribution of work function or charges on the sample surface, with the atomic resolution without the 'artifact.' This system has high possibility to identify the kind of each atom.

5:00pm **NS-TuA10 Scanning Impedance Microscopy: From Impedance Spectra to Impedance Images***, **S.V. Kalinin**, D.A. Bonnell,* University of Pennsylvania

Electrostatic force sensitive scanning probe microscopy (SPM) for quantitative imaging of dc and ac transport behavior of electrically active interfaces is presented. SPM is used to study transport properties of a metal-semiconductor junction and SrTiO@sub 3@ bicrystal grain boundary. Scanning Surface Potential Microscopy (SSPM) of laterally biased sample is used to quantify potential drops at the interface. Varying the lateral bias allows the voltage and I-V characteristics of the interface to be reconstructed. A novel scanning probe technique based on phase change of cantilever oscillations induced by a lateral bias applied to the sample is presented. This technique, further referred to as Scanning Impedance Microscopy (SIM), allows mapping of the local voltage phase angle and voltage oscillation amplitude in complex systems. The frequency dependence of the voltage phase angle shift across the interface allows interface capacitance and resistance to be determined locally. Quantitative agreement between metal-semiconductor junction capacitance obtained from SIM measurements and macroscopic impedance spectroscopy is demonstrated. Variation of the dc component of lateral bias in SIM allows reconstruction of the C-V characteristics of the junction. SSPM and SIM imaging of a SrTiO3 grain boundary has demonstrated the non-linear transport properties of the interface and identified a large density of interface states at the boundary. The combination of SSPM and SIM provides an approach for the quantitative analysis of local dc and ac transport properties from SPM data and provides spatially resolved impedance spectra of complex microstructures. Finally, the applicability of SIM to characterize complex polycrystalline materials will be demonstrated.

Organic Films and Devices
Room 131 - Session OF+NS+SS+BI-WeM
Self Assembled Monolayers/Ordered Films

Moderator: R. Maboudian, University of California, Berkeley

8:20am **OF+NS+SS+BI-WeM1 Preparation and Characterization of Nano-Scale Mixed Self-Assembled Monolayers***, S. Chen, L. Li, C. Boozer, **S. Jiang**,* University of Washington

Fabrication of nano-scale structures by mixed self-assembled monolayers (SAMs) has recently attracted much attention due to its scientific importance and potential applications to chemical and biological sensors, and biocompatible materials. However, it is still difficult to prepare nano-scale mixed SAMs since phase segregation occurs when two components are quite different. Recently, we proposed a new kinetically-trapped method to prepare nano-scale uniform mixed SAMs. In this work, we prepared various mixed SAMs, such as dodecanethiol(C12)/octanethiol(C8), tetradecanethiol (C14)/C8, 11-mercaptoundecanol(C11OH)/C8, and 11-mercaptoundecanoic acid(C10COOH)/C8 at a range of compositions using the kinetically-trapped method. Our results by low-current scanning tunneling microscopy (STM) revealed homogenous mixed SAMs with various terminal groups and a solution composition up to 25% of long chains formed at higher solution temperatures. Possible mechanism for forming uniform mixed SAMs will be discussed.

8:40am **OF+NS+SS+BI-WeM2 The Role of Linker Molecules in the Controlled Adsorption of Polystyrene (PS) Nano Particles***, **M. Himmelhaus**,* Universität Heidelberg, Germany*; H. Takei,* Hitachi Central Research Laboratory, Japan

Controlled adsorption of PS nano particles onto specific regions of flat surfaces has found increasing interest as potential applications for surface-adsorbed PS particles, such as fabrication of quantum dots, optical switches, mesoscopic lasers, biosensors, as well as dosing of biomolecules, require an easily applicable adsorption scheme capable of addressing macroscopic areas. Among the various techniques those utilizing linker molecules to promote particle-particle as well as particle-surface interaction have only recently been applied as to date the role of the linker molecules in the various physical and chemical adsorption mechanisms is only poorly understood. We have studied the effect of several water-soluble linker molecules on the adsorption behavior and packing density of surfactant-free polystyrene latex spheres from suspension. By variation of several parameters, such as molarity of the linker molecules, pH of the suspension, as well as choosing differently functionalized PS particles we can distinguish several adsorption mechanisms from each other, reaching from purely physical ones to covalent bonding. This basic study is a first step to the fabrication of 2D crystalline monolayers of macroscopic lateral extension by means of chemically driven self-assembly.

9:00am **OF+NS+SS+BI-WeM3 Characterization of Biphenyl-substituted Alkanethiol Self-assembled Monolayers by High-resolution X-ray Photoelectron Spectroscopy***, K. Heister, H.-T. Rong, M. Buck,* University Heidelberg, Germany*; L.S.O. Johansson,* University Karlstad, Sweden*; **M. Zharnikov**, M. Grunze,* University Heidelberg, Germany

Synchrotron-based high resolution X-ray photoelectron spectroscopy was applied to characterize self-assembled monolayers (SAM) of biphenyl-substituted alkanethiols CH@sub 3@(C@sub 6@H@sub 4@)@sub 2@(CH@sub 2@)@sub n@SH (BPn, n = 1-4) on Au and Ag substrates. Beyond previously identified odd-even changes in the packing density and the tilt angle of the biphenyl moieties, the high resolution spectra reveal a number of additional odd-even effects upon variation of the number of methylene groups in the aliphatic part in the BPn molecule. Their occurrence and mutual correlation suggests that a BPn SAM represents a strongly correlated, highly ordered molecular assembly. In particular, periodical changes of a shake-up feature in the C 1s region are observed, which are related to the differences in the arrangement of the aromatic matrix. The width and binding energy of the S 2p signals also exhibit odd-even changes. The width changes are associated with the occupation of either equivalent or non-equivalent adsorption sites on the polycrystalline (111) Au and Ag substrates. The comparison of the width values with those for conventional alkanethiols implies that the substrate bonding of alkanethiols on gold cannot be described by a single adsorption site. At the same time, the FWHM of the S 2p@sub 3/2,1/2@ peaks in the loosely packed BPn/Au (~0.50 eV) was found to be the smallest one among all thiol-derived SAMs investigated by HRXPS until present. Therefore, this value can be associated with the occupation of equivalent adsorption sites on the Au(111) surface. This work has been supported by the German BMBF (05 SF8VHA 1 and 05 SL8VHA 2), DAAD (313/S-PPP), and DFG (Bu820/11-2).

9:20am **OF+NS+SS+BI-WeM4 Separation via Self-assembly of Enantiomers of Chiral Aromatic Hydrocarbons Adsorbed on Metal Surfaces***, **K.-H. Ernst**, Y. Kuster, R. Fasel,* EMPA Duebendorf, Switzerland

We studied the interaction of heptahelicene ([7]H), a helically shaped, polyaromatic phenanthrene derivative, with well-defined single-crystal metal surfaces under ultra high vacuum (UHV) conditions. The molecules, racemate as well as the pure enantiomers, were deposited via molecular beam technique and subsequently characterized with surface sensitive techniques like temperature programmed desorption (TPD), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), time-of flight secondary mass spectrometry (ToF-SIMS), X-ray absorption spectroscopy (NEXAFS), and X-ray photoelectron diffraction (XPD). On Ni(111), the [7]H-molecule is adsorbed intactly at room temperature. TPD, however, shows only desorption of molecular [7]H from the multilayers. The first layer undergoes decomposition into carbon and hydrogen at 650 K. From Cu(111), molecular desorption is also observed at low coverages. The closed packed monolayers of [7]H on Ni(111) and Cu(111) show two-dimensional lattice structures. Adsorption of racemic [7]H leads to self-alignment into domaines on the surface, which are mirror images of each other. This is not observed after exposure to pure enantiomers and can be explained with a lateral separation of the enantiomers into homochiral domaines on the surface. For the pure M-enantiomer on the stepped Cu(332) surface, an azimuthal alignment of the molecular spirals is observed. Models for the monolayer structures and the mechanism of the separation will be discussed. Support by the Swiss National Science Foundation (NFP 36) is gratefully acknowledged.

9:40am **OF+NS+SS+BI-WeM5 Mesoscopic Correlation of Supramolecular Chirality in One-Dimensional Hydrogen-Bonded Assemblies***, **J.V. Barth**,* Ecole Polytechnique Federale de Lausanne, Switzerland*; J. Weckesser,* Max-Planck-Institut fuer Festkoerperforschung, Germany*; A. De Vita,* Institut Romand de Recherche Numerique en Physique des Materiaux, Switzerland*; C. Cai,* University of Houston*; K. Kern,* Max-Planck-Institut fuer Festkoerperforschung, Germany

We studied enantioselective self-assembly in two dimensions employing the molecule 4-[trans-2-(pyrid-4-yl-vinyl)] benzoic acid. Scanning tunneling microscopy observations at noble metal surfaces reveal the formation of hydrogen-bonded supramolecular twin chains in two mirror-symmetric species, each containing only molecules of a given chirality. The twin chains are ordered in µmm-gratings, where a mesoscopic correlation of supramolecular chirality over the entire domain size without intimate molecular contact persists. This novel phenomenon reflects mesoscopic chiral segregation due to chiral recognition in the formation of the supramolecular assemblies. Theoretical modelling in conjunction with direct observations indicate that twin chains act as enantioselective templates for transient molecular attachment, which process mediates self-replication of supramolecular chirality and the enantiopure gratings' evolution.

10:00am **OF+NS+SS+BI-WeM6 Controlling Molecular Orientation in Solid Films Via Self-organization in the Liquid-crystalline Phase***, I.K. Iverson, S.-W. Tam-Chang, **S.M. Casey**,* University of Nevada, Reno*; B.A. Pindzola,* University of California, Berkeley

We report the control of molecular orientation in solid films through self-organization and induced-orientation processes. We synthesized water-soluble cationic 3,4,9,10-perylene diimide (1) and studied its self-organization in aqueous solution. By UV-vis spectroscopy, H-aggregates of 1 are observed forming in solutions with concentrations as low as 10@super -7@ M. At concentrations above approximately 0.1 M (7% w/w) these solutions are observed with polarized microscopy to form a chromonic N phase (a nematic lyotropic liquid crystalline phase) at room temperature. Upon induced alignment (by shearing) of the chromonic N phase on a glass substrate and removal of solvent, anisotropic solid films of the dichroic dye are produced. These films have dichroic ratio values that routinely exceed 25 and in some cases 30, making them excellent sheet polarizers over the blue and green region. Using a combination of polarized UV-vis and FT-IR spectroscopies, the orientation of the average molecular plane in these films is determined to be perpendicular to both the shearing direction and the substrate plane. X-ray diffraction studies indicate that the molecules in the solid film possess a high degree of order.

10:40am **OF+NS+SS+BI-WeM8 Effect of Lipid Vesicle Fusion on the Ordering and Redox Activity of 11-(ferrocenyl carbonyloxy) Undecanethiols Self-assembled Monolayers***, A.T.A. Jenkins,* University of Bath, U.K., Great Britain*; **J.F. Le Meur,*** University of Bath, U.K.

Self-assembled Monolayers (SAMs) of 11-(ferrocenyl carbonyloxy) undecanethiol were made following a procedure given by Chidsey et @footnote 1@ The formation of the 11-(ferrocenyl carbonyloxy) undecanethiol SAM on gold was followed in-situ by Surface Plasmon Resonance (SPR)and showed a film of thickness 13 Å was formed. Impedance measurements indicated a high level of film coverage. Cyclic voltammetry was subsequently used to electrochemically characterise the SAM, and check its stabilty with respect to immersion in electrolyte. Egg-Phosphatidylcholine lipid vesicles were created by extrusion through a 50 nm membrane and were adsorbed on the SAM. SPR was used to follow the lipid adsorption on the SAM. Cyclic voltammetry measurements on the SAM-lipid system showed a large and reproducible increase in the peak anodic and cathodic currents after lipid adsorption, although the total quantity of charge transfered stayed the same. This is likely to be due to an increase in order of the ferrocene units in the SAM, allowing for a faster transfer of electrons on the lipid covered SAM than the SAM alone. The above experiments were repeated with binary mixtures of SAMs containing both 11-(ferrocenyl carbonyloxy) undecanethiol and mercaptoundecanol moities. It was found that the increase in anodic and cathodic current maximums measuresed by cylic voltammetery was disproportionately lower than the single component SAM (relative to the coverage). From this we propose a model for how the SAM structure changes upon lipid adsorption. @FootnoteText@ @footnote 1@ Chidsey, C.E.D.; Bertozzi, C.R.; Putvinski, T.M.; Mujsce, A.M. Journal American Chemical Society, 1990, 112, 4301-4306.

11:00am **OF+NS+SS+BI-WeM9 Temperature-dependent Morphology of Crystalline p-sexiphenyl Thin Films on KCl(001)***, **E.J. Kintzel, Jr.,*** Florida State University*; D.-M. Smilgies,* Cornell University*; J.G. Skofronick, S.A. Safron,* Florida State University

Investigations of the morphology of ultrathin films of p-sexiphenyl (p-6P) vapor deposited onto KCl(001) have been carried out using the complementary techniques of X-Ray Diffraction (XRD) and Atomic Force Microscopy (AFM). XRD studies have shown that the molecular orientation of the p-6P is dependent on the substrate temperature during deposition. For films prepared at low temperatures, the p-6P molecules take a lying orientation, with the long axis of the molecule aligned parallel to the substrate. As the substrate temperature was increased during deposition, XRD results indicate two coexisting molecular orientations, corresponding to lying and standing p-6P molecules. AFM images provide independent confirming evidence of the influence of substrate temperature on molecular orientation, consistent with the XRD results.

11:40am **OF+NS+SS+BI-WeM11 Characterization of Photoisomerization Reaction of Azobenzene-containining SAMs: Reaction Kinetics and Thermal Stability***, **K. Tamada,*** National Institute of Advanced Industrial Science and Technology (AIST), and Frontier Research System, RIKEN, Japan*; H. Akiyama, T. Wei,* AIST, Japan

We studied the change of photoreactivity of azobenzene disulfide SAMs under thermal stress. Azobenzene-containing unsymmetrical disulfide (C6AzSSC12) SAM was annealed at each temperature (70, 85, 100, 120, 140°C) for 1 hr, then the photoreaction was monitored with surface plasmon resonance spectroscopy (SPR) in hexane. The photoreaction was stable under 100°C when no decomposition of adsorbed molecules was detected, while it was suddenly reduced at over 100°C when the decomposition was taking place. After annealing at 140°C, the reactivity of the unsymmetrical disulfide SAM reached to the level of the corresponding azobenzenethiol SAMs (single component), suggesting the phase segregation of the adsorbed molecules by annealing. We designed new azobenzene thiol/disulfides (C6Az(Me)thiol, C6Az(Me)SSC12) to achieve more thermally stable photoresponse. In these molecules, CH@sub 3@-group is introduced to the azobenzene ring directly to avoid dye aggregation sterically. The C6Az(Me)thiol SAM exhibited much higher photoreactivity than conventional azobenzenethiol, which suggests that dye functions are less aggregated even in the single component SAMs. The C6Az(Me)SSC12 exhibited much higher photoresponse compared with C6AzSSC12 after annealing, since these azo dyes can react even in phase segregated domains. We also discuss photoisomerization reaction kinetics (cis to trans, trans to cis) in correlation with dye alignment.

Biomaterials
Room 103 - Session BI+NS-WeA
Nanobiology

2:00pm **BI+NS-WeA1 Light-controlled Molecular Shuttles Based on Motor Proteins***, **H. Hess**, J. Clemmens, D. Qin, J. Dennis, J. Howard, V. Vogel,* University of Washington

Molecular shuttles, an active transport system to position nanoscale objects, are needed as parts of molecular assembly stations, self-healing materials, or nanoscale actuators. The key problems of such a transport system are finding the motors, guiding the motion, loading cargo, and controlling the speed on the nanoscale. Active transport by single molecules is ubiquitous in biology and the solutions found by nature can serve as inspiration for technology. We demonstrate that molecular shuttles resembling conveyor belts can be constructed utilizing kinesin motor proteins as engines, microtubules as belts, and ATP as fuel. Two different strategies for guiding the microtubules have been explored by us: Arranging the motor proteins in nanometer-wide tracks by selective adsorption or creating micrometer-wide guiding channels by soft-lithography. Selective loading of cargo is accomplished by tagging cargo with streptavidin, and linking it to biotinylated microtubules. User-controlled exposure of caged ATP to UV-light and addition of an ATP-consuming enzyme to the buffer solution can move the microtubules in discrete steps. This forms a tool-set for the assembly of a functional molecular shuttle.

2:20pm **BI+NS-WeA2 The Direct Measurement of Drug-enzyme Interactions by Atomic Force Microscopy***, S.M. Rigby-Singleton, **S.J.B.T. Tendler**, S. Allen,* University of Nottingham, UK*; M.C. Davies,* University of Nottingham, UK, United Kingdom*; C.J. Roberts, P.M. Williams,* University of Nottingham, UK

AFM has been employed to directly probe the rupture forces upon the mechanical dissociation of the drug-enzyme complex formed between the anticancer compound methotrexate and the protein dihydrofolate reductase (DHFR). AFM probes were functionalized with methotrexate immobilized beads and rupture forces recorded between the probe and a DHFR monolayer attached via Lys residues. Three variables were studied, AFM retraction rates, the presence of the enzyme cofactor NADPH and the protonation of the key enzyme Asp26 residue. Rupture forces of 91 pN were recorded at a retract velocity of 1 micrometer per second, a ten fold decrease in velocity resulted in an observed decrease in rupture force. The influence of the enzyme cofactor was negligible suggesting little effect on the dissociation pathway, this is in marked contrast to literature fluorescent binding assays. Notably a decrease in rupture force of approximately 25pN was observed when the pH was decreased below the pKa of the key Asp26 residue which is situated deep within the methotrexate binding site. These studies indicate that the AFM will be a valuable tool in the drug discovery process.

2:40pm **BI+NS-WeA3 Single and Multiple Molecule Binding Forces Measured Using Modified Atomic Force Microscope Cantilevers***, **R.G. Rudnitsky**, F. Drees, K.S.H. Wu, T.D. Perez, W.J. Nelson, T.W. Kenny,* Stanford University

Although the energies and forces controlling protein interactions are frequently inferred from traditional equilibrium and kinetic measurements, recent developments in chemical force microscopy allow for the direct quantification of the ranges and magnitudes of binding forces between individual protein pairs and between groups of proteins. We report here on the use of specially modified Atomic Force Microscope cantilevers to measure bond strength down the single-molecule level, with pico-Newton force resolution, using the cellular binding protein E-cadherin as our model system. Previous E-cadherin studies focused on the energetics of large systems of molecules, typically in-vivo, to demonstrate their role in cellular adhesion. Our novel AFM force spectroscopy method tracks the unbinding process of single and multiple E-cadherin molecules under force loads, to quantitatively differentiate specific from non-specific binding, and single and multiple binding events, in surface bound protein. The measurements isolate the extracellular domain of the molecule, thought to be essential for stable cell adhesion, and demonstrate the dependence of binding forces at a molecular level on Ca++ concentrations. The data correlates the relationship of homophilic E-cadherin adhesion to surface protein density in a way not previously demonstrated in cellular studies.

3:00pm **BI+NS-WeA4 Selective Molecular Assembly Patterning - A New Approach to Micro- and Nanochemical Patterning of Surfaces for Biological Applications***, **R. Michel**,* Laboratory for Surface Science and Technology, Switzerland*; J.W. Lussi,* Laboratory for Biomedical Engineering, Swiss Federal Institute of Technology, Zurich, Switzerland*; I. Reviakine, M. Textor, N.D. Spencer,* Laboratory for Surface Science and Technology, Switzerland

A novel method for producing chemically patterned surfaces based on selective self-assembly of alkane phosphates on metal oxide surfaces is presented. Standard photolithography is used to create patterns of titanium oxide within a matrix of silicon oxide by successively depositing 40 nm of TiO@sub 2@, 10 nm of SiO@sub 2@ onto a silicon wafer, followed by photoresist application and anisotropic etching. Ordered SAMs of alkane phosphates form on the TiO@sub 2@, but not on the SiO@sub 2@ surfaces by self-assembly. Poly-L-lysine-g-poly(ethylene glycol) (PLL-g-PEG) is used to render the exposed SiO@sub 2@ protein-resistant. X-ray photoelectron spectroscopy and imaging time-of-flight secondary ion mass spectrometry were used to characterize the surfaces. Protein adsorption studies conclusively established that the resulting surfaces presented protein adhesive (the TiO@sub 2@/alkane phosphate SAM region) and non-adhesive (the PLL-g-PEG-coated SiO@sub 2@) areas. This novel Selective Molecular Assembly Patterning (SMAP) technique was used to grow fibroblasts in the presence of serum on 5*5 µm TiO@sub 2@ spots. Cytoskeletal organization in the fibroblasts was induced above the 5*5 µm TiO@sub 2@ patches, while no interaction with the PLL-g-PEG background was evident. The SMAP technique is considered to be highly suitable for reproducible and cost-effective fabrication of biologically-relevant patterns over large areas, by combining state-of-the-art photolithography and simple self-assembly dip-and-wash processes. Its applicability to sub-micrometer patterns is currently being evaluated.

3:20pm **BI+NS-WeA5 Studies of 20 nm Gold Particle Systems for Biosensing Applications & Optical Properties of Gold Nanostructures***, L. Olofsson, **F. Höök**, P. Delsing, D.S. Sutherland, J. Gold, B. Kasemo,* Chalmers University of Technology, Sweden

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3:40pm **BI+NS-WeA6 Nanofabricated Lipid Bilayers Patterned on Metal Electrodes***, **R.N. Orth**, I. Hafez, J. Kameoka, M. Lindau, H.G. Craighead,* Cornell University

Lipid molecules were immobilized on the surface of photolithographically patterned chromium and titanium. Large unilamellar lipid vesicles were found to bind on the native oxide surface of patterned support metals. Metal evaporation and resist liftoff techniques were used to pattern metal on a hydrophobic polymer surface. Lipids bound on solid substrates provide a biological interface for impedance measuring electrodes to detect bound cells or biomaterial. This patterning technique provides means to specifically bind lipids and conjugated biomaterials (polyethelene glycol (PEG), biotin, fluorescence dyes, and DNA oligimers) to the electrode surface. This technique may be applied to patterning biomaterial on metal inside thermally bonded microfluidic channels, to form titanium coated biomedical implants, and to create robust lipid-conjugated electrodes for biosensor applications.

4:00pm **BI+NS-WeA7 The Micropatterning of Mixed SAM Surfaces Using Inkjet Printing Technology: A Comparison Study to Microcontact Printing***, **L.F. Pardo**, T. Boland,* Clemson University

Micropatterning is a powerful method for controlling surface properties, with a myriad of applications ranging from cell biology to electronics. Self-assembled monolayers (SAMs) of alkanethiolates on gold, the structures most widely used for preparing organic films with specific surface properties, are usually patterned by partitioning the surface into regions formed from different thiols. In microcontact printing for example, patterned self-assembled monolayers (SAMs) are printed onto a surface using a polydimethilsiloxane (PDMS), made using a microfabricated mold. Although this technique is suitable, the distortion of patterns, pattern limitation to binary mixtures and expensive mold design are limiting the efficient use of stamps. In this study, a new method utilizing inkjet printing technology for patterning mixed thiols is introduced. Methyl and carboxyl-terminated hexadecanethiols were patterned onto clean gold surfaces using a modified inkjet printer. The topography of the micropatterned samples was visualized and measured by atomic force microscopy. The chemico-physical properties investigated by Fourier Transform infrared spectroscopy and dynamic contact angle measurements suggest that inkjet printer yielded high throughput patterning on surfaces. This new inkjet printing technique provides a quick and inexpensive method for micropatterning alkanethiols of surfaces.

4:20pm **BI+NS-WeA8 Fabrication of High Aspect Ratio Vertically Aligned Carbon Nanofiber-based Electrochemical Probes for the Probing of Intact Whole Cells***, **T. McKnight**,* Oak Ridge National Laboratory*; M.A. Guillorn,* Oak Ridge National Laboratory & University of Tennessee*; A.V. Melechko, D.W. Austin,* University of Tennessee*; V.I. Merkulov, M. Doktycz,* Oak Ridge National Laboratory*; D.H. Lowndes, M.L. Simpson,* Oak Ridge National Laboratory & University of Tennessee

Molecular biology and genomics are providing great insight into gene sequence, regulation and function. At the same time, imaging technology is elucidating cellular structure. Unfortunately, we have limited ability to monitor processes within and around living cells in real time and with high spatial resolution. This limitation is largely technological - our current research instruments are simply not on the same size scale as the functional components of cells. Here we present the fabrication and operation of high aspect ratio vertically aligned carbon nanofiber (VACNF)-based electrochemical probes for the probing of intact whole cells. Electron beam lithography was used to define the catalytic growth sites of the VACNFs. Following catalyst deposition, VACNF were grown using a novel plasma enhanced chemical vapor deposition (PECVD) process. Photolithography was performed to realize interconnect structures. These probes were passivated with a thin layer of SiO2, which was then removed from the tips of the VACNF, rendering them electrochemically active. We have demonstrated their functionality by selectively electrodepositing Au clusters onto the tips of the probes. We believe that these probes are ideally suited for characterizing intracellular phenomena in real time with an unprecedented degree of spatial resolution.

Nanometer Structures
Room 133 - Session NS+EL-WeA
Molecular Electronics and Patterning

Moderator: D.A. Bonnell, University of Pennsylvania

2:00pm **NS+EL-WeA1 Molecular Electronics by the Numbers***, **S.T. Pantelides**,* Vanderbilt University*; M. Di Ventra,* Virginia Tech*; N.D. Lang,* IBM **INVITED**

The paper gives an overview of recent work by the authors on first-principles, parameter-free calculations of electronic transport in molecules in the context of experimental measurements of current-voltage (I-V) characteristics of several molecules by Reed et al. The results show that the shape of I-V characteristics is determined by the electronic structure of the molecule in the presence of the external voltage whereas the absolute magnitude of the current is determined by the chemistry of individual atoms at the contacts. A three-terminal device has been modeled, showing gain. Finally, recent data that show large negative differential resistance and a peak that shifts substantially as a function of temperature have been accounted for.

2:40pm **NS+EL-WeA3 Controlled p-Doping of an Organic Molecular Semiconductor***, **W. Gao**, C. Chan, A. Kahn,* Princeton University

Electrical doping is perceived as the key to enhance the performance and versatility of organic molecular devices.@footnote 1@ Yet, few systematic investigations of the electronic structure of molecular films and interfaces doped with organic molecules have been published to date. We report here an investigation of controlled doping of zinc phthalocyanine (ZnPc) co-evaporated on Au with a strong acceptor, tetrafluoro-tetracyano-quinodimethane (F@sub 4@-TCNQ), using ultraviolet photoelectron spectroscopy (UPS) and inverse photoelectron spectroscopy (IPES). The 5.2 eV ionization energy of ZnPc is smaller than the electron affinity of F@sub 4@-TCNQ, suggesting host HOMO-to-guest LUMO charge transfer. Undoped ZnPc exhibits near mid-gap Fermi level (E@sub F@) and flat bands away from the Au interface, indicative of quasi-intrinsic purity. In ZnPc doped with ~3% (molar ratio) F@sub 4@-TCNQ, E@sub F@ shifts toward the HOMO level by 0.72eV and reaches ~ 0.16 eV above the leading edge of ZnPc HOMO, as measured from the surface of a 100Å film. At the interface with Au, the ZnPc HOMO is 0.72 eV below E@sub F@, leading to a depletion region with a 0.56eV band bending away from the interface, consistent with the p-type character of the film. The width of the depletion region in doped ZnPc is measured at approximately 32Å, consistent with a simple electrostatic model based on the doping concentration and a dielectric constant @epsilon@=3. The interface dipole barrier between Au and doped ZnPc is of the same sign and similar magnitude as for the undoped material. No evidence of chemical interaction can been seen, suggesting that pure charge transfer is the more likely mechanism for doping. The narrow depletion region in the doped layer is likely to lead to an increase in the tunneling of holes through the junction. I-V measurements will be performed to confirm this point. @FootnoteText@ * Work supported by the NSF (DMR-0097133) @footnote 1@Zhou et al., Appl. Phys. Lett., 78, 410 (2001).

3:00pm **NS+EL-WeA4 Conductance Switching in Single Molecules Through Conformational Changes***, **K.F. Kelly**, Z.J. Donhauser, B.A. Mantooth, L.A. Bumm, J.D. Monnell, J.J. Stapleton,* Penn State University*; D.W. Price,* Rice University*; D.L. Allara,* Penn State University*; J.M. Tour,* Rice University*; P.S. Weiss,* Penn State University

The viability of molecular electronics is being investigated with the aim of creating inexpensive, ultra-dense, high-capacity electronic devices. Conjugated phenylene-ethynylene oligomers have been extensively studied as candidate molecular devices. However, most experiments have required the assembly and study of these molecules in groups of thousands. We utilize self-assembly techniques in combination with scanning tunneling microscopy (STM) to study candidate molecular switches individually and in small bundles. Alkanethiol self-assembled monolayers (SAMs) on gold are used as a host two-dimensional matrix to isolate and to insulate electrically the molecular switches. The candidate molecules selectively adsorb into existing defect sites and at step edges. The molecules bind with a sulfur "alligator clip" to the underlying gold substrate, and the ordered SAM causes the molecules to adsorb nearly normal to the substrate. We then individually address and electronically probe each molecule using STM. The conjugated molecules exhibit reversible conductance switching, manifested as a change in the apparent height in STM images. The observed switching occurs randomly and reversibly, with persistence times for each state ranging from seconds (or less) to hours. Both individual molecules and bundles of molecules exhibit switching. We have demonstrated the ability to control the amount and rate of active switching by controlling the local environment of the guest molecules. Inserting the guest molecules into poorly ordered matrix films results in increased switching activity when compared to well-ordered films. Similarly, annealing the SAM after inserting the guest molecules results in decreased switching activity, when compared to unannealed SAMs. We ascribe the switching to conformational changes of the molecules that are either enhanced or reduced by the corresponding loosening or tightening of the surrounding matrix.

3:20pm **NS+EL-WeA5 Epitaxial Growth of Self-Assembled Dots and Wires***, **S. Williams**,* Hewlett-Packard Laboratories **INVITED**

Various structures with nanometer-scale dimensions can be grown on surfaces by taking advantage of lattice mismatch, crystal symmetry and surfactant species. This provides experimentalists with an array of control parameters to tune the size and shapes of the structures that form. The general principals for attaining this control will be illustrated for various types of Ge nano-islands on Si(001) and also for nano-wires of various silicides on Si(001).

4:00pm **NS+EL-WeA7 Micro and Nanoscale Patterning of SAMs and Their Functionalisation***, **S. Sun**, K. Chong, G.J. Leggett,* University of Manchester Institute of Science and Technology, UK

Lithography methods are at the heart of modern-day microfabrication, nanotechnology and molecular electronics. These methods always rely on patterning of a resistive film followed by a chemical etching of the substrates. Self-assembled-monolayers (SAMs) of alkanethiols on metals (Au, Ag or Cu) have been found to be good resists to protect underneath metals from wet etching. In addition, due to the chemical reactivity of some groups on SAMs, various kind of materials can be immobilized onto it. Therefore patterning and functionalisation of SAMs have attracted great interest since the last decade. Various methods have been employed for this purpose. Here we report experiments that generate micro- and nanometer size patterns of SAMs. Micrometer size features have been obtained through masked photo-oxidation either by a high-pressure mercury arc lamp or a lamp that only emits 254 nm light. Proteins have been immobilised onto these features successfully and can exhibit both a lateral force and topography contrast. Nanometer scale patterns have been achieved by scanning alkanethiol coated atomic force microscope (AFM) tips across Ag/Au film surface, a method called dipped-pen-nanolithography (DPN). It has been found the transportation rate of alkanethiols from AFM tip to metal surface not only depend strongly on the humidity of the environment, but also on the quantity of alkanethiol adsorbed on the tip and properties of substrate of interest. Different feature sizes from several micrometers to less than 50 nm have been obtained by controlling the scan speed and the environment humidity. Similar with the SAMs on Au, the SAMs on Ag formed by this method can also be used as resist layer to protect underneath Ag film from chemical wet etching.

4:20pm **NS+EL-WeA8 Diffusion of Alkanethiols in the Presence of Water**, ***P.E. Sheehan***, *M.L. Stevens, L.J. Whitman,* Naval Research Laboratory

The patterning of alkanethiols has become a cornerstone in the burgeoning field of nanotechnology. Several patterning techniques have been developed, the more popular of which include stamping using polymer masters, known as microcontact printing (mCP) and, more recently, the direct writing of the thiols using an AFM tip, known as Dip Pen Nanolithography (DPN). Importantly, in both techniques, diffusion of the thiol away from the contact area fundamentally limits the spatial resolution obtained. Obtaining the highest resolution possible from these techniques will require a full understanding of the rate and nature of thiol diffusion. To address this need, the radii of octadecanethiol spots deposited via DPN were studied as a function of tip-surface contact time and relative humidity. The increase in spot size with time was well described by two-dimensional radial diffusion from a constant source of finite radius. Fits using this formula revealed a diffusion constant of approximately 2500 nm2/sec with little dependence on humidity. Analysis of published images@footnote 1@ showing the spread of hexadecanethiol on gold after microcontact printing leads to comparable diffusion constants. Significantly, these values are four orders of magnitude smaller than that expected for diffusion through bulk water. Mechanisms that would explain such a low diffusion coefficient will be discussed. @FootnoteText@ @footnote 1@ Y. Xia and G.M. Whitesides, J. Am. Chem. Soc. 117 (1995) 3274.

4:40pm **NS+EL-WeA9 Chemical Nanolithography**, ***A. Gölzhäuser***, *W. Geyer, A. Küller, V. Stadler, W. Eck, M. Grunze,* Universität Heidelberg, Germany; *T. Weimann, P. Hinze,* Physikalisch Technische Bundesanstalt, Germany; *K. Edinger,* University of Maryland

The efficient fabrication of chemically defined surface nanostructures is an important objective in fields such as molecular electronics, biochips or biosensors. Chemical nanolithography utilizes electron beams to selectively modify self-assembled monolayers, for example to convert NO@sub 2@ end groups in monolayers of nitrobiphenylthiol to NH@sub 2@ groups.@footnote 1,2@ In this presentation, we show that chemical nanolithography can fabricate chemical features with lateral dimensions down to ~20 nm on a variety of different surfaces (noble metals, semiconductors or oxides). E-beam lithography as well as low energy electron proximity printing are used to fabricate chemical surface structures. These are then used as high resolution templates for the laterally controlled electrochemical deposition and for the immobilization of molecules (or macromolecular objects) on predefined surface regions. @FootnoteText@ @footnote 1@ W. Eck, V. Stadler, W. Geyer, M. Zharnikov, A. Gölzhäuser, M. Grunze, Adv. Mater. 12, 805 (2000). @footnote 2@ A. Gölzhäuser, W. Eck, W. Geyer, V. Stadler, T. Weimann, P. Hinze, M. Grunze, Adv. Mater. in press.

Tribology
Room 132 - Session TR+MM-WeA
Nanotribology

Moderator: Y.-W. Chung, Northwestern University

2:00pm **TR+MM-WeA1 Tribological Issues in MEMS**, ***R. Maboudian***, University of California, Berkeley **INVITED**

Given the dimension of most microelectromechanical systems, gravity and other body forces are negligible. In contrast, interfacial forces dominate due to their large surface area-to-volume ratios. As a consequence, adhesion, friction, and wear are prevalent problems in many MEMS devices. Additionally, MEMS technology provides us with the opportunity to study tribology on a length scale not easily accessible by other techniques, namely the mesoscopic length scale. This presentation will discuss the use of several tribological microinstruments in conjunction with other surface characterization techniques, such as atomic force microscopy, to measure the surface forces present between polycrystalline silicon surfaces and to manipulate them by utilizing various surface treatments. The successes and the limitations of current surface coating technologies as well as areas for improvement will be discussed.

2:40pm **TR+MM-WeA3 Friction Properties of Self-assembled Monolayers: Influence of Adsorbate Molecular Structure and Molecular Organisation**, *N.J. Brewer,* ***G.J. Leggett***, UMIST, UK **INVITED**

The frictional properties of self-assembled monolayers (SAMs) of alkanethiols on gold are influenced by both the chemistry of the adsorbate tail groups and the organisation of adsorbate molecules within the monolayer. Studies of mixed self-assembled monolayers composed of adsorbates with contrasting terminal group chemistries and equal chain lengths have revealed a linear relationship between SAM composition and the coefficient of friction. However, for mixed SAMs formed from molecules with differing alkyl chain lengths, molecular organisation may be quite different from that observed for single component SAMs, leading to substantial changes in the coefficient of friction. Moreover, while methyl terminated SAMs exhibit markedly different frictional properties for adsorbates of different chain length, this is not the case for SAMs formed from hydroxyl and carboxylic acid terminated adsorbates. For these polar SAMs the coefficient of friction varies little between short and long chain adsorbates. This is attributed to hydrogen bonding between adsorbate terminal groups, which has a dominating effect on SAM stability and organisation. The friction-velocity behaviour of SAMs with polar terminal groups in contact with polar tips is quite different from the behaviour observed for the same materials in contact with non-polar tips, and the expected linear relationship between the friction force and the log of the velocity is not observed; instead the friction force rises rapidly and then reaches a plateau. Finally, friction properties of specific thiols adsorbed onto gold and silver surfaces are markedly different, reflecting changes in molecular organisation and providing valuable insights into the structures of these materials.

3:20pm **TR+MM-WeA5 Interfacial Friction of Methanol Sliding on Rigid vs. Rotating Fullerenes**, ***T.S. Coffey***, *M. Abdelmaksoud, J. Krim,* North Carolina State University

Due to the ability of C60 molecules to rapidly rotate within their lattice position, tribologists had hopes that C60 molecules would work like nano-sized ball bearings. C60 has not been proven to be an effective lubricant. We measured the interfacial friction of toluene on Ag(111) in both the presence and absence of interfacial C60 layers employing quartz crystal microbalance (QCM) and atomic force microscopy (AFM) techniques.@footnote 1@ We see the friction double when C60 is present. However, the difference in interfacial friction between a rigid vs. a rotating molecule in a substrate remains an interesting topic. C60 is known to form close packed hexagonal films on both Ag(111) and Cu(111) substrates. However, on Ag(111) surfaces, C60 is known to spin freely in its lattice position, while it is not free to rotate on a Cu(111) surface.@footnote 2@ In order to determine whether the spinning of the C60 molecules affects the interfacial friction, we are employing QCM techniques to compare the friction of methanol on C60/Ag(111) vs. methanol on C60/Cu(111). We examine here whether the rolling nature of the C60 layer impacts the sliding friction as probed by QCM, AFM, and QCM/STM measurements. @FootnoteText@ @footnote 1@ T. Coffey, M. Abdelmaksoud, and J. Krim, "A Scanning Probe and Quartz Crystal Microbalance Study of the Impact of C60 on Friction at Solid-Liquid Interfaces", Journal of Physics Condensed Matter, in press. @footnote 2@ Applied Surface Science 87/88 (1995) 405.

4:00pm **TR+MM-WeA7 Superconductivity Dependent Friction of Adsorbed Monolayers on Pb(111)**, ***J. Krim***, *A. Mayer, L. Wagner,* North Carolina State University

In order to gain a fundamental understanding of friction, one must understand, at the molecular level, how the energy associated with the work to overcome friction is converted to heat. Such knowledge is key to understanding the rate at which an interface will heat, and in addition how chemical reactions and other physical processes triggered by heat will be affected by friciton. One of the simplest possible geometries in which friction can occur, and thus be studied, is that of a fluid or crystalline monolayer adsorbed on an atomically flat surface. This geometry is experimentally accessible to experiments with a Quartz Crystal Microbalance (QCM), to numerical simulation techniques, and to analytic theory. A recent QCM experiment@footnote 1@ sought to explore the nature of electronic contributions to friction by measuring the friction associated with nitrogen monolayers sliding on Pb substrates as the temperature passed through the superconducting transition at 7.2K. The work inspired a number of subsequent theoretical and experimental efforts, which yielded contradictory results. A major complication associated with the Ref. 1 result arose from the fact that the data were reported for Pb substrates which had been exposed to air. We have thus repeated the measurements on Pb substrates which have been prepared in situ for both nitrogen and rare gas monolayers. The latter have been predicted by some theories to exhibit no dependence on the superconducting state of the sample. We present these results and compare them to the various conflicting theories. @FootnoteText@@footnote 1@ A. Dayo, W. Alnasrallah and J. Krim, Phys. Rev. Lett. vol 80, 1690 (1998) Work funded by NSF.

4:20pm **TR+MM-WeA8 Nanotribology of Total Joint Replacement Prosthesis (TJR)***, **S.P. Ho,*** Clemson University*; R.W. Carpick,* University of Wisconsin - Madison*; T. Boland, P.F. Joseph, M. LaBerge,* Clemson University

Atomic force microscope (AFM) was used to represent nanotribological asperity-to-asperity nanocontact between a cast CoCr alloy and an unsterilized surgical-grade direct compression molded ultra high molecular weight polyethylene (UHMWPE) of TJR prosthesis. UHMWPE is a semicrystalline material consisting of crystalline domains within an amorphous matrix. The primary dependence of friction upon normal load during an abrasive nanocontact may involve gross plastic deformation leading to plowing of UHMWPE surface. We have studied the nanotribological properties and evolution of plastic deformation of UHMWPE, to determine the precursors to wear particle formation in TJR prosthesis. It was hypothesized that variability in friction due to the individual nano-constituents in the semicrystalline polymer could cause a stress concentration leading to the generation of nanoscale wear debris particle; the originator for osteolysis in a total joint arthroplasty. Results from AFM analyses will be presented in this work to elucidate the average coefficient of friction and wear mechanisms and to reveal friction coefficients of the individual nano-constituents in the UHMWPE. Results showed that loading the nanocontact within the elastic regime resulted in an average coefficient of friction of 0.25+/-0.04. Higher normal load ranges revealed a sudden increase in lateral force indicating ploughing of the nanocontact, eventually leading to generation of nanoscale wear debris. The sudden increase in lateral force indicated that the UHMWPE plastically deforms causing an increase in contact area leading to an increase in lateral forces. We will present data supporting the individual contribution of crystalline and amorphous regions to the coefficient of friction for the purpose of understanding the observed plastic deformation at the modeled nanocontact of total joint replacement prosthesis (TJR).

4:40pm **TR+MM-WeA9 Surface Force Dynamics and Nanotribology of Self-healing Monolayers Applied to MEMS Lubrication: A Study Using Dip Pen Nanolithography***, **J.J. Nainaparampil,*** Systran Federal/MLBT, US*; K.C. Eapen,* UDRI/MLBT*; J.S. Zabinski,* AFRL/MLBT

Self-assembled monolayers (SAMS) have good potential for lubrication of microelectromechanical systems (MEMS). However, monolayers tend to wear away relatively quickly, which limits their usefulness. Mechanisms for monolayer replenishment have the potential to expand the role of SAMS in MEMS lubrication schemes. The dynamics of adhesion and friction forces of self-healing monolayer coatings is studied using techniques derived from dip pen nanolithography (DPN). Typically, DPN makes use of an Atomic Force Microscope (AFM) to write patterns with 'ink' that is deposited on the cantilever tip or delivered through a nanometric aperture.@footnote 1,2@ An AFM is used here to write monolayer patterns of various thiols, nonane dione and aminoalkylsilane on gold, copper, aluminum and silicon surfaces. Nanotribological measurements of adhesion and lubricity are measured using a combination of topography and lateral force scans. Special patterns that constrain molecular surface diffusion were used to permit studies of wear and replenishment dynamics. Measurements made on thiol and nonane dione monolayers on gold surfaces showed that stronger adhesion occurs for thiol coatings compared to nonane dione. The effects of relative humidity, temperature and aging on surface forces and monolayer dynamics will be presented. @FootnoteText@@footnote 1@Richard D. Piner, Jin Zhu, Feng Xu, Seunghun Hong and Chad A. Mirkin, Science 283, (1999) 661. @footnote 2@Mun-Heon Hong, Ki Hyun Kim, Joono Bae and Wonho Jhe, Appl. Phys. Lett. 77(16) (2000) 2604.

5:00pm **TR+MM-WeA10 Observation and Simulation of Dislocation Emission after Nanoindentation of an FCC (100) Surface***, O. Rodríguez de la Fuente,* Universidad Complutense de Madrid, Spain*; J.A. Zimmerman, **J. de la Figuera**,* Sandia National Laboratories*; M.A. González,* Universidad Complutense de Madrid, Spain*; J.C. Hamilton,* Sandia National Laboratories*; J.M. Rojo,* Universidad Complutense de Madrid, Spain

The traditional use of indentation of materials to characterize mechanical hardness has benefited both from recent experimental and theoretical advances. The routine use of Scanning Probe Microscopes allows the detailed examination of the surface of materials after nanoindentation, using the same instrument for both deformation and analysis. Techniques used to model the defects generated during indentation have also advanced by the development of fast, parallel computations of million-atom systems governed by semi-empirical potential energy functions. Together, these advances are starting to bridge the gap between theory and experiment. We present a combined study of the emission of dislocation loops by indentation on the surface of Au(100) using Scanning Tunneling Microscope (STM) experiments and atomistic simulations employing the Embedded Atom Method (EAM). Our experiments show dislocation loops emitted in directions that extend out to distances hundreds of nanometers away from the indentation region. These loops consist of dissociated edge loops that intersect the surface. The locations of these dissociated loops are identified by the sub-angstrom height hillocks observed on the crystal surface. Atomistic simulation of nanoindentation reveals that these dislocation loops are generated close to the indentation region and glide away along directions. The sub-surface structure of the dislocation loops verifies the stacking faults beneath the hillocks, which intersect at a stair-rod dislocation. Our simulation permits an estimate of the Peierls barrier for loop glide, revealing why the dislocations can glide so far from the indentation region. We have also observed the same dislocation loops by annealing an ion-irradiated Au(100) surface. The atomistic simulations help to understand how the dislocation loops can withstand the annealing.

Magnetic Interfaces and Nanostructures
Room 110 - Session MI+NS-ThM

Magnetic Imaging and Spectroscopy

Moderator: P.N. First, Georgia Institute of Technology

8:20am **MI+NS-ThM1 Measurement of Spin Polarization using Andreev Reflection***, **R.J. Soulen**, M.S. Osofsky, G. Trotter,* Naval Research Laboratory **INVITED**

Measurement of spin polarization using Andreev reflection A new class of electronics is emerging which relies on the ability of ferromagnetic materials to conduct spin polarized currents. The performance of devices based on this phenomenon is greatly enhanced as the spin polarization, P, of the ferromagnetic material approaches 100%. In the face of difficulties in measuring this important property, we have developed a very simple method to determine P in which a superconducting point is placed in contact with the candidate ferromagnetic material. The Andreev reflection process at the interface between the two metals is influenced by the spin polarization of the ferromagnet enabling the determination of P through measurement of the conductance of the contact. In a very short time we have been able to measure the spin polarization of several metals and conducting oxides: NixFe1-x; Ni. Co, Fe, NiMnSb, La0.7Sr0.3MnO3; CrO2, whose spin polarization ranges from 25% to over 90%. Our results compare well with other magnetic spectroscopy measurements of P where available. Our search continues for a material with 100% spin polarization.

9:00am **MI+NS-ThM3 Point Contact Spectroscopy in Magnetic Fields***, **M. Tsoi**,* IBM Almaden Research Center **INVITED**

9:40am **MI+NS-ThM5 Magnetocrystalline Anisotropy Probed using X-ray Magnetic Linear Dichroism***, **S.S. Dhesi**,* ESRF, France*; G. van der Laan,* Daresbury Laboratory, UK*; E. Dudzik,* Hahn-Meitner-Institut, Germany*; A.B. Shick,* University of Davis, California

The anisotropy of the spin-orbit interaction,@lambda@@sub 2@, in vicinal Co films has been measured using x-ray magnetic linear dichroism (XMLD). A linear increase in @lambda@@sub 2@ with Co step density is found using a new sum rule and represents the first experimental confirmation that XMLD probes the magnetocrystalline anisotropy energy (MAE). X-ray magnetic circular dichroism (XMCD) is used to confirm that the XMLD arises from changes in the local step-edge electronic structure. The XMLD sum rule gives a larger MAE compared to macroscopic values and is discussed with respect to other local probes of the MAE.

10:00am **MI+NS-ThM6 Soft X-ray Microscopy to Image Magnetic Domain Structures at High Resolution***, G. Schuetz,* Universitat Wurzburg, Germany*; **P. Fischer**,* MPI-MF, Germany **INVITED**

X-ray magnetic circular dichroism (X-MCD) serves as huge element-specific magnetic contrast mechanism in combination with soft X-ray microscopy to image magnetic domains with a current lateral resolution down to 25nm. The sensitivity of X-MCD on the projection of the magnetization of the ferro(i)magnetic species along the photon propagation direction allows to study both in-plane and out-of-plane magnetized systems. The capability of this photon based microscopy to record the images in varying external magnetic fields and the high sensitivity down to thicknesses of a few nm is outlined and proofs this novel technique to be a promising tool for the study of the switching behaviour of individual layers in thin film magnetic media that are currently discussed (magnetic sensors, spintronic devices, etc.). Recent results obtained on nanostructured and multilayered systems will be presented together with micromagnetic simulations to get insight into the micromagnetic properties of these systems.

10:40am **MI+NS-ThM8 Photoemission Electron Microscopy and X-Ray Magnetic Circular Dichroism of Ultrathin FeNi Alloy Films on Cu(111)***, **Y. Sato**, T.F. Johnson, S. Chiang,* University of California, Davis*; F. Nolting, A. Scholl,* Lawrence Berkeley National Laboratory*; X.D. Zhu, D.P. Land,* University of California, Davis

We are studying the system of NiFe/Cu(111) to understand and control the surface/interface magnetism relevant to the application of the giant magnetoresistive effect to magnetic recording heads. We used the Photoemission Electron Microscope (PEEM2) at the Advanced Light Source to observe the domain structures of the alloy films. PEEM has the unique capability of imaging the film's magnetic structure with high spatial resolution and elemental specificity. Element specific magnetic contrast images and X-ray Magnetic Circular Dichroism (XMCD) spectra were obtained for eight different samples of varying Fe compositions at two different thicknesses. Samples with higher Fe content (x = 0.66, 0.74) were non-magnetic at room temperature. This trend of reduction in Curie temperature at higher Fe concentration agrees both with our XMLD data on the same system@footnote 1@ and with previous work on FeNi/Cu(100).@footnote 2@ We speculate this is a structure-driven effect related to the "Invar effect" in the bulk alloy. The PEEM images clearly show that Fe and Ni form a good alloy and have the same domain structures with their magnetization aligned. Further, we find a strong thickness and concentration dependence of the magnetic domain structures. For 5ML films, the domain structures appear to be strongly influenced by surface topography of the substrate. For 10ML films, however, the effect of the substrate features is already insignificant. At this thickness, the Fe concentration is also found to affect the size of the domains and the presence of an easy magnetization axis. @FootnoteText@ @footnote 1@T.F.Johnson, S.Chiang, Y.Sato, et al., to be published @footnote 2@F.O.Schumann, S.Z.Wu, G.J.Mankey and R.F.Willis Phys.Rev.B 56, 2668 (1997).

11:00am **MI+NS-ThM9 Imaging Magnetization in MRAM Elements with Soft X-Ray Microscopy***, **J.B. Kortright**, G. Meigs, G.P. Denbeaux,* Lawrence Berkeley National Laboratory*; J.M. Slaughter, R. Whig, S.-I. Han,* Motorola

The magnetic elements used to store information in MRAM devices will have dimensions of less than 1 micron laterally and roughly 5 nm in thickness. Such small dimensions make it difficult to directly observe field-dependent magnetization structure in individual elements, and possible interactions between elements, by conventional magnetic microscopy techniques. We are using scanning and imaging soft x-ray microscopes based on zone-plate lenses (with resolution approaching 30 nm) and resonant magnetic circular dichroism contrast to image magnetization structure during reversal in arrays of lithographically patterned bits on SiNx membrane substrates. Remnant magnetization structure and its evolution through reversal are clearly resolved, as is the dependence of this structure on element size, shape and cyclic reversal. Following a brief review of techniques, microscopy results relevant to MRAM applications and comparisons with micromagnetic theory will be presented. Work at LBNL was supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Work at Motorola Labs was partially funded by DARPA.

11:20am **MI+NS-ThM10 Imaging Magnetic Nanostructures by Spin-Polarized Scanning Tunneling Microscopy***, **M. Bode**, A. Kubetzka, O. Pietzsch, M. Kleiber, R Ravli@aa c@, R. Wiesendanger,* University of Hamburg, Germany **INVITED**

Our recent progress in spin-polarized scanning tunneling microscopy (SP-STM) will be reviewed. By using magnetic thin film tips and spectroscopic techniques we could image the surface spin-structure of different surfaces and ultrathin films with a spatial resolution down to the atomic level. Namely, we will present results obtained on the topological antiferromagnet Cr(001),@footnote 1@ on self-organized Fe-nanowires@footnote 2@ and -islands,@footnote 3@ and on the antiferromagnetic monolayer of Mn/W(110).@footnote 4@ We will demonstrate that in-plane and out-of-plane spin-contrast can be achieved by choosing appropriate magnetic tip coatings and that the use of an antiferromagnetic tip material avoids any influence of the tip´s magnetic stray field on the sample´s domain structure. In contrast to most other electron-based microscopic techniques SP-STM as a near-field method can be applied even in large external magnetic fields up to several Tesla allowing the investigation of hysteresis effects in magnetically hard materials. @FootnoteText@ @footnote 1@ M. Kleiber et al., Phys. Rev. Lett. 85, 4606 (2000).@footnote 2@ O. Pietzsch et al., Phys. Rev. Lett. 84, 5212 (2000).@footnote 3@ A. Kubetzka et al., Phys. Rev. B 63, 140407 (2001). @footnote 4@ S. Heinze et al., Science 288, 1805 (2000).

Nanotubes: Science and Applications Topical Conference Room 133 - Session NT+EL+NS-ThM

Nanotubes: Growth, Functionalization, and Sensors

Moderator: P.M. Ajayan, Rensselaer Polytechnic Institute

8:20am **NT+EL+NS-ThM1 Control of Carbon Nanofiber Growth: "Base" versus "Tip" Growth Regimes***, **A.V. Melechko,*** University of Tennessee*; V.I. Merkulov,* Oak Ridge National Lab*; M.A. Guillorn,* University of Tennesse and Oak Ridge National Lab*; D.H. Lowndes,* Oak Ridge National Lab*; M.L. Simpson,* University of Tennesse and Oak Ridge National Lab

Carbon nanofibers (CNF) show promise for many applications in such new areas as nanoelectronics and nanobiotechnology. It is very important to have a precise control of the position, orientation, and shape of the CNFs to maximize their utility for these applications. Recently it became possible to achieve such deterministic growth by nanopatterning catalyst and using Plasma Enhanced Chemical Vapor Deposition (PECVD). PECVD is a complex process that involves control of many interdependent parameters such as pressure, mass flow ratio (C2H2/NH3), substrate temperature, substrate material, plasma intensity and bias. Two different CNF growth regimes have been observed. One is when the catalyst particle is detached from the substrate surface and located at the tip of the CNF ("tip-growth" regime). Another regime is when the catalyst particle stays attached to the substrate ("base-growth" regime). We present an experimental study of the parameter space of a DC PECVD process for different regimes of CNF growth: "base-growth", "tip-growth", and intermediate regimes, where both types of CNFs were observed simultaneously. The mechanisms, which are responsible for the competition of these different growth phases, such as catalyst-substrate interaction and interdiffusion, formation of amorphous carbon film, and kinetics of catalysis and carbon diffusion through catalyst particle will be discussed.

8:40am **NT+EL+NS-ThM2 Scanning Tunneling Microscopy and Spectroscopy of Gd@@C@sub 82@-filled Single-walled Carbon Nanotubes***, J. Lee,* Seoul National University, Korea*; J.-Y. Park,* Cornell University*; **H.J. Kim**, H. Suh,* Seoul National University, Korea*; Y. Kuk,* Seoul National University, Korea, South Korea*; H. Kato, T. Okazaki, H. Shinohara,* Nagoya University, Japan

In this presentation we will show the atomic resolution STM images of single-walled carbon nanotubes filled with Gd@@C@sub 82@ metallofullerenes at ~7K. Atomic resolution images of Gd@@C@sub 82@-filled SWNTs with small tip bias voltages show nanometer-scale variations in topographic height and in atomic-scale corrugation pattern along the longitudinal axis of the nanotube. In the image with larger tip bias voltage of -1V, we could clearly observe the randomly oriented protrusions spaced roughly by integer multiples of 1.1nm which corresponds to the spacing between metallofullerenes in the nanotube. It is thought that the protrusions are caused by localized band-bending of the SWNT due to each Gd ion's field which is partially-screened by electrons in the encaging fullerene. Comparing images with different tip bias voltages, large DOS participating in the tunneling process, i.e. a large tip bias, might be needed to show enough spatial resolution. The scanning tunneling spectroscopy data of these nanotubes, which also show Gd-atom-induced local field-effect on the characteristic DOS features of SWNTs, will be presented. The possibility of 1-D Kondo effect due to the encapsulated Gd atoms will also be discussed.

9:00am **NT+EL+NS-ThM3 Using Carbon Nanotube Materials to Separate Molecular Mixtures: Predictions from Molecular Dynamics Simulations***, **S.B. Sinnott,*** The University of Florida*; Z. Mao,* The University of Kentucky*; K.-H. Lee,* The University of Florida*; R. Andrews, E.A. Grulke,* The University of Kentucky

Carbon nanotubes have been proposed as good materials for separation membranes because of their hollow, cylindrical shape and growth in ordered, close-packed bundles. We have therefore studied the manner in which molecular mixtures separate after diffusion into individual carbon nanotubes or nanotube bundles. The mixed systems considered in our study are methane/n-butane, methane/isobutane, methane/ethane, nitrogen/oxygen, nitrogen/carbon dioxide and oxygen/carbon dioxide. The computational approach used is classical molecular dynamics simulations where the forces on the atoms are calculated using empirical potentials that vary with distance.@footnote 1@ Short-range interactions are calculated using a many-body, reactive empirical bond-order hydrocarbon potential and the long-range interactions are characterized with Lennard-Jones potentials. Some of these molecular mixtures separate within individual nanotubes while others do not. The mechanisms by which the molecules diffuse through the nanotubes are found to play an important role in the separation of some mixtures. Molecular structure also has a large effect on the separation of the molecular mixtures. The helical structure of the nanotube walls is predicted to have no effect on results while the nanotube diameter has a large effect. As the diameter of the nanotubes increases, the amount of separation between the molecules decreases. In nanotube bundles, the diffusion behavior and coefficients of binary molecular systems change relative to the diffusion behavior in individual nanotubes. This research is sponsored by the NASA Ames Research Center and the Advanced Carbon Materials Center through the NSF (DMR-9809686). @FootnoteText@ @footnote 1@S.B. Sinnott, L. Qi, O.A. Shenderova, D.W. Molecular Dynamics of Clusters, Surfaces, Liquids, and Interfaces, Ed. W. Hase (JAI Press, Inc., Stamford, CT, 1999, pp. 1-26.

9:20am **NT+EL+NS-ThM4 Chemical Disentanglement of Single-Walled Carbon Nanotube Bundles***, N. Choi,* Joint Research Center for Atom Technology (JRCAT), Japan*; **H. Tokumoto**,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; Y. Maeda, T. Wakahara,* Niigata Univ., Japan*; T. Akasaka,* Univ. of Tsukuba, Japan*; H. Kataura, M. Kimura, S. Suzuki, Y. Achiba,* Tokyo Metropolitan Univ., Japan

Carbon nanotubes (CNTs) exhibit unique electronic and mechanical properties and chemical stability that cannot be realized in other materials, and therefore can be an important material in nanotechnology. Many applications have been demonstrated in the fields of materials science and technology, molecular electronic devices, and reliable probe tips for scanning probe microscopy. However, as-grown CNTs contain various contaminants such as catalysts and amorphous carbons, and have various lengths from a few nano-meters to milli-meters, and various sizes of bundles. These prevent us to use CNTs for various applications. Then, we have to develop several important key techniques such as how to purify, how to control length, how to disentangle the bundles, and how to disperse individuals in solvents. An important and essential technique to realize these keys is believed to be the chemical modification of CNTs combined with their sonication and centrifugation. In this paper, we will show the chemical process and their characterization techniques. After purifying single-walled CNTs, we put them into N,N-dimethylformamide (DMF) at a concentration of 0.4 mg/10 ml with the small amount of amine. At the same time, we sonicated and centrifuged them under optimized time, frequency and rotational speed. At each step, we measured a transmission electron microscopy (TEM), a Raman scattering spectroscopy, and an atomic force microscopy (AFM). These three techniques have proved that our technique has indeed worked out properly. Especially, the chemical modification of the CNT ends was confirmed by the AFM observation of CNTs covalently attached to gold colloidal particles.

9:40am **NT+EL+NS-ThM5 Electromechanical Properties of Carbon and Boron-Nitride Nanotubes***, **A. Zettl,*** University of California, Berkeley **INVITED**

The electronic properties of single- and multi-walled carbon nanotubes have been investigated via transport measurements under controlled environmental conditions, and in-situ electro-mechanical measurements inside a high resolution transmission electron microscope (TEM) and scanning tunneling microscope (STM). Our transport measurements show that the electronic structure of nanotubes is exceedingly sensitive to adsorbed gases. For example, the thermoelectric power for pure vacuum annealed tubes is negative, while that for oxygen-dosed samples is positive. Similarly, the electrical resistivity for individual tubes is sensitive to chemical environment, and nanotubes form robust oxygen and other chemical sensors. The theoretical basis for these sensitivities are explored via quantum transport models. For electromechanical studies, a special nanotube manipulator has been constructed for insertion into a TEM. Individual multi-walled nanotubes have been variously manipulated. We have discovered ways to peel and sharpen individual nanotubes (much like the sharpening process of a china marker pencil), pull the central core tubes out from (and reinsert them into) the outer nanotube shells of multi-walled tubes (nanotube "telescoping"), and induce nanotube collapse of cylindrical tubes into nanotube ribbons. Similarly, boron nitride nanotubes have been synthesized and the electromechanical response characterized in bulk and individually inside the TEM.

10:20am **NT+EL+NS-ThM7 Magnetic "Smart-Wires": Magnetic and Electronic Properties of Nickel and Iron Nanotubes Grown on Polypeptide Templates***, H. Matsui, S. Pan, E. Goun, M. Klimov, **B.P. Tonner**,* University of Central Florida

We describe a new architecture for spin-tronic magnetic devices, using a biologically modified, metal coated, peptide nanotube process which results in tubular, magnetic nanowires.@footnote 1,2@ The magnetic nano-wires are formed from a polypeptide backbone, coated with nickel, or iron, or with multilayers. The morphology of the tubes is that of a hollow, cylindrical metal pipe, with widths from 20-500nm, and lengths of up to a few microns. By functionalizing the ends of the tubes with special molecules, the nano-tubes can be "wired" to specific attachment sites on a substrate by molecular recognition. We call this a "smart-wire" concept, since the instructions for "wiring" the circuits are built into the molecular nanostructures themselves. In this paper, we describe magnetic and electronic transport measurements on aligned Nickel nanotube arrays and individual nanotubes, using both conventional and scanned-probe techniques. @FootnoteText@ @footnote 1@ Matsui, H.; Gologan, B., J. Phys. Chem. B. 2000, 104, 3383. @footnote 2@ Matsui, H.; Pan, S.; Gologan, B.; Jonas, S., J. Phys. Chem. B. 2000, 104, 9576.

10:40am **NT+EL+NS-ThM8 Chemical Reactivity of Carbon Nanotubes and Fullerenes***, **S. Park**,* Stanford University*; D. Srivastava,* NASA Ames Research Center*; K. Cho,* Stanford University

In most applications of carbon nanotubes and fullerenes, molecules are attached to either external or internal surface of carbon nanotubes and fullerenes to functionalize them. Therefore, the chemical reactions on nanotubes or fullerenes play an important role in understanding how to functionalize nanotubes and fullerenes. We have analyzed and compared the chemical reactivity of both external and internal surfaces of carbon nanotubes and fullerenes. The chemical reactivity analysis can be used to control the localized functionalization process as well as to predict energies and configurations of chemical reactions. Also this analysis can be applied to examine the storage capacity of carbon nanotubes and fullerenes. The chemical reactivity of carbon nanotubes and fullerenes can be characterized by a pyramidal angle, which is defined as the angle between @sigma@ bond and @pi@ orbital minus 90 degree. We analyze the chemical reactivity in terms of pyramidal angle. All analyses have been done by total energy density functional theory pseudo-potential method, and we have used a hydrogen atom as a point probe to investigate the chemical reactivity. We have developed a way to express the chemical relativity as function of pyramidal angle. We have found that the external chemical reactivity depends strongly on the initial pyramidal angle but the internal chemical reactivity is less sensitive to it. And we have also found that the internal chemical reactivity has more complex behavior than external chemical reactivity.

11:00am **NT+EL+NS-ThM9 Atomic Resolution Imaging of WS2 Nanotubes***, L. Scheffer, **S.R. Cohen**, R. Rosentsveig, R. Popovitz-Biro, R. Tenne,* Weizmann Institute of Science, Israel

Recent improvements in synthetic yields of inorganic nanotubes of metal dichalcogenides have enhanced the possibility of their technological applications.@footnote 1@ The unique optical and wear characteristics of these nanotubes make them ideal candidates for electromechanical systems.@footnote 2@ Correlation of the structural and electro-optical properties is a first step in this direction. Theory predicts delicate interplay between size, structure, and electrical properties of these nanotubes.@footnote 3@ Until now, correlation of the nanotube chirality with electrical properties has been indirect and scarce. In this work we present high resolution transmission electron microscopy (TEM) and atomic-resolution scanning tunneling microscopy (STM) images of nanotubes of WS@sub 2@. By relating the atomic registery to the tube-axis direction, the chirality of the tubes is determined. Current-voltage (I/V) spectroscopy in the STM was then applied to individual nanotubes to examine correlation between bandgap, density of states, and the nanotube chirality and size. @FootnoteText@ @footnote 1@ A. Rothschild, G.L. Frey, M. Homyonfer, R. Tenne, M. Rappaport, Mat. Res. Innovat. 3, 145 (1999). @footnote 2@ L. Rapoport, Y. Feldman, M. Homyonfer, H. Cohen, J. Sloan, J.L. Hutchison, and R. Tenne, Wear 229, 975 (1999). @footnote 3@G Siefert, H. Terrones, M. Terrones, G. Jungnickel, T. Frauenheim, Phys. Rev. Lett. 85, 146 (2000).

11:20am **NT+EL+NS-ThM10 In-situ Observed Atomic Structures at Carbon Nanotube Tips under Applied Electric Field***, **T. Kuzumaki**, Y. Horiike,* The University of Tokyo, Japan*; T. Kizuka,* Nagoya University, Japan*; T. kona, C. Oshima,* Waseda University, Japan

Carbon nanotubes show characteristics that are of particular interest as electron sources for field emission displays. In this study, tip structures of the nanotubes were in-situ observed under applied electric field by using a high-resolution transmission electron microscopy (HRTEM), field ion microscopy (FIM) and also field emission microscopy (FEM). HRTEM used in this experiment equipped with newly designed two specimen holders system. HRTEM observation successfully revealed that the tip of the nanotube bent during the field emission and protrudent structure was formed along the normal to the electric field. The results demonstrate that the electric field exerted mechanical stress on the surface structure. The in-situ observations lead us to development of nano-processing technology of the nanotubes. We found that burst and evaporation, and bonding of individual nanotube tips can be performed by the contact with another nanotube, amorphous carbon, or metals at the applied voltage. The tip of the nanotube was burst and evaporated at the contact at the applied voltage of more than 2V. At the burst tip, each carbon layer was often connected with the neighbor layers. After the tip burst, however, two nanotubes were bonded at the contact when the applied voltage was less than 2V. A rod specimen in which the nanotubes are sticking out of the tip was fixed on the tungsten wire with carbon binder, and was introduced into the ultra-high vacuum chamber of 3X10@super-8@ Pa for FIM and FEM experiments. Prior to the FEM observation, we evaluated the cap structure of the nanotubes by FIM and confirmed that several bright areas as emission sites, and they were either deformed honeycomb structures composed of hexagonal or pentagonal carbon rings. The bright area sites of the honeycomb structures observed in FIM moved with increment of the applied voltage.

11:40am **NT+EL+NS-ThM11 Characterization of CVD Grown Carbon Nanotubes and Field Emission Properties***, **C. Dong**, M. Gupta,* Old Dominion University*; G.R. Myneni,* Jefferson Lab, US

Carbon nanotubes(CNT) were synthesized by the thermal chemical vapor deposition with the decomposition of acetylene gas in the argon carrier gas under temperature of 700 ºC on Ni or hastelloy substrates. Carbon nanotubes were characterized by X-ray photoelectron spectroscopy (XPS), Raman Scattering, Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). Field emission properties of well characterized carbon nanotubes was extensively studied. Low turn-on electric field of ~ 1V/um was achieved. Long-term stability of emission was studied. Field emission profile was examined by imaging using phosphor screen. Carbon nanotubes appear to have better field emission properties and stability comparing to Spindt type emitters.

Nanometer Structures
Room 133 - Session NS-ThA

Quantum Dots & Single Electronics

Moderators: J. Murday, Naval Research Laboratory, L. Samuelson, Lund University, Sweden

2:00pm **NS-ThA1 Self-Organized Growth of Semiconductor Nanostructures**, ***G. Springholz,*** University of Linz, Austria **INVITED**

Strained-layer heteroepitaxy has evolved as a novel method for direct synthesis of self-assembled quantum dots based on the Stranski-Krastanow growth mode where nano-scale 3D islands spontaneously form on the surface of a thin wetting layer. In multilayers, the buried dots tend to influence the dot nucleation in the subsequent layers due to the existence of long range elastic interactions. As a result, vertical and lateral correlations within the dot ensembles are formed, which can lead to a lateral ordering and size homogenization of the dots. Here, it is shown that for various materials systems, different correlated structures are formed depending on the elastic anisotropy of the materials and depending on the growth orientation. As a most prominent example, in IV-VI semiconductor dot superlattices a nearly perfect lateral ordering and a fcc-like ABCABC... vertical stacking of the dots is obtained, and the spacing between the dots can be tuned continuously just by changing of the superlattice period. The basic mechanisms and the limits of the ordering process is discussed on the basis of theoretical calculations and Monte Carlo growth simulations.

2:40pm **NS-ThA3 Applications of Quantum Dots in Photonic and Resonant Tunneling Devices**, ***L. Samuelson***, *M. Borgstrom, T. Bryllert, B. Gustafson, S. Jeppesen, M.-E. Pistol, W. Seifert, V. Zwiller,* Lund University, Sweden

3:00pm **NS-ThA4 Single-electron Transistor Based on a 7 nm Gold Particle with Carbon Nanotube Leads**, ***C. Thelander***, *M.H. Magnusson, K. Deppert, L. Samuelson,* Lund University, Sweden; *P.R. Poulsen, J. Nygaard, J. Borggreen,* Niels Bohr Institute, Denmark

We have used CVD grown carbon nanotubes to electrically contact an individual 7 nm gold particle by scanning probe manipulation. The result was a single-electron transistor showing a periodic modulation of the current as a function of gate voltage for temperatures up to ~ 200 K. Based on a theoretical fit we conclude that the particle was responsible for the main features of the electron transport, whereas charging effects in the nanotube leads only appeared as a fine-structure. This interpretation could later be verified when the gold particle was removed and the two nanotubes were moved into electrical contact.

3:20pm **NS-ThA5 Control Over Spin Effects in Quantum Dot Structures**, ***S. Tarucha,*** University of Tokyo, Japan **INVITED**

Experimental studies on a few-electron spin state in semiconductor quantum dots and double quantum dots will be presented. Control and electronic properties of a few-electron spin states and a technical approach for tuning an exchange coupling between two different spin states will be discussed.

4:00pm **NS-ThA7 Probing the Dependence of the Spin Splitting in Quantum Dots on Residual Disorder**, ***M. Morgenstern,*** Hamburg University, Germany; *V. Gudmundsson,* Science-Institute, Iceland; *R. Wiesendanger,* Hamburg University, Germany **INVITED**

A scanning tunneling microscope is used to induce a quantum dot into the InAs(110) surface. This quantum dot provides the unique possibility to be moved in a controlled manner across the surface. Thus charged impurities of the substrate are positionable in the quantum dot area (diameter 100 nm). Working at low temperatures (6 K) in magnetic field (6 T) allows to detect the energies of the spin split states corresponding to different Landau indices. While the state energies closely follow the disorder potential in the quantum dot, the energy difference between spin split states does not. From comparison with detailed Hartree-Fock calculations we conclude that this behaviour is directly guided by the non-local character of the exchange-interaction.

4:40pm **NS-ThA9 Electronic Devices Using Single Electron Effects**, ***S. Tiwari,*** Cornell University **INVITED**

The single electron effect is a consequence of reduced capacitance in confined islands when dimensions are reduced, usually to the sub-30 nm range. Small capacitances, of the order of aF's, result in a measurable discreteness in the transfer of electrons through the islands because of the large electrostatic energy needed for transfer of charge. In semiconductors, single electron effects occur together with strong quantum-confinement effects due to the smaller density of states. In a single electron transistor, the discrete transfer of the charge is modulated by a gate voltage, and circuits analogous to CMOS can be fabricated. In most single electron memories, the effect of the single electron charge influences transport in a field-effect channel through screening, i.e., discreteness effects are coupled to the traditional field-effect of the transistor. While powerful demonstrations of room temperature operation of single electron transistors, single charge transfer devices, and simple gates with gain have been made, the use of the devices in general purpose electronics is limited by large impedance, low currents, and fluctuation effects. One particularly unique use of single electron transistor has been in charge profiling due to the strong intrinsic charge sensitivity. Memories based on single electron effects, however, are finding wider appeal because of large improvement in power, speed, voltage, and reliability characteristics over traditional non-volatile memory alternatives and their strong compatibility with present-day practice of silicon microelectronics. Such memories have been demonstrated at large dimensions (100's of nm) where numerous discrete nanocrystal islands are employed as well as in the ultimate limits of field-effect when device dimensions reduce to nearly 10 nm in dimension. We will discuss the properties of the single electron device structures and relate them to the underlying physics.

Organic Films and Devices
Room 131 - Session OF+EL+TF-ThA

Electronic Properties of Organic Thin Films

Moderator: M. Himmelhaus, Universität Heidelberg, Germany

2:00pm **OF+EL+TF-ThA1 Interface Formation in Organic Thin Film Transistors: A Photoemission Spectroscopy Study**, ***N.J. Watkins***, *L. Yan, Y. Gao,* University of Rochester

Pentacene, perylene, and sexithiophene are all materials being used in organic thin film transistors due to their relatively large mobilities. It has been suggested that the functional behavior in organic thin film transistors occurs within the first few molecular layers of the device at the interfaces between the organic and the metals and dielectrics used in fabrication of the thin film transistors. This makes understanding the electronic behavior of the interfaces involved in these devices critical. In order to better understand these interfaces we investigated the interface formation of pentacene, perylene, and sexithiophene on conductors and dielectrics using photoemission spectroscopy to examine layer by layer organic growth onto these materials. We observed indications of dipole formation at the interfaces between the metals and organics for organic on metal deposition, ranging from a 1eV dipole at the interface between sexithiophene and gold to a -0.46eV dipole at the interface between pentacene and calcium. There appears to be a linear relation between the interface dipole and metal workfunction. On the other hand, for metal on organic deposition, more complex material intermixing takes place and as a result, the electronic structure of the interface differs from that of organic on metal deposition. Possible charge transfer, dipole formation and energy level bending at these interfaces will be discussed.

2:20pm **OF+EL+TF-ThA2 Controlling Metallic Contacts to Self-Assembled Monolayers and Molecular Electronic Devices**, ***A.V. Walker,*** *B.C. Haynie, T. Tighe, D.L. Allara, N. Winograd,* Pennsylvania State University

An understanding of the nature of the metal â€“ atom organic monolayer interaction is vital in the development and design of molecular electronic devices. To fully characterize these interactions, we employ a multi technique approach using time-of-flight secondary ion mass spectrometry (ToF SIMS), infrared spectroscopy (IRS), x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Using a methoxy terminated alkanethiol monolayer on Au{111}, we demonstrate that the metal organic monolayer contact can be varied from complete destruction of the monolayer to contact formation at the terminal group to complete penetration through the layer. For metals of intermediate reactivity, e.g. Cu, we observe that the metal atoms interact with the terminal group and penetrate through the layer to the monolayer / Au{111} interface. We have also studied the interaction between promising molecular wire and electronic and device candidates and metal atoms. By using a variety of metals, the formation of the metal molecule contact can also be controlled. This leads us to suggest new metallic contact materials for molecular electronic devices.

2:40pm **OF+EL+TF-ThA3 Dependence of Electrical Properties of Metal/Organic/Metal Systems on Interface Electronic Structure, Morphology and Chemistry**, *C. Shen, **A. Kahn**,* Princeton University **INVITED**

Interactions between metals and organic molecules are varied, and depend sensitively on the nature of the metal, of the organic molecule, and on the mode of the formation of the interface. In general, an interface formed by deposition of a metal on an organic film is broader than the interface formed by reverse deposition sequence. Metal atoms diffuse and/or react in the organic layer, acting as electrically active dopant and altering the electronic properties and the structure of the molecular film. These interactions have a profound impact on the injection of charge carriers across these organic interfaces. We present here a comprehensive investigation of these effects performed on a series of metal/organic/metal structures. All experiments are performed in ultra-high vacuum to eliminate extrinsic effects. The organic materials are Alq@sub 3@ (tris-(8-hydroxy quinoline) aluminum), amorphous emissive material extensively used in molecular OLEDs; and F@sub 16@-CuPc (hexadecafluoro copper phthalocyanine), a good electron-transport material that forms molecular stacks. The metals are Al and Au. Combinations of structures including permutations of Al and Au as top and bottom contacts, and even ultra-thin metal layers inserted into the bulk of the organic film, are used to investigate the effects. Key results are: 1. The predominant role of chemistry-induced electronic gap states in leading to identical metal/organic barriers for systems like Al-on-Alq@sub 3@ and Alq@sub 3@-on-Al; 2. the "p-like" doping induced by Au atoms deposited on, and diffused deep into, organic films like Alq@sub 3@ and F@sub 16@-CuPc; and the structural disruption in the F@sub 16@-CuPc stacks resulting from Al-F@sub 16@-CuPc chemical reaction, leading to considerable decrease in electron mobility through the material. General conclusions concerning metal/organic contacts will be discussed. Work supported by the MRSEC program of the National Science Foundation (DMR-9809483) and the NJCOE.

3:20pm **OF+EL+TF-ThA5 Organic Modified Schottky Contacts: Barrier Height Engineering and Chemical Stability***, **D.R.T. Zahn**, T.U. Kampen, S. Park,* TU Chemnitz, Germany*; A. Bushell,* University of Wales Aberystwyth*; M. Rus,* TU Chemnitz, Germany

The electronic properties of metal-GaAs(100)-contacts have been modified using 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) and dimethyl-3,4,9,10-perylen-tetracarboxylicdianhydride (DiMe-PTCDI). Silver is used as a top electrode. The influence of the organic films on the electronic transport properties was investigated using in situ current-voltage (IV) and capacitance-voltage (CV) measurements. The IV curves show a strong dependence on the modification of the Schottky contacts with PTCDA. The effective barrier height varies between 0.81 ~ 0.64 eV by changing the thicknesses of the PTCDA interlayer between 0 ~ 60 nm. For layer thickness above 60 nm space-charge limited currents in the organic layer determine the carrier transport in the diodes. The CV characteristics do not vary upon introducing an organic interlayer, indicating that the overall capacitance is dominated by the depletion layer within the GaAs substrates and that the width of the depletion region is hardly affected by the PTCDA modification. Therefore, the change in the effective barrier height can be explained by an increasing image-force lowering in the presence of the organic interlayer. The decrease in barrier height as a function of the organic layer thickness is not observed after an exposure of the samples to air. Here, barrier heights are independent of the organic layer thickness and have a value similar to the one of a bare Ag/GaAs(100) Schottky contact. This sensitivity to air is attributed to a reaction of the anhydride groups of the PTCDA with oxygen and/or water leading to carrier type conversion in the organic layer. Similar experiments are currently being performed using DiMe-PTCDI. First results also reveal a comparable decrease in barrier height. In addition, the DiMe-PTCDI modified Schottky contacts are found to be less sensitive to exposure to air because the imide groups are chemically more stable compared to the anhydride groups of the PTCDA.

3:40pm **OF+EL+TF-ThA6 Characterization of Organic/organic' Heterojunctions using UV and X-ray Photoemission Spectroscopies and Luminescence Quenching***, **D. Alloway**,* University of Arizona*; D. Schlettwein,* University of Bremen and University of Oldenburg, Germany*; N.R. Armstrong,* University of Arizona

Heterojunctions based on ultrathin films of perylenedicarboxylicbisimide (PTCDI) dyes, and various phthalocyanine (Pc) overlayers, have been explored using combinations of UPS and XPS, to define the band-edge offset of these systems, and quenching of the luminescence response of the PTCDI layers as a function of coverage of the Pc layer. Depending upon initial PTCDI coverage, the quenching of its luminescence response is extremely efficient using less than 1-2 monolayer coverages of Pc, and can be seen to be due to a combination of energy transfer, and exciton dissociation events. UPS measurements suggest small interface dipoles are formed for some of the PTCDI/Pc heterojunctions, especially those which are based on perfluorinated Pcs, which have high electron affinities. These interface dipoles have the potential to accelerate exciton dissociation, and may be of importance in the application of these systems to organic photovoltaic applications.

4:00pm **OF+EL+TF-ThA7 The Influence of Substrate Interactions on the Metallicity of Polyaniline Films****, **B. Xu**,* University of Nebraska, Lincoln*; J. Choi,* Louisiana State University*; P.A. Dowben,* University of Nebraska-Lincoln

Both Na doped and undoped short chain vapor deposited polyaniline (PANI) thin films were studied using angular-resolved photoemission spectrascopy (ARPES) and X-ray photoemission spectrascopy (XPS). Films, grown on two different substrates, Si and Au, using vapor deposition method show distinctly different properties. Some indication of preferential molecular orientation was observed for ultrathin film deposited on Au substrate, but not on the Si substrates. Clear indication of metallic character was observed for the undoped polyaniline films consistent with recent theory suggesting that for alignment of chain parallel with a metal substrate enhances metallicity. The polyaniline films became more insulating with sodium doping, suggesting that Na doping leads to an increase in insulating behavior that may due to the completion of band filling. @FootnoteText@ *Supported by the Office of Naval Research and the Nebraska Research Initiative.

4:20pm **OF+EL+TF-ThA8 The Electronic Structure Studies of Fluoride Layer Insertion between Al and Organic EL Material@footnote 1@***, **Y. Park**,* Korea Research Institute of Standards and Science, Korea*; J. Lee,* Korea Research Institute of Standards and Science*; D.Y. Kim,* Hallym University, Korea*; S.K. Lee,* Chonnam University, Korea

We have investigated the electronic structures of interfaces between Al and tris-(8-hydroxyquinoline)aluminum (Alq@sub 3@), which is a prototypical organic electroluminescent (EL) material. It has been well known that the insertion of alkali metal fluoride, such as LiF, greatly enhances the EL performance and the origin of such behaviors have been controversial. We used photoelectron spectroscopy techniques including X-ray and UV photoelectron spectroscopy (XPS and UPS) to probe the electronic structures of Al/fluorides/Alq@sub 3@ interfaces. While the presence of LiF layer exhibited enhanced gap states and concomitant formation of shoulder peak in N 1s core level peaks, insertion of other fluorides showed distinctively different behaviors. For example, the presence of MgF@sub 2@ does not form N 1s shoulder peak although weak gap states were observed. Other fluorides including CsF and CaF@sub 2@ are also studied. In addition, the mixture of Al, LiF, and AlF@sub 3@ sequentially deposited on Alq@sub 3@ were investigated. The various core level peaks in this system revealed that this combination does not distinguish LiF and AlF@sub 3@, rather it is more like a homogeneous mixture of LiF, AlF@sub 3@ and Al, which is in contrast to the view that the deposition of Al on LiF/Alq@sub 3@ forms AlF@sub 3@ and liberated Li. We discuss the implications of these results in the electrical properties of the interface and eventually the organic ELD performance that employs this type of electrodes. @FootnoteText@ @footnote 1@ This work was supported in part by MOST of Korea through NRL Program and ASSRC.

4:40pm **OF+EL+TF-ThA9 Direct Observation of Fermi Level Pinning at LUMO in Alkali Metal Doped Organic Films***, **L. Yan**, N.J. Watkins,* University of Rochester*; C.W. Tang,* Eastman Kodak Company*; Y. Gao,* University of Rochester

The electronic structures of pristine and alkali metal doped organic films are investigated using the combination of photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES). The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) can be directly observed by IPES and UPS simultaneously. We found that the Fermi level position in the organic film can be modified by alkali metal doping. For example, in CuPc films, the observed LUMO of the CuPc film is shifted by the Cs doping to less than 0.2eV above the Fermi level. This pinning may be explained by the charge transfer process from Cs to CuPc. Our observation is the direct confirmation of widely used assumption that the LUMO can be inferred from HOMO position in organic films when a valance band shift is observed. The result indicates that energy alignment and charge injection properties of the organic materials can be modified by a simple doping process. Our findings could lead to various interface-engineering methods useful in organic optoelectronic devices. Possible interface dipoles, energy level shifts, charge transfer, metal diffusion and chemical reactions at the interface will be discussed.

Nanometer Structures
Room 134/135 - Session NS-ThP
Poster Session

NS-ThP1 Manipulation of Organic Monolayers Confined in Molecule Corrals*, **A. Schnieders**, T.P. Beebe, Jr.,* University of Utah

Nanometer-scale organic surface structures have significant potential applications, e. g. in the field of nanoelectronics. Therefore the characterization but also the controlled production of these structures is of increasing importance. In recent years, it has been shown that scanning tunneling microscopy (STM) is, besides its wide use in the characterization of organic monolayers, also well suited for manipulation of these layers. In this study we investigate the possibility to use molecule corrals to confine the effects of manipulation of organic monolayers to small areas. Molecule corrals are nanometer-sized etch pits in the basal plane of highly ordered pyrolytic graphite (HOPG). They are formed by heating HOPG to 650° C in air. This technique produces corrals, which are uniformly circular and one monolayer deep. The radius is easily controlled by the etching time. Molecule corrals have previously been used to contain and study small numbers of molecules in their interiors and as highly controllable surface defects on graphite. We used a home build STM and a commercial STM (Multimode Nanoscope, Digital Instruments) for both, manipulation and characterization of self-organized organic monolayers on HOPG, with and without molecule corrals. Most of the experiments were performed under a liquid droplet of the organic compound in solution at room temperature. In this presentation, we will show, among others, results on diacetylene monolayers.

NS-ThP2 Bistability in Scanning Tunneling Spectroscopy of Ga-Terminated Si(111)*, **I.B. Altfeder**, D. Chen,* Rowland Institute for Science

Demonstration of a Tunable Bistable Tunnel Device with a Low Temperature STM and A Self-organized Ga Array on Si(111)@footnote 1@ Bistable electron transport, a phenomenon usually associated with double-barrier structures, has been observed with a conventional STM junction formed between a metal tip and a Ga-terminated Si(111) surface at 77 K. Large hysteresis loops appear in the current-voltage characteristics when electrons are injected from the tip to the surface. The turn-on bias varies from -3.1 to -4.0 V and shows an inverse dependence on the tip-sample distance, indicating a strong field effect. The turn-off bias, however, is essentially pinned at a conductance threshold of -2.7 V.

NS-ThP3 Nanostructures of Si Luminescence Materials Fabricated by Microwave Plasma CVD*, H. Kezuka,* Tokyo University of Technology, Japan*; **I. Kato**, T. Matsumoto, R. Saito,* Waseda University, Japan*; T. Suzuki,* Tokai University, Japan

The double-tubed coaxial line-type microwave plasma CVD(Chemical Vapor Deposition) system has been developed for obtaining a stable plasma with a low gas pressure in order to fabricate electro-microdevices and photonic devices. In this paper, the microwave plasma CVD is applied for the fabrication of nano-particles of a-Si:H. In this system, the microwave power is confined in the the cavity, and not injected into the plasma in the chamber. Thus,in the deposition chamber,the gas flow forms spatial afterglow plasma with no microwave power injected. He outer discharge tube is composed of fused quartz and the inner tube is made of stainless steel. The Ar gas is fed to the outer discharge tube and the SiH4 gas is fed to to the inner tube.The Ar gas is ionized in the cylindrical cavity region by the microwave power. The SiH4 gas flows into the Ar plasma at the discharge tube end through the inner tube, and then the SiH4 is dissorciated by the microwave power.The substrate table area is 40cm2 and is placed at z = 10 cm. The Ar gas flow rate is 110 ml/min and the SiH4 gas flow rate is 30 ml/mi.After heat-treatments of 72 hrs in air for as-deposited a-Si:H partiles, it is assumed that nano-particles(nanoball) of a-Si:H include nano-crystal(nc) Si characterized from XPS-spectrum of the oxygen 1s region and of the silicon 2p region.From SEM- and AFM-observation of the oxidized surface of nano-particles, the size of nanoballs of a-Si:H is about 20-30nm in diameter.

NS-ThP4 Si Stems Produced by Annealing Au/Si(111) Surface*, T. Takami,* Visionarts Research*; **I. Kusunoki**,* Tohoku University, Japan

Nano-tubes, fibers, and wires are interested as an intelligent material supporting the "nano-technology". Silicon nano-wire@footnote 1@ and other semiconductor nano-wires@footnote 2@,@footnote 3@ had already been produced before the discovery of carbon nano-tube by Iijima.@footnote 4@ Recently, Homma et al.@footnote 5@ succeeded to form Si nano-columns on a Si substrate arranged with Au-islands by using vapor-liquid-solid (VLS) reaction of disilane (Si@sub 2@H@sub 6@). In the present work, we have demonstrated the formation of the Si stem (a bundle of nano-fibers) without using VLS reaction. Small Si particles for the seeds of the Si stems were scattered on a Si(111) wafer. After introducing the wafer in an ultrahigh vacuum (UHV) chamber, monolayer-equivalent Au atoms were deposited on the wafer by the vacuum evaporation. After the deposition, the wafer was annealed at 1000°C for 260 minutes. Then the Si stems were formed on the Si surface, which were observed by scanning electron microscope (SEM). The stems looked like tiny mushrooms in micro-meter scale. The Au atoms worked as a catalyst for the stem formation by inducing the surface segregation of the bulk-materials. @FootnoteText@ @footnote 1@ R.S. Wagner, W.C. Ellis, Appl. Phys. Lett. 4 (1964) 89. @footnote 2@ G.A. Boostma, H.J. Gassen, J. Cryst. Growth. 10 (1971) 223. @footnote 3@ E.I. Givargizov, J. Cryst. Growth. 32 (1975) 20. @footnote 4@ S. Iijima, Nature 354 (1991) 56. @footnote 5@ Y. Homma, P. Finnie, T. Ogino, H. Urisu, J. Appl. Phys. 86 (1999) 3083.

NS-ThP5 A Simple Method of Forming Small Gold Particles on a Thin Gold Film*, **M. Xiao**,* CCMC-UNAM, Mexico

We have produced gold particles whose sizes range from several tenth nanometers up to about one micrometer. The small gold particles are distributed on a gold thin film of thickness $50\sim 80$\AA. The method for the formation is simple. We first evaporated the gold thin film, and then applied DC field along the film. When the field increases from zero to 30 V, and the measured current increases from 0 to 650 mA, the particles were formed. The sizes and the distribution distances could be controlled by the applied DC field.

NS-ThP6 Theoretical Studies on One-dimensional Photonic Band-gap Structures*, M. Xiao,* CCMC-UNAM, Mexico*; **D. Soto Puebla**,* CIFUS and CICESE, Mexico*; F. Ramos Mendieta,* CIFUS, Mexico

We present numerical results of dispersion relations and transmission spectra for one-dimensional photonic band-gap structures composed of periodic metallic thin films separated by dielectric layers. In the calculation, both published experimental data and the Drude model are used to obtain the refraction index of the silver film. Influences fo various parameters on the quality of the band-gap structures are discussed on the base of the results.

NS-ThP7 CdS Self-assambled Nanostructures Produced by Pulsed Laser Deposition@footnote 1@*, C. Manzano, R. Castro,* Cinvestav-IPN, México*; J.L. Peña,* CICATA-IPN, México*; M.A. Santana-Aranda,* Cinvestav-IPN, México, Mexico*; **M. Meléndez-Lira**,* Cinvestav-IPN, México

Low-dimensional structures are very attractive due to their potential application in the production of high-efficiency opto-electronic devices. Until now, most of the semiconductor self-assembled nanostructures (SSN) have been fabricated employing epitaxial deposition techniques. The formation mechanism of SSN has been identified as the misfit strain involved during the heteroepitaxial growth. We report results of the production, and optical and structural characterization of CdS nanostructures deposited by pulsed laser deposition on Corning glass substrates (CGS), two possible mechanisms for the production of these nanostructures are discussed: 1) stress due to differences in the thermal expansion coefficients of the CdS film and CGS; 2) CdS droplets ejected from the target and directly deposited on the CGS. The samples were grown using a Nd:YAG laser focused on a rotating CdS target. Depositions were performed with 50 lasers shots employing substrate temperatures of 250, 350 and 500°C under a pressure of 10@super -6@ Torr. The morphology of the deposited CdS layers was examinated by atomic force microscopy finding the presence of elliptic islands with typical dimensions around 60 and 30 nm for the major and minor axis lengths, respectively. There is no evidence of degradation with time or handling. A clear blue shift, with values up to 100 meV, of the absorption band edge was observed in the room temperature transmission spectroscopy (TS) measurements, and was attributed to quantum confinement. Room temperature modulated transmission spectroscopy (MTS) measurements indicated a blue shift of only 7 meV. The differences between the results from TS and MTS are discussed taking in account the islands size distribution. These results are correlated with those obtained from 10 K photoluminescence, x-ray diffraction and scanning electron microscopy measurements. @FootnoteText@ @footnote 1@ Work partially supported by CONACyT-México.

NS-ThP8 Atomistic Simulation Studies of Stresses and Grain Boundaries by Cu Nanowire Deformations*, J.W. Kang*, *H.-J. Hwang,* Chung-Ang University, Korea

We investigated mechanical properties of Cu nanowires with grain boundary by various mechanical deformations using classical molecular dynamics simulation. We simulated the cases of elongation, shearing, rotation, rotated elongation, and compression. Before the first yielding, nanowires preserve the elastic stages, and after this, the mechanical deformation proceeds in alternating quasi-elastic and yielding stages. For Cu nanowires with grain boundary, most of the slip events occurred in the interfaces of grain boundary. For Cu {100} nanowires in this work, all slips occurred in the [110] directions on the {111} planes. In compression case, whole nanowires region, which has originally {100} planes, was transformed into {111} planes during temporary state. However, in other cases, such as elongation, [100] shear, [110] shear, and rotation, only part of nanowires region were transformed into {111} planes.

NS-ThP9 Micro-Fabrication of Sub-wavelength-Size Aperture for Near-Field Optical Probe*, M.Y. Jung*, *J.W. Kim, D.W. Kim, S.S. Choi,* Sun Moon University, Korea

There have been considerable interests about the microfabrication of the submicron size hole due to the potential application of the near field optical sensor array for gigabyte storage device. We have previously reported fabrication of the submicronsize oxide aperture.@footnote 1@ In this report, the 5 micron size dots were photo-lithographically patterned on the Si (100) wafer. After formation of the V-groove shape utilized by anisotropic KOH etching, the orientation dependent oxide growth was performed to have an etch-mask for dry etching. The reactive ion Cl2 etching using inductively coupled plasma (ICP) system will be performed in order to etch thin SiO2 layer on the bottom of the etch stop and to etch the Si on the bottom. After etching, the fabricated submicron-size oxide aperture followed by a proper metal deposition and silicon nitirde deposition procedures can be utilized as a near field optical probe. @FootnoteText@@footnote 1@Seong S. Choi, J.W. Lee, J.W. Kim, M.Y. Jung, D.W. Kim, American Physical Society Meeting, G32.011, March 21, 2000, Minneapolis, MN. USA.

NS-ThP11 An Apparatus for Deposition of Size-selected Clusters and Fabrication of Cluster-assembled Films*, N. Tarras-Wahlberg*, *M. Andersson, A. Rosén,* Chalmers Univ. of Tech. and Göteborg Univ., Sweden

We present the design of an apparatus for deposition of size-selected metal clusters. The clusters are fabricated in a laser vaporization source. It consists of a cavity where pulsed light from a Nd:YAG or excimer laser vaporizes metal atoms into a continuous flow of He atoms at a pressure of 10 - 50 mbar and clusters are formed. The cluster-buffer gas mixture exits the cavity through a nozzle (0.5 - 1 mm diameter) and the beam passes a differential pumping stage until it reaches the vacuum chambers for characterization and deposition. At several positions along the cluster beam quartz crystal microbalances and Faraday cups can be inserted to measure the total mass and ion yields. In the first vacuum chamber, just outside the nozzle the deposition rate is high, e.g. 4 Å/s of non size-selected Fe-clusters at 10 Hz repetition rate. A time-of-flight mass spectrometer is used to monitor the cluster production and to characterize the cluster size distribution, and a quadrupole mass filter will be used for size selection and deposition of monodisperse clusters. In previous deposition experiments we have made iron cluster films on HOPG and characterized their magnetic properties [C. Johansson et al., Nanostr. Mater. 12 (1999) 287].

NS-ThP13 Gas-Phase Purification of Single-Wall Carbon Nanotubes using H@sub 2@S and O@sub 2@ Mixture*, T. Jeong*, LG Innotek, Korea*; Y.B. Hahn,* Chonbuk National University, Korea

A purification process combining both a gas-phase purification using H@sub 2@S and O@sub 2@ mixture to remove impurity carbon particles and an acid treatment to remove metal particles has been developed for single-wall carbon nanotubes (SWNTs), synthesized by an arc-discharge method. Acid solution of 3 M HCl was used to remove catalyst metal particles out of the as-grown SNWTs. Thermal oxidation using the H@sub 2@S-O@sub 2@ gas mixture was followed to preferentially remove unwanted carbon particles. Hydrogen sulfide played a role of enhancing the removal of carbon particles as well as controlling the oxidation rate of oxygen with carbon. The optimum gas ratio was 10 ml H@sub 2@S/min and 20 ml O@sub 2@/min. After the acid treatment and thermal oxidation at 500 °C for 1 h, we achieved carbon nanotubes purity of > 90 % with yield of 20 - 50 %, depending on the purity of starting material.

NS-ThP14 Growth of Spherical Diamond Tips on Small Cylindrical Substrates*, V. Baranauskas,* ***A.C. Peterlevitz****, H.J. Ceragioli, S.F. Durrant,* Faculdade de Engenharia Eletrica e Computacao - UNICAMP, Brazil

This work demonstrates the possibility of growing spherical diamond tips on the top of metallic rods using chemical vapor deposition (CVD). Spherical diamond tips are of interest for diverse applications, including micro-drilling tools, waveguides, field-emission devices, biomedical instruments and so on. A hot-filament CVD system fed with ethanol highly diluted in hydrogen was used. The nucleation and growth parameters for such spherical diamond tips differ from those for deposition on flat surfaces since there is no competition for space between the neighboring grains to growth in their preferred crystalline direction, which often results in columnar structured materials on flat surfaces. A model for scaling-down or scaling-up the diameter of the diamond tips will be presented. Morphological data obtained by scanning electron microscopy (SEM) and results of Raman spectroscopic analyses of the samples produced with different diameters are discussed.

NS-ThP15 The Carbonitride Nanostructures Synthesized by Microwave Plasma Enhanced Chemical Vapor Deposition in an Acetylene / Ammonia Plasma System*, S.-H. Lai*, *K.-H. Hong, H.C. Shih,* National Tsing Hua University, Taiwan

The carbonitride nanostructures consisting of nanotubes and nanofibers have been synthesized on Pd-coated porous silica by microwave plasma enhanced chemical vapor deposition (MPECVD) at a temperature of about 600°C and the precursors are H@sub2@, C@sub2@H@sub2@, NH@sub3@, and N@sub@2. The condition of Pd clusters was varied with the power density and the bias to the substrate during the plasma immersion ion implantation (PIII) process. Samples were analyzed by SEM, HRTEM, EELS, and XPS. It was found that carbonitride nanostructures are strongly affected by the surface morphology of the Pd implant layer and the N content. HRTEM and EELS studies showed that the degree of linearity and graphitization of the nanostructure decreases as the N content increases. Nevertheless, the field emission properties of the nanostructures are enhanced due to the N doping. Form the XPS results, N is either bonded to two C atoms (sp@super2@ pyridine-like type) or to three (sp@super3@ bridgehead-nitrogen type) in the hexagonal sheets.

NS-ThP16 STM Observation of Nanoscale Defects Formed by Annealing the 6H-SiC Surface*, M. Yoshimura*, *K. Ojima, K. Ueda,* Toyota Technological Institute, Japan

It was recently reported that the carbon nanotube can be produced on the SiC surface by annealing at high temperature around 1800K. Carbon-terminated surface is considered to be more appropriate for the growth of nanotube than the Si-terminated surface. The transimission electron microscopy (TEM) has been utilized to investigate the growth mechanism for both surfaces. However the determination of the precise atomic structure, such as the location of the pentagons and defects, is difficult only by TEM observation. Here we demonstrate scanning tunneling microscopy (STM) study of the elucidation of Si-terminated SiC surface by annealing. A commercially available 6H-SiC wafer (CREE) was used as a specimen. It was annealed up to 2000K in UHV. STM observation was performed at room temperature with a tungsten tip. After annealing at 1600K, following defect structures were observed on the flat graphite layer; (1)Protruded particles with 4-5nm in diameter were observed and its surface showed /3x/3 superstructure. (2) Nanotube-like structures lie on the surface. They are probably formed by rolling of a graphite layer from the step. (3) Star-shaped defects of 3nm size were frequently observed. The surrounding graphite area also shows the /3x/3 superstructure. The surface was then annealed to 2000K, however, the surface structure was basically unchanged and no nanotube formation normal to the surface was detected. We discuss detailed structure of the defects and its formation mechanism.

NS-ThP17 Scanning Spreading Resistance Microscopy of MOCVD Grown InP and GaAs Optoelectronic and Microelectronic Structures*, St.J. Dixon-Warren*, *G. Pakulski, A.J. SpringThorpe, G. Hillier, D. Macquistan, R. Streater,* Nortel Networks, Canada*; R.P. Lu,* Simon Fraser University*; K.L. Kavanagh,* Simon Fraser University, Canada

Scanning spreading resistance microscopy (SSRM) is a new scanning probe microscopy technique that provides localized resistance profiling over a semiconductor surface. The technique, which is based on contact-mode atomic force microscopy (AFM), provides information on the two dimensional distribution of charge carriers and on the position of pn junctions in semiconductor structures. We have used SSRM to examine the cleaved edge of a number of MOCVD grown InP and GaAs optoelectronic and microelectronic structures, such as heterojunction bipolar transistors and buried heterojunction laser structures. We have also performed careful measurements on dopant staircase structures. Information on the spatial distribution of dopants in the epitaxial layers was obtained, and the effect of the applied tip voltage was investigated. We will also compare the SSRM results with those obtained using Scanning Capacitance Microscopy (SCM) on the same samples. Finally, we plan to report preliminary results for SSRM and SCM measurements for devices under operating bias conditions.

NS-ThP18 Active Feedback Noise Cancellation Low Temperature Scanning Tunneling Spectroscopy*, **D. Chen**, S.L. Pryadkin,* The Rowland Institute for Science*; B. Wang, H. Wang,* University of Science and Technology of China

A scanning tunneling microscope (STM) is one of the most sensitive mechanical and acoustical noise sensors. This in turn makes it difficult to perform fine resolution spectroscopy. Here, we describe a novel UHV and low temperature (4.2K) STM consisting of two tips which can be actuated independently. In the spectroscopy mode, one of the tips serves as the noise sensor whose signal is phase inverted and fed to the second tip to lock the tip-to-sample separation during an I-V measurement. This active feedback method effectively improves the signal-to-noise ratio. More importantly, under the low thermal drift conditions, such as in low temperature operation, it allows the long-time averaging of the measurement while avoiding artifacts due to residual mechanical instability of STM. Examples o the tunneling electron spectroscopy performed on quantized nano-structure will be demonstrated.

Nanotubes: Science and Applications Topical Conference
Room 133 - Session NT+EL+NS-FrM

Nanotubes: Field Emission

Moderator: T. Yamada, NASA Ames Research Center

8:20am **NT+EL+NS-FrM1 Nanotube Electronic and Transport Properties*, J. Bernholc,*** North Carolina State University **INVITED**

Carbon nanotubes can be either metallic or semiconducting. Their properties change significantly with doping and strain, and they are excellent candidates for nanoscale electronic devices and sensors. We have investigated the electronic and quantum transport properties of bent, deformed and tapered nanotubes, as well as nanotube-metal contacts, which will likely form components of future nanotube-based devices. Bent armchair nanotubes keep their metallic character up to fairly high angles, while metallic chiral nanotubes open a sizable gap at the Fermi level, indicating that they can be used as nanoscale strain sensors. Tapered armchair tubes remain metallic, while their zigzag counterparts are semiconducting, as expected. Ballistic transmission is very sensitive to interactions with the substrate and coupling to the contacts. Our ab initio calculations for NT/Al structures show substantial charge transfer and rehybridization effects, which strongly affect the quantum conductance. We have also investigated BN nanotubes that are intrinsically polar. For BN tubes in chiral or zigzag structures, the symmetry permits a pyroelectric field along the tube axis, which is of the order of kV/cm per nanotube. The pyro- and piezo-effects will likely be useful in nanoscale switches, resonators, actuators, and transducers. Another important aspect of nanotubular structures is their high Li uptake, with potential applications in high performance batteries. Our quantum simulations show that Li cannot penetrate nanotube walls unless large defect structures are present, and that high concentration of Li leads to aggregates in the interstitial channels. In collaboration with M. Buongiorno Nardelli, J.-L. Fattebert, V. Meunier, D. Orlikowski, C. Roland and Q. Zhao.

9:00am **NT+EL+NS-FrM3 Laser Irradiation Effect on Field Emission of Carbon Nanotubes*, T.W. Jeong,*** *S. Yu, J.H. Lee, J.N. Heo,* Samsung Advanced Institute of Technology, Korea*; W.S. Kim,* Sungkyunkwan University, Korea*; W. Yi,* Samsung Advanced Institute of Technology, Korea*; J.B. Yoo,* Sungkyunkwan University, Korea*; J.M. Kim,* Samsung Advanced Institute of Technology, Korea

Recently, field emission properties of carbon nanotubes (CNTs) have been intensivly studied as electron emission sources in field emission displays, since CNTs exhibit a good emission stability, low operating voltages, and high saturation electric field for field emission. Through current-voltage measurment, we have investigated the effect of laser irradiation on the field emission characteristics of CNT films. Multi-walled CNT thin layers were grown on the Ni/TiN sputtered alumina substrate by thermal chemical vapor deposition (CVD) process, and single-walled CNT layers were fabricated by screen printing of CNT paste onto the glass and subsequent heat treatment. In case of the CNT film grown by the thermal CVD, laser irradiation does not influence the field emission characteristics significantly. On the while, in case of the CNT film prepared by paste process, the field emission current was enhanced up to 10 times after the irradiation. Main reason for the current increase is considered as thermal heating by the laser, since organic materials existing in the paste-processed CNTs are detached out by the heat exposure leading to a clean surface of electron emitting CNTs. When the intensity of the laser was increased over a certain level, the emission current was reduced due to CNT deterioration by the heat. Therefore, laser irradiation onto the paste-processed CNTs is worthwhile for further study since currently available CNT based FEDs are fabricated mainly by paste process.

9:20am **NT+EL+NS-FrM4 Saturated Emission Near E@sub F@ from Multiwall Carbon Nanotubes*, J.L. Shaw,*** *D.S.Y. Hsu,* Naval Research Laboratory

Energy distributions of the beam emitted from gated multi-wall carbon nanotube arrays@footnote 1@ are measured in UHV as a function of gate voltage (emission current), temperature, and gas exposure. The emitters were grown by catalyzed CVD on silicon. At low currents (~1nA), the shape of the energy distribution was similar to that of metal emitters. At moderate current, emission could be detected at energies up to several volts below the Fermi level. The spectral shape at lower energies varied among specimens, after degassing, and after exposure to water. The intensity at the lower energies was reduced after degassing and increased by water adsorption. Operating the emitters removed the water at a rate related to the emission current. At increasing voltage, the fraction of the current emitted at the lower energies increased, while the emission current near the Fermi level saturated. That is, the additional current emitted after increasing the gate voltage occurred only below a specific energy, and that specific energy moved further below the Fermi level at higher voltages. The saturation effect was reduced by elevated temperatures (up to 600C) but still dominated the spectra, indicating that transport through the silicon substrate or at the silicon-nanotube interface was not responsible. Instead, we believe the emission at a specific energy is limited by the ability of the nanotube to replace electrons near the Fermi level, leaving only lower energy electrons available for emission. @FootnoteText@ @footnote 1@ D.S.Y Hsu, these proceedings

9:40am **NT+EL+NS-FrM5 Integrally Gated In-situ Grown Carbon Nanotube Field Emitter Arrays*, D.S.Y. Hsu,*** *J.L. Shaw,* Naval Research Laboratory

We report on the fabrication of two different configurations of integrally gated carbon nanotube field emitter arrays and the associated field emission. Local control of field emitter arrays, usually by gating, is necessary for most applications. Although several designs of gated carbon nanotube field emitter arrays, all based on a nanotube paste or slurry technology, have been demonstrated, to date no integrally-gated microfabricated carbon nanotube field emitter arrays based on in-situ-grown carbon nanotubes have been reported. We grew carbon nanotubes directly on gated cell structures in a cold-walled hot-filament CVD reactor at 650- 700 C using ammonia and acetylene or ethylene reactant gases and Ni or Fe catalysts. In one configuration, multi-walled carbon nanotubes with 20-30nm average diameter were grown on the tips of standard gated silicon tip-on-post field emitter arrays with 2.5 micron diameter gate apertures. Typical threshold voltages were less than 20V. For a 37 thousand cell array our highest collected anode current to date was 1.1 mA at a gate voltage of 41V. Stable emission even at 600 C has been obtained. Exposure to water vapor shifted the current-voltage curve to lower voltages, consistent with work of Dean and Chalamala@footnote 1@ on ungated single SWNT emitters. We also investigated electron energy distributions under various experimental conditions.@footnote 2@ In a second configuration, we grew multi-walled carbon nanotubes on the bottoms of hole structures with horizontal gate apertures having 1.5 - 2.5 micron diameters. Average emission currents up to 60 nA per cell with anode to gate current ratios greater than 10 have been measured. Economical manufacture of both configurations is projected because the first configuration does not require a sharp tip and the second requires only a much reduced number of steps. @FootnoteText@ @footnote 1@ K.A. Dean and B.R. Chalamala, App. Phys. Lett. 76, 375 (2000). @footnote 2@ J.L. Shaw and D.S.Y. Hsu, this proceedings.

10:00am **NT+EL+NS-FrM6 Field Emission in Cylindrical Geometry with Carbon Nanotube Cathodes: Characterization and Application to Luminescent Tubes**, *J.-M. Bonard, M. Croci, O. Noury, T. Stöckli, A. Chatelain,* Ecole Polytechnique Fédérale de Lausanne, Switzerland*; **I. Arfaoui,*** IPE, Switzerland

There have been in the past some attemps to realize tubular lighting elements with field emitters to offer a mercury-free alternative to incandescent or fluorescent lamps. To ensure a uniform light emission from the cylindrical anode, the cathode itself must be cylindrical, and the problem of depositing field emitters on a non-planar surface has up-to-now prevented the demonstration of such devices. We report here on the successful realization of a field emission diode in a cylindrical geometry, with multiwall carbon nanotubes deposited on the metallic cathode as the electron sources. The deposition was carried out by chemical vapor deposition of acetylene over metallic wires, and we observed a significant influence of the wire material. The field emitters show excellent performances: electron emission is observed below 1 kV and currents up to 1 A cm@super -2@ can be obtained. The cathodes can be used to realize luminescent mercury-free tubes: our most recent tube has a length of 30 cm and a diameter of 4 cm, and reaches luminances equivalent to those of commercial fluorescent elements. We show also that the cylindrical geometry allows one to gain information on the different parameters involved in the field emission. Space-charge related problems and the influence of residual gas pressure have been addressed. Field emission microscopy measurements show also that modifications of the structure of the nanotubes can occur during the emission, especially during or following heating. Spectacular observations of the failure of single nanotube emitters also offer direct clues to the degradation mechanism.

10:20am **NT+EL+NS-FrM7 Fabrication and Electron Field Emission Properties of Carbon Nanotube Films by Electrophoretic Deposition***, **G.Z. Yue**, B. Gao, Q. Qiu, Y. Cheng, H. Shimoda, L. Fleming, O. Zhou,* University of North Carolina

Carbon nanotubes have recently attracted considerable interests as electron field emitters for potential vacuum microelectronic applications such as field emission flat panel displays. Compared to the conventional field emitters, they show lower emission threshold fields and enhanced high current capabilities. However, their utilization in practical devices has been hindered, in part, by difficulties in processing. In this paper, we demonstrate that the electrophoretic deposition (EPD) method can be utilized effectively to deposit pre-formed carbon nanotubes on various substrates with good homogeneity and packing density. The films show very good emission stability at high current densities.

10:40am **NT+EL+NS-FrM8 Field Emission Energy Distribution for an Undergate Type Triode CNT-FED***, S.H. Jin, **S. Yu**, J.H. Kang, W. Yi, T.W. Jeong, Y.S. Choi, J.H. Lee, J.N. Heo,* Samsung Advanced Institute of Technology, Korea*; W.S. Kim, Y.H. Lee,* Sungkyunkwan University, Korea*; J.M. Kim,* Samsung Advanced Institute of Technology, Korea

We have measured I-V characteristics and field emission energy distribution (FEED) for an undergate-type triode carbon nanotube (CNT) field emission display (FED), which has gate electrodes located under the cathode electrodes. The emitters of an undergated CNT-FED were fabricated by the printing method on the glass plate with single walled CNT paste, which was mostly consisted of CNTs and glass powders. For the diode emission, the FEED peaks shifted from the Fermi level with the ratio of 67 meV/V by the change of the applied voltage, and the field enhancement factor was found to be 26,000 cm@super-1@ from the I-V measurement. On the while, the peaks for the triode emission shift with 270 ~ 500 meV/V, and it is expected mainly due to the strong electric field induced by the gate electrodes. Several subpeaks were also observed below the main FEED peaks, which indicated existence of other minor electron transition mechanism within CNTs. The full width at half maximum of FEED peaks for the diode and triode emissions were broader than those reported by others, i.e., 0.7 ~ 1.9 eV, which may be caused by field emission from various geometry of CNTs. In summary, we have measured the FEED of the undergate type triode CNT-FED for the first time, and the FEED peaks are shifted as the applied voltage increased, which may be ascribed to the energy band bending of dielectric materials on CNTs.

11:00am **NT+EL+NS-FrM9 Integrated Field Emission Devices with Single Carbon Nanofiber Cathodes***, **M.A. Guillorn**, V.I. Merkulov,* Oak Ridge National Laboratory*; A.V. Melechko, E.D. Ellis,* University of Tennessee*; G.J. Bordonaro,* Cornell University*; L.R. Baylor, J.H. Whealton, M.L. Simpson, D.H. Lowndes,* Oak Ridge National Laboratory

The fabrication of robust integrated field emission (FE) devices is currently an area of intense research. FE devices require an electron source with a low threshold field and stable operating characteristics. Recently, we have focused on vertically aligned carbon nanofibers (VACNFs)@footnote 1@ as FE sources for these reasons.@footnote 2@ In this paper we will present field emission data on isolated VACNFs measured by a scanned probe technique and device performance of integrated gated cathode and triode structures that use a single VACNF as the FE element. Isolated high aspect ratio VACNFs were grown on Si substrates using a DC acetylene/ammonia PECVD process from catalyst sites defined with electron beam lithography (EBL). FE properties of individual VACNFs were measured with a scanned probe system capable of positioning a 1-micron diameter probe tip above an individual VACNF. Gated cathode and triode structures using individual VACNFs as FE elements were fabricated using a combination of traditional micro- and nanofabrication techniques.@footnote 3@ EBL was used to define the first layer of features consisting of catalyst sites for VACNF growth and alignment marks for subsequent photolithography steps. Alternating layers of PECVD silicon dioxide and metal were then deposited onto the substrate and patterned using photolithography creating electrostatic extractor and focus electrodes aligned with the catalyst site. The dielectric layers were reactive ion etched until the buried catalyst sites were released. To complete the devices the growth of the VACNF was performed as described above. The FE current from these devices was measured using a micro channel plate system. @FootnoteText@ @footnote 1@V.I. Merkulov, D.H. Lowndes, Y.Y. Wei, G. Eres, E. Voelkl, Appl. Phys. Lett., 76, 3555 (1999) @footnote 2@V.I. Merkulov, D.H. Lowndes, L.R. Baylor, J. Appl. Phys, 89, 1933 (2001) @footnote 3@M.A. Guillorn, V.I. Merkulov, G.J. Bordonaro, et al, J. Vac. Sci and Tech. B, 19, 573 (2001).

11:20am **NT+EL+NS-FrM10 Advances in Conception of Flat Panel Displays Based on Carbon Nanotube Field Emitters***, **I. Arfaoui**, J.-M. Bonard,* EPFL, Switzerland*; D. Sarangi,* EPFL, Switzerland, France*; J. Dijon,* CEA, France*; A. Chatelain,* EPFL, Switzerland

Because of their unusual sharpness and conducting properties, Carbon NanoTubes (CNT) are an ideal candidate material for field emitting tips. In order to develop a technology allowing the fabrication of low cost large area Field Emission Displays (15 - 40), we therefore used CNT as field emissive materials. For that, it is important to have an optimised deposition method of well-aligned and well-distributed carbon nanotubes on large area substrate at low or moderate temperature. Our work deals with the growth and FE properties of CNT films on Si substrates. These patterned emitting films are made by Chemical Vapour Deposition: the CNT grow preferentially on Si substrates where a metallic catalyst (i.e. Ni, Co, Fe...) is deposited by sputtering followed by standard lithography, by microcontact printing or ink jet printing. We have optimised growth parameters (catalyst, temperature, ...) in order to obtain the lowest threshold emission fields and the highest emitting site density. However, we have shown that emitting site density is the most important parameter for Flat Panel Displays. Two particular points are discussed: structural and FE properties of diode and triode structures and a model of the emission process. In order to improve the cost issue as well as the reliability of FED, we have studied innovative triode structures. Finally, a microscopic model of the emission process is used to predict emission life and spatial uniformity of CNT films.

11:40am **NT+EL+NS-FrM11 Huge Secondary Electron Emission from Coated Carbon Nanotubes***, **J.N. Heo**,* Samsung Advanced Institute of Technology, Korea*; W.S. Kim,* Sungkyunkwan University, Korea*; T.W. Jeong,* Samsung Advanced Institute of Technology, Korea*; Y.M. Shin, H.J. Jeong,* Sungkyunkwan University, Korea*; S. Yu, J.H. Lee, W. Yi,* Samsung Advanced Institute of Technology, Korea*; Y.H. Lee,* Sungkyunkwan University, Korea*; J.M. Kim,* Samsung Advanced Institute of Technology, Korea

Carbon nanotubes (CNTs) have been reported to show very attractive properties such as high geometric anisotropy, high mechanical strength, and chemical stability, which leads to potential applications in the areas of display, nanoelectronics, and nano-sensors. According to the recent report by W.Yi and et al.(J. Appl. Phy. 89, 4091(2001)), huge secondary electron emission (SEE), i.e., value higher than 10@super 4@, was obtained for the MgO coated CNTs. In order to understand this high SEE feature systematically, a seres of samples have been fabricated by varying several parameters such as the thickness of the MgO layer, openness of the CNT tip, selectively growing of CNTs on patterned catalytic layer. CNTs were grown vertically by a thermal chemical vapor evaporator on the Si substrates with Ni and TiN thin layer. MgO or other dielectric layers were deposited on CNTs by an electron beam evaporator. Among the sample grown parameters, especially MgO thickness variation resulted in significant SEE yield change. From the thickness variation of coated CNTs from 60 to 450 nm, the maximum SEE yield was obtained for 150nm. From the energy distribution of secondary electrons, this huge SEE yield for a coated CNT is illustrated with the help of field enhanced SEE due to high geometrical aspect ratio. In addition, experimental results for different dielectric layers such as SiO@sub 2@ or LaF@sub 3@ will also be presented.

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