

Nanometer-scale Science and Technology

Room: 616 - Session NS-MoM

Nanoscale Assembly and Manipulation I

Moderator: L.E. Ocola, Argonne National Laboratory

8:00am **NS-MoM1 On-Surface Synthesis of Metallo-Porphyrin Nanotubes by Vacuum Sublimation onto Noble Metals Substrates**, *M. Trelka, C. Urban, D. Ecija*, Universidad Autonoma de Madrid, Spain, *P. de Mendoza*, Instituto Catalan de Investigaciones Quimicas (ICIQ), Spain, *J.M. Gallego*, Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), Spain, *R. Otero*, Universidad Autonoma de Madrid, Spain, *A. Echavarren*, ICIQ, Spain, *R. Miranda*, Universidad Autonoma de Madrid, Spain

Molecular electronics is a promising alternative for the continuing miniaturization of electronic devices. The capability of synthesizing and depositing molecular wires on solid surfaces is a key step within this context. The majority of the most promising current candidates to molecular wires, such as carbon nanotubes, DNA strands or individual polymer molecules, are too large and fragile for depositing them on solid surfaces by in-vacuum sublimation. Other kinds of wet deposition methods, such as drop-casting, are not so well controlled, which, in turn, hinders the understanding and design of their conductivity. Since the molecular mass of the chemical species well-suited for deposition on solid surfaces by in-vacuum sublimation is limited, one could envisage a mechanism to grow the polymeric molecular wires by depositing smaller subunits that would subsequently assemble into the polymer on the surface. This approach has successfully been used to steer the assembly of organic molecules into 1D structures. The 1D molecular wires so created are mostly like 'ribbons', due to the fact the molecules tend to lie flat on the surface to maximize substrate-adsorbate interaction. The on-surface synthesis of molecular wires with more complex geometrical shapes, such as tubular or cylindrical, has only been described for the case of carbon nanotubes, and only on surfaces covered with catalytic nanoparticles or on silicon carbide surfaces, where the constituent carbon for the nanotube growth arises from bulk segregation. The aforementioned ideal situation in which molecular subunits assemble into 1D structures with cylindrical symmetry has not been described so far in the literature. In this work we describe the growth of 1D tube or cylinder-looking structures obtained after deposition of a metallo-porphyrin (Zn-Tmp) on the noble-metal surfaces Au(111) and Cu(100) by vacuum sublimation with the substrate held at room temperature (RT). Our experiments indicate that the 'nanotubes' are only a meta-stable structure, since they disassemble into flat-lying Zn-Tmp monomers upon annealing to 500 K. The disassembled Zn-Tmp adsorbates are tightly bound to the surface, as evidenced by the fact that they can be easily imaged by Scanning Tunneling Microscopy even at room temperature, and the difficulty to manipulate them even under the harsher tunnelling conditions. Two mechanisms for such a phenomenon will be discussed.

8:20am **NS-MoM2 Interactions of Nanoparticles with a Dewetting Solid Film**, *J.S. Palmer, P. Swaminathan, J.H. Weaver*, University of Illinois at Urbana-Champaign

Capillary forces at the interfaces between particles, fluids, and solid substrates lead to the self assembly of structures during liquid film evaporation. We introduce a related process that involves nanoparticle assembly during dewetting and sublimation of a solid thin film. Metal atoms evaporated onto condensed inert gas films form clusters that can be delivered to a substrate of choice by subliming the film. Warming leads to hole formation at defects or grain boundary triple points and surface tension causes hole spreading and film breakup. For Au on Xe we show that, as for liquids, the physics underlying aggregation involves capillary forces as films dewet amorphous carbon substrates. The cluster mobility reflects the dynamics of the boundary of the retreating solid film and results in the formation of nanostructures, whose sizes and densities are controlled by adjusting the film thickness. Kinetic Monte Carlo simulations reproduce the experimentally-observed shapes and distributions and provide insight into the particle assembly process. In contrast to liquid films, particle motion is limited to the dewetting front where capillary forces drive cluster aggregation. This nanoparticle assembly process is not limited to noble metals on rare gas films but occurs in a variety of systems where particles are deposited onto thin volatile films, e.g. II-VI semiconductor particles and condensed CO₂ layers.

8:40am **NS-MoM3 Solidification and Melting of Mercury in Nanotube Cavities**, *A. Kutana, K.P. Giapis*, California Institute of Technology

We present molecular dynamics simulations of solidification and melting of mercury nanoparticles inside carbon nanotubes as a function of nanotube diameter. The mercury liquid is described by an ab initio potential for mercury dimer, rescaled to match the experimental density at 300K and melting point of mercury. The liquid-wall interactions are optimized based on the wetting angle of a mercury drop on graphite. The liquid-solid phase transition is marked by a discontinuity of the energy when monitored as a function of temperature. A significant depression of the melting point of mercury nanoparticles is predicted as the nanotube diameter decreases from 5.4 nm to 1.4 nm. The transition is less pronounced in smaller tubes, as the limit of one-dimensional system is approached. Below the freezing point, the crystal structure of solid nanoparticles is represented by a set of concentric shells in small nanotubes, while larger nanotubes show multiple domains with bulk crystal structure. Above the melting point, the central part of the nanoparticle is amorphous, while the liquid within a few atomic layers of the wall remains partially ordered. Near-wall liquid density profiles exhibit oscillation with the amplitude that increases as the tube diameter becomes smaller. In overall, the ordering inside nanotube cavities is stronger in comparison with the liquid near a flat wall. The contact angles are predicted to be larger inside nanotubes than on flat graphene sheets, indicating less favorable conditions for wetting on concave surfaces.

9:00am **NS-MoM4 Template Guided Self-Assembly of Metal Oxide Quantum Dots**, *Y. Du, I. Lyubinetzky, D.R. Baer*, Pacific Northwest National Laboratory, *J.F. Groves*, University of Virginia

This talk reports the use of focused ion-beams (FIB) to direct the self-assembly of Cu₂O quantum dots (QDs) on SrTiO₃ (100) substrates via point implants of Ga⁺. Oxygen plasma-assisted molecular beam-epitaxy (OPA-MBE) is used to grow Cu₂O QDs. It is found that, for high FIB implant dose (>10¹⁸ ions/cm²) and large interdot spacing (~1000 nm), multiple QDs can be formed preferentially on the edges of FIB modified pits. For lower doses (<10¹⁵ ions/cm²) and/or smaller interdot spacings (~100 nm), individual QDs nucleate first within the pits. Under carefully controlled conditions, the separation and arrangement of the Cu₂O QDs follows the FIB patterned template. This study finds that the FIB directed self-assembly technique works for different FIB doses, interdot spacings and deposition thicknesses, suggesting that this method is robust and flexible. Examination of QD growth on low-dose implant surfaces revealed a multi-step growth process. To further interpret the low dose implant results, calculations of total free-energy changes have been performed to study the differences between nucleation on a flat substrate surface and nucleation within a surface pit. This analysis shows that nucleation within a pit is almost always energetically favorable. In some special cases, assuming the pits have an inverted pyramidal shape, calculations show that island formation within the pits lowers the system total free-energy from the beginning of growth, i.e. there is no critical radius or energy barrier before a stable nucleus can be formed. Continued study of directed self-assembly of metal oxide quantum dots should lead to better understanding of the creation of well ordered, precisely controlled, high density QD arrays, ultimately contributing to the development of next generation nanoelectronic, magnetic, and optical devices.

9:20am **NS-MoM5 A Generic Method for Coupling Quantum Dots to Biomolecules**, *A.S. Blum, C.M. Soto*, Naval Research Laboratory, *C.D. Wilson*, SAIC, *K.E. Sapsford*, George Mason University, *J.L. Whitley*, SAIC, *A. Chatterji, J.E. Johnson*, Scripps Research Institute, *B.R. Ratna*, Naval Research Laboratory

We present a new technique that allows the generic coupling of quantum dots to any biomolecule without the use of specially engineered domains. Using well-developed chemistry short histidine-containing peptides can be conjugated to lysine-containing protein scaffolds to controllably attach quantum dots (QDs) to the scaffold. This technique was used to bind quantum dots from aqueous solution to both chicken IgG and Cowpea mosaic virus (CPMV), a 30 nm viral particle. These quantum dot-protein assemblies were studied in detail. The IgG-QD complexes were shown to retain binding specificity to their antigen after modification. The CPMV-QD complexes have a local concentration quantum dot greater than 3000 nmol/mL, and show a 15% increase in fluorescence quantum yield over free quantum dots in solution.

9:40am **NS-MoM6 Luminescent Nanocrystals Labelled Beads for Directed Patterned Assembly**, *E. Fanizza*, Università di Bari, Italy, *L. Malaquin*, LPN CNRS, France, *T. Kraus*, *H. Wolf*, IBM Research GmbH, Zurich Research Laboratory, Switzerland, *M. Striccoli*, *A. Agostiano*, *M.L. Curri*, CNR Italian National Research Council IPCF, Italy

Polystyrene (PS) beads have been functionalized with luminescent (CdSe)ZnS core shell type nanocrystal (NC), generating a versatile core-shell type of material, able to combine the size dependent optical property of (CdSe)ZnS NCs with the versatility and prompt processability for assembly of micrometer sized PS beads. The novel colloidal nanocomposite system has been fabricated by using a layer-by-layer (LbL) approach.¹ Polystyrene beads have been firstly coated with polyelectrolyte (PE) layers and subsequently functionalized with fluorescent (CdSe)ZnS nanocrystals, synthesizing following established procedure with minor adjustment. The obtained luminescent NC functionalized beads have been subsequently assembled onto patterned polydimethylsiloxane (PDMS) substrate by means of a capillary force induced process,² thus providing an original example of physical directed assembly. Here the patterned stamp, fabricated with a top-down approach, act as template for the construction of well-defined discrete nanoscale structures at two- and three dimensions. The ordered fluorescent nanoparticle arrangement has been successful preformed by using two different patterns. A precise positioning of the PS functionalized beads has been achieved. Such original structures based on colloidal particles, which now carry the unique spectroscopic signatures of the luminescent NCs, are of considerable interest either in optoelectronic systems, and the ability to assemble and precisely positioning the functionalized nano-object into ordered assembly the venue to their prompt integration in bio-engineering due to their potential application in multiplexed bioassays, medical diagnostic, drug screening.³

¹V. Salgueirino-Maceira, F. Caruso, L. Liz-Marzan, *J. Phys. Chem. B*, 2003, 107, 10990; M. Correa-Duarte, A. Kosiorek, W. Kandulowski, M. Giersig, L. Liz-Marzan, *Chem. Mater.*, 2005, 17, 3268; F. Caruso, M. Spasova, A. Susha, M. Giersig, R.A. Caruso, *Chem. Mater.* 2001, 13, 109; H. Singh, O.E. Laibinis, T.A. Hatton, *Langmuir* 2005, 21, 11500; D. Wang, A. L. Rogach, F. Caruso, *Nano Lett.* 2002, 2, 857

²T. Kraus, L. Malaquin, E. Delamarche, H. Schmid, N.D. Spencer, and H. Wolf. *Adv. Mater.*, 2006, 17, 2438. L. Malaquin, T. Kraus, H. Schmid, E. Delamarche, H. Wolf, manuscript submitted.

³The partial support of the EC-funded project NaPa (Contract no. NMP4-CT-2003-500120) MIUR SINERGY programme (FIRB RBNE03S7XZ) is gratefully acknowledged.

10:20am **NS-MoM8 Selecting and Driving Nanoscale Assembly in Monolayer Films through Tailored Intermolecular Interactions**, *T.J. Mullen*, *C. Srinivasan*, *M.J. Shuster*, *J.N. Hohman*, *M.W. Horn*, *A.M. Andrews*, *P.S. Weiss*, Penn State University

Active chemical surfaces that selectively capture and separate specific analytes from competitive environments are useful for detecting and isolating complex biological molecules as well as small molecules found in chemical weapons and toxic industrial waste. The development of self- and directed assembly strategies is key to the fabrication of molecularly precise structures for such applications. As the dimensions of patterned surface structures have decreased to the sub-100 nm scale, traditional lithographic techniques have not demonstrated the ability to fabricate reproducible structures over larger areas with molecular-scale organization. We have developed, utilized, and evaluated self- and directed nanoscale assembly strategies to fabricate, to register, and to functionalize chemical surface structures at the supramolecular 1-100 nm scale. We will highlight two hybrid soft-lithography strategies - microdisplacement printing and microcontact insertion printing - where monolayers with specifically tuned intermolecular interactions were engineered and the chemical and physical properties of the resulting patterned structures were characterized on both the ensemble and the molecular scales. Additionally, we will demonstrate that these chemical films can be functionalized with small-molecule probes that selectively capture large biomolecules while resisting nonspecific binding.

11:00am **NS-MoM10 Assembly and Transfer of Functional Nanoparticle Arrays**, *H. Wolf*, *T. Kraus*, *L. Malaquin*, *A. Decker*, *H. Schmid*, IBM Research GmbH, Zurich Research Laboratory, Switzerland, *N.D. Spencer*, Swiss Federal Institute of Technology, Switzerland **INVITED**

Nanoparticles provide multiple properties that make them potential building blocks of novel optical and electronic devices. Significant progress has been made in the bulk synthesis of nanoparticles with controllable composition, shape, structure, and size. However, in general the products are disordered colloidal suspensions or powders, whereas devices usually require ordered arrangements of particles on a substrate. Self-assembly processes can order large numbers of particles in parallel on surfaces, but they usually provide only dense regular arrays without the long-range order required for large-scale integration. In addition to particle order, also the particle-substrate junction is often crucial for device performance, and the reliable creation of well-defined particle-surface interfaces remains a challenge. We will show in this talk how directed self-assembly can be combined with a transfer step to produce arbitrary patterns of nanoparticles on a substrate. The combined

process, called "SATI" for "Self-Assembly, Transfer and Integration", maintains the advantages of self-assembly but relaxes the requirements on the substrates, and is more flexible than single-step self-assembly. Directed self-assembly uses a topographically or chemically patterned template to assemble nanoscale objects. Compared to template-free self-assembly it has less requirements and restrictions with regard to the assembled object. It is not limited to regular patterns but still a highly parallel process. Directed self-assembly comes at the cost of producing a template. However, the template can be re-used or fabricated as a low-cost replica of a topographical master made by standard top-down patterning techniques. After assembly, the nanoscale objects are printed in the transfer and integration steps onto the target substrate, retaining the parallel nature of the process. The transfer requires to tailor adhesion in a way that makes the nanoparticles leave the template or intermediate carrier and stay on the target substrate. Further processing of the arrays allows to exploit the specific particle functionality, e.g. as a catalyst, optical activity, or simply as a resist.

11:40am **NS-MoM12 Cyanuric Acid and Melamine on Au(111): Structure and Energetics of Hydrogen Bonded Networks**, *W. Xu*, *M. Dong*, *H. Gersen*, *E. Rauls*, *T. Linderoth*, *F. Besenbacher*, Interdisciplinary Nanoscience Center (iNANO), University of Aarhus, Denmark

Supramolecular chemistry based on non-covalent interactions is a powerful synthetic tool for the preparation of complex molecular architectures. In particular hydrogen bonds are considered to be useful for controlling molecular self-assembly due to the reversibility, specificity, directionality, and co-operative strength of this class of interactions. The highly specific interaction between the molecules Cyanuric Acid (CA) and Melamine (M), based on three complementary hydrogen bonds, is a key structural motif in supramolecular chemistry. Here we investigate the adsorption and co-adsorption M and CA on a Au(111) surface under Ultra High Vacuum conditions using Scanning Tunneling Microscopy with submolecular resolution. In addition to the expected structure with a 1:1 CA:M ratio, we identify a novel phase with 1:3 CA:M ratio formed upon sequential deposition. The hierarchy of binding energies for homo and heteromolecular dimers as well as for the observed network structures has been evaluated through theoretical modeling by the SCC-DFTB method, rationalizing the experimental observations.

Monday Afternoon, October 15, 2007

Electronic Materials and Processing

Room: 612 - Session EM+NS-MoA

Semiconductor Nanostructures for Electronics and Optoelectronics I

Moderator: N. Gergel-Hackett, National Institute of Standards and Technology

2:00pm **EM+NS-MoA1 Effect of Organic and Inorganic Capping Agents on Optical Properties of CdS Nanoparticles**, *N. Hullavarad, S. Hullavarad*, University of Alaska Fairbanks

Vast research interest on the synthesis and characterization of II-VI semiconductor nanoparticles for size-dependent optical properties and their potential applications in optoelectronic devices is developed over the few years. A blue shift in the energy is observed due to the quantum confinement effect as the dimensions of nanoparticles approach the Bohr radius of exciton. Size tunable properties of nanoparticles give an opportunity for various photonic applications which might find restrictions because of nonradiative recombinations due to surface defects. Organic and inorganic capping agents are used to stabilize and passivate during the synthesis of nanoparticles in order to overcome these kind of difficulties associated with the nanoparticles. Cadmium sulfide (CdS) is an important II-VI semiconducting material having a direct band gap of 2.42 eV. However, when synthesized chemically through a bottom-up approach by the capping method, the narrow band gap material can be grown with enhanced band gap in the ultraviolet region. In this paper, the synthesis of CdS nanoparticles through a simple, inexpensive and straightforward method will be discussed. The synthesis of CdS nanoparticles using organic and inorganic capping agents by chemical colloidal method will be discussed. The capping agents used are thioglycerol, mercaptoethanol, 1-6 hexanedithiol and tetraethyl orthosilicate (TEOS) and tetraethyl orthotitanate (TEOT). It is observed that nature of optical absorption spectra changes depending on the capping agents for CdS nanoparticles synthesized under same parameters. The effect of capping agent on the photoluminescence and UV absorption will be discussed in the light of metal induced defects. The thioglycerol capped CdS nanoparticle sample will be taken as a special case to study the effect of X-ray irradiation.

2:20pm **EM+NS-MoA2 Initial Metallization and Transition Metal Diffusion in ZnO Single Crystals, CVD-Grown Epi-films, and Nanostructures**, *S. Rangan, S. Katalinic, R. Gateau, D. Hill, R.A. Bartynski, P. Wu, Y. Lu*, Rutgers University

Transition metal doped ZnO is a promising candidate room temperature dilute magnetic semiconductor for spintronic applications. In previous studies of MOCVD-grown epitaxial ZnO films and nanostructures, either ion-implanted or diffusion doped with Fe or Mn, we have observed that these two metals exhibit significantly different diffusion properties. To explore whether this is an inherent property of ZnO or if it is related to non-ideal aspects of the films or nanostructures, we have studied the initial stages of Mn, Fe, and Cu metallization of the single crystal ZnO(0001)[Zn-terminated] and (11-20) surfaces, as well as MOCVD-grown epitaxial films [for which the (11-20) surface is exposed], using scanning tunneling microscopy and spectroscopy (STM and STS). The subsequent diffusion of these metals into the oxide upon annealing to various temperatures was studied with ion scattering spectroscopy. The as-prepared surface of the epitaxial film shows the same nanoscale morphology as the single crystal (11-20) surface, organized in row-like structures tens of nm in width and 2-4 nm in height. While Cu deposition results in well defined islands, all three surfaces exhibit apparent disruption upon Fe deposition, even at room temperature. The surfaces exhibit substantial morphological changes on the nm length scale, with a significant change in terrace widths and a significantly smaller fraction of atomic height steps. Upon annealing, Cu islands become mobile and coarsen, but the underlying ZnO structure is not strongly affected. In contrast, with Fe present on the surface, significant coarsening and roughening of the substrate occurs even at the modest annealing temperature of 200C, and this effect is enhanced upon annealing to 400 C. A comparison of the diffusion of Fe and Mn into the single crystals and the film will be presented. Initial results suggest that uptake of metals into the epi-film is predominantly determined by the properties of the (11-20) surface that terminates the film.

Support for this work from NSF grant 0224166 is gratefully acknowledged.

2:40pm **EM+NS-MoA3 Electron Spin Dynamics in Colloidal ZnO Quantum Dots**, *K.M. Whitaker, D.R. Gamelin*, University of Washington

Conduction band electrons in colloidal ZnO quantum dots have been prepared photochemically. This presentation will describe the use of electron paramagnetic resonance (EPR) spectroscopy to probe the spins of these conduction band electrons. Spectroscopic g-values for 3-7 nm diameter nanocrystals containing single S-shell conduction band electrons have been determined. Room-temperature ensemble spin dephasing times for these electrons were estimated from EPR linewidth analysis. The effects of electron-nuclear hyperfine interactions on T_2^* were investigated systematically by varying the concentration of ^{67}Zn ($I = 5/2$) ions synthetically. A clear relationship between T_2^* and nuclear spin concentration was observed and will be discussed.

3:00pm **EM+NS-MoA4 Characterization of Ion Beam Deposited Quantum Dots Thin Films from Colloidal Solution**, *Y. Tani, S. Kobayashi, H. Kawazoe*, HOYA Corporation, Japan

Distinctly monodispersed core/shell structured semiconductor nanocrystals (NCs) quantum-dots (QDs) prepared by chemical synthetic methods in liquid solutions are fascinating fluorescent materials because of efficient saturated chromatic luminescence. In the consideration of applications to light emitting flat panel displays, ready-synthesized NCs can be expected to be pieces of a light emitting component being deposited on a heterologous large areal polycrystalline or amorphous substrates, in contrast with a restrictive conditioned Stranski-Krastanov mode QDs. However, it has been a daunting challenge to form an organic-free luminescent QD structured film from the wet QDs, which are stably dispersed in an organic solvent or water with hundreds of ligand molecules on their surface. We developed a very low energy NC ion beam deposition technique,¹ which is capable of forming QD ion beam from the colloidal solution to deposit fluorescent thin films without significant organic contamination. In present study fabrications of high efficient luminescent QD structured thin films from CdSe/ZnS colloidal NC source are demonstrated. Semiconductor device requires a compatible technology with the colloidal source and a high-vacuum deposition process for simultaneous pursuit of a preservation of NC configuration and an exclusion of the organics derived from the ligand and solvent. An electrospray technique was employed for a soft ionization process to obtain nanocrystalline ions. From the requirement of a transportation of the ultraheavy ions and a nonequilibrium deposition, a supersonic flow with a speed of 1.1×10^3 m/s was formed with a free jet nozzle arrangement attaching a differential pumping system, which also works as a neutral molecular evacuator. Furthermore, for preventing the depositing films from an exposure with lighter ions such as the ones originated from the organic solvent and surfactant, ion optics including an energy analyzer are applied. Microstructural observations and chemical composition analysis evidenced that the deposited film has a closely packed polycrystalline structure with less organic contamination. Its photoluminescence spectrum reproduces the original distinct single peak spectrum from the colloidal dispersed NCs. The NC ion with kinetic energy of 0.1-0.4 eV/atom provides appropriate energy dissipation for a deposition of NCs.

¹S. Kobayashi et al Jpn. J. Appl. Phys. 46 (2007) L392.

3:40pm **EM+NS-MoA6 Interdiffusion during Growth of Self-Assembled InAs/InP Quantum Dots by Chemical Beam Epitaxy: A Combined Experimental and Theoretical Study**, *C. Dion, P. Desjardins*, École Polytechnique de Montréal, Canada, *N. Shtinkov*, Université d'Ottawa, Canada, *M.D. Robertson*, Acadia University, Canada, *F. Schiettekatte*, Université de Montréal, Canada, *P.J. Poole, S. Raymond*, National Research Council, Canada

The formation of atomically sharp interfaces during the epitaxial growth of heterojunctions is a challenging task since atomic intermixing between the different materials is often unavoidable due to the relatively high growth temperatures involved. This effect has been found to be particularly important during the growth of self-assembled quantum dots (QDs) for which evidence of highly alloyed structures have been reported by several authors for a wide variety of semiconductor systems.¹ In the present work, we investigate intermixing during the growth of self-assembled InAs/InP QDs by chemical beam epitaxy. Using a careful combination of photoluminescence (PL) and transmission electron microscopy (TEM) measurements as well as tight-binding (TB) calculations, we have devised a procedure that enables an unambiguous assignment of QD heights (h_{QD}) and composition to the observed PL transitions. PL spectra from ensembles of QDs are characterized by distinctive peaks which can be attributed to the ground state emission of QD families having the same thickness in terms of an integer number of monolayers (ML).² Consequently, QDs electronic

transitions are analogous to those of quantum wells and can be analyzed accordingly. TB calculations were performed by assuming (i) InP/InAs_{1-x}P_x/InP structures of varying P concentration ([P]) with abrupt interfaces and (ii) InP/InAs/InP structures with P diffusion concentration profiles described by the diffusion length L_D. Both calculation frameworks lead to similar, realistic descriptions of the as-grown material. However, the above procedure yielded two solutions sets of (h_{OD} : [P] or L_D) compatible with experimental results. In order to determine which solution set is the most suitable, they were used as input data in a Bloch-wave simulation of TEM image contrast providing a sequence of contrasts versus h_{OD}. A unique solution set was compatible with observed TEM data, therefore allowing an unambiguous assignment of h_{OD} and [P] to the observed PL transitions. For the samples under investigation, it was concluded that the electronic transitions can be best attributed to a 3 ML-thick wetting layer and 4 to 13 ML-thick QDs with a relatively constant [P] of 10 ± 1 %.

¹ N. Liu, et al., Phys. Rev. Lett. 84, 334 (2000).

² S. Raymond, et al., Semicond. Sci. Technol. 18, 385 (2003).

4:00pm EM+NS-MoA7 Improved Long-Term Thermal Stability of InGaN/GaN Multiple Quantum Well Light-Emitting Diodes using TiB₂- and Ir-based p-Ohmic Contacts. *L. Stafford, L.F. Voss, S.J. Pearton, H.T. Wang, F. Ren*, University of Florida

InGaN/GaN multiple quantum well light-emitting diodes (MQW-LEDs) are commercially available in a broad range of wavelengths for use in applications such as full color displays, traffic signals, and exterior lighting. There is also interest in shorter wavelength LEDs with AlGaIn active regions which can be used in conjunction with down conversion phosphors to produce white light, and hold significant promise for next generation lighting technology. Nevertheless, to compete with fluorescent and other high-efficiency lighting sources, it is essential to drive GaN-based LEDs at very high current densities to maximize light output. One drawback of the high current densities is self-heating of the heterostructure. This can produce either indiffusion of the Ohmic contact elements, leading to an electrical short of the pn junction, or intermixing of the contact scheme, producing very rough surface morphology. One possible way to prevent excessive Ohmic contact degradation is to use a high-melting-point diffusion barrier in the contact stack. TiB₂, with a melting temperature of ~3000°C, reasonable electrical resistivity (28 μΩ.cm) and thermal conductivity (26 W.m⁻¹.K⁻¹), and heat of formation comparable to those for silicides or nitrides, shows promise as a diffusion barrier. In this work, we report on the long-term annealing characteristics at 200-350°C of InGaN/GaN MQW-LEDs with TiB₂- and Ir-based p-Ohmic contacts. This high-temperature stress stimulates accelerated aging of GaN-based LEDs and gives an idea of the expected reliability of the Ohmic contacts. By comparison with companion devices with conventional Ni/Au Ohmic contacts fabricated on the same wafer, MQW-LEDs with TiB₂- and Ir-based Ohmic metallization schemes showed superior long-term thermal stability after 45 days at 200°C and 350°C, as judged by the change in turn-on voltage, leakage current, and output power. This is a promising result for applications where high-temperature operation is required.

4:20pm EM+NS-MoA8 Effects of N Incorporation on the Electronic Properties of GaAsN Alloy Films and Heterostructures. *Y. Jin, M. Reason, H. Cheng, R.S. Goldman, C. Kurdak*, University of Michigan

(In)GaAsN alloys with a few percent nitrogen have potential applications in infrared laser diodes, high efficiency solar cells, and other electronic devices. However, as-grown materials often exhibit poor photoluminescence efficiencies and electron mobilities substantially lower than those of (In)GaAs. In this work, we investigate the effects of N incorporation on the electronic properties of GaAsN alloy films and heterostructures grown via molecular-beam epitaxy. The total N concentrations and substitutional N fractions were determined by nuclear reaction analysis and Rutherford backscattering spectrometry studies of the bulk-like GaAsN films. Four-terminal magnetoresistance and Hall measurements were performed from 1.6K to room temperature on both bulk and heterostructure films. In GaAsN bulk films, N-composition dependent free carrier concentrations were observed at room temperature, suggesting that N acts as an electron trap. In addition, a strong T dependence of sheet resistivity and electron mobility was observed. This suggests the localization of carriers due to N-induced potential fluctuations in the conduction band, which may be explained in the framework of Anderson localization. Using modulation-doped AlGaAs/GaAs(N) heterostructures, we determine the N-related scattering effects in the GaAs(N) channel, with minimal contributions from ionized impurity scattering from dopants. Low temperature magnetoresistance and Hall measurements of the heterostructures were performed while the carrier densities in channel layer were manipulated via front-gating and illumination. An increase in electron mobility with free carrier density was observed for all heterostructure samples. For control samples (GaAs channel), the mobility depends exponentially on carrier density, i.e., μ~n^α, where α is typically 1~1.5,

suggesting the dominant scattering mechanism is long-range ionized impurity scattering. For the nitride samples (GaAsN channel), α is 0.2~0.3, and the mobility saturates for n>1.5x10¹¹cm⁻², suggesting that N atoms act as short-range neutral scattering centers. The effects of rapid thermal annealing on the substitutional and interstitial N concentrations and the resulting transport properties of GaAsN films will also be discussed.

4:40pm EM+NS-MoA9 Interface- and Photo-Based Manipulation of Point Defects for Nanoelectronics. *Y. Kondratenko, R Vaidyanathan, C.T.Z. Kwok, E.G. Seebauer*, University of Illinois, Urbana - Champaign

As electronic devices scale deeper into the nanometer regime, key aspects of device performance become increasingly dominated by point defects within the semiconductor. An obvious example is current flow in silicon nanowire devices, which is heavily influenced by residual point defects. The present work discusses two new mechanisms for controllably manipulating point defect concentrations in semiconductors at the nanoscale, using silicon as a specific example. In the first mechanism, the ability of free surfaces or solid interfaces to annihilate point defects within the solid can be altered by several orders of magnitude through either chemical state modification or mild ion bombardment. The resulting dangling bonds at the surface or interface interact with the defects through direct bond-addition reactions and through electrostatic attraction or repulsion. In the second mechanism, low-level photostimulation to produce excess charge carriers changes the average charge state of certain varieties of point defects, which in turn affects their diffusion rates toward nearby interfaces. Depending on the temperature and time of exposure, diffusion rates can be either enhanced or inhibited. Experiments using arsenic and boron diffusion as markers for defect behavior in silicon are described that demonstrate both mechanisms. Rate-equation-based modeling accurately describes all qualitative and most quantitative aspects of the results.

5:00pm EM+NS-MoA10 Programmable Memory Devices using Gold Nanoparticles Capped with Alkanethiol of Different Carbon Chain Lengths. *P.-Y. Lai, J.-S. Chen*, National Cheng Kung University, Taiwan

In recent years, organic nonvolatile memory devices have attracted much attention due to its high potential for fabricating high density, low cost and flexible electronic components. In this work, we have fabricated an organic memory consisting of gold nanoparticles and polystyrene sandwiched between aluminum (Al) electrodes. The gold nanoparticles capped with three different carbon chain lengths of the alkanethiol ligand are prepared by the two-phase arrested growth method. The pristine device, which is initially at a low-conductivity state, exhibits an abrupt increase of current when the device is scanned up to the certain voltage. The high-conductivity state can be returned to the low-conductivity state by applying a positive voltage. The length of the alkanethiol which encapsulates gold nanoparticles affects the distribution of threshold voltage to turn on the memory device. The carbon chain length of alkanethiol varies the electron tunneling ability due to the modification of energy barrier. The results correlate the length of the alkanethiol with switching speed, cyclic write-read-erase-read times, and retention time of memory devices will also be discussed.

Nanometer-scale Science and Technology

Room: 616 - Session NS-MoA

Nanoscale Assembly and Manipulation II

Moderator: H. Schiff, Paul Scherrer Institute, Switzerland,
H. Wolf, IBM Research GmbH, Zurich Research Laboratory

2:40pm NS-MoA3 Controlled Manipulation of Self-Organized Ni (II)-Octaethylporphyrin Molecules Deposited from Solution on HOPG with a Scanning Tunneling Microscope. *L. Scudiero, K.W. Hipps*, Washington State University

We have investigated the controlled manipulation of self-assembled NiOEP molecules adsorbed from a benzene solution onto a freshly cleaved high ordered pyrolytic graphite surface using the scanning tunneling microscope (STM) under ambient conditions. STM images acquired before and after scans of different patterns at a high current setpoint value reveal the creation of molecule free regions. In these cleared regions STM images reveal a 2D HOPG lattice with atomic spacing of 2.5 Å and a pattern depth of about 1.2 Å which is a typical STM height value for a monolayer NiOEP film on graphite. These molecule free regions are created by the transfer of NiOEP molecules from the surface to the tip when the STM is operated at very high current setpoint (tunneling resistance of about 120 MΩ or less). Once the

molecules are picked up by the tip they then diffuse along the wire as confirmed by the absence of molecular build-ups around the patterned areas of the STM images. Furthermore, once the molecular film is damaged the size of the uncovered area keeps on growing larger with subsequent scans. In the case of square scans performed at high current setpoint values the freshly created regions exhibit straight edges with directions that are dictated by the lattice vectors of the underlying graphite substrate.

3:00pm NS-MoA4 Manipulation and Electrical Characterisation of Carbon Nanotubes by using Nanomanipulators in the SEM System. *M. Passacantando, F. Bussolotti, V. Grossi, S. Santucci, L. Lozzi*, University of L'Aquila - Italy

The results of in situ manipulation and electrical transport characterisation of individual MWCNT grown on nickel tip by using a piezoelectric nanomanipulation system operating in a SEM chamber have been reported. The growth of MWCNT directly on nickel wire by chemical vapour deposition technique ensures a good electrical contact with the catalyst substrate. Using the electron beam induced welding a fully characterization of electronic properties of several MWCNT has been explored without the usual postprocessing methods which may alter, in principle the intrinsic properties of the CNT. Thanks to the high mechanical and electrical stability ensured by the electron beam welding procedure a detailed study of the CNT electrical transport properties modification under CNT buckling has been performed. The crucial role played by the structural defects in determining an irreversibility of a long MWCNT IV characteristic under mechanical stress has been clearly evidenced. Finally, by a proper sequence of CNT/tip welding and movement the potentiality in creating ohmic junction between two nanotubes has been demonstrated opening the route to a systematic investigation of one of the most fundamental aspect of the CNT physics.

3:40pm NS-MoA6 Automatic Manipulation of Nanoparticles with a Software-Compensated AFM. *B. Mokaberi, D.J. Arbuckle, J. Yun, A.A.G. Requicha*, University of Southern California

Manipulation of nanoparticles by pushing them with the tip of an Atomic Force Microscope (AFM) has been under development for over a decade, and is now routinely performed in several laboratories around the world. However, AFM nanomanipulation of small particles with sizes on the order of 10 nm has been until now a time-consuming and labor-intensive process. Automation has remained a desirable but elusive goal, primarily because of the spatial uncertainties associated with the positioning mechanisms of the AFM and with the manipulation process itself. Extensive user intervention has been required, resulting in very low throughput and severely limiting the complexity of structures that could be built with a reasonable amount of time and labor. This talk describes an automatic system for building patterns of nanoparticles by AFM manipulation. A planner determines the paths required to convert an initial, random distribution of particles on a surface into a desired pattern. The planner generates a sequence of motion commands for positioning the tip and pushing the particles. The commands are executed through software that compensates for thermal drift, creep and hysteresis. Experimental results show that the system can build in minutes a pattern that would take an experienced user several hours to construct interactively.

4:00pm NS-MoA7 Directed Assembly of Metal Contacts to Silicon Nanowires using Electrodeposition. *S. Ingole, P. Aella*, Arizona State University, *S.J. Hearne*, Sandia National Laboratories, *S.T. Picraux*, Los Alamos National Laboratory

A technique based on electrodeposition for electrically contacting semiconductor nanowires (NWs) is presented. In the majority of exploratory studies electron-beam lithography has been utilized for establishing the metal-nanowire contacts. While useful for laboratory investigation this technique requires a post nanowire-assembly photolithography step and is too slow for large scale assembly. Thus new techniques are needed that are easy to integrate, low cost and involve minimum additional time for integration of nanowires onto device platforms. In the present work we report a process based on electrodeposition for establishing metal contacts to silicon nanowires (SiNWs). In this technique nanowires are first aligned between pairs of planar metal electrodes using dielectrophoresis. These electrodes have been predefined on top of an oxidized silicon substrate using photolithography. After the alignment, the ends of SiNW are resting on top of the metal electrodes and held in place by the Van der Waals attraction with the electrodes. In order to achieve good electrical contacts, metal has to be conformally deposited encapsulating the ends of these nanowires. In the present work this has been achieved via electrodeposition where prefabricated metal electrodes act as selective sites for deposition of metal. As the deposition proceeds the ends of nanowire become encapsulated by the electrodeposited metal. This avoids post NW-assembly photolithography, reducing the associated processing complexity. Metal

doesn't deposit on the SiNW surfaces because of the native oxide present around them. We have demonstrated this process using electrodeposited Ni on electrically doped Si nanowires. Good coverage and control for nanowires aligned between Au/Cr pre-defined electrodes has been achieved and post-electroplating annealing resulted in specific contact resistivities $\sim 10^{-6}$ Ohm-cm². Although native oxide is useful for avoiding metal plating on the surface of NW, it acts as barrier for metal-SiNW reaction during annealing of such contacts. Also Au is not a desirable metal for devices. Therefore we have explored the use of other electrode array metals such as Ni/Ti to replace Au as well as to assist in reducing the native oxide during annealing for good metal-SiNW contacts. The results are promising for development of a general self-assembly technique for the integration of nanostructures on device platforms.

4:20pm NS-MoA8 Multi-Island Single-Electron Transistors Made by Lithographic Contacting of Gold-Nanocrystal Chains. *D.N. Weiss*, Washington Technology Center, *X. Brokmann, L.E. Calvet*, CNRS, France, *M.A. Kastner, M.G. Bawendi*, Massachusetts Institute of Technology

We demonstrate a fabrication scheme that bridges the dimensional gap between lithographic dimensions and nanocrystal sizes. The method involves lithographic contacting of previously self-assembled, alkanethiol-coated nanocrystal chains. Because one nanocrystal is incorporated into the edge of the larger electrode, all of the important tunnel junctions are defined by self-assembly rather than lithography. This method allows the fabrication of one-dimensional island arrays, similar to those used for metrology, with predictable electronic characteristics. Specifically, we show that the electronic behavior of a double-island device can be fully explained using the standard theory of Coulomb blockade, with very few adjustable parameters.

4:40pm NS-MoA9 Dip Pen Nanolithography using NanoInk's NSCRIPTOR System: Nanolithography and Nanoscale Assembly Using Biological and Metal Inks. *E.R. Tevaarwerk, M. Parpia, N.A. Amro, S. Rozhok, J. Haaheim, F. Villagran, T. Renner, M. Nelson, J. Fragala, T. Levesque*, NanoInk

Precision nanoscale deposition of biological, organic, and inorganic materials is a fundamental need in nanoscience research. Relative to other nanopatterning techniques, dip-pen nanolithography-DPN is a direct-write technique maintaining high resolution (30 nm line widths, 50 nm pitches), and among sub-50 nm techniques, DPN is the only one that can directly deposit molecules under ambient conditions. A wide variety of biological, organic and inorganic materials can be deposited. We will discuss the development of a silver nanoparticle based ink for the writing of conductive metal traces, as well as recent developments in "Just Add DNA" inks for DNA nanopatterning for the making of DNA nanoarrays. We demonstrate results of DPN patterning with these two inks using NanoInk's one dimensional probe arrays, and microfluidic ink delivery tools. We discuss the implications of these results and tools in furthering the application of dip-pen nanolithography as a large scale, multi-ink patterning tool, including recent developments for massively parallel patterning using the two-dimensional nanoprint array (2DnPA).

Applied Surface Science

Room: 610 - Session AS+BI+NS-TuM

Surface Analysis and Related Methods for Biological Materials

Moderator: J. Soares, University of Illinois at Urbana-Champaign

8:00am **AS+BI+NS-TuM1 Nano-bio Chemical Image of Single Cells and Tissues for Bio-medical Applications**, *D.W. Moon, T.G. Lee, J.Y. Lee*, Korea Research Institute of Standards and Science **INVITED**

Biochemical imaging of cells and tissues is a basic infra-technology in various bio-medical applications. Instead of conventional labeling methodology for biomolecular imaging with fluorescent dyes, label-free single cell and tissue biochemical imaging methodologies such as a nonlinear optical technique, coherent anti-Stokes Raman scattering (CARS) and an ion beam sputtering analysis technique, Secondary Ion Mass Spectrometry (SIMS) using cluster ion beams were developed. They were used to measure in a complementary manner 2D or 3D biochemical images of various cells and tissues such as Hella cells, adipogenic stem cells, fat liver tissues, cancer tissues, and skin tissues. Preliminary results will be discussed on the following issues. 1) Interactions of fibroblasts with native and denatured collagen thin films were studied with CARS and SIMS. It was extended to study the interactions of fibroblasts with 500 nm nano-fibers and 5 μm micro-fiber made of 40% poly (glycolic acid) (PGA) and 60% collagen. 2) Photoaging effects of skin by UV radiation were studied with SIMS, which showed significant changes in the biochemical imaging of amino acids representing collagen fibers and lipid molecules. 3) It was shown that SIMS imaging of colon cancer tissues has some potential to develop personalized cancer therapy with new drugs. Finally, the present status and future prospects of nano-bio technology based on laser, mass spectrometry, and nanoprobe for biochemical imaging of single cells and tissues at KRISS will be discussed for practical applications in bio, medical, and pharmaceutical researches.

8:40am **AS+BI+NS-TuM3 SIMS Imaging of Polymer Membranes and Single Cells**, *G. Jiang, R. Michel, D.J. Responde, L. Mayorga, K. Greenland, T.N. Davis, T.A. Horbett, D.G. Castner*, University of Washington

The ability to obtain 3-D images of drug distributions in polymers can provide information about drug loading and release profiles. Likewise 3-D images of biological species (lipids, proteins, sugars, etc.) in cells can provide information about the distribution of those species within the cell. With the advent of C_{60} cluster ion beam sources, it is now possible to use time-of-flight secondary ion mass spectrometry (ToF-SIMS) to examine these important biological problems. This study used a dual beam approach (C_{60}^+ for sputtering and Bi_1^+ or Bi_3^+ for analysis) to generate 3-D images from drug (dipyridamole) loaded polyurethane (PEU) films cast onto glass and single cells (yeast and monocytes) adsorbed onto porous polycarbonate (PC) membranes. 3-D images were successfully obtained from all samples. For PEU films without the drug, the intensity of organic fragment ions from the PEU remained constant until the PEU/glass interface was reached, then decreased as the intensity of fragments from the glass increased. In the initial stages of sputter profiling drug loaded PEU films, the intensity of the drug peaks decreased while the intensity of the PEU fragments increased. Then intensities from both components remained relatively constant until the PEU/glass interface was reached. Molecular ions from the drug were readily detected throughout the entire PEU film. ToF-SIMS 2-D and 3-D images of single yeast (size ~ 5 microns) and monocyte (size ~ 10 microns) cells were obtained for cells adsorbed onto the surface of the PC membrane and within the pores of the PC membrane. Fragments from biological species from these cells (e.g., phospholipid at $m/z = 184$) could be detected in the ToF-SIMS images. These results indicate the possibility of 3-D chemical state mapping of single cells and other biomedical samples with the spatial resolution of a few microns.

9:00am **AS+BI+NS-TuM4 Surface Energy Control Within Copolymer Libraries Synthesised as Micro Arrays for Biological Screening**, *M. Taylor, A.J. Urquhart*, The University of Nottingham, UK, *D.G. Anderson, R. Langer*, Massachusetts Institute of Technology, *M.C. Davies, M.R. Alexander*, The University of Nottingham, UK

There is currently much interest in polymer microarrays in the field of high-throughput materials development.^{1,2} Although combinatorial material synthesis is relatively advanced, methods for characterising the surface chemical properties of such libraries are less well developed. We report on methods to characterise the surface chemistry and surface energy of 480 polymers on a microarray formed using on-slide copolymer synthesis. We used X-ray Photoelectron Spectrometry and Time of Flight Secondary Ion Mass Spectrometry to provide surface chemical information from each spot. Water and diiodomethane contact angle measurements were made from individually dosed picolitre volume droplets to estimate surface energy of each copolymer formulation.³ Such arrays provide extra challenges for characterisation due to the large sample numbers, small sample size and increased data volume. Here, we will focus on the correlations determined between the monomer structures and the surface energy. The information XPS and SIMS can provide on the actual surface chemistry is presented and contrasted to the bulk surface chemistry. We highlight the ability to tune the surface energy using certain polymerised monomer combinations by varying their relative concentrations. This has great utility in controlling the biological response to polymer surfaces.

¹ J. A. Hubbell, Nature Biotechnology 2004, 22, 828.

² D. G. Anderson, S. Levenberg, R. Langer, Nature Biotechnology 2004, 22, 863.

³ Taylor, M.; Urquhart, A. J.; Zelzer, M.; Davies, M. C.; Alexander, M. R., Picolitre water contact angle measurement on polymers. Langmuir Letters (2007, in press).

9:20am **AS+BI+NS-TuM5 Surface Characteristics of Listeria Monocytogenes Mutants with Variable Pathogenicity Levels**, *N.I. Abu-Lail, B.-J. Park*, Washington State University

Despite being an important food-borne pathogen, *L. monocytogenes* in fact comprises a diversity of strains with varying virulence. Whilst many strains of *L. monocytogenes* have pathogenic potential and can result in disease and mortality, others have limited capability of establishing infections and relatively avirulent. Although very important, the question of how the composition of the bacterial surface and the properties of bacteria vary between strains that have different level of virulence at the molecular level needs to be answered. To answer this question, interaction forces between five different *L. monocytogenes* mutants that vary in their virulence and a model surface of silicon nitride were investigated using atomic force microscopy (AFM). Adhesion measurements between the strongest *Listeria* mutant and silicon nitride revealed that although both surface polysaccharides and surface proteins contributed significantly to the total adhesion, polysaccharides contribution (1.0 ± 0.2 nN) was larger than that of proteins' contribution (0.38 ± 0.1 nN). Adhesion forces were also dependent on the pH value of the solution, temperature, and media type. Experiments on intermediate virulence mutants and avirulent mutants are currently ongoing. Successful completion of these experiments will improve our understanding of the main molecular differences between virulent and avirulent strains of *L. monocytogenes*. Such findings would be very important, because it will allow for the first time and at a molecular level, to define a criteria that can distinguish virulent *L. monocytogenes*' strains from avirulent ones and therefore reduce unnecessary recalls of food products and help in preventing disease outbreaks.

9:40am **AS+BI+NS-TuM6 First Observation of Charge reduction and Desorption Kinetics of Multiply Protonated Peptides Soft Landed onto Self-assembled Monolayer Surfaces**, *O. Hadjar, J.H. Futrell, J. Laskin*, Pacific Northwest National Laboratory

Soft-landing (SL) of hyperthermal ions onto semiconductive surfaces is a promising approach for highly-selective preparation of novel substrates using a beam of mass-selected ions. In addition, controlled deposition of complex ions onto surfaces presents a new approach for obtaining molecular level understanding of interactions of large molecules and ions with a variety of substrates relevant for biology and catalysis research. In this work we present a first study of the kinetics of charge reduction and desorption of peptide ions soft-landed onto a fluorinated self-assembled monolayer (FSAM) surface at hyperthermal energy (40 eV). An *in situ* 8 keV Cs^+ secondary ion mass spectrometry (SIMS) in a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer is used. Doubly protonated peptide ions are produced by electrospray ionization, mass-selected and transferred to the surface. The experiment allows the Cs^+ beam to merge with the peptide ion beam on the surface facilitating real time soft landing process monitoring. The surface is regularly probed using SIMS

during and after ion soft-landing. All peptide-related peaks in SIMS spectra show a gradual increase during the soft-landing. Rapid decay of the $[M+2H]^{2+}$ signal accompanied by increase of the $[M+H]^+$ signal is observed after soft-landing is stopped. The $[M+H]^+$ signal maximizes 2-3 hours after the end of the soft-landing and shows a relatively slow time decay at longer delay times. Several peptide fragments followed a very different kinetics behavior showing very slow, almost linear decay after soft-landing. We attribute this time signature to fragments that originate from neutral peptide molecules on the surface. Other peptide fragments show a mixed behavior suggesting that they are formed from different charge states of the soft-landed peptide ions. Our results demonstrate for the first time that various peptide-related peaks follow very different kinetics, signatures for doubly protonated, singly protonated and neutral peptides retained on the surface. The experimental results are in excellent agreement with a simple kinetic model that takes into account charge reduction and desorption of different species from the surface. The kinetic modeling allowed us to obtain for the first time desorption and charge exchange rate constants for different peptide species on the surface.

10:40am **AS+BI+NS-TuM9 Ultra Fast Mid Infrared Spectroscopic Imaging for Biomedical Applications**, J. Phillips, H. Amrania, J. Plumridge, M. Frogley, Imperial College London, UK

We discuss the potential biomedical applications for a unique infrared spectroscopic micro-imaging system. A table top tuneable solid state laser has been coupled to a commercial infrared microscope to create a unique mid-IR imaging tool. By integrating with a modified high resolution infrared camera that has previously only been available to the military market, we have constructed a broadband imaging system capable of performing diffraction limited spatially resolved spectroscopy of biological specimens. The narrow line-width of the laser allows us to take spectra at a resolution of 20cm⁻¹. A polymer film sample with a micron scale structure has also been imaged in reflective mode to resolve details down to 8 microns in size. We also discuss results from spectrally imaging cancerous cervical tissue samples. The high peak power of the laser (10MW) offers signal to noise levels previously unobtainable with stand-alone laboratory based commercial instruments. This coupled with a short pulse duration will for the first time enable time resolved imaging at a 100psec resolution.

11:00am **AS+BI+NS-TuM10 X-ray Spectromicroscopy and Ion Spectroscopy to Evaluate a Blend of Poly(L)lactic Acid and Fluorine End-capped Poly(L)lactic Acid**, D. Wells, J.A. Gardella, University at Buffalo

Blending polymers is a versatile method for tuning the physical and chemical characteristics of a material such as strength, thermal stability, optical properties, and degradation rates. As the field of nanomaterials continues to grow it is essential to be able to evaluate the microstructure of polymeric materials as well as to characterize the chemistry that occurs at the interfaces of blended polymer films. Two techniques capable of such analysis are scanning transmission X-ray microscopy (STXM) and imaging time of flight secondary ion mass spectrometry (ToF-SIMS). STXM is a spectromicroscopy technique, that is, it combines both imaging and chemical spectral information. Recent advancements in cluster primary ion sources for ToF-SIMS have extended the range of its applications. The system of primary interest in this work is a blend of poly(L)lactic acid (PLLA) with fluorine end-capped poly(L)lactic acid (F-PLLA). This material has potential as a drug delivery device whose degradation could be controlled by changing the ratio of hydrophobic F-PLLA to hydrophilic PLLA. It is known that the fluorine containing component will preferentially surface segregate.¹ By reducing the concentration of F-PLLA we predict that we can create lateral surface segregation as well as vertical segregation. Both STXM and ToF-SIMS generate images containing chemical information and are useful to evaluate lateral phase segregation. Our intent is to use these two techniques as the primary means to evaluate the effects of changing the ratio of F-PLLA to that of pure PLLA.

¹Won-Ki Lee, I. L., Joseph A. Gardella Jr., Synthesis and Surface Properties of Fluorocarbon End-Capped Biodegradable Polyesters. *Macromolecules* 2001, 34, (9), 3000-3006.

11:20am **AS+BI+NS-TuM11 Influence of Molecular Environment on ToF-SIMS Detection of Bio-Active Molecules on Self-Assembled Monolayers**, Z. Zhu, Pacific Northwest National Laboratory

Bio-active molecules can be immobilized on solid substrates to form a monolayer or sub-monolayer. Because interactions between bio-active molecules are typically special, this structure is very useful in bio-recognition. So far, it has been widely used in bio-analysis or disease diagnosis. Alkanethiol self-assembled monolayer (SAM) on Au substrate is one type of commonly used solid substrate due to its versatile surface properties. During the last decade, time-of-flight secondary ion mass spectrometry (ToF-SIMS) has proven one of the most convenient techniques to detect sub-monolayer of organic molecules on alkanethiol SAMs. We have earlier described the possibility of quantitative detection of

peptide molecules on COOH-terminated SAMs. However, we found that molecular environment greatly affect the signal intensity. For example, Au⁺ signal from -S(CH₂)₂(CF₂)₉CF₃ film is much stronger than Au⁺ signal from S(CH₂)₁₁CO₂H film. Therefore, quantitative comparison of the density of bio-active molecules on different SAMs by ToF-SIMS is difficult unless effect of molecular environment can be quantitatively considered. In this work, a number of bio-active molecules were deposited on -S(CH₂)₁₁CH₃, -S(CH₂)₁₀OH, -S(CH₂)₁₀CO₂H, and -S(CH₂)₂(CF₂)₉CF₃ films with similar density, and ToF-SIMS measurements were made. Two major factors are found to affect SIMS signal intensity. Firstly, electron-attraction organic functional groups are found to enhance positive ion signals but depress negative ion signals. For example, positive ion signals are enhanced on -S(CH₂)₂(CF₂)₉CF₃ film but negative ion signals are depressed. In addition, active H-atoms such as those from COOH groups are able to enhance signal of positive molecular ions since they are normally protonated.

11:40am **AS+BI+NS-TuM12 Advances in Organic Depth Profiling Using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) under Optimized Ion Beam Conditions**, H.-G. Cramer, T. Grehl, ION-TOF GmbH, Germany, N. Havercroft, ION-TOF USA Inc., F. Kollmer, R. Moellers, E. Niehuis, D. Rading, ION-TOF GmbH, Germany

Depth profiling of inorganic materials has been one of the most important applications of SIMS in general, and more recently also of ToF-SIMS. In contrast, depth profiling of organic materials has always suffered from the fact that high-mass molecular information, to a large extent, is rapidly lost under high-dose sputtering conditions. With the advent of cluster ion beams, however, more and more examples of successful organic depth profiling have been presented, such as C₆₀ profiling of PMMA, PLA, etc. On the other hand, it also became obvious that the projectiles and conditions commonly used were not successful for profiling of every organic material analyzed. In this paper we used the so-called dual beam mode of depth profiling to start a systematic investigation of organic depth profiling with a ToF-SIMS instrument. Similar to the case of inorganic profiling, we found the dual beam mode beneficial because sample erosion and the sample analysis are decoupled and can be independently optimized. We applied different primary projectiles, such as C₆₀, Bi_n cluster ions, O₂ and Cs with a wide range of impact energies to a variety of organic specimens. The results will be discussed with respect to the specificity of the detected ions, their yields, the damaged and removed sample volume per primary ion, and classical figures of merit such as depth resolution.

12:00pm **AS+BI+NS-TuM13 Fragment Free Mass Spectrometry for Bio-Molecular Surfaces with Size Selected Cluster SIMS**, J. Matsuo, S. Ninomiya, K. Ichiki, Y. Nakata, T. Aoki, T. Seki, Kyoto University, Japan

Polyatomic and cluster ions have been utilized for bio-molecular analysis as the primary ion beam for SIMS. Enhancement of sputtering and secondary ion yields, and the capability for depth profiling of bio-materials have been reported for cluster ions, and are due to the effects of multiple collisions and high-density energy deposition of such ions on solid surfaces. In bio-molecular analysis, not only molecular ions, but also fragment ('daughter') ions are usually observed in the mass spectra, and this makes interpretation of the spectrum difficult. Therefore, reducing fragment ions is very important especially for practical applications. These phenomena strongly depend on cluster size, which is a unique parameter, and one of the fundamental questions is what size of cluster ion is most appropriate for bio-SIMS. To date there have been very few studies on the effect of size on secondary ion emission from bio-molecules. We have examined the size dependence of the secondary ion emission from amino acid, sugar and small peptide films with large cluster ion (N>100) by using the double deflection technique. When the total energy of the cluster ion is fixed, the secondary ion emission (SI) yield of molecular ions increases with size due to the non-linear effect. However, when the cluster size is too large, the SI yield is gradually diminished, because the energy per atom becomes too low to emit secondary ions. The maximum molecular SI yield from amino acid film was obtained for Ar clusters with the size of a few hundred at the energy of 20keV. The ratio of fragment ions to molecular ions was also measured as a function of cluster size. The ratio decreases quite rapidly with increasing the cluster size. When the cluster size was larger than 1000, very few fragment ions were observed in the mass spectrum. In this case, each incident Ar atom has kinetic energy of a few eV, which is comparable to the bonding energy of peptides. Ultra-low energy SIMS can be realized by using large cluster ions. The size effect in secondary ion emission and damage cross-section will be discussed.

Imaging of Nanostructures

Moderator: N.P. Economou, Carl Zeiss SMT, S. Hasegawa, University of Tokyo, Japan

8:00am **NS-TuM1 Atomic-Scale Studies of Complex Oxide Interfaces Using Aberration-Corrected Z-Contrast Imaging and EELS, R.F. Klie, G. Yang,** University of Illinois - Chicago **INVITED**

Interfaces in complex oxide materials have been an enduring theme in materials physics, where the interplay of the reduced dimensionality, proximity effects, as well as surface relaxation, reconstruction and segregation creates interfacial states that are distinct from their bulk counterparts. It has long been recognized that the perovskite oxides provide a unique opportunity to bring materials with diverse and even mutually exclusive properties into intimate contact, thereby creating interfaces with excellent structural and chemical compatibility that potentially can be implemented in novel electronic devices. In recent years, novel techniques have been developed in analytical scanning transmission electron microscopy (STEM) that can be used to directly study the atomic-scale structure-property relationships of interfaces in complex oxides, both at room and LN₂ temperature. In particular, by using aberration-corrected Z-contrast imaging and electron energy-loss spectroscopy (EELS), the structure, composition and bonding can all be characterized directly with a spatial and energy resolution that cannot be achieved by any other technique. Here, we will demonstrate that the combination of aberration-corrected Z-contrast imaging and EELS can be used to analyze a wide range of properties in complex oxide materials, such as CMRs, high-k dielectrics and high-temperature superconductors. In particular, I will concentrate on my recent discovery of the cooperative doping-effect in the high-T_c superconductor YBa₂Cu₃O_{7-x} (YBCO), where the presence of grain boundaries causes a significant reduction in the critical current density (J_c). I will explain the atomic-level origin of the improved J_c across grain boundaries in Ca-doping YBCO, and propose a number of potential dopants to further improve the materials properties.¹ Further, I will discuss the effects of oxygen vacancy segregation on the dielectric property of ultrathin SrTiO₃ on GaAs(001)² and conclude with our recent discovery that the Co-ion spin-state in Co-based perovskite oxides can be directly measured by EELS.

¹ Klie, R.F., J.P. Buban, M. Varela, A. Franceschetti, C. Jooss, Y. Zhu, N.D. Browning, S.T. Pantelides, and S.J. Pennycook, *Nature*, 2005. 435(7041): p. 475-478.

² Klie, R.F., Y. Zhu, E.I. Altman, and Y. Liang, *Applied Physics Letters*, 2005. 87(14).

8:40am **NS-TuM3 In-situ Observation of Active Electronic Devices using Electrically Biased TEM Holder, D.S. Ko, S.D. Kim,** Seoul National University, Republic of Korea, X.S. Li, K.S. Park, Y.K. Kim, Samsung Advanced Institute of Technology, Republic of Korea, C.G. Park, National Center for Nanomaterials and Technology, Republic of Korea, Y.W. Kim, Seoul National University, Republic of Korea

In-situ transmission electron microscopy (TEM) became one of the major fields in physics and materials science as the advanced technologies were adopted to observe real-time changes of microstructures in a confined space of TEM.^{1,2,3} We developed an in-situ TEM holder to investigate the live operation of electronic devices and we present step-by-step manufacturing procedures of nano-manipulator-electrical signal holder applied to investigate the transport of matters in Light Emitting Diode (LED) and Phase-changing Random Access Memory (PRAM). The TEM sample of active electron device was prepared by focused ion beam followed by plasma etching as reported earlier⁴ to remove the Ga-contamination at the surface. The removal of surface layer with Ga was essential to remove a leakage path of current. As-FIB-prepared LED sample showed illumination only after the plasma etching process. In order to make electrical contact to the samples of electronically active device, tungsten tip was fabricated using electro-chemical polishing technique in 10% NaOH. The tip fabricated was small enough to locate the contact pad with 30-40 nm in apex diameter. The apex radius of commercially available tungsten tip was too big for probing to make electrical contact to the target device. Tungsten probe was mounted on the 4-mm diameter, quadrant piezo tube, which was linked to micrometer for the coarse movement. In-situ observation of intermixing and materials transport in commercially available GaN LED and phase-changing of chalcogenide material in PRAM device, is investigated and the recorded.

¹C.M. Grimaud and O. Lourie, *In Situ Electrical Probing by TEM-STM: instrumentation and applications for nanocharacterization*, *Microsc. Microanal.* 10(suppl 2), 1112 (2004)

² T. Kizuka et al, *Metal-Insulator Transition in Stable One-Dimensional Arrangements of Single gold Atoms*, *Jpn. J. Appl. Phys.* 40 L170 (2001)

³ D. Golberg, et al, *In situ electrical probing and bias-mediated manipulation of dielectric nanotubes in a high-resolution transmission electron microscope*, *Appl. Phys. Lett.* 88 123101 (2006)

⁴D.S. Ko, et al, *Effective removal of Ga residue from focused ion beam using a plasma cleaner*, *Ultramicroscopy* 107, 368 (2007).

9:00am **NS-TuM4 Measuring Atomic Size Objects on Electrically Insulating Surfaces in Ultrahigh Vacuum, S.C. Fain, N. Ruzycski, J. Morales, T.C. Lovejoy, E.N. Yitamben, M.A. Olmstead, F.S. Ohuchi,** University of Washington

Frequency modulation non-contact atomic force microscopy (ncAFM) provides a way to measure atomic size objects on electrically insulating surfaces in ultrahigh vacuum. Computer simulations indicate that the apparent height of clusters one atomic layer high is much less than the actual height when the lateral extent of the cluster is much less than the tip radius.¹ For example the apparent height of a 1.4 nm diameter, one-atomic-layer-high cluster of 19 atoms on a flat surface is expected to be 12% of its actual height when imaged by a typical probe tip of 20 nm radius. The apparent height of the cluster is predicted to be much closer to the real height as the cluster height increases. We have performed measurements on semiconducting surfaces with various cluster sizes by both ncAFM and scanning tunneling microscopy (STM) using various probe tips. Evidence in qualitative agreement with the computer simulations has been obtained for clusters on a surface with Cr co-deposited with Ga₂Se₃ on Si(100):(2x1)As. We acknowledge support from NSF NER-0508216, NSF DMR-0605601, and an IGERT Traineeship to TCL from NSF and NCI grant DGE-0504573.

¹S. C. Fain, Jr., C. A. Polwarth, S. L. Tait, C. T. Campbell, and R. H. French, *Nanotechnology* 17, S121-127 (2006).

9:20am **NS-TuM5 Ambient Dynamic Mode AFM Non-contact Operating Regime Determination, C.C. Wang, B. Liu, B. Leung, Y. Uritsky,** Applied Materials Inc.

Dynamic mode AFM, which uses a cantilever vibrating near its natural mechanical frequency, is the most popular AFM imaging method in the ambient. As AFM tip approaches the sample, it enters the non-contact regime first due to attractive force interactions and, as tip continues to descend, it starts to contact surface intermittently.¹ During tip descend, the vibration amplitude continuous to decrease. Therefore, using a feedback loop that maintains a constant amplitude set-point during AFM imaging, the AFM can be operated in either non-contact mode or intermittent contact mode and the set-point of former is higher than that of the latter. Non-contact mode is desirable, because it affords higher spatial resolution and longer tip life.² Hence, accurate determination of the non-contact amplitude operating range is needed. A unique characteristic of phase signal of cantilever is that, in non-contact regime, phase changes monotonically with tip-to-sample distance, but as soon as tip makes intermittent contact with sample, the phase signal abrupt jumps in the other direction.¹ Therefore, non-contact regime can be determined by approaching tip to surface in open-loop condition, monitoring the amplitude and phase signals at the same time and determining the amplitude corresponding to phase reversal point. However, this popular method causes tip and sample damage and inaccurate non-contact regime determination. A new method is reported here. In this method, the tip approach is stopped at the start of non-contact interaction regime and the feedback loop is turned on; the tip descend is then resumed by lowering the amplitude set-point continuously and at the same time monitoring the phase signal; as soon as the phase signal makes a sudden discontinuous reversal, the intermittent contact mode is reached. By recording the amplitude set-point at the onset of intermittent contact, the non-contact regime can be determined more precisely. It is shown that this range depends on tip material, sample material and the cantilever initial vibration amplitude. Therefore, this method can be used to image sample surface properties and to optimize non-contact operating parameters.

¹ R. Garcia and A. S. Paulo, *Phys. Rev. B* 60, 4961 (1999)

² C. Wang et al., *Proceedings: the 2005 International Conference on Characterization and Metrology for ULSI Technology*, 194 (2005).

9:40am **NS-TuM6 Atomic Resolution AFM with a Purely Electrical QPlus Sensor, B. Uder, M. Maier, A. Bettac, A. Feltz,** Omicron NanoTechnology, Germany

In contrast to conventional optical detection AFM, self-sensing or purely electrical detection schemes have not yet been established as reliable and routine techniques for atomic resolution under UHV conditions. The QPlus sensor however, has successfully been used for LT STM with 5 K operation and is now introduced for variable temperature operation with the VT STM. The QPlus sensor employs a quartz tuning fork for force detection in non-contact AFM operation mode. One prong of the tuning fork is fixed while the SPM probe tip is mounted to the second prong. It thus acts as a quartz lever transforming its oscillation into an electrical signal as a result of the piezo-electric effect. The feedback signal is based on frequency shift

originating from tip-sample force interaction. A dedicated pre-amplification technique ensures distance control based on the vibrational signal. The main motivation for the QPlus sensor is to improve AFM resolution for short range forces by the high spring constant of the sensor (approx. 1800 N/m, cantilever typ. a few ten N/m) and small oscillation amplitudes in the range of 1nm or below (cantilever typ. 10 nm), which more precisely match the range of the involved (chemical) forces. Optimal image performance was achieved using conventionally wet-chemically etched tungsten tips, glued onto the tuning fork. This allows for highest performance in simultaneous or alternative STM/STS operation. Measurements on Si(111) 7x7 show that tunnelling current and vibrational signal are clearly separated. In addition, benchmark measurements on NaCl with a typical corrugation of approx. 10pm prove that resolution on insulation samples is competitive to best cantilever based AFM results.

10:40am **NS-TuM9 Imaging Performance Variations in Organic Solar Cells with Time-Resolved Electrostatic Force Microscopy and Photocurrent-sensitive Atomic Force Microscopy**, *D.S. Ginger*, University of Washington **INVITED**

We study organic/organic and organic/inorganic interfaces in polymer solar cells using time-resolved Electrostatic Force Microscopy (trEFM), and photoconductive Atomic Force Microscopy (pcAFM). These techniques allow us to measure charge generation, collection, and trapping with sub-100 nm resolution so we can correlate variations in performance directly with variations in local film morphology. This talk will describe our trEFM and pcAFM studies of polymer/polymer and polymer/fullerene solar cells. In model blends of polyfluorenes we present surprising evidence that the majority of the collected photocurrent arises away from the visible domain interfaces. In polymer/fullerene cells we show that even the best devices exhibit a distribution of local quantum efficiencies and fill factors that vary on two characteristic length scales. First, we observe performance variations over tens of nanometers that we associate with vertical connectivity of the fullerene domains. Second, in these same devices we observe performance variations over several hundred nanometer length scales (much larger than the characteristic polymer or fullerene domain sizes). We explore the possibility that these larger-scale performance variations are associated with the interface between the polymer blend and the underlying indium tin oxide contact.

11:20am **NS-TuM11 Investigation of Charge Trapping in GaN Films using Scanning Kelvin Probe Microscopy and Conductive Atomic Force Microscopy**, *J.C. Moore, M.A. Reshchikov, J. Xie, H. Morkoc, A.A. Baski*, Virginia Commonwealth University

A new combination of conducting atomic force microscopy (CAFM) and scanning Kelvin probe microscopy (SKPM) was used to study localized charge trapping for MBE-grown GaN films. Charge was injected into the near-surface region of a GaN film by scanning local regions using CAFM with a reverse bias applied to the sample. Time-resolved local surface potential measurements were then obtained using SKPM after charge injection, where an induced band bending caused by charging of surface/interface states was observed. In dark environments and for applied CAFM biases greater than 10 V, the density of charged states ($2 \times 10^{12} \text{ cm}^{-2}$) doubled immediately after scanning as compared to unscanned regions. This increase in charged states resulted in an increase of surface band bending of ~ 3 eV that dissipated quasi-exponentially with time. Induced band bending greater than 0.5 eV was still observed up to 4 hr after charge injection, indicating that charge trapping is relatively stable in a dark environment. Initial values for band bending depend on the applied CAFM bias during injection, where nominal band bending (< 0.5 eV) occurs for biases less than 8 V and a saturation value of ~ 3 eV occurs at biases greater than 10 V. A phenomenological model was used to model the CAFM charge injection via a tunneling mechanism, where electrons travel from the tip through a thin surface gallium oxide barrier and become trapped at the oxide/GaN interface. Saturation occurs due to the existence of a finite density of chargeable interface states. After charging occurs via CAFM, the decrease in induced band bending with time was found to be consistent with a thermionic model of charge transfer from the interface to the bulk. As expected, charged interface states could be rapidly neutralized (< 1 s) via photovoltage caused by illumination with UV light. Funding provided by NSF and AFOSR.

11:40am **NS-TuM12 Sinc or Sine? The Band Excitation Method and Energy Dissipation Measurements by SPM**, *S. Jesse, S.V. Kalinin*, Oak Ridge National Laboratory

Mapping energy transformation pathways and energy dissipation on the nanometer scale and understanding the role of local structure on dissipative behavior is a grand challenge for nanoscale imaging in areas ranging from electronics and information technologies to efficient energy production and use. To date, dissipation measurements are invariably based on either phase and amplitude detection in constant frequency mode, or as amplitude

detection in frequency-tracking mode. Sampling of a single frequency in the Fourier domain of the system allows only two out of three parameters (amplitude, resonance, and Q) to be determined independently. The analysis in both cases implicitly assumes that amplitude is inversely proportional to the Q-factor and is not applicable when the driving force is position dependent, as is the case for virtually all SPM measurements. Here, we developed and implemented a new approach for SPM detection based on the excitation and detection of a signal having a finite amplitude over a selected region in the Fourier domain. The detected signal is Fourier transformed and fitted by appropriate model. This data acquisition scheme substitutes standard lock-in or PLL detection. This band excitation (BE) SPM allows very rapid acquisition of the full frequency response at each point in an image and in particular enables the direct measurement of energy dissipation through the determination of the Q-factor of the cantilever-sample system. This band excitation method allows acquisition of the local spectral response at a ~ 10 ms/pixel rate, compatible with fast imaging. We demonstrate this technique with electromechanical imaging, the investigation of dissipative defects in magnetic force microscopy, and force-distance spectroscopy. The BE method thus represents a new paradigm in SPM, beyond traditional single-frequency excitation and is applicable as an extension to many existing SPM techniques. Research was sponsored by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy at Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

12:00pm **NS-TuM13 Electromechanical Imaging, Polarization Switching, and Intermittent-Contact PFM in a Liquid Environment**, *B.J. Rodriguez, S. Jesse, A.P. Baddorf, S.V. Kalinin*, Oak Ridge National Laboratory

Electromechanical activity is a universal feature of molecular and biological systems, ranging from piezoelectricity in calcified tissues to voltage-controlled ion channels and the functionality of cardiac myocytes and cells for auditory signal transduction. Here, we study the mechanisms of electromechanical imaging by Piezoresponse Force Microscopy (PFM) in liquid environments using model ferroelectric systems. The effects of the conductive properties of the liquid on the localization of the dc electric field are studied from the polarization patterns created by the voltage pulses applied to the tip. Under ambient conditions, the biased tip establishes a highly-localized electric field that decays rapidly with distance from the tip-surface junction, resulting in small, well-defined domains. For solvents with intermediate conductivities, the electric field is localized, but the characteristic length scale is significantly larger than the tip size and is mediated by pulse length via the mobile ion diffusion length. The switching in this case results in the formation of irregular fractal domains. In conductive solvents, the solution is uniformly biased, resulting in a homogeneous electric field across the film thickness and partial or complete uniform switching. Notably, high resolution imaging is possible even in polar solvents because of the high excitation frequencies, minimization of the diffusion paths, and high localization of the strain that transmit predominantly through the mechanical (rather than electrical) contact. The same screening effect in solution enables a mechanically modulated approach for intermittent-contact PFM in solution. In air, this mode is dominated by electrostatic forces, which are screened in solution, allowing the electromechanical signal to dominate. These results elucidate a strategy for high resolution imaging of electromechanical activity in biological and molecular systems in liquid environments.

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Tuesday Afternoon, October 16, 2007

Electronic Materials and Processing

Room: 612 - Session EM+NS-TuA

Semiconductor Nanostructures for Electronics and Optoelectronics II

Moderator: S.E. Mohney, The Pennsylvania State University

1:40pm **EM+NS-TuA1 Epitaxial NiFe Contacts on GaAs via Electrodeposition.** *Z.L. Bao, K.L. Kavanagh, A.S. Arrott*, Simon Fraser University, Canada, *A.A. Talin*, Sandia National Laboratories

We report the electrodeposition of epitaxial $\text{Fe}_x\text{Ni}_{(1-x)}$ films on n-GaAs (001) substrates from aqueous metal ammonium sulphate solutions. Structural measurements using x ray diffraction show that the films have single crystalline BCC or FCC structure at Fe and Ni-rich compositions, respectively. The ratio of Fe concentration in the FCC films to that in the electrolyte is surprisingly close to unity (1.1). BCC $\text{Fe}_x\text{Ni}_{(1-x)}/\text{GaAs}$ diodes have constant Schottky barrier heights independent of Fe composition consistent with a constant interfacial composition while the FCC Ni-rich alloys barriers increase with increasing Ni composition consistent with room temperature reactions.

2:00pm **EM+NS-TuA2 Medard W. Welch Award Lecture - Growth of Semiconductor Nanostructures: Simple Models for Complex Behavior.** *J. Tersoff**, IBM T.J. Watson Center **INVITED**

Epitaxial islands and wires can "self assemble" during growth, producing quantum dots and nanowires with sub-lithographic dimensions. Such growth exhibits many remarkable and puzzling features, which must be understood in order to grow well controlled nanostructures. I will describe simple models that can explain many of the phenomena observed during growth of quantum dots in strained-layer heteroepitaxy, and also some recently discovered phenomena in growth of nanowires via the vapor-liquid-solid mechanism.

2:40pm **EM+NS-TuA4 Fast Synthesis Method for Binary and Ternary alloy Quantum Dots.** *N. Shukla, M.M. Nigra, A.J. Gellman*, Carnegie Mellon University

We have developed a one step synthesis process for binary and ternary alloy quantum dots with photoluminescence ranging from the red through to the violet region of the solar spectrum. This synthesis method allows us to control particle size and composition of quantum dots. We have also studied the effect of solvent boiling point and the addition of various chemical precursors on the synthesis and the photoluminescence properties of quantum dots. The photoluminescence peak in this synthesis method can be controlled by using different reaction time to produce quantum dots of different sizes. Photoluminescence peaks can also be controlled through varying composition of the chemical precursors. In addition, we have also studied the effect of solvent boiling point and the type of solvent on the physical and photoluminescence properties of these quantum dots. The type of solvent plays an important role in the photoluminescence properties of quantum dots. High boiling point non-polar solvents shift the photoluminescence peak to higher wavelength and low boiling point polar solvents shift the photoluminescence peak to lower wavelength.

3:00pm **EM+NS-TuA5 Zinc Oxide Nanowalls and its Optical and Field Emission Properties.** *D. Pradhan, K.T. Leung*, University of Waterloo, Canada

Vertically grown ZnO nanowalls, with typical dimensions of 40-80 nm thick and several micrometers wide, were electrodeposited on an ITO-glass substrate at 70 °C. XRD study shows that these nanowalls have the wurtzite structure and are highly crystalline. The corresponding Raman and photoluminescence spectra further indicate the presence of oxygen deficiency. These ZnO nanowalls exhibit excellent field emission performance, with not only a considerably lower turn-on field of 3.6 V/ μm (at 0.1 $\mu\text{A}/\text{cm}^2$) but also a higher current density of 0.34 mA/ cm^2 at 6.6 V/ μm than most of ZnO nanowires and other one-dimensional nanostructures reported to date. We will also discuss a plausible growth mechanism for these nanowalls, and our recent work on the growth of these and other novel ZnO two-dimensional nanostructures on ITO-plastics.

4:00pm **EM+NS-TuA8 Bright and Color-Saturated Light Emitting Devices Based on Colloidal Nanocrystal Quantum Dots.** *J. Xu*, Pennsylvania State University, *Q. Sun*, University of Dayton, *T. Zhu*, Pennsylvania State University, *A. Wang*, Ocean NanoTech LLC., *Y. Li*, Chinese Academy of Science, China **INVITED**

Recently, the development of low cost, solution-based synthesis of monodisperse, well characterized colloidal quantum dots (QDs) has generated a new class of material for the next generation-light emitting devices. Electroluminescent (EL) devices have been fabricated from thin films of colloidal QDs and exhibit saturated colors and broad wavelength coverage. Emission of EL devices can be easily tuned by varying the size and/or the material composition of nanoparticles during the synthesis process, while their chemical properties remain largely the same. Therefore, one device fabricating procedure can be adopted for different nanocrystals to produce emissions over a broad wavelength, covering the visible (0.4 μm – 0.8 μm) and NIR (0.8 μm - 2.5 μm) regions of the spectrum. In addition to the broad wavelength tunability, high fluorescence quantum yield and photochemical stability can be achieved by careful modification of the nanocrystal surface, and this may favor the efficiency of the EL device. All these unique properties have made semiconductor NQDs promising candidates for a broad range of applications, including flat panel display (FPD), light illumination, lightwave communication, and bio/chemical sensing. In this talk we present our work on the design and optimization of colloidal quantum dot (QD)-based light emitting diodes (LEDs) by tailoring the structure and layer thickness of the emissive QDs in the LED active region, the device configuration, as well as the electrode composition. The maximum brightness of red (?peak=619nm), orange (?peak=595nm), yellow (?peak=575nm), and green (?peak=526nm) QD-LEDs were measured to be 9064 cd/m², 3200 cd/m², 4470 cd/m², and 3700 cd/m², respectively, representing the highest brightness reported for QD-based EL devices. These devices were characterized with low turn-on voltages (3-4 V), high efficiency (1.1-2.7 Cd/A), and longer operation time at high brightness (t50%=300hrs at 1100 cd/m²), indicative of the superior radiative properties and adequately-tailored carrier-injection and transport functions of the QD-active region in the LEDs.

4:40pm **EM+NS-TuA10 Ligand Quenching of CdSe Quantum Dot Photoluminescence Investigated by Single Molecule Spectroscopy.** *A.M. Munro, I. Jen-La Plante, D.S. Ginger*, University of Washington

Colloidal quantum dots are a unique class of solution processable chromophores with high photoluminescence quantum yields, good photostability, and narrow, size-tunable emission spectra that make them potentially useful for many optoelectronic and photonic applications. Surface chemistry strongly affects the optical and electrical properties, as well as the solubility and stability of the quantum dots. However, many properties of ligand-quantum dot interactions remain unresolved. For instance, it is not known exactly how different ligands alter quantum dot photoluminescence and a better understanding of ligand effects is necessary in order to tailor quantum dot surface chemistry for specific applications. We investigate changes in the photoluminescence of colloidal CdSe quantum dots as we bind different ligands to quantum dot surfaces using both single-molecule and ensemble averaged spectroscopy. Using single-molecule spectroscopy, we monitor the photoluminescence of single CdSe quantum dots over time in the presence of varying concentrations of octadecanethiol and determine the average quantum dot intensity, the average number of emissive quantum dots, and the blinking statistics of the quantum dots. This allows us to determine that the binding of a single thiol molecule to the surface of a CdSe quantum dot creates a trap state that decreases the photoluminescence intensity of the individual quantum dot by a significant amount, but that there is no change in the quantum dot blinking rate. We use this single-molecule data to refine our previously reported Langmuir isotherm quenching fits to ensemble solution photoluminescence spectra. By modeling the effects of octadecanethiol on CdSe quantum dots, we develop a better general understanding of ligand exchange and ligand binding to quantum dots.

5:00pm **EM+NS-TuA11 Controlling the Electronic Structure of Graphene Layers.** *T. Ohta*, LBNL; Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *A. Bostwick*, LBNL, *J.L. McChesney*, LBNL; Montana State University, *T. Seyller*, Univ. Erlangen-Nürnberg, Germany, *K. Horn*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *E. Rotenberg*, LBNL

Much recent attention has been given to the electronic structure of graphene, the honeycomb carbon sheet which is the building block of graphite, carbon nanotubes, C₆₀, and other mesoscopic forms of carbon. Following recent developments in synthesizing or isolating graphene films,

* Medard W. Welch Award Winner

experiments have revealed many interesting and physical properties, including an anomalous quantum Hall effect, ballistic electron transport at room temperature, and micron-scale coherence lengths. These unconventional properties are the direct consequence of graphene's peculiar and structure, with massless "Dirac Fermions" as charge carriers at the Fermi level. We have determined the layer-dependent electronic properties of graphene sheets prepared on silicon carbide, using angle-resolved photoemission spectroscopy. We examine this unique two-dimensional system in its development from single layers to multilayers in the π band, the highest occupied state, and the dispersion relation in the out-of-plane electron wave vector in particular.¹ By exploiting the sensitivity of graphene's electronic states to the charge carrier concentration, changes in the on-site Coulomb potential leading to a change of π and π^* bands can be examined. We demonstrate that, in a graphene bilayer, the gap between π and π^* bands can be controlled by selectively adjusting relative carrier concentrations, suggesting a potential application in switching functions in electronic devices.²

¹T. Ohta, A. Bostwick, J. L. McChesney, T. Seyller, K. Horn, E. Rotenberg, Phys. Rev. Lett., 2007, in press.

²T. Ohta, A. Bostwick, T. Seyller, K. Horn, E. Rotenberg, Science 313, 951, 2006.

Nanometer-scale Science and Technology

Room: 616 - Session NS+MS-TuA

Characterization of Nanostructures

Moderator: R.F. Klie, University of Illinois - Chicago

1:40pm **NS+MS-TuA1 Atomic-scale Deformation in N-doped Carbon Nanotubes**, C.-L. Sun, Academia Sinica, Taiwan, H.-W. Wang, M. Hayashi, L.-C. Chen, National Taiwan University, K.-H. Chen, Academia Sinica, Taiwan

We present the N-doping induced atomic-scale structural deformation in N-doped carbon nanotubes (CNTs) by using energy-filtered transmission electron microscopy (EFTEM) and density functional theory calculations. EFTEM N mapping image shows that N is indeed incorporated in the bamboo-like CNTs with non-uniform distribution. The interlinked parts in CNTs are brighter than the sidewall, indicating that they contain higher N concentration. We then construct the finite cluster models for CNTs with pure and two doping types in order to study the detailed structural changes in atomic scale. For substitutional-N-doped nanotube clusters, the N dopant with an excess electron lone pair exhibits the high negative charge and the homogeneously-distributed dopants enlarge the tube diameter in both zigzag and armchair cases. On the other hand, in pyridine-like-N-doped ones, the concentrated N atoms result in positively curved graphene layer and thus can be responsible for tube wall roughness and the formation of interlinked structures. Several examples for its relevant applications in energy conversion and storage will be briefly introduced in the end.

2:00pm **NS+MS-TuA2 Four-Tip Scanning Tunneling Microscope for Measuring Transport in Nanostructures**, S. Hasegawa, University of Tokyo, Japan **INVITED**

Since the establishment of techniques for surface conductivity measurement by microscopic four-point probes (M4PP).¹⁻⁵ with four-tip scanning tunneling microscope (4T-STM) and monolithic four-point probes, electronic transport through single-atomic layers on semiconductor crystals has attracted considerable interests. The electrical conduction through atomic chains and nanowires can also be measured by the methods. Interesting transport properties of such atomic-scale structures have been revealed; the instability and atomic-scale defects intrinsic to such nano-scale structures play decisive roles in transport. I will introduce and summarize the following several topics in the talk. Recent advancements with metal-coated carbon nanotube tips in 4T-STM are also introduced.¹¹⁾ (1) A metal-insulator transition and strong anisotropy in conductivity of Indium atomic wire arrays.^{1,6} (2) Resistance caused by monatomic steps on surface.¹² (3) Non-metallic conduction of metallic Au wires and monolayers.^{7,10} (4) Conductance of individual silicide nano-wires and carbon nanotubes.^{8,9,13}

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⁵R. Hobara, et al., Rev. Sci. Instr. 78, 053705 (2007).

⁶T. Tanikawa, et al., Phys. Rev. Lett. 93, 016801 (2004).

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⁸H. Okino, et al., Appl. Phys. Lett., submitted.

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¹⁰S. Yamazaki, et al., submitted to Phys. Rev. Lett.

¹¹Y. Murata, et al., Jpn. J. Appl. Phys. 44, 5336 (2005); S. Yosimodo, et al., ibid. 44, L1563 (2005).

¹²I. Matsuda, et al., Phys. Rev. Lett. 93, 236801 (2004).

¹³S. Yoshimoto, et al., Nano Letters 7, 956 (2007).

2:40pm **NS+MS-TuA4 A Novel Approach for Electronic Nanotechnology of Carbon Nanotubes**, K.E. Hurst, National Institute of Standards and Technology, R.K. Ahrenkiel, National Renewable Energy Laboratory, T. Campbell, ADA Technologies, J.H. Lehman, National Institute of Standards and Technology

We present a new measurement technique for measuring the recombination lifetimes of carbon nanotubes called the resonant-coupled photoconductive decay (RCPCD) method.¹ The carrier recombination lifetime is a fundamental property of carbon nanotubes which is typically determined by contact-based techniques or spectroscopic methods which do not readily allow characterization of bulk material properties. The measurement is based on a pump-probe technique in which an optical pump and a low frequency microwave probe are employed. RCPCD offers the first rapid, non-contact technique for routine nanometrology of carbon nanotube electronic properties. We demonstrate measurements of carrier lifetimes for multi-walled carbon nanotube and single-walled carbon nanotube thin films, where the ~30 μm thick films are deposited on a glass slide by an air-brush technique. We also consider the influence of material purity on the measurement of lifetimes in these nano-scale systems. Raman spectroscopy and UV-VIS absorption measurements provide further identification and characterization of nanotube samples to enable correlation of nanotube properties with the efficiency of charge transport in these samples. RCPCD is shown to be a fast and effective method for measuring the lifetimes of bulk carbon nanotubes, thereby overcoming present issues of routine carbon nanotube electronic nanometrology.

¹R.K. Ahrenkiel, S.W. Johnston Mater. Sci. Eng. B 102 (2003) 161

3:00pm **NS+MS-TuA5 Properties of the Surface and Core Region of Single CdS Nanowires**, S.F. Alvarado, IBM Research, Zurich Research Laboratory, Switzerland, O. Hayden, Siemens AG, Germany

The properties of the surface and core region of single CdS nanowires are characterized by STM-based cathodoluminescence under ultrahigh-vacuum conditions at room temperature. The CdS nanowires were fabricated using pulsed laser deposition via metal-cluster-catalyzed growth. A diluted nanowire suspension was used to flow-align the nanowires on a p-type Si substrate using microfluidic channels. Cathodoluminescence is excited by using the tip of an STM as a source of low-energy electrons ($100 < E_{\text{kin}} < 1000$ eV) at currents in the pico- to microampere range. The penetration depth of the incident electrons is approx. 1 nm at 100 eV and increases with kinetic energy up to a few nanometers at 1 keV. Therefore this technique allows one to probe the surface region of single nanostructures. A typical spectrum collected on a single nanowire exhibits a relatively sharp emission line centered at approx. 510 nm, with a full width at half maximum of 20 nm, and a much broader band centered at 750 nm. The intensity ratio of the 510 nm to the 750 nm line increases with increasing electron energy, indicating that the 750-nm emission arises from the surface regions of the nanowires, whereas the 510 nm line originates mainly from their core regions. In addition, cathodoluminescence images of single CdS nanowires, collected at different wavelengths, exhibit regions of enhanced emission as well as local variations of the ratio of surface and core contributions. A comparison of cathodoluminescence spectra collected on nanowires, on a CdS nanosheet, and on other structures, suggests a relationship between the ratio of surface-to-core emission and the quality of the nanowires.

4:00pm **NS+MS-TuA8 Helium-ion Microscopy for Nanostructure Characterization**, N.P. Economou, B. Ward, J. Notte, R. Hill, L.A. Stern, Carl Zeiss SMT **INVITED**

We have developed the first practical He ion microscope, based on a unique gas field ion source. The source has highly desirable performance characteristics for building scanning ion microscopes with sub-nanometer probe sizes. A unique construction allows the source to provide stable output over useful lifetimes of several hundred hours, thus enabling the development of practical systems for microscopy and nanostructure characterization. An important aspect of the He ion microscope is the interaction of He ions with the sample being observed. As compared with electrons interacting with the same sample, He ions penetrate less deeply, scatter less and produce higher yields of secondary electrons; back-scattered ions are also present. Images produced with a He ion beam exhibit greater material contrast, higher resolution due to reduced interaction volume, and better signal-to-noise ratio. These factors combine to produce He ion images that often contain more and better information than electron images. Because of these inherent advantages, we believe the He ion microscope will become an important tool for the study of nanostructures. We will discuss the unique characteristics of the source, and present images

produced from the microscope that demonstrate its advantages over currently available instruments.

4:40pm **NS+MS-TuA10 Study of Characteristic Fragmentation of Nano Carbon by the Scanning Atom Probe.** *O. Nishikawa, M. Taniguchi, Kanazawa Institute of Technology, Japan, Y. Saito, Nagoya University, Japan, M. Ushirozawa, Japan Broadcasting Corporation*

Since the characteristic fragmentation of a material is closely related with the binding state between the atoms forming the material, multiwall carbon nanotubes (MWCNT), graphite nanofibers (GNF) and ultrapure graphite are studied by field evaporating these specimens and by mass analyzing the fragmented cluster ions with the scanning atom probe. Two kinds of MWCNT were analyzed: commercially available and laboratory fabricated MWCNTs. GNF is grown on a 304 stainless steel tip by thermal CVD. Purity of the analyzed graphite is 99.9999%. The mass spectra of both MWCNTs are quite similar, particularly mass to charge ratio M/n from 0 to 100. However, the commercial MWCNT exhibits many unidentifiable small mass peaks throughout the mass range up to a few thousands. The most significant feature is the large mass peak at $M/n = 340$ which could be $C_{28}H_4$. The proposed structure of this cluster is a square arranged 8 hexagonal rings. This structure is suitable to form a tube. The mass spectrum of GNF is quite different from that of MWCNT and shows the highest mass peak at $M/n = 278$, $C_{23}H_2$. The proposed structure of this cluster is the triangularly arranged six hexagonal cells. Two corner carbon atoms of the triangle are hydrogen-terminated and third corner carbon atom is bound with an extra carbon atom. Two dimensional extension of the fragments shows a hexagonal ring formed by 6 hydrogen atoms terminating the carbon bonds and 6 extra carbon atoms forming a hexagon. The hydrogen hexagonal ring is quite similar to that of a kekulene molecule. The graphite exhibits two completely different mass spectra. One is quite similar to that of MWCNT showing the characteristic large mass peaks. The other closely resembles those of silicon and diamond. The number of detected ions decreases with mass. Thus, the largest mass peak is C^{2+} and then C^+ . The clusters formed by the odd number of carbon atoms are more abundant than those of even number. Most clusters are doubly charged. This implies that the binding between carbon atoms in this analyzed section is strong and uniform and that the graphite has two phases: diamond and graphite. Although only few H^+ ions are detected from MWCNTs and GNF, most fragments contain more than 1 hydrogen atom. On the other hand few ions detected from the diamond-like graphite are bound with hydrogen.

5:00pm **NS+MS-TuA11 Nano-scale Surface Effects of Field Electron Emission from Zirconium and Hafnium Carbide.** *W.A. Mackie, G.M. Magera, K.J. Kagarice, Applied Physics Technologies*

An electron source for a high resolution SEM/TEM application should produce a high brightness, have a minimal energy distribution, and should be highly stable. In an application in which the resolution is limited by chromatic aberrations, one can improve the performance over a commonly used thermal field emission source, such as a ZrOW Schottky emitter, by using a cold field emission source (CFE). In CFE, the emitting area of the usable beam is small and understanding surface chemistry and effects are crucial to controlling emission stability. Single crystalline transition metal carbides have electron emission properties making them attractive candidates for CFE applications. We are reporting on field emission from (310) oriented single crystal ZrC and HfC. ZrC(310) has a relatively low work function axial emitting surface (3.4 eV) that has a low evaporation rate, is resistant to ion bombardment and sputtering, has a high melting point (~3800 K), and a very low surface mobility. The robustness of this material allows for repeated cleaning via high temperature flashing without changing the geometry of the emitting end form. These crystals are electrochemically etched and mounted in a mini Vogel mount to enable flash cleaning. Experimental $I(V)$ data were taken from which angular intensity and reduced brightness were calculated. Experimental $I(t)$ data were then taken and analyzed for current stability in both long term drift and short term noise. Results are highlighted from a 160 nm ZrC (310) operating at 0.02 mA/sr. Noise spectra were analyzed by FFT and found to be consistent with step and spike like noise associated with foreign atom migration and ion bombardment. Emission from small areas comprising <100 atom sites are dominated by the mobility of foreign atoms from ion back streaming and surface diffusion both arising from the high electric field. Using an annular area surrounding the beam emission area as a current monitor we were able to control fluctuations in the beam. This control ability results from the overlapping currents from both areas. Data are presented which demonstrate improved stability over a variety of vacuum conditions.

Tuesday Afternoon Poster Sessions

Nanometer-scale Science and Technology

Room: 4C - Session NS-TuP

Nanometer-scale Science and Technology Poster Session I

NS-TuP1 Orderly Fabrication of Nanometer-Scaled Triangular Structure using Bridge Phenomenon of Polystyrene Beads, B.K. Lee, K.S. Kim, J.H. Lee, N.H. Kim, Y.H. Roh, Sungkyunkwan University, Republic of Korea

Recently, nanometer-scaled materials have used for fabrication of nanostructure. Polystyrene bead (PSb) has many advantages for fabrication of nanostructure. For example, the PSb could fabricate the particular pattern array structures using for its self-assembled monolayer property. The PSb could be integrated with the established semiconductor process technologies because the PSb has excellent compatibility with silicon substrate. In this experiment, a spin coating was used for well-ordered array of the PSb. The PSb could be reduced its size using an oxygen plasma ashing process. During the plasma ashing process, the bridge phenomenon was occurred between the adjacent PSBs according to the plasma ashing conditions. The main reason for the occurrence of PSb bridges during the plasma ashing process is estimated that the PSb on the silicon surface was not sufficiently ashed by plasma. The ashed PSBs showed the triangular structures and the adjacent bridge distance was under 35 nm. The metal thin film was deposited on the bridges of the PSBs and then the PSBs as a deposition mask were removed by ultra sonication process. After the metal deposition on the ashed PSBs mask, we could obtain the nanometer-scaled triangular island less than 30 nm with the well-ordered array. Consequently, the triangular island would be applied to the nanometer-scaled devices such as single-electron transistor and biosensors.

NS-TuP2 Deposition of Gold Nanoparticles on HOPG using Atmospheric Plasma, F. Demoisson, Universite Libre de Bruxelles, Belgium, **M. Raes, J. Vereecken,** Vrije Universiteit Brussel, Belgium, **F. Reniers,** Universite Libre de Bruxelles, Belgium

The interest for gold nanoparticles in the field of nanocatalysis and of nanosensors is growing. Nanotubes covered with gold nanoclusters could present interesting properties in these fields. However, due to the weak carbon-gold bond, the adhesion of this metal to carbon is not trivial. It is generally accepted that the carbon surface must be activated, either by the creation of surface defects and/or by the adsorption of reactive species, such as oxygen containing groups. Most of the time, activation is done using wet chemistry techniques, such as hot nitric acid solutions. Some studies present activation and deposition experiments realized using vacuum techniques, with ion guns, low pressure plasmas, and/or thermal evaporators. In this preliminary study, we used highly oriented pyrolytic graphite (HOPG) as a model surface that could present the same chemical properties as the one of carbon nanotubes. An atmospheric plasma torch was used to activate the HOPG surface and to realize the gold deposition. The atmospheric plasma torch runs in the RF mode (13.56 MHz), using argon as the main gas. Oxygen was added as secondary gas, in order to provide the active species able to activate the surface. The plasma post discharge was spatially characterized by optical emission spectrometry. Immediately after activation, metal particles were injected into the plasma post-discharge. The surface Au/C elemental composition was analysed using XPS and shows the presence of gold, whereas field emission gun scanning electron microscopy allowed to study the size distribution of the gold particles on the surface as a function of the plasma parameters. This work is financially supported by the Nano2Hybrids (EC-STREP-033311) and PAI 7/3 (Plasma surface interactions - Belgian federal government) projects.

NS-TuP3 Laser Transfer of Organic Molecules through a Liquid Layer, Y. Pihosh, M. Goto, A. Kasahara, M. Tosa, National Institute of Materials Science (NIMS), Japan

Previous results of implantation of Coumarin 6 (C6) molecules on a target polymer surface by laser molecular implantation technique showed that the achieved minimum size of dots could be 3 μm in diameter. However, the implantation of organic molecules into conductive organic or inorganic materials on the nanometer scale is one of the challenging problems in materials research that has to be solved. Here, we report the process of laser molecular implantation of pyrene acid and pyrene sublimed molecules onto different materials by generating a laser-induced water channeled jet through a liquid-filled space-gap between the source film and target materials. This process leads to significant reduction in the size of

implanted organic molecular dots to a sub-micrometer region on the surface of solid materials such as glass and copper. The pyrene source films were prepared by means of thermal evaporation onto a cover glass with the thickness of about 600 nm. The source film and the target were brought into contact, and the distance between them was filled with liquid. A four nanosecond pulse laser beam was focused on the surface of the source film by special array of lenses, and those photo-excited organic molecules. As a result, the molecules could be ejected from the source film in a form of a plume through a strait path, which was created by laser induced plasma. Later the molecules were implanted onto or into the target materials in the form of dots or rings depending on laser fluence. Those experiments focused on the implantation process of pyrene organic molecules in the submicron region on glass and copper substrates through polar and non-polar liquids. The size of the smallest implanted pyrene acid dots implanted through water and diiodomethane layer was estimated to be about 0.4 μm and 0.3 μm at laser fluences of 235 Jcm^{-2} and 326 Jcm^{-2} , respectively. From fluorescence spectra it was noticed that the implanted molecules did not decompose during the implantation process no matter which liquid filled the gap. In the case of pyrene sublimed molecules it was found that implantation occurs only through a water layer, and, also, that the implanted dots have a very short life time.

NS-TuP4 Effect of Surface Potential on Formation of DNA-Templated Gold Nanowires by pH Change of Gold Nanoparticles, S.W. Cha, J.-S. Kim, H.J. Kim, N.H. Kim, Y.H. Roh, Sungkyunkwan University, Republic of Korea

Biological molecules such as DNA are especially useful as the material for the nanoscale electronic construction because their strand is possible to regulate and their width has nanometer-size diameter of about 2 nm. And also, the negatively charged phosphate group in DNA is possible to bind the surface-functionalized gold nanoparticle (AuNP). However, the location of AuNP with the uniform interval along DNA molecules as template is generally considered to be difficult because precise control of the electrostatic force for conjugation between negatively charged DNA molecules and positively charged AuNPs is hard. In this study, we developed a new method to control the interval between AuNPs on stretched DNA molecules by changing pH of oxidized aniline-capped AuNPs (AN-AuNPs). DNA molecules were stretched and fixed on 3-aminopropyltriethoxysilane (APS) coated Si wafer by the tilting method. Then, pH of AN-AuNPs solution was changed by adding NaOH solution, and DNA molecules were treated with AN-AuNPs solution for the certain time. As NaOH solution was added in AN-AuNPs solution, the surface electric charge of AN-AuNPs was decreased. Atomic force microscopy (AFM) was used to analyze the intervals of AN-AuNPs attached on DNA molecules. The surface electric charge of AN-AuNPs was measured with the change of pH by the Zeta-potential measurement to confirm the interval of AuNPs when the surface electric charge of AN-AuNPs was changed. The effect of AN-AuNPs size on the intervals of AN-AuNPs was also investigated because the AuNPs would be aggregated with the change of pH of AN-AuNPs.

NS-TuP5 Nanostructured Growth of Cobalt on Cu(775): An STM and Photoemission Study, M. Yilmaz, N. Zaki, S. Wang, K. Knox, D.V. Potapenko, J. Dadap, R.M. Osgood, Columbia University, **T. Valla, P. Johnson,** Brookhaven National Laboratory

Vicinal metal surfaces have attracted much attention in recent years as templates for self assembled nanostructures. We will present an STM and photoemission study of Co/Cu(775). Using STM, we observed that the substrate acts as a template for the growth of Co. Cobalt grows in the form of anisotropic islands, the structure of which changes with coverage. The effect of these nanostructures on the surface electronic structure is investigated by means of high resolution angle resolved photoemission spectroscopy (ARPES). At very low coverages, cobalt alters the modulation plane of the Cu surface state from surface modulation to terrace modulation. As the coverage increased an additional Cu derived surface state at a higher binding energy appears. Both states are suppressed as more cobalt is deposited on the surface. Cobalt d-band features are relatively flat and consistent with experiments performed on other Co/Cu systems.

NS-TuP6 Influence of Preparation Condition on Electrical Properties of Cobalt(Co²⁺)-Metallic-DNA Molecules, S.D. Cheon, N.H. Kim, Y.H. Roh, Sungkyunkwan University, Korea

Recent works have showed many attractive interests in the formation of nanowires to make nano-device using the deoxyribonucleic acid (DNA) molecules. Because of DNA molecule has narrow width (2nm) and the length of DNA easy to control. Metallic DNA (M-DNA) is a modified DNA by incorporating divalent metallic ions (i.e., Zn²⁺, Co²⁺, Ni²⁺, etc.) to the

each base pair of B-DNA. It is one of the methods to form the metallic nanowires with metallic electrical conductivity by contrast with B-DNA of semiconductor like electrical properties. M-DNA has the higher and the more stable current-voltage (I-V) characteristic than B-DNA. Most experiments of electrical properties of M-DNA were made up by Zn-M-DNA. Cobalt and nickel divalent ions are generally known to be also possible to make M-DNA. Particularly, cobalt (Co^{2+}) is comparatively easy to make M-DNA because of its good synthesis rate and fast incorporating speed. In this work, Co-M-DNA could be made using poly(dG)-poly(dC), poly(dA)-poly(dT) or lambda DNA. The Co-M-DNA was prepared with the various conditions such as concentration of divalent metallic ions, preparation pH and temperature. The Co-M-DNA was prepared with heating processes, which contributed to decrease of incorporating time. The prepared Co-M-DNA molecules were attached on Au electrodes with the nanometer size gap. The current through Co-M-DNA measured on vacuum (10^{-2} torr) to minimize humidity effects by HP4145 semiconductor parameter analyzer. The current through Co-M-DNA showed the metallic electrical properties and larger conductivity than B-DNA. The conductivity of Co-M-DNA became larger by preparation over pH 8. Furthermore, the conductivity of M-DNA was affected by Co^{2+} concentration.

NS-TuP7 A Study on the Patterned Molecular Wires Based on Carotenoids by Electrostatic Force Microscopy and I-V Measurement. *J.W. Yoo, J.W. Kim, Y.J. Choi, Y.S. Kim, S.H. Koo, C.J. Kang*, Myongji University, Korea

Electrical properties of single carotenedithiol molecules lithographed on Au by micro channel have been investigated by electrostatic force microscopy (EFM) and current versus voltage (I-V) measurement. The Carotenedithiol molecules have three different species of end-groups substitutive. To make a wire pattern, polydimethylsiloxane (PDMS) micro channel carrying carotenedithiol molecules are used and the molecules are inserted into an octadecane monolayer that is previously patterned on Au substrate. After removing the PDMS channel, EFM and I-V measurement was performed on the remained wire pattern. For the efficient microscopy, we adopted cantilever oscillation method using Lorentz force. The results show that the organic molecules of carotenoid based patterned nano wires can be a candidate of the element for nano devices.

NS-TuP8 Real-time Single-molecule Detection on Random Arrays for Biosensing Applications using Total Internal Reflection Fluorescence. *A. Gunnarsson, P. Jönsson, R. Marie, J. Tegenfeldt, F. Höök*, Lund University, Sweden

Development of ultrasensitive biological sensors has attracted significant scientific interest due to its many possible application areas such as biomedical diagnostics, proteomics and forensic analysis. DNA sensing using nanoscale devices based on electrical^{1,2} or optical^{3,4} detection has shown great promise for achieving high sensitivity and specificity. We report of a novel biosensor assay capable of detecting non-labeled low-abundant DNA targets based on surface adsorption of lipid vesicles through DNA hybridization. Using total internal reflection fluorescence (TIRF) microscopy, single DNA molecule detection at 10 fM concentrations is achieved. Various biomolecules besides DNA can be probed with the assay, including soluble and membrane proteins utilizing the lipid bilayer of the vesicles. Not only achieving ultra-sensitive detection, the novel approach also offers great potential for studies of biomolecular interactions on a single molecule level in real time.

¹ Hahn, J.; Lieber, C. M. *Nano Letters* 2004, 4, (1), 51-54.

² Brousseau, L. C. *Journal of the American Chemical Society* 2006, 128, (35), 11346-11347.

³ Bailey, R. C.; Nam, J. M.; Mirkin, C. A.; Hupp, J. T. *Journal of the American Chemical Society* 2003, 125, (44), 13541-13547.

⁴ Ho, Y. P.; Kung, M. C.; Yang, S.; Wang, T. H. *Nano Letters* 2005, 5, (9), 1693-1697.

NS-TuP9 Siloxane, including Amine Terminal, Coated Stable Silicon Nanoparticles for Interaction with Negative Charged Materials. *B.-Y. Jeong*, SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Republic of Korea, *J.-W. Park*, Sungkyunkwan University, Republic of Korea, *J.-S. Kim*, SAINT, Sungkyunkwan University, Republic of Korea, *N.H. Kim, Y.H. Roh*, Sungkyunkwan University, Republic of Korea

Silicon nanoparticles (Si NPs) have many interesting electronic properties such as controllable electron mobility and energy band-gap through doping impurities despite their nanometer-scaled size. They are widely used in LED, photo-luminescent label, sensor, etc. Si NPs could be also applied to nano-size semiconductor. However, pure Si in nature makes natural oxide-layer. Moreover, Si NPs which were not functionalized lost their characteristics of nanoparticles for aggregating each other because the pure Si has unsatisfactory stability. Therefore, the surface of Si NPs should be modified in order to disperse and stabilize Si NPs. In this study, Si NPs were coated by siloxane that has amine terminal to stabilize and modify the surface of Si NPs to the positively charged surface coincidentally. It led to

prevent an aggregation and chemical reactions of surface. After treatment, Si NPs were dispersed in solution and had positively charged surface. The raw Si NPs were treated with piranha etch to remove the oxide layer and make a hydroxyl surface. In order to induce hydrosilylation, we added 3-aminopropyltriethoxysilane with gentle stirring. TEM was carried out to check the rate of dispersion. EDX and FTIR analyses were performed to confirm the hydrosilylation reaction. Zeta-potential was measured in order to estimate the charge of particle surface. Consequently, we expected that the stable siloxane-coated Si NPs with positively charged surface have possible applications to conjugate with phosphate of DNA or other polymer with negative charge.

NS-TuP10 Fabrication of Well-defined Microdomains Composed of Aldehyde- and Carboxy-terminated Self-assembled Monolayers. *A. Hozumi*, National Institute of Advanced Industrial Science and Technology (AIST), Japan, *H. Taoda, T. Saito*, AIST, Japan

Organosilane self-assembled monolayers (SAMs) have been widely applied to the artificial control of surface chemical functionalities. Among the various types of SAMs, both aldehyde (CHO)- and carboxy (COOH)-terminated SAMs are of particular interest owing to their chemical reactivities to biomolecules. Here, we report on the fabrication of microdomains composed of CHO- and COOH-terminated SAMs on a Si substrate covered with native oxide. The cleaned substrate was first exposed to a vapor of 12.5 vol % solution of triethoxysilylundecanal (TESUD) diluted with absolute toluene for 3 h at 403 K. This vapor phase treatment produced the CHO-terminated SAM on the native oxide/Si surface. The thickness of this SAM was estimated by ellipsometry to be about 1.2 nm. Next, some of the samples were irradiated for 1-60 min with 172 nm vacuum UV light in air. Due to this treatment, the hydrophobic surface became hydrophilic gradually with irradiation time. Although film thickness remained almost unchanged even after irradiation for 25 min, water-contact angle decreased from 86 degree to about 25 degree. Both contact angle and film thickness decreased markedly after about 25 min and reached their minimum of 5 degree or less and 0.3 nm, respectively, at the irradiation time of 60 min. We further confirmed by X-ray photoelectron spectroscopy and attenuated total reflection spectroscopy, the irradiation time of 25 min was determined the optimum time to yield reproducible COOH-terminated SAM. Finally, the CHO-SAM was irradiated site-selectively through a photomask. As confirmed by lateral force microscopy, the microstructures composed of 5 micron x 5 micron square features photoprinted on the CHO-terminated SAM surface were clearly imaged through the friction force contrast between the photoirradiated and masked regions. The former regions were expected to have been converted to COOH-terminated SAM.

NS-TuP11 Conducting Polymer Nanofilm Growth on a Nanoscale Linked-Crater Pattern Fabricated on an Al Surface. *H. Kato, S. Takemura, A. Ishii, Y. Takarai, Y. Watanabe, T. Sugiyama, T. Hiramatsu, N. Nanba*, Kanto Gakuin University, Japan, *O. Nishikawa, M. Taniguchi*, Kanazawa Institute of Technology, Japan

A nanoscale linked crater structure was fabricated on an Al surface by wet chemical and electrochemical processes. The surface of an Al plate was treated with Semi Clean and Semico Clean in order to create crater-shaped erosion on the surface. The successive electrochemical anodization in H_2SO_4 solution created a nanoscale finer linked-crater structure on the surface. The authors conducted the nanofilm growth of conducting polymer polythiophene on the nanoscale structured Al surface by the electrochemical polymerization method. The electrochemical polymerization was performed in acetonitrile containing thiophene monomer and $(\text{Et})_4\text{NBF}_4$ as a supporting electrolyte and the polymerization on the linked-crater surface was conducted by applying positive voltage to the Al plate. The dynamic force microscopy (DFM) image of the Al surface after the polymerization process suggested that the polymer was grown on the nanoscale linked-crater structure. In the DFM measurements, the dimmer contour image of each crater was still recognized even after the polymerization process was fulfilled suggesting that the polymer film was grown on the Al surface. The cross section analysis of the DFM measurement demonstrated that the nanofilm was grown on the linked crater because the crater depth became shallow. X-ray photoemission spectroscopy (XPS) measurement also supported the polymer growth because C 1s and F 1s due to the polymer origin were detected. Furthermore, the authors tried to inject copper phthalocyanine (CuPc) molecules into the polythiophene nanofilm on the nanoscale structured Al in order to functionalize the nanoscale hybrid materials. The XPS measurement detected C 1s, N 1s and Cu 2p lines due to the injected CuPc molecules. This work was supported by High-Tech Research Center Project aided by MEXT.

NS-TuP12 Fabrication of Nanoscale Organic Patterns on a Highly-Oriented Grooved Structure Created on an Electrochemically Treated Aluminum Surface. *H. Kato, Y. Watanabe, S. Takemura, S. Kimura, D. Okumura, R. Nakano, T. Sugiyama, T. Hiramatsu, N. Nanba,* Kanto Gakuin University, Japan

The surface of an aluminum plate was treated with a combination of chemical and electrochemical processes. A chemical treatment with acetone and a successive electrochemical process created a nanoscale highly-oriented grooved structure on an aluminum surface. The distance between the oriented lines was estimated as 30-40 nm by dynamic force microscopy (DFM) measurements. The present work intended to make an organic-inorganic nanoscale pattern using this nanoscale structure. Copper phthalocyanine (CuPc) and fullerene C60, which were highly-functional molecules, were selected in fabrication of nanoscale patterning. CuPc and C60 molecules were deposited on the highly-oriented line-structure on Al. A toluene droplet containing CuPc molecules was cast on the Al plate and extended on the surface. CuPc deposition on the Al surface was made by evaporation of toluene. Cross section analysis of the DFM measurements clarified that each aligned groove was filled with CuPc molecules because the depth of the channel became shallow and in some area the row width became narrower after the CuPc deposition. X-ray photoelectron spectroscopy (XPS) measurements clarified that N 1s and Cu 2p lines appeared, which also supported the CuPc deposition on the nanoscale structure creating a nanoscale organic line-pattern. The spectral profile difference of Al 2p pre- and after deposition of CuPc suggested the molecular-surface interaction. Furthermore, the authors tried to make a polyaniline nanowire along the row channel fabricated on an Al surface. A droplet of HCl solution containing aniline molecules was cast and extended on the nanoscale-structured Al plate. Successively, a droplet containing APS was put and extended on the surface in order to trigger the polymerization in the nanoscale area. The DFM and XPS measurements clarified that aniline molecules were polymerized in the channel. This work was supported by High-Tech Research Center Project aided by MEXT.

NS-TuP13 Quenching of Photoluminescence in Silicon Oxide Layers with Silicon Nanocrystals under Ion-Beam Irradiation: Analysis of Experimental Data. *V.A. Stuchinsky, S.G. Cherkova, G.A. Kachurin, D.V. Marin,* Russian Academy of Sciences

A quantitative analysis of experimental data on photoluminescence (PL) quenching in silicon oxide layers with embedded Si nanocrystals (nc's) under ion-beam irradiation is presented. The analysis was performed using the data of¹, obtained for an nc-system with mean nc size $R=2.9$ nm irradiated with 2 MeV He, Ge, and Au ions, and our data obtained for an nc-system with $R=3.8$ nm, irradiated with 130-200 keV He, F, and P ions. A method to allow for the PL lifetime degradation is proposed, which can be applied if the available dataset for a particular nc-system contains data obtained using irradiation of this system with light ions. A simple model is considered to predict the number N_{lum} of luminescing nc's versus the fraction η of atoms displaced in the system at low irradiation doses with allowance for the density of collision cascades and the size distribution of nc's. In this model, the well-known expression for N_{lum} vs η in the case of random rare displacements is used (see, e.g.,¹), with the density of atomic displacements corrected for the damage factor of individual nc's. The experimental PL quenching curves were used to determine the average number of stable nonradiative centers introduced into one nc (N_{exp}). The quantity N_{exp} was then compared with the mean number N of displacements per nc obtained in a computer analysis of TRIM simulation data on 3D coordinates of displacements. The yields N_{exp}/N of stable nonradiative centers with respect to primary displacements in the nc-systems irradiated with the various ions were determined. The obtained values suggest that in dense collision cascades close vacancies choose to combine in divacancies, whereas in rare cascades they prefer to form nonradiative centers individually, possible coming to the nc/matrix interface with the formation of dangling bonds there. A physical interpretation is given to the curves of PL lifetime versus the damaged fraction of nc's. The exciton tunneling times between adjacent nc grains in the nc-systems under consideration were evaluated (120 and 15 μ s for the systems with $R=2.9$ and 3.8 nm). Based on these values, estimates of the decay length of the excitonic wavefunction into the dielectric matrix, and the excitonic recombination cross section at deep traps introduced by ion-beam irradiation in the host dielectric, were obtained.

¹ D. Pacifci et al. Phys. Rev. B 65, 144109 (2002).

NS-TuP14 Segmented Nanowire Fabrication Through Templated Electrodeposition. *A.J. Murray, S. Evoy,* National Institute for Nanotechnology, Canada

Metal oxide nanowires have recently attracted considerable attention in electrochemical sensing. Templated electrodeposition of metals within porous aluminum oxide (PAO) membranes has proven to be a simple and reliable method of nanowire synthesis.¹ The PAO self ordered pore array

consists of honeycomb packed hexagonal cells with central cylindrical pores. Pore diameters exhibit high uniformity across the membrane can be easily tailored from 4 to 400 nm, while a pore depth of several hundred nanometers has been achieved. Electrodeposition of WO_3 has been explored for its electrochromic effects. Application of WO_3 to gas sensing was first explored by Reyes et al.² We here report on the development of WO_3 segmented nanowires for chemical sensing. The basic layout of these sensing structures consists of a short metal oxide segment intercalated between gold electrical contacts. During the initial step, a 500 nm silver layer is sputtered onto the back of Whatman Anodisc 25 PAO filters. The resistive nature of aluminum oxide forces wire growth to initiate at the seeding layer, the deepest point within each pore, and continue towards the surface of the membrane. Silver (Technic Inc. Cy-less Silver RTU Plating solution) is backfilled into the pores and acts as a sacrificial contact, restricting gold and metal oxide growth to a uniform portion of the membrane. 3 μ m of gold is subsequently deposited from Technic-Gold 25 E (Technic Inc.) at a current density of 250 μ m/cm². A 0.1 molar aqueous sodium tungstate (Na_2WO_3) solution is then prepared and subsequently deposited at 0.5 mA/cm². Plating is completed with a final 3 μ m Au deposition. The resulting wires are then released by selective etching of the silver seeding layer and the porous alumina template. Extensive structural characterization of these nanowires using XPS, SEM and Auger will be presented. We plan to present both morphological material analysis as well as preliminary electrical response and chemical sensing results.

¹ A. Kolmakov, Y. Zhang, G. Cheng, M. Moskovits, "Detection of CO and O₂ using tin oxide nanowire sensors", Adv. Mater. 15(12), 997-1000 (2003).

² L.F. Reyes, A. Hoel, S. Saukko, P. Heszler, V. Lantto, C.G. Granqvist, "Gas sensors of pure and activated WO_3 nanoparticle films made by advanced reactive gas deposition", Sensors and Actuators B 117, 128-134 (2006).

NS-TuP15 Local Gating Behaviors in Nanowire Heterojunction Transistors. *J.-H. Lim, H.J. Ji, G.E. Jeong, G.T. Kim, J.S. Ha, S.-J. Kahng,* Korea University

Electronic transport properties of ZnO nanowire transistors were studied with atomic force microscope (AFM). The nanowire transistors were fabricated with ebeam lithography and characterized in a probing system embedded in the AFM. Clear gate dependence was observed in the source-drain current by using the non-local back-gate in the transistor. When Ti-Pt-coated AFM tip was used as a local and mobile gate, it was observed that the gating behavior is strongly dependent on the position of the local gate. The transistor could be made on and off repeatedly with the AFM tip locating above the nanowire heterojunction, implying that the active region in the transistor behavior is mostly confined to the small junction area.

NS-TuP16 Nanoindentation Rate Depend Mechanical Properties of Nickel and Titanium. *E. Tam, P. Berke, T.J. Massart, M.P. Delplancke-Ogletree,* Universite Libre de Bruxelles, Belgium

Rate dependent nano-indentation experiments have been performed on pure polycrystalline nickel and titanium and also on anodized titanium samples. During indentation, the load is linearly increased, then held constant for various intervals of time then reduced linearly to zero. The extent of "creep", sample displacement at constant load, varies with the loading rate. Finite element calculations have been performed to model these experiments. Using time independent material properties, the slope of the loading curve is significantly underestimated. When rate-dependent material properties are used in the model calculations accurate load slopes and creep behavior are obtained. Additional experiments have been carried out to analyse the effect of sample roughness and indentation depth. Implications for determination of material properties through nano-indentation will be discussed.

NS-TuP17 Flipping of Atomic Image Contrast of Graphite. *J. Choi, G.S. Khara,* Wayne State University

Flipping of atomic image contrast of graphite is studied by using scanning tunneling microscopy (STM) and spectroscopy (STS). Tunneling gap-distance, gap-voltage and bias polarity play an important role in the flipping of atomic image contrast. The study revealed that the flipping of atomic image contrast is natural because of the electronically active and mechanically soft beta-carbon atoms of graphite. The brightest contrast in the scanning tunneling microscopic images does not always represent a specific site of graphite such as beta-site. The flipping mechanism of atomic image contrast will be discussed.

NS-TuP18 Construction of a Ultra Low Temperature Scanning Tunneling Microscope System¹. *Y.J. Song, S.R. Blankenship, J.N. Crain, J.A. Stroscio,* National Institute of Standards and Technology

We describe the design and construction of an ultra-low-temperature (20 mK), high magnetic field (15 T) scanning tunneling microscope (ULT STM) system. This ULT STM consists of an ultra-high-vacuum-compatible dilution refrigerator (DR) and associated UHV systems. The DR was

designed and constructed to allow two independent modes of ^3He condensation: a traditional 1K pot condenser, or a Joule-Thomson condenser for possible lower noise operation. The system includes extensive vibration isolations and RF shielding. We describe the cooling power characteristics and temperature measurement system of this versatile DR, which reaches a base temperature of 10 mK without STM running. For STM/STS measurements a custom-designed STM module suitable for operation at mK temperatures is described. The STM body is made from coin silver which is rigid and thermally conductive in the mK regime. The whole STM module can be transferred from the upper, room-temperature chamber where the sample and tip can be easily exchanged. The sample holder has five isolated electrical contacts which are also used for kinematic mounting of the sample. This allows 4-probe electrical measurements to be performed simultaneously with STM measurements for microscopic transport studies. This STM module has ± 2 mm of x and y travel and in-situ deposition capabilities on the STM sample mount. Current progress and research plans will be discussed.

¹ This work is supported in part by the Office of Naval Research and Korea Research Foundation.

NS-TuP19 High Selectivity Detection of Trace Explosives using Piezoresistive Microcantilevers, A.R. Krause, University of Tennessee, Oak Ridge National Laboratory, D. Yi, T.G. Thundat, Oak Ridge National Laboratory

Microcantilever arrays offer a miniature, cost effective, and real-time sensor platform for trace explosive detection for combating the terrorist threat. Selectivity in detection in microcantilever arrays is achieved by using receptor layers immobilized on the cantilever surfaces. Despite their high sensitivity and the ability for array-based detection of multiple analytes in real-time, cantilever-based sensor platforms exhibit poor selectivity due to the lack of highly selective receptor layers. Selectivity based on array-based detection and pattern recognition often fails due to the lack of orthogonality in sensor array responses due to the limited number of interactions forming a basis for receptor-analyte interactions. We have developed a receptor-free detection method that can provide high selectivity in explosive vapor detection. In this method adsorbed explosives molecules are allowed to undergo chemical reactions with locally generated ozone to provide an analyte specific cantilever response. The explosive molecules from a vapor generator calibrated with GC-mass spectrometer were first allowed to condense on the cantilever surface. The adsorbed molecules were then exposed to ozone created by a miniature UV lamp for a short period of time and the cantilever responses were recorded as a function of exposure time. We have used a piezoresistive cantilever array in common mode rejection to achieve high selectivity and sensitivity. Recent results for selective and sensitive detection of TNT, RDX, and PETN using this method will be presented.

NS-TuP20 Reactions of Atomic Oxygen on Nanoporous Gold Sponges, A. Wittstock, University Bremen, Germany, J. Biener, M. Biener, Lawrence Livermore National Laboratory, D. Kramer, J. Weissmueller, Forschungszentrum Karlsruhe, Germany, M. Baeumer, V. Zielasek, University Bremen, Germany

In recent years there has been a rising interest in nanoporous gold sponges due to their promising features in low temperature heterogeneous catalysis. Preparation by selectively leaching silver from a gold-silver alloy with acid or a combination of applied voltage and acid leads to a sponge-like morphology with structures in the range of only a few nanometers. Model studies on Au(111) single crystals show a strong interaction of atomic oxygen with the gold surface.¹ The chemisorbed oxygen extracts Au atoms from the surface leading to gold-oxygen complexes on top of it. Inspired by this work we treat nanoporous gold-sponges with atomic oxygen under an ozone-containing ambient atmosphere. We show that in contrast to molecular oxygen the atomic oxygen reacts strongly with the surface leading to a macroscopically detectable shrinking. Measurement of shrinking depending on the concentration of ozone is carried out with a dilatometer. We detect a change of length of nearly 0.5 % of the edge size. The process was accompanied by a black staining which affirms that the oxygen reacts with gold and leads to the formation of gold oxide clusters in the range of a few nanometers on top of the surface. Staining and shrinking can be changed reversibly by reduction with carbon monoxide. In catalytic measurements it is shown that the surface oxygen produced by ozone reacts immediately with carbon monoxide leading to the product of oxidation, the carbon dioxide. These results provide fundamental insight into the allocation of reactive oxygen on catalytically active gold surfaces, the key step of the oxidation reaction on gold catalysts. Furthermore, ozone detection is of great interest in the context of environmental monitoring. Our experiments show that application of gold sponges as chemical gas sensors for determination of ozone is an interesting and promising possibility.

¹ Min, BK; Alemezafar, AR; Biener, MM; Biener, J.; Friend, CM, *Top. Catal.*, 2005, 36, 77.

Wednesday Morning, October 17, 2007

Nanometer-scale Science and Technology

Room: 616 - Session NS+EM-WeM

Nanoscale Devices and Nanowires I

Moderator: S. Pang, University of Michigan, C. Eddy, Naval Research Laboratory

8:00am **NS+EM-WeM1 Self-Organization of SiGe Quantum Dots Grown on Ultrathin Si Nanomembranes**, *F.S. Flack, C.S. Ritz, M.G. Lagally, H.J. Kim, K. Turner*, University of Wisconsin-Madison, *M. Huang, F. Liu*, University of Utah

Self-assembly in nanostructures is a linchpin of the bottom-up design technique essential to the advance of nanoscale fabrication. In particular, the self-assembly demonstrated by quantum dots (QDs) in strain-mismatched systems has potential for applications in lasers, high-density memory, and thermoelectric devices. Self-assembled arrays of QDs have been fabricated by several techniques with varying degrees of success and usability. We demonstrate an entirely new route for investigating the nucleation and ordering of QDs: growth on ultrathin semiconductor nanomembranes, substrates that are so thin, usually on the order of tens of nm, that they allow the strain created by a QD to penetrate the entire structure. Such freestanding thin films are truly compliant and, when thin enough, regions of high strain will bend. Thus, we must address the effects of both strain and bending on the preferential nucleation of SiGe QDs. Tethered Si nanomembranes (cantilevers, ledges, wires, and ribbons) with thicknesses ranging from 20 nm to 60 nm are fabricated from silicon-on-insulator (SOI) substrates. SiGe QDs are then grown epitaxially by ultrahigh vacuum chemical vapor deposition. To ensure appropriate strain, the QDs are grown to have dimensions of the same order as the membrane thickness - roughly 8 nm in height. CVD allows for QD nucleation simultaneously on both sides of the membrane, so that nucleation of a QD on one side influences nucleation on the other. In addition, the nanomembranes are thin enough to be semi-transparent in an SEM, granting us a direct view of the alignment of QDs on the top surface to those on the bottom. We model this growth system with finite element analysis and see that a SiGe island nucleated on the top creates regions of high strain on the bottom along preferential crystallographic directions. These strained regions act as sites for preferential nucleation for QDs on the bottom, which will then seed the next QDs on the top layer and so on to create highly ordered, anticorrelated, arrays on both the top and bottom of the membrane. We discuss the simulations and observations in the limits of QD nucleation due to substrate bending and strain modulation. Research supported by DOE and AFOSR.

8:20am **NS+EM-WeM2 Synthesis of Si_{1-x}Ge_x Nanowire Alloys by Chemical Vapor Deposition**, *S.G. Choi*, Los Alamos National Laboratory, *P. Allea*, Arizona State University, *S.B. Chikkannavar, E. Akhadov, S.T. Picraux*, Los Alamos National Laboratory

There is an increasing interest in semiconductor nanowires (NWs) as a result of their unique physical properties which have resulted in new conceptual devices at the "nano" scale. Among a large number of NWs explored so far, Si and its related NWs have received much attention, in part due to their potential for easy integration into the well-developed Si microelectronics. Recently, attention has been given to SiGe alloy NWs which offer bandgap tuning from 0.7 to 1.1eV and possible applications in various devices. In order to synthesize these SiGe alloy NWs in a controlled manner and to realize nanoscale devices with optimum performance, it is important to understand the nature of alloy NWs growth. Although the two binary endpoints - Si and Ge NWs - have been well investigated, studies of SiGe alloy NWs are still in a formative stage. In this work, we studied effects of growth conditions on the structural characteristics of SiGe alloy NWs. SiGe alloy NWs were grown by chemical vapor deposition (CVD) on Si(111) substrates by the vapor-liquid-solid (VLS) mechanism. Au nanoparticles were used as the catalysts, and SiH₄ and GeH₄ were used as the source gases. Partial pressures were controlled precisely by mass-flow controllers for the flow rate of individual gases and a pressure controller for the total process pressure. NWs were grown at temperatures between 450 and 600°C. Morphology and composition of the grown NWs were investigated by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDXS), respectively. The NWs are observed to become more tapered as growth temperature or Ge composition is increased. Also for the same Au nanodot seeding conditions, the epitaxial Ge-rich alloy NWs grow primarily in the four <111> directions with a substantial fraction of these being vertical [111]-directed NWs, whereas the Si-rich alloy NWs

exhibit a noticeable amount of the smaller diameter <110> oriented NWs as well as the four <111> NW orientations. In this work, we examined possible dependences of composition on: (1) diameter of NWs, (2) growth orientations, (3) growth temperature, (4) ratio of GeH₄ to the total partial pressure (i.e., P[GeH₄]/(P[SiH₄] + P[GeH₄])). In this presentation, we will contrast alloy growth with Si and Ge end point growth, and discuss possible mechanisms for explaining the observed effects of growth parameters on composition, morphology, and structure of SiGe alloy NWs.

8:40am **NS+EM-WeM3 In Situ Kinetic Measurements during the Nucleation and Growth of Si and Ge Nanowires**, *F.M. Ross*, IBM T. J. Watson Research Center **INVITED**

In this presentation we will discuss the growth of epitaxial nanowires in Si and Ge using Au as the catalyst, focusing on the kinetic processes that influence nucleation and wire shape. We grow wires in an environmental TEM, which has capabilities for evaporating Au onto a clean Si substrate and for introducing the precursor gases while the sample remains under observation. In situ video rate imaging allows us to measure nucleation events and growth kinetics and to observe structures during growth. We will start by showing the nucleation of Si nanowires within the catalyst particles, and will discuss the buildup of supersaturation that leads to nucleation. After nucleation, the variation of growth rate with pressure, temperature and droplet size allows us to determine the rate limiting step and evaluate the relevance of curvature-driven effects to wire growth. For Si wires, the simple picture that results is complicated by some interesting phenomena caused by the high mobility of Au on the wire surface. And for Ge wires, we show that the growth-driven supersaturation can stabilize the droplets and allow growth far below the eutectic temperature. We finally discuss the growth of hybrid nanowires composed of group IV and group III-V components, showing how the balance of interface energies determines the overall structure. Thus we find that nanowires provide a unique window into fundamental crystal growth processes, as well as an opportunity to fabricate precisely controlled structures for novel applications.

9:20am **NS+EM-WeM5 Self-Catalyzed Growth of Defect-Free Indium Phosphide Nanowires on Silicon**, *R.L. Woo*, University of California, Los Angeles, *Y. Kobayashi, T. Mallouk*, Penn State University, *R.F. Hicks*, University of California, Los Angeles

Compound semiconductor nanowires exhibit promising properties for high-speed nanoelectronic devices. However, in order to realize their full potential, growth processes must be developed for the precise control of the nanowire shape, density, uniformity, and crystalline quality. In this study, we report on the fabrication of indium phosphide nanowires on silicon (100) and (111) by metalorganic vapor-phase epitaxy. Nanoscale indium droplets were used instead of gold catalyst to nucleate wire deposition. High-resolution transmission electron microscopy with selected area electron diffraction have revealed that the InP nanowires are free of crystal defects and grow along either the <110> or the <113> axis. This may be contrasted to gold catalyzed growth, where the preferential orientation is <111>, and there is a relatively high density of stacking faults. Through careful control of the substrate preparation and the MOVPE process conditions, it has been possible to grow vertical InP nanowires of uniform diameter and lengths over 1.0 micron. At the meeting, we will present data on the novel electrical and optical properties of the indium phosphide nanowires.

9:40am **NS+EM-WeM6 Plasma-stimulated Control of Silicon Nanowire Nucleation, Orientation and Growth Kinetics**, *P. Aella, W.T. Petuskey*, Arizona State University, *S.T. Picraux*, Los Alamos National Laboratory

Plasma-enhanced chemical vapor deposition is shown to significantly alter the nucleation rate and activation energy for vapor-liquid-solid (VLS) growth of silicon nanowires compared to thermal growth, providing new control over nanowire morphologies and new insight into the rate-limiting mechanisms of VLS growth. Initially, catalytic gold films (0.5 - 2 nm thick) were thermally evaporated onto hydrogen terminated Si (100) substrates at room temperature in a UHV deposition system. Subsequently, Si nanowires were grown in a cold wall reactor at 0.5 Torr in atmospheres of 10% SiH₄ in H₂ between 350 to 510°C and RF plasma powers of 2.5 to 10 W. SEM images show that thermally grown nanowires on Si (100) substrates nucleate and grow predominantly in <111> directions. In contrast, plasma stimulation significantly enhances the nucleation rate of smaller diameter <110> Si nanowires and also reduces coarsening of Au dots. A two step growth process is demonstrated whereby initial plasma excitation nucleates <110> nanowires followed by thermal growth to preferentially form a high density of small diameter <110> nanowires on Si (100) surfaces, greatly limiting the large diameter <111> nanowire formation found under thermal growth conditions with identical Au seeding. This demonstrates the overall

effect of the plasma on shortening nucleation times, favoring thinner wires, and thereby dominating the rest of the growth process. A comparison of the growth rate vs. temperature for both $\langle 111 \rangle$ and $\langle 110 \rangle$ nanowires shows a large reduction in the activation energy (from 0.74 to 0.26 eV) due to the plasma. The overall growth rate is also greatly enhanced at low temperatures by plasma excitation, with growth rates at 350°C an order of magnitude greater than for thermal growth. Under our low temperature thermal conditions the predominant source gas is silane, while in the case of plasma stimulation SiH₃ radicals are also present. Our results unequivocally demonstrate that the rate limiting step for Si nanowire growth under these conditions is due to the kinetics of silicon incorporation at the vapor-liquid interface and not at the liquid-solid interface as has also been previously proposed in some cases. Based on our measured incorporation coefficients and activation energies under thermal and plasma-enhanced growth we suggest the first model for the rate-limiting kinetic steps for Si nanowire growth by the VLS mechanism.

10:40am **NS+EM-WeM9 Nanowires in Nanoelectronics: Problems and Promise**, *D.K. Ferry*, Arizona State University **INVITED**

Progress in microelectronics has generally followed the well known scaling rules known as Moore's Law. By the end of this decade, we will approach some well recognized limits in traditional semiconductor devices. Nanowires have been put forward as a new technology with new promise to extend nanoelectronics. For this to be the case, the nanowires must fit into the scaling rules and must offer important new options, primarily in circuit cleverness. In this talk, I will review the scaling rules, and where they have led us, then discuss how the constraints of these rules, particularly Si area cost, dictate how new technologies can be used. These suggest that the impact of nanowires will likely be in providing new options for architectural revolutions, as opposed to merely clever new devices.

11:20am **NS+EM-WeM11 Electrical and Mechanical Characterization of Nanowire Properties using In-Situ SEM**, *D.F. Ogletree*, Lawrence Berkeley National Laboratory

Nanowires have unique electrical and mechanical properties with a wide range of potential applications in electronics, opto-electronics and nanomechanics. Local measurements of the electrical and mechanical properties of individual nanowires in controlled environments are required to develop these applications and to optimize nanowire growth conditions. A flexible system for nanowire characterization based on a high-resolution environmental scanning electron microscope (SEM) has been developed combining sample heating in controlled gas environments with nano-positioning of local probes. This system has been used to investigate the evolution of size-dependent nanowire mechanical properties between room temperature and the melting point of the nanowires.

11:40am **NS+EM-WeM12 Four Independent STM Navigated by High Resolution UHV SEM: Transport Measurements on In-Situ Grown Titanium Silicide Nanowires on Si(111)**, *J. Koebler, M. Maier*, Omicron NanoTechnology, Germany, *B. Grandier*, IEMN, Lille, France

A major challenge in Nanotechnology is the incorporation of single nano-devices into larger integrated circuits. Traditional instrumentation suffers from one fundamental issue: How to cover the dimensional range of a fully integrated circuit down to the nanometer range (or even atomic scale) of single devices and have an adequate integrated navigation system. To meet these requirements, we have established and being advancing a new approach to integrating state-of-the-art SPM technology via high resolution electron microscopy and spectroscopy: (1) Bridging dimensions and rapid navigation; (2) Combining different surface analysis methods at the very same sample area to gain complementary information; (3) Integrated position-readout of sample and probe positioning; (4) Pushing each single technology to its inherent limits. The system facilitates four independent Scanning Tunneling Microscopes and the UHV version of the Zeiss Gemini SEM column with ultimate resolution below 4nm for probe navigation and rapid localisation of sample features or devices. STM imaging is used to pro-actively position and contact the probe(s) on nano-devices. Using STM probe approach technology, a controlled electrical contact is ensured to finally perform a four-point measurement on the nano-scale. We report on electrical measurements on self-assembled titanium silicide nanowires (NWs) in-situ grown on a Si(111) surface. Transport measurements have been taken in 2-point and 4-point configuration. The transport measurements indicate metallic behavior for the silicide nanowires and that the NWs are electronically decoupled from the Si surface and reveal a Schottky barrier between the NWs and the Si surface.

12:00pm **NS+EM-WeM13 Anisotropic Plasmon and Electronic Structure of Ag Nanowires on Cu(110)**, *P.T. Sprunger, I. Senevirathne, W. Zhao, B.M. Watson, O. Kizilkaya, A.K. Sekharan, R.L. Kurtz*, Louisiana State University

Epitaxial Ag nanowires have been found to self-assemble on Cu(110) for Ag coverages exceeding 1.2 ML. The electronic and plasmon loss structure of the nanowires have been characterized by ARPES and EELS. STM images reveal that Ag nanowires grown on Cu(110) are approximately 2 nm high and ~12 nm wide. The nanowires grow oriented with the long axis parallel to the $\langle 110 \rangle$ substrate direction and they have aspect ratios up to 20:1. The ARPES results show that the valence bands within the Ag nanowire are strongly anisotropic with clear band dispersion in the along-wire direction, but no dispersion in the across-wire direction. This strongly suggests that the valence electrons of Ag behave as quasi-one-D conductors along the wire yet confined with atomic-like states perpendicular. Fermi surface crossings have been observed, confirming that metallic behavior is realized along the wire axis. In accord with the ARPES measurements, EELS reveals that the plasmon excitation is red-shifted at the zone-center and is nearly dispersionless perpendicular to the nanowire direction. These results will be discussed in light of recent band-structure calculations of Ag nanowires and models for plasmon behavior in quasi-1D structures. We would like to acknowledge the support of the LSU CAMD synchrotron light source and the support of and LA-R&D and NSF through DMR-0504654.

Plasma Science and Technology

Room: 606 - Session PS1+NS-WeM

Plasmas in Nanotechnology

Moderator: S. Kodambaka, University of California, Los Angeles

8:00am **PS1+NS-WeM1 Spectroscopic, Spatial, and Temporal Investigation of Fe Nanoparticle Synthesis by Through Thin Film Ablation**, *A.R. Waite*, University of Dayton, Air Force Research Laboratory and UTC, Inc., *P.T. Murray*, University of Dayton, *J.G. Jones*, Air Force Research Laboratory, *E. Shin*, University of Dayton, *A.A. Voevodin*, Air Force Research Laboratory

Nanoparticles of Fe have been formed by the process of Through Thin Film Ablation (TTFA). In the TTFA process, the target consists of a thin film (10-20 nm thick) of material that has been applied to an optically transparent support. The thin film target is ablated in vacuum through the transparent support, and this produces a directional plume of nanoparticles. Optical Emission Spectroscopy (OES), Time-of-Flight (TOF) analysis, and high-speed Intensified Charge Coupled Device (ICCD) imaging are utilized to study the plume dynamics and characteristics. OES measurements indicate the ejected nanoparticles to have a temperature of 2232 K, suggesting they are liquid. TOF analysis indicated that there are two main size constituents in the ablation plume, higher speed atomic species and slower nanoparticles. ICCD imaging is used to further study the plume dynamics in both time and space. Ablation in vacuum and in the presence of a background gas will be discussed.

8:20am **PS1+NS-WeM2 Size Manipulation and Control of Nanoparticles Produced from Atmospheric-Pressure Microplasmas**, *N.A. Brunelli, K.P. Giapis*, California Institute of Technology

Size manipulation and control of nanoparticles produced from atmospheric-pressure microplasmas Atmospheric-pressure microdischarges have been shown to produce silicon nanoparticles between 1-2 nm in diameter, which exhibit intense photoluminescence emission at 420 nm with quantum efficiency of 30%.¹ For imaging applications, it is desirable to have an emission at longer wavelengths which requires larger diameter nanoparticles. However, it has been exceedingly difficult to manipulate the nanoparticle size in a single microdischarge, where perturbations to the growth conditions seem to only influence the number of particles produced while the size remains invariant. We demonstrate here that the combination of a microdischarge with a CVD reactor can overcome this problem by achieving overgrowth of the seed particles produced in the microdischarge. For example, silicon nanoparticles can be enlarged from 2.5 nm to 3.5, 4.5 and 5 nm by mixing an additional 150, 300 and 600 ppm of sila4ne in argon, respectively. In fact, the CVD overgrowth allows not only tuning of the particle size but also permits selection of an alternate overgrowth layer, creating core-shell structures. Examples of Ge and Fe cores overgrown with Si will be shown. We quantify this claim by using a new ultrafine radial differential mobility analyzer immediately after the furnace to monitor in

real-time the particle size. We characterize the nanoparticles by AFM, photoluminescence (PL) spectroscopy and transmission electron microscopy. As oxidation has been shown to affect the PL emission,² we have encapsulated the particles in thin films to ensure observed light emission is from radiative recombination. Beyond enlarging the seed particle diameter, we demonstrate the synthesis of core-shell structures consisting of an inexpensive metallic core and a thin overlayer of catalytically active material as the shell. Electrochemical measurements demonstrate the catalytic activity and performance of Fe-Pt and Co-Pt core-shell nanoparticles for fuel cell type applications.

¹ Sankaran, R. M., D. Holunga, et al. (2005). "Synthesis of blue luminescent Si nanoparticles using atmospheric-pressure microdischarges." *Nano Letters* 5(3): 537-541.

² Biteen, J. S., N. S. Lewis, et al. (2004). "Size-dependent oxygen-related electronic states in silicon nanocrystals." *Applied Physics Letters* 84(26): 5389-5391.

8:40am PS1+NS-WeM3 Ionic Plasmas Yielding Novel-Structured and -Functional Nanocarbons, R. Hatakeyama, T. Kaneko, W. Oohara, Y.F. Li, Tohoku University, Japan **INVITED**

Nanocarbons of carbon allotropes have attracted a great deal of attention due to their high potential for novel properties and a variety of applications. Since fullerenes and carbon nanotubes among them are furnished with hollow inner nanospaces, it is a fascinating challenge to inject various kinds of atoms and molecules into the nanospaces based on plasma nanotechnology, which could lead to innovative functionalization of the pristine ones. For that purpose original approaches using nanoscopic plasma processing mainly in ionic plasmas have been performed in order to develop fullerene-, SWNT(single-walled carbon nanotube)- and DWNT(double-walled carbon nanotube)-based materials with new functions corresponding to electronic and biological applications. Firstly, the encapsulation of charge-exploited alkali atoms inside the fullerene is realized (Li@C₆₀ etc.) using alkali-fullerene plasmas as ionic plasmas, which consist of positive alkali ions and negative C₆₀ ions. Then the atomic nitrogen as a spin-exploited atom is also encapsulated inside C₆₀ (N@C₆₀). In relation to the inner nanospace modification of the carbon nanotubes, another ionic plasmas, i.e., alkali-halogen plasma and pair-ion plasma are generated, which consist of positive alkali ions and negative halogen ions, and positive-C₆₀ and negative-C₆₀ ions with an equal mass, respectively. Furthermore, an electrolyte solution plasma including DNA negative ions is prepared. The substrate bias method is utilized mainly in these plasmas, where positive and negative ions with their energies and fluxes controlled are irradiated to an immersed substrate coated with the pristine carbon nanotubes. In addition, a thermal and plasma combined process is also devised for the treatment of both charge- and spin-exploited atoms. Consequently, we have innovatively created alkali-metals encapsulated SWNTs and DWNTs (Cs@SWNTs, Cs@DWNTs), halogen-elements encapsulated SWNTs (I@SWNTs), ferromagnetic-atoms encapsulated SWNTs (Fe@SWNTs), fullerene molecules encapsulated SWNTs and DWNTs (C₆₀@SWNTs, C₆₀@DWNTs, C₇₀@DWNTs, C₈₄@DWNTs), and DNA molecules encapsulated SWNTs (DNA@SWNTs). Finally, their electronic and magnetic properties are intensively investigated. As a result, we have for the first time succeeded in realizing the continuous transition of air stable electronic transport from p-type to n-type semiconducting property by adjusting an amount of dosed atoms and molecules inside SWNTs and DWNTs (Cs@SWNTs, Cs@DWNTs, I@SWNTs, C₆₀@SWNTs, C₆₀@DWNTs), and in forming nano structures of magnetic semiconductor (Fe@SWNTs), nano pn junctions with rectifying characteristic [(Cs/I)@SWNTs]), and nano structures with distinct negative differential resistance of high peak-to-valley ratio (C₆₀@DWNTs, C₇₀@DWNTs, C₈₄@DWNTs). In the case of DNA@SWNTs an experimental system utilizing an interfacial region between the gas and liquid phases has been constructed in order to enhance the DNA encapsulation rate. Here an ionic liquid consisting of only positive and negative molecules is introduced into the liquid phase, which can be regarded as an ionic plasma, i.e., fully ionized electrolyte plasma.

9:20am PS1+NS-WeM5 Continuous-Flow Microplasma Synthesis of Metal Nanoparticles for Catalytic Growth of Carbon Nanotubes, W.-H. Chiang, R.M. Sankaran, Case Western Reserve University

Carbon nanotubes (CNTs) have been synthesized in a continuous-flow, gas-phase catalytic process. The synthesis technique consists of two steps: 1) production of well-defined metal nanoparticles in an atmospheric-pressure microplasma and 2) catalytic growth of carbon nanotubes in a tube furnace reactor. In the first step, nanoparticles are generated using a direct-current (dc) hollow cathode microplasma made-up of a stainless steel cathode with a pin-hole (d~180 μm) and an arbitrarily-shaped tube anode. Gaseous precursors are introduced into the microplasma at atmospheric-pressure and decomposed non-thermally by electron impact to generate reactive radical species. Under appropriate precursor saturation conditions, the radicals polymerize to nucleate particles homogeneously in the gas phase. Particle growth is limited to the small reactor volume (less than 1 nL) created by the

microplasma geometry. As a result of the large concentration gradients and short residence time, the technique is capable of producing very small (1-3 nm diameter) nanoparticles with narrow size distributions. The particle-laden flow is then continuously fed to a second reactor to grow carbon nanotubes in free flight with addition of acetylene and hydrogen and heating at fixed temperatures between 500 and 1000 °C. Nanotube size and distribution are determined on line using a gas-phase electrophoretic mobility macromolecular analyzer (GEMMA). In situ aerosol classification allows experimental conditions to be directly related to growth parameters. We have recently investigated the catalytic properties of iron and nickel nanoparticles toward growth of carbon nanotubes. Process parameters were optimized to prevent amorphous carbon formation and obtain high-quality CNTs. Ex-situ techniques such as Raman spectroscopy and transmission electron microscope (TEM) were used to characterize the structure of the carbon nanotubes. The combination of continuous-flow synthesis using microplasmas and the GEMMA system opens new possibilities for nanocatalyst synthesis and provides a methodology for enhancing our fundamental understanding of catalytic behavior.

9:40am PS1+NS-WeM6 Low Temperature Growth of Single-Walled Carbon Nanotubes by Oxygen-Assisted Inductively Coupled Plasma Chemical Vapor Deposition, C.-H. Hsiao, C.-H. Weng, Z.-Y. Juang, K.-C. Leou, C.-H. Tsai, National Tsing Hua University, Taiwan

Single-walled carbon nanotubes (SWNTs) have attracted a great deal of attention recently due to their unique physical properties and a wide range of potential applications, in particular, field effect transistors (FET) and nano-phonic devices. It is highly desirable to develop a method compatible with standard semiconductor microfabrication processes for direct synthesis of high quality SWNTs. In this work, we demonstrated a low temperature growth process of SWNTs on silicon substrates by inductively coupled plasma chemical vapor deposition (ICP-CVD) method with CH₄/H₂ gas mixture as base processing gases. A unique Ni/Al/SiO₂ nanocatalysts/support system has also been developed to allow the growth of high quality SWNTs. To further improve the crystalline structure of SWNTs, oxygen was added to the processing gas mixture to remove amorphous carbons during the growth process. Both the scanning electron microscopy and micro-Raman spectra were employed for characterizations of the SWNTs. Parametric experiments were conducted to optimize the O₂ fraction in the gas mixture. The SWNTs were successfully synthesized at a temperature as low as 600°C.

10:40am PS1+NS-WeM9 Fabrication of Defect-Free and Diameter-Controlled Silicon Nanodisks for Future Quantum Devices by using Neutral Beam Etching, T. Hashimoto, T. Kubota, C.H. Huang, Tohoku Univ., Japan, M. Takeguchi, National Inst. for Mtls Sci., Japan, K. Nishioka, Japan Adv. Inst. of Sci. and Tech., Y. Uraoka, T. Fuyuki, Nara Inst. of Sci. and Tech., Japan, I. Yamashita, Matsushita Electric Industrial Co., Ltd, Japan, S. Samukawa, Tohoku Univ., Japan

Nanometer-scale structures, such as quantum dots, are widely studied because of their possible application in the development of quantum-effect devices, such as quantum-dot lasers and single-electron transistors. To develop practical and robust quantum-effect devices, manufacturers must be able to fabricate selectively arranged, defect-free, sub-10-nm-scale structures of uniform size on substrates. To realize a nanometer-scale structure, we used a ferritin iron core (7 nm in diameter) as a uniform and high-density template and our developed neutral beam (NB) etching process for damage-free etching. We fabricated a "nanodisk," a nanometer-thick disk-shaped silicon structure by patterning <3.5-nm poly-Si layer / 1.4-nm SiO₂ layer / Si substrate> by using NB etching with a ferritin iron-core mask. To precisely control the diameter of the nanodisk, we must selectively remove the surface native silicon oxide layer before Cl neutral beam etching because the Cl neutral beam has extremely high selectivity to SiO₂ film. SEM and TEM observations revealed that the nanodisk was successfully fabricated and that the buried SiO₂ layer was not damaged during etching. When the nanodisk was only etched by using the Cl neutral beam with the iron core mask, the diameter of the nanodisk was about 13 nm. To shrink the diameter of nanodisk, we developed a dry process to remove native oxide by using NF₃ gas and hydrogen radicals ("NF₃ treatment"). By using the NF₃ treatment to remove the native oxide, we decreased the nanodisk diameter to 10 nm. We found that removing the surface native oxide is very important for controlling the diameter of nanodisk. We then measured the I-V characteristics by using atomic force microscopy (AFM) with a conducting probe. Coulomb staircases were observed from the I-V measurements of the nanodisks at 25 K and at room temperature. These results indicate that the nanodisks we fabricated have a precise quantum-effect structure, and they attained single-electron properties. This research has great potential in the development of practical and robust fabrication processes for future quantum-effect devices. A part of this work was supported by the Nanotechnology Support Project and the

11:00am **PS1+NS-WeM10 Parallel Writing of Complex Nanofeatures using Nanopantography**, *L. Xu, A. Nasrullah, M. Jain, Z. Chen, V.M. Donnelly, D.J. Economou, P. Ruchhoeft*, University of Houston

Nanopantography is a technique for massively parallel writing of nano-sized features. A broad-area, collimated, monoenergetic ion beam is directed to an array of sub-micron-diameter electrostatic lenses fabricated on a conductive substrate (e.g., doped Si wafer). By applying appropriate voltages to the lens electrodes, each "beamlet" entering the lens is focused to a spot on the wafer surface. The spot size can be up to 100X smaller than the diameter of the lens. With the choice of an Ar⁺ beam in the presence of Cl₂ gas, 10 nm-dia holes were etched in Si; while with the choice of a Ni⁺ beam, ~10 nm nickel dots were deposited on Si. Nanopantography has the capability to write arbitrary nano-sized features since the focal points can be displaced by tilting the substrate. A second-generation nanopantographic system was built to allow writing of complex nano-features. The improved system design had an ion flux ~ 15X higher than the first generation reactor. A LabView-controlled motorized stage could be tilted in both the X- and Y-axes with an accuracy of 0.011° degrees. This corresponds to translation of the focal point by 1.5 nm on the substrate. The energy distribution of the extracted ion beam was measured to have a spread of 2.2 eV, for a 100 eV beam. By continuously tilting the substrate in one direction, nanotrenches with ~15 nm (FWHM) width and ~40 nm depth were etched in a Si wafer. More complex patterns, such as letters of the alphabet, were also etched into Si in a massively parallel fashion by two-dimensional tilting of the substrate.

11:20am **PS1+NS-WeM11 High Aspect Ratio Deep Trench Chamber and Process Development for Silicon Etch in DRAM Applications below 50 nm**, *S. Wege, S. Barth*, Qimonda Dresden, Germany, *A. Kersch*, Qimonda Munich, Germany, *M. Reinicke*, Dresden University of Technology, Germany, *G. Wenig*, Qimonda Munich, Germany, *M. Rudolph, J. Sobe, A. Steinbach*, Qimonda Dresden, Germany

For Qimonda's DRAM Technology the deep trench etched into silicon is the base for the capacitor concept. The shrink of lateral dimensions at approximately constant capacity specifications leads to increased deep trench aspect ratio requirements. Therefore high selectivity to the etch mask and excellent uniformity is needed, especially for technologies below 50nm. In this paper we describe the development of advanced DT plasma etch chamber and process to fulfill these requirements. New process regimes, e.g., RF pulsing and high temperature showed promising results. Simulations were combined with in-situ plasma measurement techniques, e.g., QMS with ion energy analysis, high resolution OES, insitu IR absorption spectroscopy, and technological experiments, to characterize hardware features and process conditions. To achieve high Si etch rate and selectivity, plasma density and electron energy distribution in the plasma bulk, and ion energy distribution on the wafer surface can be optimized through multi frequency cathode excitation. The selectivity is further enhanced by using advanced hard mask materials and combining with RF pulsing. The optimization of the side wall passivation stoichiometry is a key for high aspect ratio silicon etch. In addition, the etch process chamber includes new features for process control, in-situ wafer surface temperature and trench depth measurement. The equipment and process development was accomplished through close cooperation between Qimonda and the tool supplier.

11:40am **PS1+NS-WeM12 Etch Selectivity and Surface Roughening of Polystyrene and Poly(methyl methacrylate) in Plasma Etching of Block Copolymers**, *Y.-H. Ting, S.-M. Park, C.-C. Liu, X. Liu, F.J. Himpsel, P.F. Nealey, A.E. Wendt*, University of Wisconsin-Madison

Polystyrene -block-poly(methyl methacrylate), (PS-b-PMMA) diblock copolymers are a promising lithography alternative for nanometer scale features. The two components segregate into nanoscale domains when the polymer solution is spun on to form a thin film and annealed above the glass transition temperatures of both components. Preferential removal of PMMA domains through plasma etching to leave behind a PS mask for subsequent etching of underlying layers is the focus of this work. The quality of the PS mask is characterized by the thickness and lateral dimension of the PS structures after removal of the PMMA, as well as the smoothness of its surfaces. We have characterized the effects of different plasma chemistries including O₂, Ar/O₂, Ar, CF₄ and CHF₃/O₂ on etch selectivity and surface/sidewall roughness for PS and PMMA. The surface roughness of PS and PMMA after Ar/O₂ plasma etching (which gave the best overall etch performance) was further examined as a function of ion bombardment energy to understand the roughening mechanisms, as the two polymers show different responses to changing plasma conditions. Specifically, the surface roughness of PMMA increases with increasing ion bombardment energy, while that of PS decreases. An oxidation-induced

micro-masking process on PS surfaces upon plasma exposure has been proposed to explain the different in roughening of PS and PMMA. Surface chemical analysis using NEXAFS shows that chemical change occurs on the PS surface during exposure to oxygen containing plasmas. Evidence of inhomogeneities in the composition of the PS film suggests that surface inhomogeneities in chemical composition may persist and change chemically upon plasma exposure. Variations in etch resistance associated with the inhomogeneities may in turn be responsible for observed surface roughness. Roughening caused by this "micro-masking" effect is reduced under conditions that minimize selectivity, such as high ion bombardment energies. We acknowledge support from the UW NSF MRSEC for Nanostructured Materials.

12:00pm **PS1+NS-WeM13 Comparison between NF₃ and CF₄ Chemistries for the Selective Etching of SiGe Sacrificial Layers in a 300mm Chemical Dry Etching Reactor**, *S. Borel*, CEA-Leti MINATEC, France, *C. Arvet*, STMicroelectronics, *D. Watanabe*, Shibaura Mechatronics Corporation, Japan

The selective removal of a SiGe sacrificial layer is a key step in the realization of several architectures that are based on the SON technology. Such a process has been developed and studied in 200mm, showing very good results in terms of selectivity by using CF₄ as an etching gas. This competence has been transferred in 300mm by using a new generation chemical dry etching tool that offers an additional and alternative source of fluorine which consists in NF₃. A process based on this environment-friendly molecule has been developed and compared with the CF₄ reference in terms of SiGe:Si selectivity while keeping a comparable etch rate. In that aim, a strong dilution (1:10) was necessary because of the high dissociation level of NF₃ that results in high etch rates. Morphological analyses clearly show that the selectivity obtained by using NF₃ is prohibitive for the realization of advanced devices. Indeed, the selectivity value is around 3, which means that the thinning of the Si cap is only 3 times lower than the SiGe tunnel depth whereas it needs to be higher than 30 (it reaches 70 by using CF₄). Surface analyses by XPS reveal that a Si substrate exposed to the CF₄ process presents some carbon, which suggests a passivation mechanism that may be involved in the selectivity. With the carbon-free NF₃ molecule, this phenomenon does not occur, hence the lack of selectivity we observe. As a conclusion, even if it is possible to etch SiGe faster than Si by using NF₃, the reference process made of CF₄ remains the best solution for the tunnel etching of advanced devices where a controlled etch rate is necessary and a high SiGe:Si selectivity is mandatory.

Wednesday Afternoon, October 17, 2007

Applied Surface Science

Room: 610 - Session AS+BI+NS-WeA

Fabrication and Characterization of Functional Soft Material Surfaces

Moderator: R.T. Haasch, University of Illinois at Urbana Champaign

1:40pm **AS+BI+NS-WeA1 UPS Work Function Measurements on Polymers Combined with C60 Depth Profiling.** *S. Raman, J. Moulder, J.S. Hammond*, Physical Electronics, *N. Sanada, M. Suzuki*, ULVAC-PHI, Inc.

The performance of ultra thin organic films in organic LED's (OLED) is dependent on the work functions of the electrodes and polymers forming the OLED junctions. Historically, the work functions have frequently been derived from the secondary electron emission edges measured with UPS. The recent applications of C60 ion beams for the sputter removal of a surface layer of many organic materials, leaving the remaining surface with minimal chemical damage, have offered a new tool for studying surface modified polymers. By combining these two techniques, the work function and composition as a function of depth of polymers targeted for OLED applications can be characterized by XPS and UPS. The surface characterization of OLED component polymers exposed to deleterious environments will also be discussed. The possible chemical surface damage induced by the C60 ion beams will be examined by both XPS and UPS spectra and secondary electron emission edge spectra.

2:00pm **AS+BI+NS-WeA2 Patterning and Bonding of Poly(dimethylsiloxane) A Simple New Method for Creating Optically Transparent Biocompatible Surfaces and Robust Microfluidic Devices.** *P.R. Norton, N. Patrio, J. McLachlan, J. Chan, S. Faria, S. Tadayyon*, University of Western Ontario, Canada

Our group has developed a simple protocol to prepare inexpensive, single-component substrates capable of confining cell attachment and growth. In the presence of an argon plasma, thin metal films are deposited onto poly(dimethylsiloxane) (PDMS). Removal of the metal layer exposes regions of the polymer surface that are enriched in oxygen and promote the adhesion of fibroblast, epithelial and myoblast cells. This method produces bioactive arrays of controlled size (down to scales in the order of μm), shape, pitch and symmetry on which cells can be grown to confluency. The treated material is storable and can be activated just before use; this eliminates stability problems inherent in a number of previously reported PDMS surface treatments, most notably oxygen plasma modification. The patterned arrays offer highly adaptable means to probe cell-cell interactions, cell motility and cell signaling in response to varied spatial or geometric organization and they are being incorporated into microfluidic channels for combined optical and proximal probe studies of live cells. Serendipitously, this surface treatment alters the mechanical properties of PDMS, rendering the modified material sensitive to tensile stresses imposed by cells. Cellular traction forces generate nanoscale ripples in the elastic substrata which extend outward from the cell bodies and which can be imaged by dark-field microscopy and AFM. Detailed analyses of these ripples can potentially provide a direct measure of cellular traction forces and mechanical signaling. In related experiments, we have also developed a novel means of bonding PDMS to a host of materials relevant to microfluidic device fabrication, including glass, Si, SiO₂ and polystyrene. To quantify the adhesive strength, closed PDMS-glass and PDMS-PDMS microfluidic devices were fabricated and subjected to tensile and leakage testing. The data indicate a significant improvement in performance over previously reported bonding technologies, resulting in the production of more robust, longer-lasting microfluidic devices and the concomitant possibility of using higher pressures and flow-rates.

2:20pm **AS+BI+NS-WeA3 Interfacial Structure of Polymer Brush and Gel Investigated by Sum Frequency Generation Spectroscopy.** *K. Uosaki, H. Noguchi, S. Nihonyanagi, H. Minowa, R. Yamamoto*, Hokkaido University, Japan

Polymer brush and gel plays very important roles in biological systems. Information on the interfacial structure is essential to understand the function of these materials. Here we employed sum frequency generation (SFG) spectroscopy, which is known to possess high surface specificity, to investigate the molecular orientation/conformation of polymer brush under

various environment and water structure at PVA gel/solid interface. SFG spectra of alkylated poly (vinyl pyridine) in contact with dry nitrogen, water vapor, and liquid water were obtained. The peaks due to CH vibration of CH₃ dominated in nitrogen, showing that the side chains are highly ordered. When the polymer layer is in contact with water vapor, in addition to the two peaks due to CH₃ group, two peaks of CH₂ group were observed, indicating that many gauche defects existed. The SFG spectrum of the polymer brush in contact with liquid water showed no peaks in CH stretching region except for small shoulder due to the ring CH modes, indicating the alkyl side chain was completely disordered. SFG spectra of the polymer brush in OH stretching region were also obtained. A broad band assigned to the OH stretching was observed in water vapor. Two bands corresponding to the OH stretching of the interfacial water molecules at 3200 cm⁻¹ due to "ice-like water" and at 3400 cm⁻¹ due to "liquid-like water" dominated in liquid water. Poly vinyl alcohol (PVA) gel is considered to be one of the possible candidates for an artificial articular cartilage in artificial joints because of very low friction between PVA gel and solid. SFG measurement proved that while the fractions of the "ice-like" and "liquid-like" water were almost equal at water/quartz interface, the fraction of the "liquid-like" water became much higher when the PVA gel was pressed against the quartz surface, showing that the weakly hydrogen bonded water dominate at PVA gel/quartz interface where friction is very low. SFG measurement in Ar showed only weakly hydrogen bonded water was present at the PVA gel/quartz interface. The effect of PVA gel contact was less obvious at the octadecyltrichlorosilane (OTS) coated quartz, where the friction is much higher. These results suggest the important role of weakly hydrogen bonded water for very small friction at PVA gel/solid interface. In conclusion, SFG is demonstrated to be a very useful technique to characterize molecular structure at solid/liquid interfaces including biological interfaces.

2:40pm **AS+BI+NS-WeA4 Multiphoton Patterning of Planar and Topographically Complex Surfaces for Control of Photon, Electron, and Chemical Transport.** *P.V. Braun*, University of Illinois at Urbana-Champaign **INVITED**

Multiphoton patterning enables fabrication of complex structures with minimum feature sizes on the order of the volume of the focal point. Using a pulsed laser source coupled to a laser scanning confocal microscope, we have concurrently written and imaged various complex structures and patterns. Recently, along with formation of complex structures, we have initiated efforts to locally modify the surface chemistry of both planar and topographically complex (three-dimensional) surfaces to create pathways for photon, electron, and chemical transport. A series of organic chemistries have been developed to enable this patterning, which revolve around the grafting of photoswitchable molecules or polymer brushes to the various surfaces. Once the local chemistry of the surface has been modulated, this chemistry can be amplified through quantum dot attachment, electroless plating, or surface initiated polymerization to create two and three-dimensional patterns for control of photon, electron, and chemical transport. Colloidal crystals and porous glasses are used as model three-dimensional substrates; standard materials are used for two-dimensional structures.

4:00pm **AS+BI+NS-WeA8 Chemical Modification of Self-Assembled Monolayer Surfaces using Soft-Landing of Mass-Selected Ions.** *P. Wang, O. Hadjar, J. Laskin*, Pacific Northwest National Laboratory

Stable immobilization of peptides on solid supports plays an important role in biochemistry. Existing techniques for linking peptides to surfaces are based on a variety of solution-phase synthetic strategies and require relatively large quantities of purified material. Here, we report a novel approach for preparation of peptide arrays on self-assembled monolayer (SAM) surfaces using soft-landing (SL) of mass-selected ions. This approach takes advantage of the exceptional selectivity in preparation of projectile ions by mass spectrometry. We demonstrate efficient reactive landing (RL) of several model peptides onto the SAM of N-hydroxysuccinimidyl ester terminated alkylthiol on gold (NHS-SAM). This method introduces unprecedented selectivity and specificity into the surface preparation step by eliminating the effect of solvent and sample impurities on the quality of the film. Peptide ions produced by electrospray ionization are mass-selected and deposited onto SAM surfaces using a novel ion deposition chamber designed and constructed in our laboratory. NHS-SAM, which readily reacts with accessible primary amino groups in proteins or peptides by forming amide bonds, is used as a target for soft-landing experiments. Freshly prepared SAMs and modified surfaces are characterized ex situ using time-of-flight secondary ion mass spectrometry (ToF-SIMS) and infrared reflection absorption spectroscopy (IRRAS). Mass-selected ions of model peptides including cyclo(-RGDfK-), GRGDSPK and RGDGG were soft-landed onto the NHS-SAM surface.

ToF-SIMS and IRRAS characterization suggested efficient covalent binding between the two lysine-containing peptides and the NHS-SAM by the formation of an amide bond through the lysine side chain. Systematic studies were carried out to understand the factors that affect the efficiency of reactive landing. We found that the reaction takes place upon collision and is promoted by the kinetic energy of the ion. The reaction yield is independent of the charge state of the projectile ion suggesting efficient neutralization of peptide ions upon collision. Chemical reactivity and physical properties of the SAM surface are also important factors that affect the outcome of RL. RL of mass- and energy-selected peptide ions on surfaces provides a highly specific approach for covalent immobilization of biological molecules onto SAM surfaces.

4:20pm **AS+BI+NS-WeA9 TOF-SIMS Analysis of Polypropylene Films Modified by Isotopically Labeled Methane Flames.** *S.J. Pachuta, M.A. Strobel*, 3M Company

Flame treatment is a common industrial process for modifying polymer surfaces. Surfaces exposed to flames are known to oxidize, but studies of the oxidation mechanism have been largely confined to correlating simple surface properties with models of the flame composition due to the lack of direct experimental data on the flame-surface interaction. In this work, polypropylene film surfaces were oxidized by exposure to a flame fueled by isotopically-labeled methane (CD₄). The isotopic sensitivity of time-of-flight secondary ion mass spectrometry (TOF-SIMS) was then used to gain new insights into the mechanism of flame treatment. TOF-SIMS analysis indicates that much of the oxidation of polypropylene occurring in fuel-lean flames is not accompanied by deuteration, while for polypropylene treated in fuel-rich flames, deuteration is extensive, and some of the affixed oxygen is deuterated. These observations imply that O₂ is the primary source of affixed surface oxygen in fuel-lean flame treatments, but that OH may be a significant source of affixed oxygen in fuel-rich flame treatments. Application of principal component analysis (PCA) and multivariate curve resolution (MCR) to the TOF-SIMS data was found to provide information beyond that which could be obtained by traditional peak-ratio methodology.

4:40pm **AS+BI+NS-WeA10 The Analysis of Oxidation Profiles in Elastomers Using ToF-SIMS.** *J.A. Ohlhausen, M.C. Celina, M.R. Keenan*, Sandia National Laboratories

As elastomeric materials age, their mechanical properties can change such that they do not perform their desired function. It is important to understand the aging behaviour of such elastomers, so that predictive aging models can be developed. In that light, much work has been done to understand oxygen diffusion limited aging processes under accelerated aging conditions for a range of elastomers.^{1,2} In these studies, mechanical properties as a function of depth were determined under differing temperature/time conditions. In addition, chemical changes were measured by analyzing microtomed sections using FTIR. Unfortunately, these measurements were difficult to perform on carbon-black filled samples and were also relatively time consuming. Ideally, an alternative method is needed to measure the chemical oxidation profiles of commercial o-rings containing fillers in a quick and efficient manner. In this talk, the usefulness of ToF-SIMS as a technique to measure the position-dependent extent of oxidation in filled elastomers will be discussed. Accelerated aging in 18O is used to demonstrate the ability of SIMS to directly measure the extent of oxidation. Examples of 18O- cross section line scans in aged elastomers will be discussed and compared to known diffusion limited degradation mechanical profiles. It will be shown that filled elastomers can be analysed using these methods. Additionally, the ability to measure oxidation profiles in air-aged samples will also be shown. Thus, ToF-SIMS is seen as a rapid evaluation tool for the measurement of elastomer oxidation for engineered elastomers. The benefits and limitations of the technique will be discussed. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

¹ M. Celina, J. Wise, D. K. Ottesen, K. T. Gillen, R. L. Clough, *Polymer Degradation and Stability* 60 (1998) 493-504

² M. Celina, J. Wise, D. K. Ottesen, K. T. Gillen, R. L. Clough, *Polymer Degradation and Stability* 68 (2000) 171-184.

5:00pm **AS+BI+NS-WeA11 Surface Chemical Analysis of Nano-Scaled r.f. Plasma Polymer and Co-Polymer Films by using a Combination of "In-Situ" and Ex-Situ Characterization Tools: Hydroxylated and Aminated Surfaces by XPS, ToF-SIMS and NEXAFS Spectroscopy.** *W.E.S. Unger, A. Lippitz, S. Swaraj, E. Yegen*, Federal Institute for Materials Research and Testing (BAM), Germany

The formation of plasma-polymerized materials made from organic molecules is a technologically highly attractive way to obtain films with unique properties. Surface properties like bio-compatibility, wettability, etc., can be adjusted by tailoring the chemical functionalization. A controlled deposition of those films requires the development of surface

analytical procedures which are able to derive useful information on relevant parameters. This can be a hard job for an analyst because plasma-polymerized or plasma-modified materials are extremely complex samples. Their complexity is caused by the co-existence of a relatively high number of chemical species. This leads to a kind of mixture analysis at surfaces but without the possibility of a separation step as it is possible, e.g., by using GC-MS techniques in the analysis of organic mixtures. Relevant parameters for film characterization are primarily (1) qualitative and (2) quantitative determination of functional groups. However there are other important parameters as for instance (3) the cross-linking and branching within the films or even the concentrations of (4) radicals and (5) unsaturated species in the films. It is well known that plasma-polymerized materials may undergo ageing processes. It is assumed that many of them will be initiated by radicals in the films. These radicals are inherently produced by plasma processing. Approaches have to be developed enabling a study of ageing processes on the molecular level including the respective reaction kinetics. So-called "in-situ" techniques of surface chemical analysis are required to investigate the real fresh state of samples. Using a selection of hydroxylated or aminated model plasma polymers and co-polymers it will be demonstrated how analytical approaches based on a combination of photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) and x-ray absorption spectroscopy (XAS) may provide solutions for the analytical challenges summarized above.

Nanometer-scale Science and Technology

Room: 615 - Session NS1+BI-WeA

Biological and Molecular Applications of Nanoscale Structures

Moderator: J. Randall, Zyvex Corporation

1:40pm **NS1+BI-WeA1 Multiplexed DNA and Protein Arrays Printed via Dip Pen Nanolithography.** *N.A. Amro, S. Rozhok, T. Renner, J. Fragala, M. Nelson*, NanoInk, Inc.

Miniaturized nucleic acid in the form of nanoarrays will dramatically enhance the sensitivity, and spatial density of chip-based bio-assays. These nanoarrays will improve applications ranging from point-of-care diagnosis to genomic arrays used in basic research by enabling the development of next generation screening technologies that are faster, more sensitive, more reliable, and possibly more cost effective than those presently available in the life sciences market. Nucleic acid bioarrays can be printed using Dip-Pen Nanolithography® (DPN®), a new direct-write spotting technology which generates sub-micron sized features of DNA or protein on solid surfaces. This printing technique offers significant advantages over current microarray printing technologies that suffer from poor spot to spot reproducibility in terms of size, shape, and oligonucleotides density, as well as reproducibility across microarray slides. In this talk we report on recent technical advances in patterning DNA and protein patches with submicron dimensions on glass and metal coated substrates, using new commercially available DPN accessories such as multiple pen arrays and microfluidic pen loading which allows performing multiplexed DNA and protein patterning to fabricate arrays with nanoscale registration and high throughput printing. DNA and protein dot features as small as 200 nm in diameter can be routinely generated. DPN patterning of proteins and oligos, as well as screening for their biological activity, will be shown and discussed in detail.

2:00pm **NS1+BI-WeA2 Cell-Surface Interactions: The Extracellular Matrix as Mechanotransducer.** *V. Vogel*, ETH Zürich, Switzerland
INVITED

While cells initially respond to the surface chemistry presented on synthetic materials, they rapidly begin to assemble their own matrix. Cells can thereby sense and transduce a broad range of mechanical forces into distinct sets of biochemical signals that ultimately regulate cellular processes, including adhesion, proliferation, differentiation, and apoptosis. But how is force translated at the molecular level into biochemical signal changes that have the potential to alter cellular behavior? The molecular mechanism of fibronectin's (Fn) extensibility within extracellular matrix fibrils is controversial. Does it originate from the force-induced extension of a compactly folded quaternary structure, or from unfolding of fibronectin modules? Clarification of this issue is central to our understanding whether or not the extracellular matrix can act as a mechanotransducer that converts mechanical forces into well regulated biochemical signal changes. Different fluorescence resonance energy transfer (FRET) labeling schemes were used to differentiate between these two models and we quantified how the conformational changes of fibronectin probed by FRET relate to changes of

its overall end-to-end extension. The data clearly demonstrate that cells do indeed mechanically unfold fibronectin. The functional implications of the findings are discussed as well as high resolution structural models derived from steered molecular dynamics (SMD) how force might change the functional states of this and other multidomain proteins.

2:40pm NS1+BI-WeA4 Carbon Nanotube - Chitosan Sites for Direct Electrical Sensing of Biomolecular Events in BioMEMS, S.L. Buckhout-White, S.K. Gupta, M.S. Fuhrer, G.W. Rubloff, University of Maryland

Direct electrical sensing of biomolecular events is highly desirable in bioMEMS applications such as metabolic engineering platforms or biosensor systems. We are pursuing the development and integration of carbon nanotube (CNT) thin film biosensing devices in the microfluidic systems we employ for recreating metabolic pathways for drug discovery. Since these systems exploit chitosan electrodeposition as a spatiotemporally programmable reaction site for biomolecular binding and enzymatic activity, CNT biofunctionalization using chitosan would enable fabrication of the microfluidics environment with embedded CNT devices so that the devices could serve as active sites for biomolecular events and simultaneously read out those events electrically. We have developed integrated CNT devices, for use as conductance elements and/or FET's, and an easily fabricated, reusable microfluidic system using SU8 channels and a PDMS gasket for non-permanent sealing. In addition, we have electrodeposited chitosan, an amine-rich polysaccharide, onto CNT mats exposed as active sites for biomolecular binding down to 1 μm resolution. Since we have already demonstrated that proteins,¹ nucleic acids, and viruses² can be conjugated to localized chitosan sites in bioMEMS and retain their biomolecular functionality, we believe the integrated CNT devices are promising for sensing and controlling biomolecular assembly in multi-site bioMEMS networks that recreate metabolic pathways. This work is supported in part by the Robert W. Deutsch Foundation.

¹Park, J.J., et al., Chitosan-mediated in situ biomolecule assembly in completely packaged microfluidic devices. *Lab on a Chip*, 2006. 6(10): p. 1315-1321.

²Yi, H.M., et al., Patterned assembly of genetically modified viral nanotemplates via nucleic acid hybridization. *Nano Letters*, 2005. 5(10): p. 1931-1936.

3:00pm NS1+BI-WeA5 The Study of FET Flow Control and Separation of Proteins in Nanofluidic Channels, Y.-J. Oh, University of New Mexico, D. Bottenus, Washington State University, D.N. Petsev, University of New Mexico, C.F. Ivory, Washington State University, S.R.J. Brueck, G.P. Lopez, S.M. Han, University of New Mexico

We have studied field-effect-transistor (FET) flow control and separation of proteins in a parallel array of nanochannels (100 nm W \times 500 nm D), using scanning laser confocal fluorescence microscopy (SL-CFM) and multiple internal reflection Fourier transform infrared spectroscopy (MIR-FTIRS). For fluidic FET, a DC potential is applied to the gate surrounding an isolated mid-section of the channels under longitudinal electric field along the nanochannels. The gate potential controls the surface charge on SiO₂ channel walls and therefore the ξ -potential. Depending on the polarity and magnitude, the gate potential can accelerate, decelerate, or reverse the flow of proteins. We also analyze a pH shift in the nanochannels according to the surface charge modulation and longitudinal electrical field, using Fluorescein as a pH indicator. Our MIR-FTIR analysis shows that Fluorescein dye molecules are hydrogenated and dehydrogenated in response to the gate bias and subsequent pH shift. We demonstrate that the pH shift affects the FET flow control with SL-CFM analysis. A nanochannel device containing multiple gates is used to improve the controllability of protein flow and to introduce a pH gradient along the channels for isoelectric focusing. A different potential is applied to each gate to differentially control the surface charge on the SiO₂ channel walls and to create a pH gradient along the channels. We also generate a pH gradient along the nanochannels, induced by controlled water electrolysis under longitudinal electrical field. The control and separation of proteins, which have different isoelectric points (pI), by the pH gradient along the nanochannels as a function of gate bias and longitudinal electrical field will be further discussed in this presentation.

4:00pm NS1+BI-WeA8 Microfabricated Cantilever Arrays for Drug Screening Based on DNA-Drug Intercalation, R. Desikan, Oak Ridge Associated Universities, H.M. Meyer III, T.G. Thundat, Oak Ridge National Laboratory

The ability of a cantilever sensor to generate nanomechanical motion from biomolecular interactions can have wide applications in drug discovery. Microfabricated cantilever arrays offer high sensitivity multiplexed detection in real-time in liquid medium. DNA strands when selectively immobilized on one side of the cantilever surface exhibit surface stress variation during interaction with different chemicals. We have used microfabricated piezoresistive cantilever arrays to demonstrate surface stress variation due to immobilization of ssDNA, hybridization and drug interaction that could form the basis for multiplexed detection of chemicals

and drugs intercalating with dsDNA. It is shown that immobilization of ssDNA results in a compressive stress while hybridization results in tensile stress. Intercalation between adjacent base pairs results in stiffening, lengthening and unwinding of the double helix, causing it to expand and lose native conformation. Intercalation of chemicals into immobilized dsDNA produces a characteristic oscillatory response pattern. We have investigated the surface stress pattern due to interaction of chemicals such as ethidium bromide and anti-tumor drugs with dsDNA immobilized on cantilever arrays. The dynamic signature pattern can provide new insight on the kinetics and nanomechanics of DNA-drug intercalation. We have used x-ray photoelectron spectroscopy to carry out elemental analysis in order to confirm the presence of the intercalating agent in the DNA. Microfabricated cantilever arrays find potential applications in drug screening, identification of various toxins, and biological sensing.

4:20pm NS1+BI-WeA9 Nanofluidic System for Investigating DNA-Force and DNA-Protein Interactions, V.R. Dukkupati, S.W. Pang, University of Michigan

Nanofluidic systems are useful in the studies of single-molecule DNA-protein interactions, nanofluidics, and polymer dynamics. DNA is a flexible polymer with a large aspect ratio of 2 nm in width and length in the order of the micrometers. Due to its unique properties, it is ideally suited for investigations using nanofluidic systems for both biological and mechanical characteristics. We present an integrated nanofluidic system, which is applied to study DNA-protein interactions and DNA-force dynamics. In this system, electrodes are integrated in sealed Si nanochannels by PMMA bonding. Cr/Au electrodes are patterned on a 100 μm thick glass followed by PMMA coating and patterning to expose the electrodes. The 100 μm thick glass allows high resolution imaging of DNA at single molecule level. Si nanochannels varying from 350-500 nm in width are sealed with electrodes using PMMA bonding. A 150 μm wide, 1 μm deep microchannel is connected to each of the fluidic ports as an interface to the nanochannels. The microchannel allows the DNA molecules from the inlet port to have an easy access to the nanochannels. The DNA molecules are pumped into the nanochannel array using both hydrodynamic force and electric field. Using the hydrodynamic force, the DNA molecules near the inlet are pumped by evaporation from the outlet port, which is open to atmosphere. Using 100-300 KHz electric field generated by ac voltage applied across the electrodes integrated in the microchannel, the DNA molecules are driven from the microchannel into the nanochannel array. The linear motion generated by the electric field causes the DNA molecules to move in the nanochannels with velocity varying from 5-40 $\mu\text{m/s}$. This corresponds to a viscous drag force of 0.04-3.80 pN acting on the DNA molecules, assuming the values of viscosity of the water and the radius of the DNA molecules of 0.5 μm in nanochannels. The nanofluidic system is also used to immobilize and stretch T2-DNA molecules using the protein assisted DNA immobilization (PADI) technique. 350 nm wide and 100 nm deep channels are used to immobilize and stretch λ -DNA molecules up to 12 μm long. Further studies will be conducted on the influence of multiple sources of electric field on DNAs in nanochannels.

4:40pm NS1+BI-WeA10 Plasma Assisted Production of Chemical Nano-Patterns: Study of the Biosensing Efficiency, A. Valsesia, P. Colpo, I. Mannelli, P. Lisboa, F. Bretagnol, G. Ceccone, F. Rossi, European Commission - Joint Research Centre, Italy

The next challenge for the development of analytical devices for biological analysis relies on the ability to design advanced surfaces able to interact properly with the biological world. An increase of several order of magnitude of analysis capacity in biosensing devices together with lower detection limits is envisaged, due to the special interactions between the biomolecules and the nanostructured materials. The most important consequences of the nano-structuring of the bio-interacting surfaces is the immobilization of the biomolecular probes in an active state, limiting the non specific adsorption and the optimisation of their binding site accessibility for the bio-recognition of the target molecules. In our laboratory, we have developed alternative fabrication strategies for the creation of chemically nanostructured surfaces by combining Colloidal Lithography and Electron Beam Lithography with Surface Functionalization Techniques such as Plasma Enhanced Chemical Vapour Deposition (PE-CVD) of bio-functional polymers and Self Assembled Molecular Monolayers (SAM). In particular carboxylic functionalized nano-domes in a PEO-like anti-fouling matrix have been produced. We showed that these chemical nano-patterns are able to immobilize proteins selectively in the carboxylic functional nano-domains, leaving the anti-fouling matrix clear. Moreover, we have compared the detection performances between uniformly functionalized surface and chemically nano-patterned surfaces when applied as platforms for antigen/antibody interactions. In particular, homogeneous PAA was compared with the PAA nano-areas in anti-fouling matrix previously described. Nano-patterned surfaces showed a considerable enhancement of the immunoreaction

efficiency with respect to the non-structured surfaces, demonstrating the capability of nano-patterns to improve the binding site accessibility of the immobilized biological probes.

Nanometer-scale Science and Technology

Room: 616 - Session NS2+EM-WeA

Nanoscale Devices and Nanowires II

Moderator: D.K. Ferry, Arizona State University, F.M. Ross, IBM T. J. Watson Research Center

1:40pm **NS2+EM-WeA1 Real-time Studies of Metallic Nanodroplet Formation and Motion on Semiconductor Surfaces.** *J.H. Wu, W. Ye, T. Sun, H.-Y. Chen, K. Thornton, R.S. Goldman*, University of Michigan

Arrays of metallic nanodroplets are of interest for a broad range of applications including magnetic memory arrays, plasmonic waveguides, nanowire growth seeds, and negative index of refraction materials. Although nanometer-sized metallic droplets often form on compound semiconductor surfaces during epitaxial growth, thermal annealing, and/or ion irradiation, the mechanisms of their formation are not well understood. In this work, we are examining the formation and motion of metallic droplets during ion-irradiation of a variety of semiconductor surfaces. We use real-time imaging in a dual-beam focused-ion-beam system followed by quantitative analysis of the instantaneous positions, sizes, and velocities of the droplets in each movie frame. On GaAs and GaSb surfaces, randomly distributed nearly pure liquid-like Ga droplets are observed to form above a critical dose. Subsequent ion beam irradiation results in growth, motion, and coalescence of the droplets. Since droplets are not observed on Si surfaces prepared under similar conditions, the droplet formation is likely associated with the preferential sputtering of group V elements and liberation of Ga from the substrate as it is milled. Under ion beam irradiation, Ga droplet motion is observed, possibly due to Marangoni motion, which is usually driven by a surface tension gradient. Since the Ga droplets are essentially liquid spheres, the weak atomic bonds and droplet shape lead to enhanced sputtering in comparison with the surrounding substrate. The enhanced sputtering at liquid droplets leads to both thermal and surface tension gradients between the droplets and the substrate, thus providing the driving force for droplet motion. Interestingly, a higher droplet velocity is observed on GaSb than on GaAs surfaces, suggesting that droplet motion is dependent on the energetics of the Ga-substrate interface. On GaAs surfaces, most droplets move in a direction opposite to the ion beam scanning direction, presumably due to the FIB-induced thermal gradient on the surface. In addition, the droplet velocity is size-dependent, with higher velocities for larger droplets, suggesting the thermal/surface tension gradients increase with droplet size. The velocity is apparently correlated with the rate of droplet size change, suggesting that a mass transfer/exchange process occurs during droplet motion. This phenomenon is less significant for droplets that have merged with other droplets.

2:00pm **NS2+EM-WeA2 A Periodic Table of Silicon-Metal Nano-Templates for Cluster-Assembled Materials.** *G.K. Gueorguiev, S. Stafström, L. Hultman*, Linköping University, Sweden

The structure and bonding properties of MSi_n clusters, containing 1 to 14 Si atoms together with one transition metal atom among 24 different elements: Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ti, Zr, Hf, V, Nb, Ta, Ni, Pd, Pt, Cu, Ag, Au, were studied by first-principles calculations. Some of these clusters are known to have been synthesized. The transition metal atoms work as nucleation sites for MSi_n . We find that species with $n=3, 5, 7, 10, 12$ are stable and exhibit shapes independent on the metal atom evolved which establishes a systematic behavior for MSi_n . For most metals, due to p-d orbital hybridization, both MSi_{12} and MSi_{10} (the smallest endohedral species) are highly symmetric, exhibiting the shapes of a hexagonal prism (D_{6h}) and of a bicapped tetragonal antiprism (D_{4d}), respectively. For such clusters, we predict similar packing rules, but considerably different electronic properties. Nano-wires (hexagonal nanocylinders) assembled from MSi_{12} are stable and with tunable electronic properties. These attributes suggest MSi_n as building blocks for cluster assembled materials. We have systematized the results on MSi_n by the organization of the transition metals in the Periodic Table.

2:20pm **NS2+EM-WeA3 Sc Silicide Epitaxial Nanowires on Si(001): A Comparison with Rare Earth Silicide Nanowires.** *J. Nogami, Y. Chai*, University of Toronto, Canada, *G. Ye, M.A. Crimp*, Michigan State University

Rare earth (RE) metals can form self-assembled silicide nanowires when grown epitaxially on Si(001) substrates. These nanowires form due to an anisotropy in lattice mismatch between the hexagonal form of the silicide and substrate, with extended growth occurring along the direction of low mismatch.^{1,2} In this context, the growth of scandium silicides is interesting since Sc_2Si_5 has the same crystal structure as the RE silicides, but with the direction of close match along the c rather than the a axis. This raises the intriguing possibility of growing nanowires that are naturally perpendicular to RE silicide nanowires. The initial stages of Sc silicide growth on Si(001) was studied by scanning tunneling microscopy, transmission electron microscopy (TEM) and atomic force microscopy. The nanostructures can be divided into two classes: tabular rectangular islands with small aspect ratios, and highly elongated nanowires with triangular cross section. Surprisingly, there is no indication that the common growth direction of the nanowires is rotated with respect to RE nanowires. At the same time, TEM shows that the triangular nanowires have a two phase crystal structure, with a Sc rich silicide growing on top of a Si rich silicide. The differences in growth behavior with respect to the RE silicides will be explained in terms of the differences in stable silicide phases seen in the phase diagrams of these systems.

¹Y. Chen, D. A. A. Ohlberg, G. Medeiros-Ribeiro, Y. A. Chang, and R. S. Williams, *Appl. Phys. Lett.* 76, 4004 (2000).

²J. Nogami, B. Z. Liu, M. V. Katkov, C. Ohbuchi, and N. O. Birge, *Phys.Rev.B* 63, 233305 (2001).

2:40pm **NS2+EM-WeA4 Time-resolved X-ray Excited Optical Luminescence Characterization of Si Nanowires***. *R.A. Rosenberg, G.K. Shenoy*, Argonne National Laboratory, *P.S.G. Kim, T.K. Sham*, University of Western Ontario, Canada

Due to quantum confinement effects nanostructures often exhibit unique and intriguing fluorescence behavior. X-ray excited optical luminescence (XEOL) provides the capability to chemically map the sites responsible for producing low energy (1-6 eV) fluorescence. By taking advantage of the time structure of the x-ray pulses at the Advanced Photon Source (APS, ~80 ps wide, 153 ns separation) it also possible to determine the dynamic behavior of the states involved in the luminescence. In this presentation we show how this technique can be utilized to understand the XEOL from silicon nanowires (~50 nm diameter). Analysis of the XEOL spectra revealed the presence of three peaks at 475, 540, and 640 nm whose breadth increased with increasing wavelength. To gain insight into the dynamic nature of the luminescence, time-gated spectra were obtained as the x-ray energy was varied through the Si K edge. Data were obtained using 15-140 ns and a 0-10 ns gates. For the long time gate the areas are roughly evenly distributed among each of the peaks. However, in the short time gated data the 640 nm peak is dominant. This clearly demonstrates that the relative lifetime of this state is shorter than the other two. This is in contrast to the conventional wisdom for homo-structured and single component materials, for which the lifetime usually increases with wavelength. By extracting the intensity of each peak as the x-ray energy is scanned thru the Si K edge we are able to demonstrate that the 540 nm luminescence emanates from the Si nano crystallites imbedded in the wire, the 475 nm peak originates from the oxide shell, and the 640 nm peak comes from defects located near the Si-SiO interface.

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3:00pm **NS2+EM-WeA5 Enhancement of CHEI Programming Efficiency Using Extended SixZr1-xO2 Interface Formed by ZrO2 Charge Trapping Layer.** *G. Zhang, W.J. Yoo*, Sungkyunkwan Advanced Institute of Nano-Technology, Korea

Channel hot electron injection (CHEI) programming is widely used for NOR Flash memory operations, whose efficiency is determined by both hot electron (HE) injection level and electron capture rate in which an electron excitation and relaxation process is involved.¹ Inelastic phonon scattering is considered as the main mechanism to cause HE relaxation, where HE energy loss rate decays with larger electron/phonon temperature divergence.² As a result, electron capture rate of deep traps decays sharply with the increase of HE temperature (Te).³ We consider that phonon scattering occurs actively at interfacial junction of different layers, where regularity of lattice structure is disturbed. In this work, we investigated capture rate dependent CHEI programming efficiency for different junction widths or phonon temperatures (Tp). It is found that HEs are injected into the gate stack as lucky electrons,⁴ resulting in small capture rate or low programming efficiency; instead, warm electrons (WE), which are generated by thermally enhanced F-N tunneling, play a more important role in programming with higher capture rate. In this work, a practical method to effectively enhance programming speed using extended SixZr1-xO2

interfacial junction between tunnel SiO₂ and ZrO₂ trapping layer in SONOS type Flash memory is proposed. Cross-sectional TEM image shows that the ZrO₂ is highly reactive with SiO₂ to form a Si_xZr_{1-x}O₂ interface of graded composition over the thickness of ~2 nm. HfO₂ has a similar band structure with ZrO₂ but a thinner (0.5~0.7nm) interface and Si₃N₄ has a smaller conduction band energy offset to SiO₂. We observed effectively enhanced programming efficiency at various operation temperatures for the devices using a charge trap layer of ZrO₂, compared to those using Si₃N₄ by ~3.2 times and HfO₂ by ~2.2 times. Furthermore, ZrO₂ demonstrates clear advantages in low-voltage operation and large V_{th} window over Si₃N₄ and HfO₂, being a very attractive material contender for next-generation NOR Flash application.

¹B. Govoreanu, et. al., IEDM Tech. Dig., p479, 2006.

²W. Cai, et. al., Physical Review B, p8573, 1986.

³R. Passler, Solid-State Electronics, p155, 1984.

⁴S. Tam, et. al., IEEE Trans. Electron Devices, vol.31, n.9, p1116, 1984.

4:00pm **NS2+EM-WeA8 Nano-Structured Surface Fabrication for Higher Luminescent LED by Self-Assembled Block Copolymer Lithography**, A. Fujimoto, K.A. Asakawa, Toshiba Corporation, Japan
INVITED

Light-Emitting Diodes (LEDs) are widely used for cell phones, display panels, LCD backlights, traffic signals, and automobile rear lamp. They are expected to be used for automobile head lamps, and interior illumination. Higher luminance LEDs are required for these purposes. The total efficiency of LEDs is determined by the product of the internal quantum efficiency and the extraction efficiency. The internal quantum efficiency has been improved more than 80 %. But, the extraction efficiency remains 10 %, because of the large difference of the refractive index between substrates (n=3-3.5) and the air. Therefore, to improve the extraction efficiency is the key for higher luminance LEDs. In order to improve the extraction efficiency, we fabricated nanostructures having the antireflection and the diffraction effect onto the semiconductor surface. Nanostructures have the cone, cylinder, and the mesa part. Since nanostructures have the cone and the mesa part and the refractive index from the semiconductor to the air changes smoothly within the critical angle, the incident light within the critical angle can be extracted without a loss, and the transmittance increases about 30 % compared with that of the flat surface. Furthermore, since nanostructures have the cylinder and the cylinder has the diffraction effect, the incident light over the critical angle can be extracted as the -1st order light. Nanostructures having two functions can be expected to improve the light-extraction efficiency greatly. Such structures are usually fabricated by electron beam (EB) lithography, but are too costly for mass production. To overcome this challenge, block copolymer lithography was employed. The polystyrene (PS) - polymethyl methacrylate (PMMA) diblock copolymer was used in this study. The PMMA was removed by reactive ion etching (RIE) since the PMMA has a much faster etch rate than the PS by RIE. The gallium phosphide (GaP) substrate was dry-etched by chlorine-based inductively coupled plasma RIE using the remaining PS dots as a mask. The optical extraction efficiency of the substrates with subwavelength columnar structures improved 2.6 times compared to unprocessed flat substrates; the pillars' height was 350 nm, diameter was 130 nm, and pitch was 180 nm. We also manufactured a real LED and increased light emission volume 1.8 times compared with conventional LED at the same energy consumption.

4:40pm **NS2+EM-WeA10 Current-Voltage Characteristic of Organic Molecular Wires by Conducting Atomic Force Microscopy**, N.J. Lee, S.B. Kim, I.C. Hong, S.H. Koo, Y.J. Choi, J.W. Kim, Y.S. Kim, C.J. Kang, Myongji University, Korea

Using a atomic force microscope (AFM), with conducting cantilever the current versus voltage (I-V) characteristics of difference group substituted carotenedithiol molecules are measured. The molecules are inserted into 1-methylsulfanyl-octadecane monolayer on gold surface, and a Au nanoparticle is attached to each molecule via the protruding thiol group. To measure the current a gold coated AFM probe is used to contact with the molecule through the Au nanoparticle. A self-assembled monolayer of 1-methylsulfanyl-octadecane was analyzed by the surface plasmon resonance, ellipsometry and X-ray diffraction, which were employed to identify suitable preparation conditions of the substrate. The I-V curves of two kinds of carotenedithiol molecules substituted for different end groups appear quite different because of the different electron transport properties, bromophenyl substituted group put a crimp in electron transport. The phenyl-substituted carotenoid is significantly more conductive than the bromophenyl-substituted carotenoid. In this talk, we'll present the molecular wires possibility. The carotenoid candidate "molecular wire".

5:00pm **NS2+EM-WeA11 Fabrication, Dynamics, and Electrical Properties of Shielded Probes**, P.D. Rack, B.J. Rodriguez, K. Seal, S. Jesse, A.P. Baddorf, S.V. Kalinin, Oak Ridge National Laboratory

Many biological systems respond to stimuli such as electrical bias. The application of naturally occurring local biases in biosystems can be mimicked with an atomic force microscope tip. In order to minimize capillary forces and obtain high resolution images of biosystems, a liquid environment, typically with a high ionic strength, is required. A bias applied via traditional cantilevers will cause electrochemical reactions in the solution. The use of shielded probes may allow biases to be applied locally, and minimize any electrostatic force contribution to the signal being measured, whether the tip is used as an electromechanical probe or a probe of local electric force. In this case, the bias is applied locally and the signal is measured locally, both on the nanoscale. The fabrication of suitable shielded probes requires (a) good dynamic properties of the lever, (b) good insulation everywhere except for the apex, (c) high apex conductivity, and (d) apex geometry consistent with high resolution. In this presentation, we describe a process for fabricating shielded probes, and measure their dynamic and electrical properties. The commercial doped-Si tips were coated with an oxide prior to etching a small via (~200nm diameter) with a focused ion beam. Subsequent to the via etch, a tungsten contact was deposited in the via using electron beam induced deposition. The dynamic properties of the fabricated probes, as well as their performance in Piezoresponse force microscopy in ambient and liquid environment and I-V characteristics are discussed. The choice of other coatings or other metal plugs may allow for further improvements, and/or tunable properties. The use of shielded probes may allow precise control over the application and measurement of local fields in solution.

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Thursday Morning, October 18, 2007

Nanometer-scale Science and Technology

Room: 616 - Session NS-ThM

Nanotube Devices and Processes

Moderator: S.V. Kalinin, Oak Ridge National Laboratory, S. Evoy, University of Alberta, Canada

8:00am NS-ThM1 Single Charge Sensing by Carbon Nanotube Single-Hole Transistor, *K. Matsumoto*, Osaka University, Japan

We have succeeded in detecting the single charge transition near the channel of single walled carbon nanotube (SWNT) single-hole transistor (SHT). Abrupt discrete switching of the source-drain current is observed in the electrical measurements of SWNT SHT. These random telegraph signals (RTS) are attributed to charge fluctuating near the SWNT SHT conduction channels. The sample has a back gate FET structure with the source-drain spacing of 73 nm. The channel is formed by thermal CVD grown single walled carbon nanotube on the SiO₂ substrate. The silicon dioxide layer was deposited on the SWNT SHT to prevent the adsorption & desorption of the molecules to the carbon nanotube channel. In the drain current-voltage characteristics of SWNT SHT under the drain voltage of 11 mV at 7.3 K, drain current showed periodic peaks and valleys structure, with two. The large period of 3 V was attributed to Coulomb oscillation characteristic, the small period of 0.5 V to the quantum interference property of hole. The drain current was observed only in negative gate voltage region, which indicates that the measured SWNT SHT has the p type semiconductor property. The SWNT SHT shows random telegraph signals (RTS), which were attributed to fluctuating charge traps near the SWNT SHT conduction channels. The RTS appeared two levels, upper level and lower level in drain current, the occupation probabilities of which was depended on the applied gate voltage. Using the simple model we assumed, we could estimate the distance between the trap and the channel of SWNT SHT to be $L=1.03$ nm. The potential energy barrier between the trap state and the Fermi level of carbon nanotube channel was also founded to be 3.2 meV. Thus, using the carbon nanotube single hole transistor, we have succeeded in detecting and analyzing the single charge transition.

8:20am NS-ThM2 Single Molecule Sensing with Carbon Nanotubes, *B.G. Goldsmith, J.G. Coroneus, V.R. Khalap, A.A. Kane, G.A. Weiss, P.G. Collins*, University of California at Irvine

Due to their extremely small size, single walled carbon nanotubes (SWCNTs) provide a promising framework for building single molecule electronic devices. We have developed a procedure to controllably form single carboxyl groups on a CNT's sidewall. By limiting the chemically sensitive region of a nanostructure to a single binding site, single molecule bonding dynamics become visible. Discrete changes in the circuit conductance reveal chemical processes happening in real-time and allow SWNT sidewalls to be deterministically broken, reformed, and conjugated to target species, creating new possibilities for chemical sensing and molecular electronics.

8:40am NS-ThM3 STM and STS Studies of SWCNT on NaCl/Ag(100), *H.-J. Shin, S. Clair, Y. Kim*, Riken, Japan, *M. Kawai*, Riken and University of Tokyo, Japan

Single-walled carbon nanotubes (SWCNTs) have been considered as one of the most promising candidates for future electronic devices due to their unique electrical properties. Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) have provided a lot of information about the structure and electronic properties of SWCNTs.^{1,2} In most STM studies of SWCNT, it was carried out on metals or semiconductors so far. In these cases, the electronic structure of SWCNT can be perturbed by the presence of the electrons of the surface. For example, the charge transfer between metal substrate and SWCNT results in the shift of Fermi-level of SWCNT on Au(111) to the valence band.² In this study, we studied electronic structure of SWCNT on NaCl thin film by STM and STS. We introduced insulating layer to reduce the influence of metal surface. We deposited SWCNT on the NaCl(100) film, grown on Ag(100) single crystal by dry contact transfer technique in UHV.³ Interestingly, the Fermi-level of SWCNT shifted to the conduction band on Ag(100), while it shifted to the valence band on NaCl film. The charge transfer due to work function difference between Ag(100) (4.3eV) and SWCNT (4.8 ~ 5.0eV) was the main reason for the Fermi-level shift of SWCNT on Ag surface. On NaCl film, it is thought that the dipole moment at the interface between NaCl and

Ag brought about Fermi-level shift to the conduction band, though the work function of NaCl on Ag(100) is 3.6 ~ 4.0eV, much lower than that of Ag(100). The influence of dipole moment on the electronic structure of SWCNT will be discussed in details.

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² M. Ouyang, J.-L. Huang, and C.M. Lieber, *Annu. Rev. Phys. Chem.* 53, 201 (2002).

³ P.M. Albrecht and J.W. Lyding, *Appl. Phys. Lett.* 83, 5029 (2003).

9:00am NS-ThM4 Evaluation of High k Dielectric Films for Carbon Nanotube FETs, *W. Miller, S.V. Krishnaswamy, J.M. Murduck, H. Zhang, J. Baumgardner, A.A. Pesetski, J.X. Przybysz, J.D. Adam*, Northrop Grumman Electronic Systems

Carbon nanotube FETs are promising candidates for future RF applications because they simultaneously offer high speed, high linearity, low power and low noise. Carbon nanotube FETs are projected to have a cut-off frequency of over 1 THz due to their small size and high carrier mobility, 1000x lower dissipated power than current GaAs devices without sacrificing linearity. Successful development of CNT electronics will enable the fielding of RF systems that are not currently possible because of prime power requirements. CNT FETs will have a large impact in RF electronics applications where linearity is critical. Based on our simulations, CNT FETs can be designed to be intrinsically linear provided one uses a gate dielectric material with dielectric constant >15. In our work we have evaluated several candidate materials such as HfO₂, ZrO₂, Ta₂O₅, TiO₂ etc. Thin films of these gate dielectric materials have been grown at various laboratories using different techniques. While sputtering is a standard technique used in the semiconductor industry, sputtering of these materials on to CNT significantly deteriorated the performance of the devices. Dielectric for gate oxide in our CNT IC process must have high dielectric constant, be compatible with CNT, have good dielectric integrity and have reasonable breakdown voltages. We will report our results on atomically smooth TiO₂ films using rf magnetron sputtering with auxiliary magnet under the substrate. In addition we will report on ALD HfO₂ and evaporated Ta₂O₅ films along with our results obtained from CNT FETs using these different gate dielectrics.

9:20am NS-ThM5 Erbium and/or Ytterbium Doped Yttrium Oxide Nanotubes for Optical Amplifier Application, *Y. Mao, J.P. Chang*, University of California at Los Angeles

Yttria is one promising hosting material for rare-earth-ion-activated phosphors with applications including amplifiers, lasers, waveguides, X-ray imaging, bioimaging, and displays due to their luminescent characteristics and stability in high vacuum. In fact, in our most recent study, we have deposited Er-doped Y₂O₃ thin films by radical-enhanced atomic layer deposition (ALD)¹ and demonstrated that the Er incorporated in Y₂O₃ can reach a concentration as high as 10²¹ cm⁻³ with outstanding room temperature photoluminescence (PL) at 1.54 μm in thin Er-doped (6-14 at. %) Y₂O₃ films deposited at 350°C.² Meanwhile, nanomaterials exhibit physical properties, in particular, increased luminescence efficiency, which are not observed with their bulk counterparts. Hence, in this talk, we present our recent work on the synthesis of nanotubes of rare-earth (RE, Er and Yb) doped Y₂O₃, by a solution synthetic method. The processing temperature, pH, time, addition rate of NaOH, the concentration of precursors, and the annealing temperature dictated the nucleation/growth of RE doped Y(OH)₃ nanotubes. These tubes were converted to RE doped yttria by high temperature annealing and the resulting nanotubes had varying RE dopant concentrations (0-100%) with sizes ranging from 40-500 nm in diameter and 2-10 μm in length. X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), and extended x-ray absorption fine structure (EXAFS) were combined to delineate the structure and composition of these nanotubes. The erbium coordination number and local bonding environment are assessed by synchrotron based EXAFS analysis, and are shown to dictate the measured photoluminescence intensity.³ Their room luminescent properties (PL and cathodoluminescence, CL) are outstanding and even superior than the thin films synthesized by ALD. Finally, we will discuss their electronic properties and the application of these doped yttria nanostructures as small and compact planar optical amplifier.

¹ T.T. Van and J.P. Chang, *Appl Phys Lett*, 87, 011907 (2005).

² T.T. Van, J. Hoang, R. Ostroumov, K. L. Wang, J. R. Bargar, J. Lu, H.-O. Blom, and J.P. Chang, *J Appl Phys*, 100, 073512 (2006).

³ T.T. Van, J. R. Bargar, and J.P. Chang, *J Appl Phys*, 100, 023115 (2006).

9:40am **NS-ThM6 Ultrahigh-Vacuum Scanning Tunneling Microscopy Study Into the Adsorption of N-methyl-pyrrolidone Molecules on Carbon Nanotubes**, *Z.T. Wang, P.M. Ryan, N.P.P. Niraj, J.J. Boland*, Trinity College Dublin, Ireland

The most common processing technique for carbon nanotubes involves dispersing them in a liquid media. However, due to their high molecular weight, nanotubes suspend and are not soluble in all known solvents. Usually, surfactants are used to overcome this obstacle.¹ Recently people found that pristine single wall carbon nanotubes can be spontaneously dispersed and even exfoliated in an N-methyl-pyrrolidone (NMP) solvent, forming a carbon nanotube solution.² The negative free energy of mixing NMP with nanotubes leads to the strongly adsorption of a huge number of NMP molecules on the nanotubes in NMP solution and even dried-powder. In our experiments, carbon nanotubes processed by the NMP solvent are deposited on clean Si(001) substrates using a dry deposition method³ and investigated using an ultrahigh-vacuum (UHV) scanning tunneling microscope (STM). We find that NMP molecules diffuse from the nanotubes and become irreversibly chemically adsorbed on Si(001) surfaces due to the strong interaction of nitrogen with Si dangling bonds, indicating NMP molecules remain bound to nanotubes even under UHV conditions. However a few remaining molecules reversibly bound to the nanotubes are observed using STM and are seen to emerge from tube bundles. The molecules can migrate on the bundles during imaging and finally become bound to the Si(001) substrate. After all NMP molecules are removed, there is no defect left on the nanotubes.

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² S. D. Bergin et al, unpublished.

³ P.M. Albrecht and J. W. Lyding, App. Phys. Lett. 83, 5029 (2003).

10:00am **NS-ThM7 Growth Promotion and Etching of Carbon Nanotubes by CO₂ in Chemical Vapor Deposition using CH₄ Gas**, *Y. Suda, T. Saito, A. Okita, J. Takayama*, Hokkaido University, Japan, *J. Nakamura*, Tsukuba University, Japan, *Y. Sakai, H. Sugawara*, Hokkaido University, Japan

Oxidant has been used for growth promotion of carbon nanotubes (CNTs) in CVD since the work by Hata, et al.¹ We report the effect of CO₂ addition to CH₄ gas on CNT growth. The CVD chamber is evacuated down to 10⁻⁶ Torr by a turbo-molecular pump followed by a rotary pump. We used Mo_{(0.025)/Fe_{(0.05)/MgO_(0.925)} or Mo_{(0.025)/Ni_{(0.05)/MgO_(0.925)} as a catalyst, H₂ gas as a reductant and CH₄ gas as a feedstock.² CO₂ gas was introduced during the CNT growth at a temperature of 800°C and its concentration in CH₄ was varied from 0.0037% (37 ppm) to 50%. The other experimental parameters are as follows: H₂ gas pressure = 100 Torr and flow rate = 100 sccm for reduction; CO₂/CH₄ gas pressure = 100 Torr and flow rate = 76 sccm for growth. The CNT yield and the G/D ratio in the Raman spectra of CNTs grown in 10%-CO₂/CH₄ were slightly higher (~86%) than that grown in CH₄ only (~71%). However, CNTs were hardly grown when the CO₂ concentration was more than 20%. Decreasing the CO₂ concentration down to 37 ppm, it was found that single-walled CNTs (SWCNTs) with a yield of ~10% were grown and that the yield for 60 min was 1.5 times higher than that for 10 min. This suggests that the SWCNT growth in a CO₂/CH₄ gas mixture continued for 60 min. The G/D ratio obtained from 37 ppm-CO₂/CH₄ was almost the same as that grown from CH₄ only. The radial breathing mode (RBM) obtained by a 632.8 nm excitation shows that the SWCNT diameter ranges from 0.9 to 1.3 nm and that a few metallic SWCNTs were eliminated but most of semiconducting SWCNTs remained.}}

¹ K. Hata, et al, Science, 306 (2004) 1362-1364

² L.-P. Zhou, et al, J. Phys. Chem. B, 109 (2005) 4439-4447.

10:40am **NS-ThM9 Effect of Nitrogen Dopant on the Structure and Electrocatalytic Activity of Arrayed Multi-Walled Carbon Nanotubes**, *Y.-G. Lin*, National Chiao Tung University, Taiwan, *Y.-K. Hsu*, Academia Sinica, Taiwan, *J.-L. Yang, S.-Y. Chen*, National Chiao Tung University, Taiwan, *K.-H. Chen*, Academia Sinica, Taiwan, *L.-C. Chen*, National Taiwan University

With the recent advancements in nanoscience and nanotechnology, carbon nanotubes (CNTs) have drawn a great deal of attention as novel catalyst supports due to their unique structure, high surface area, stability, and excellent mechanical and electrical properties, all of which could offer improvements for fuel cell applications. We have developed a method to synthesize well-aligned nitrogen-containing carbon nanotube (CNx NT) by microwave-enhanced chemical vapour deposition with a source gas of CH₄, N₂, and H₂. Here we report our recent results on employing different flow rate of nitrogen to control the structure and electrochemical activity of CNx NTs. The effect of nitrogen on the structure and electrochemistry has been examined by Raman spectroscopy, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry (CV) using the redox probe of Fe(CN)₆³⁻/Fe(CN)₆⁴⁻. From the structural investigation, as the flow rate of N₂ gas is higher than 120 sccm, the average diameter of the nanotubes goes beyond 100 nm. The intensity ratio

of the D band to G band of Raman spectrum increased with increasing N₂ flow rate from 0 to 40 sccm, and then rapidly decreased with further increase in the flow rate of N₂. Similarly, XPS results showed the highest nitrogen concentration occurred at 40 sccm and the intensity of pyridine-type N bonding which causes the interlinked node morphology inside the CNx NTs increased with increasing N₂ gas flow rate. Hence, the nitrogen-incorporation promotes the disorder in graphitic structure in the initial stage; however, further increase in the N₂ flow rate won't enrich the nitrogen concentration in CNx NTs, but raise the growth temperature leading to enhanced graphitization. In addition, CNx NT electrode with N₂ flow rate of 40 sccm was found to significantly improve the electron transfer kinetics of Fe(CN)₆^{3-/4-} redox couple, approaching almost reversible electron transfer kinetics. The reason could be ascribed that the nitrogen treatment at 40 sccm creates disordered and chemically active sites which play a key role to facilitate electron transfer.

Tribology

Room: 617 - Session TR2+BI+NS+MN-ThM

Biolubrication, Sensing and Adhesion

Moderator: R.W. Carpick, University of Pennsylvania

8:00am **TR2+BI+NS+MN-ThM1 Resonant Nanomechanical Sensors for Protein Detection**, *P.S. Waggoner, H.G. Craighead*, Cornell University

Micro- and nanoelectromechanical systems (MEMS and NEMS) are of interest in sensing applications due to their high sensitivity, label-free operation, and potential for multiplexed detection on a single chip. Resonant MEMS and NEMS devices have demonstrated detection of masses on the order of femtograms or less, transducing changes in mass into changes in resonant frequency. Appropriate functionalization of the sensor surface allows specific, label free detection for analytes of choice. In this work we have detected prostate specific antigen (PSA), a biomarker used in the early detection of prostate cancer, as a model system using immunospecific functional layers present on the resonator surfaces. We have also studied the surface chemistry in order to minimize non-specific binding during sensor functionalization and use. In addition, sandwich assay techniques have been investigated for use in secondary mass tagging in order to enhance sensor response for dilute analytes while still preserving specificity.

8:20am **TR2+BI+NS+MN-ThM2 Correlation between XPS Data and Liquid Phase Self-Assembly of Alkanethiols**, *H.M. Meyer III, T.G. Thundat, R. Desikan*, Oak Ridge National Laboratory, *R.G. White*, Thermo Fisher Scientific, UK

The relative ease in which self-assembled monolayers (SAM) can be applied have made them part of the standard tool set used for functionalizing and patterning surfaces at the nanoscale. Recently, alkanethiol-based SAMs have been used for immobilizing selective chemical receptors on the gold-coated side of a microcantilever. In this configuration, adsorption on the functionalized side of the microcantilever generates nanomechanical motion (i.e. bending) which can be accurately sensed and used for detecting a variety of chemical and biological molecules. Achieving reliable selectivity and sensitivity depends primarily on the reproducible formation of the functional layer on one side of the microcantilever. We have recently investigated the effect of chain length on the packing density of the alkanethiols and, in turn, how this affects the sensitivity of the sensor. We present XPS characterization of microfabricated cantilevers functionalized with alkanethiol-based SAMs. The results are correlated with similar cantilevers that have been monitored during adsorption/immobilization of the same alkanethiols in the liquid phase. Previous liquid phase results indicated an unusual change in packing density of the thiol molecules as the chain length was increased and were difficult to correlate with preliminary XPS data, indicating major difference between how these films form in liquid phase vs. post-formation analysis in-vacuo. These new results attempt to illuminate those differences. Research sponsored in part by grant NSF Award ID 0330410 in collaboration with Drs. V.P. Dravid, G. Shekhawat, and A. Majumdar and in part by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies, as part of the High Temperature Materials Laboratory User Program, Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract number DE-AC05-00OR22725.

8:40am **TR2+BI+NS+MN-ThM3 Surface-Chemical Aspects of Implant Biotribology and Biomimetic Lubrication**, *N.D. Spencer*, ETH Zurich, Switzerland

INVITED

Following implantation of a hip prosthesis, the synovial membrane reforms and generates a liquid, pseudo synovial fluid (PSF), which is comparable in composition to synovial fluid itself. This complex solution of proteins, glycoproteins, polysaccharides and lipids is then responsible for the lubrication of the implanted joint. Surprisingly, the interactions of PSF components with the surfaces of joint materials, such as UHMWPE, CoCrMo, or alumina, remain remarkably unexplored. Not only is their relative propensity for adsorption unknown, but, once adsorbed, their efficacy for lubrication remains to be determined. We have investigated these issues by means of tribometry (on both macro and nano scales), combined with fluorescence microscopy, and determined, for example, that while albumin, the major component of PSF and the model protein used for implant testing, is strongly adsorbed on the surface of implants, it can be displaced during sliding by $\tilde{\Lambda}$ -glycoprotein, a species present at much lower concentrations, but a much more effective lubricant. The fluorescence approach has also enabled us to detect transfer of polyethylene under conditions where it was not previously thought to occur. Natural lubricated surfaces tend to be soft and covered with species such as polysaccharides that have the ability to retain large amounts of water. We have attempted to imitate and understand this mechanism of lubrication by means of tethering various highly hydrated polymer chains in a brush-like structure onto both hard and soft surfaces and measuring their tribological properties. Interestingly, on soft surfaces, the effect of chain tethering seems to be to effectively eliminate boundary lubrication entirely. Fluid-film-like behavior is thought to persist to very low sliding speeds, by virtue of water retention in a thin layer between the brush-covered surfaces.

9:20am **TR2+BI+NS+MN-ThM5 In-situ Measurement of Boundary-Lubrication on Articular Cartilage Surfaces**, *J.M. Coles*, Duke University, *G.D. Jay*, Brown University, *F. Guilak*, *S. Zauscher*, Duke University

The diarthrodial (synovial) joints of the body enable locomotion and activity while withstanding millions of cycles of loading at several times body weight. Recent macroscopic tribological experiments and biochemical analyses suggest that heavily glycosylated proteoglycans encoded by the gene proteoglycan 4 (Prg4), which are expressed by synoviocytes in synovial fluid as lubricin and by superficial zone chondrocytes of articular cartilage as surface zone protein (SZP), provide boundary lubrication in cartilage in the absence of interstitial fluid pressurization. Improved understanding of the role of Prg4 on the cartilage surface could thus provide important insight into the development of new therapies for joint diseases such as OA. The development of powerful new methods for the genetic manipulation of mice has led to the creation of modified murine strains in which specific gene inactivation (PRG4^{-/-}) results in age-related joint degeneration that recapitulates the symptoms of OA. Here we show that atomic force microscopy with a colloidal probe is uniquely suited to study boundary lubrication of murine cartilage in-situ and in absence of other lubrication mechanisms. Here we report on friction measurements on the superficial surface layer of articular cartilage from the femoral head of Prg4 knockout and wildtype mice under boundary lubrication conditions. Furthermore, we report on the measured RMS roughness and Young's modulus to quantify morphological and mechanical changes of the cartilage superficial zone induced by the absence of Prg4. Our measurements suggest that the absence of Prg4 leads to increased friction, as well as degradation of the mechanical and topographical properties of cartilage. We propose that, while lubricin plays a role as a boundary lubricant, its role in chondroprotection is equally, if not more, vital.

9:40am **TR2+BI+NS+MN-ThM6 Humidity Dependent Ordering of Water and its Effect on Adhesion and Friction between Silica Surfaces**, *B.I. Kim*, *J. Bonander*, Boise State University

Adhesion and friction related to water are major problems limiting both the fabrication and long-term use of micro-machines. Adhesion and friction between two silica surfaces were measured as a function of separation distance using interfacial force microscope (IFM) for different relative humidity (RH) between 3% - 78%. The IFM provides force-distance curves without having the "snap-to-contact" problems associated with atomic force microscopy using voltage-controlled force feedback. The measured friction force-distance curves show that the friction force is oscillatory as the separation changes below thickness of water droplet. The oscillatory period is close to the mean diameter of a water molecule. The number of oscillation increased as the relative humidity increases up to RH 60% while it decreased with humidity above RH 60%. The origin of the oscillatory feature in the "interfacial" water may come from the "solid-liquid transition" between solid (ordering) and liquid (disordering). Strong correlation between the number of oscillation and the strength of the adhesion and friction indicates that the humidity dependent adhesion and

friction may be attributed to the ordered structure of water molecules between two silica surfaces.

10:00am **TR2+BI+NS+MN-ThM7 Nanomechanical Properties of Arachidic Acid Langmuir Blodgett Films**, *G. Oncins*, University of Barcelona, Spain, *J. Torrent-Burgues*, Universitat Politècnica de Catalunya, Spain, *F. Sanz*, Universitat de Barcelona and Center of Nanobioengineering of Catalonia (IBEC), Spain

Scanning Probe Microscopies development has given biophysics the possibility to deal with the interactions arisen in biological membranes from a nanometric point of view, revealing that van der Waals, hydrogen bonding and electrostatic interactions play a crucial role in the membrane cohesion. Unfortunately, although interesting experimental conclusions have been reported in the past, these systems are complex and difficult to study.¹ In order to isolate the effect of the different cohesive interactions, Langmuir-Blodgett (LB) fatty acid monolayers provide excellent model systems because of the controlled area per molecule, linear hydrocarbon chain geometry, amphiphilic nature, high mechanical stability and the possibility to test solid and liquid phases at room temperature. The nanomechanical properties of arachidic acid LB films extracted at surface pressures of 1, 15 and 35 mN/m and deposited on mica are investigated by Atomic Force Microscopy, Force Spectroscopy and Friction Force Microscopy. It is experimentally demonstrated that the molecular ordering depends on the extraction pressure, while discrete molecular tilting angles of 50°, 34° and 22° are detected and identified as conformations that maximize van der Waals interactions between alkyl chains. The vertical force (F_v) needed to puncture the monolayer strongly depends on the molecular tilting angle, ranging from 13.07±3.24 nN at 1 mN/m to 22.94±5.49 nN at 35 mN/m. The friction force (F_f) measurements performed from low F_v until monolayer disruption reveal three friction regimes corresponding with a low F_f elastic monolayer deformation at low F_v , followed by a sharp increase in F_f due to a sudden plastic deformation of the monolayer. The last regime corresponds with the monolayer rupture and the contact between tip and substrate. Interestingly, as the extraction pressure increases, the friction coefficient of the monolayer reduces while the F_v needed to trigger the monolayer plastic deformation increases, facts that are discussed in terms of sample compactness and monolayer rupture mechanism.²

¹ Garcia-Manyes, S.; Oncins, G.; Sanz, F. *Biophys. J.* 2005, 89, 1812.

² Oncins, G.; Garcia-Manyes, S.; Sanz, F. *Langmuir* 2005, 21, 7373.

10:20am **TR2+BI+NS+MN-ThM8 Optimal Roughness for Minimal Adhesion**, *D.L. Liu*, Worcester Polytechnic Institute, *J. Martin*, Analog Devices Inc., *N.A. Burnham*, Worcester Polytechnic Institute

Differing views on the effect of surface roughness on adhesion have appeared in the literature recently. Molecular dynamics has been used to simulate the contact of two surfaces and found that atomic-scale roughness can have a large influence on adhesion, causing the breakdown of continuum mechanics models.¹ An experimental study showed that roughness can determine the adhesion in nanometer contacts and indicated that continuum mechanics still works down to nanometer length scales.² In this work, we use a single-asperity model to describe a smooth tip in contact with a rough surface and predict that there is an optimal size of asperity that will yield a minimum of adhesion. Experimentally, adhesive forces on silicon wafers with varying roughness from 0.2 nm to 39 nm were measured using AFM (atomic force microscope) cantilevers with varying tip radii ranging from 75 nm to 9.08 μ m. It is found that for all tip radii, the adhesion falls significantly for roughness greater than 1-2 nm and drops at higher roughness for larger tips. Minimum adhesion was observed as predicted in the 1-10 nm range and the optimal roughness for minimal adhesion increases as the tip radius increases, which is also consistent with our predictions. The work presented here should help minimize adhesion in future MEMS devices and progress the understanding of adhesion between the atomic- and macro-scale.

¹ B. Luan and M.O. Robbins, *Nature* 435, 929-932 (2005).

² E.J. Thoreson, J. Martin, N.A. Burnham, *J. Colloid Interface Sci.* 298, 94-101 (2006).

10:40am **TR2+BI+NS+MN-ThM9 A Tribological Study of Bound plus Mobile Lubricants for MEMS Application from the Nano- to the Macro-scale Regime**, *B.P. Miller*, *M. Brukman*, North Carolina State University, *C.C. Baker*, Naval Research Laboratory, *R.J. Nemanich*, North Carolina State University, *K.J. Wahl*, Naval Research Laboratory, *J. Krim*, North Carolina State University

One possible solution to the in-use stiction problem in Micro-Electro-Mechanical systems (MEMS) is the introduction of a bound plus mobile lubricant combination.¹ For this system, one monolayer of the bound lubricant (perfluorodecyltrichlorosilane, PFTS) bonds to the surface of the device. The mobile lubricant (tricresyl phosphate, TCP) can replenish the layer after rubbing contacts wear it away, thus keeping the device free of contamination. Friction behavior of this lubricant combination was

examined over three different regimes using a macroscopic tribometer, an AFM, and a quartz crystal microbalance (QCM). A comparative study of bound only versus bound plus mobile lubricants showed a decrease of the coefficient of friction with the addition of the mobile lubricant to the bound layer. Dynamic properties of the mobile film were characterized with the QCM. This work is funded by AFOSR Extreme Friction MURI Grant #FA9550-04-1-0381.

¹W. Neeyakorn, M. Varma, C. Jaye, J. E. Burnette, S.M. Lee, R. J. Nemanich, C. Grant, J. Krim, Dynamics of Vapor-Phase Organophosphates on Silicon and OTS, Tribology Letters, in press.

Thursday Afternoon, October 18, 2007

Biomaterial Interfaces

Room: 609 - Session BI+AS+NS-ThA

Surface Analysis and Related Methods for Biological Materials

Moderator: S.L. McArthur, University of Sheffield, UK

2:00pm **BI+AS+NS-ThA1 Creating and Probing Model Biological Membranes**, S.G. Boxer, Stanford University **INVITED**

During the past few years, our lab has developed a wide range of methods for patterning lipid bilayers on solid supports.¹ These 2D fluids are interesting both as a model for biological membranes and as a physical system with unusual properties. Methods have been developed for controlling the composition of patterned membrane corrals by variations on microcontact printing and microfluidics. Charged components can be moved around within these fluid surfaces by a form of 2D electrophoresis. The planar geometry of supported bilayer systems is ideal for high resolution imaging methods. The lateral (x-y) composition of membranes can be analyzed by high spatial resolution secondary ion mass spectrometry (SIMS) using the NanoSIMS 50 (Cameca) at the Livermore National Laboratory. Results will be described for simple membrane compositions² and phase separated domains³ suggesting the potential of this method for the analysis of membrane organization in complex membranes. Extensions of this approach to more complex systems including membrane-associated proteins will be described. If time permits, a complimentary optical imaging method offering sub-nm resolution in the z-direction (perpendicular to the membrane surface) will be described in the context of imaging conformational changes in membrane proteins.

¹J. T. Groves and S. G. Boxer, *Accounts of Chemical Research*, 35, 149-157 (2002).

²C. Galli Marxer, M. L. Kraft, P. K. Weber, I. D. Hutcheon and S. G. Boxer, *Biophysical Journal*, 88, 2965-2975 (2005).

³M. L. Kraft, P. K. Weber, M. L. Longo, I. D. Hutcheon, S. G. Boxer, *Science*, 313, 1948-1951 (2006).

2:40pm **BI+AS+NS-ThA3 Activation Thermodynamics for Phospholipid Flip-Flop in Planar Supported Lipid Bilayers Measured by Sum-Frequency Vibrational Spectroscopy**, T.C. Anglin, H. Li, J.C. Conboy, University of Utah

Basic transition state theory is used to describe the activation thermodynamics for phospholipid flip-flop in planar supported lipid bilayers prepared by the Langmuir-Blodgett / Langmuir Schaeffer method. Kinetics of flip-flop are determined as a function of varying temperature and lateral surface pressure for model bilayers of 1,2-distearoyl-sn-glycero-3-phosphocholine (DSPC) using sum-frequency vibrational spectroscopy (SFVS). The temperature and pressure dependence of the kinetics of DSPC flip-flop provide a complete description of the activation thermodynamics for flip-flop in the gel state, including free energy of activation, area of activation, and entropy of activation. This is the first description of phospholipid flip-flop according to basic transition state theory with explicit treatment of the free-energy dependence of the process and determination of the entropic contribution to the transition state.

3:00pm **BI+AS+NS-ThA4 Observation of Electrical Characteristics at Cells Membrane using by Electrostatic Force Microscopy**, Y.J. Kim, Myongji University, Korea, H.D. Kim, Seoul National University, Korea, Y.S. Kim, Myongji University, Korea, K.H. Lee, Seoul National University, Korea, C.J. Kang, Myongji University, Korea

Recent advances in atomic force microscopy (AFM) made it possible to investigate the biological materials in a single molecule level. Moreover, the AFM has been used to measure the fine structure of individual live cell even under physiological liquid. The images of cells measured show finer structure of cell boundary compared with those of SEM after fixation. Since electrostatic force microscopy (EFM) using conducting cantilever to AFM allows us to observe the electrical properties of the surface, it is also used to study the various properties of the cell membrane. Reportedly, it is known that protein expression depends on the cell kinds and shows the non uniform distributions, which causes the electrical potential difference on the cell surface in the local area. Thus mapping the electrical potential of a cell using EFM and comparing it with that of reference group, we are able to extract the information to differentiate the cells. In this work, we have identified the breast cancer cells (MCF7) and normal breast epithelial cells (MCF10A) derived from the same origin by fractal dimension analysis using AFM and the electrical properties of the cell membrane measured

from the EFM will be also discussed. The results show that AFM imaging with EFM measurement might be feasible methods for analyzing surface structures of living cells with high resolution, and it could provide new insights into cell surface structure.

3:40pm **BI+AS+NS-ThA6 Two and Three Dimensional Analysis of C. Albicans Biofilms with Cluster SIMS**, B.J. Tyler, S. Rangarajan, University of Utah, J. Moeller, H.F. Arlinghaus, University of Muenster, Germany

The high tolerance of microbial biofilms to important antimicrobial agents creates an import problem for treatment of infections associated with implanted medical devices. Several important hypotheses for this drug resistance involve mass transport limitation within the biofilms. We have been using 2_D and 3_D ToF-SIMS analysis to investigate transport of drugs and nutrients through *C. albicans* biofilms. Analysis has been performed using a novel ToF-SIMS system which incorporates a cryo-sectioning chamber and precise temperature control during analysis. This instrument has allowed us to map the distribution of key nutrients and drugs within the biofilm as well as to identify viable vs. nonviable cells. Through these studies, we have determined that the multiple cellular layers and extracellular polymers are not the most important mass transport barrier. Common drugs are able to permeate to the bottom of the biofilm within 5 minutes but are still unable to penetrate the cell wall of persister cells found at the base of the biofilm. Current work is focusing on cell wall and membrane changes within a subpopulation of the biofilm cells which apparently limits transport of antimicrobials into the cells. Multivariate statistical techniques have been crucial for the analysis of these samples and discussion of the relevant statistical methods employed will be presented.

4:00pm **BI+AS+NS-ThA7 XPS, ToF-SIMS and NEXAFS Investigation of Peptide Adsorption onto SAMs**, J.S. Apte, L.J. Gamble, D.G. Castner, University of Washington

The interactions between proteins and surfaces are critical to the success or failure of implants in the body. When adsorbed onto a synthetic surface, proteins often denature which can trigger the foreign-body response. It is therefore essential to develop methods to examine these interfacial phenomena. This work uses X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS) and near-edge X-ray absorption spectroscopy (NEXAFS) to characterize the structure of α -helix and β -sheet peptides adsorbed onto self-assembled monolayers (SAMs). The α -helix peptide is a 14-mer made up of lysine (K) and leucine (L) residues with a hydrophobic periodicity of 3.5. The β -sheet peptide is a 15-mer also made up of L and K residues with a hydrophobic periodicity of 2. A β -sheet peptide with the same structure but with valine (V) substituted for L was also studied since V has a higher tendency than L to form β -sheet structures. All peptides have the hydrophobic side-chains on one side of the peptide and the hydrophilic on the other. The SAMs studied were thiols on gold containing the ω -groups $-\text{CH}_3$, $-\text{OH}$, $-\text{COOH}$, $-\text{NH}_3^+$ and $-\text{CF}_3$. XPS nitrogen atomic percent was used to measure adsorption isotherms for the peptides. The α -helix peptide forms a monolayer (8.2% N) on the COOH-terminated SAM at an adsorption concentration 50 times lower than on the CH_3 -terminated SAM (0.01 mg/mL compared to 0.5). The surface coverage on the CH_3 SAMs appeared to be patchier compared to the COOH SAMs, since they had standard deviations of 2-3% N. Atomic force microscopy images of the adsorbed peptides were generated to examine this patchiness. Also, the adsorption process depended on buffer salt concentration. Little peptide adsorption was detectable on the methyl SAMs when adsorbed from a 0.1x buffer. ToF-SIMS was used to investigate the ratio of K to L characteristic mass fragments at 84 and 86 m/z, respectively. The 84/86 (K/L) ratio on CH_3 SAMs (1.2) was the same, within experimental error, as the ratio on COOH SAMs (1.1). Polarization dependent NEXAFS experiments at the nitrogen K-edge indicated the β -sheet was lying down on the SAM surfaces. The α -helical peptide exhibited significantly less polarization dependence than the β -sheet peptide, probably due to the different structure of the backbone amide groups in the α -helical peptide.

4:20pm **BI+AS+NS-ThA8 Isolation and Detachment of Small Cell Populations from a Thermoresponsive Polymer**, H.E. Canavan, K. Gallagher-Gonzales, J.A. Reed, University of New Mexico

Poly(N-isopropyl acrylamide) (pNIPAM) has proven to be an efficient and non-destructive means of detaching intact sheets of mammalian cells. In addition, cell sheets detached from pNIPAM maintain their association with the extracellular matrix (ECM) during and following detachment from a coated surface, enabling their use in tissue engineering. To date, the majority of those studying cellular interactions with pNIPAM have focused on harvesting large domains of cells for such tissue engineering applications. However, there are many other applications for which the non-

destructive release of smaller populations, or even isolated cells, is desirable. For example, isolated cells are required to ascertain the extent of transmembrane protein receptor upregulation when assaying the efficacy of cancer therapeutics on cell populations via flow cytometry (FC). In this work, arrays of thermoresponsive domains were fabricated to isolate defined populations of cells using a variety of techniques. The surface chemistry, thermoresponse, and topography of the films generated were verified via X-ray photoelectron spectroscopy (XPS), contact angle measurements, and atomic force microscopy (AFM), respectively, and compared to controls. The cell releasing properties of the films were characterized by incubating baby hamster kidney (BHK) and bovine aortic endothelial cells (BAECs). The behavior of the cells from isolated cells and small cell populations were characterized and compared to large cell population controls.

4:40pm **BI+AS+NS-ThA9 Surface Characterization of Ordered Nanopatterns made from Self-Assembly of Mixed Nanoparticles**, S. Pillai, G. Singh, The University of Aarhus, Denmark, C. Blomfield, A. Roberts, Kratos Analytical Ltd, UK, R.L. Meyer, P. Kingshott, The University of Aarhus, Denmark

Controlled patterning of surfaces with different chemistries and structures at nanoscale length scales is highly desirable for understanding the fundamental mechanisms of protein and cell interactions with biomaterials. The use of nanoparticles (NPs) to pattern surfaces by colloidal lithography or templating using one type of NP is well known for applications such as biosensors,¹ biomaterials² and tissue engineering.³ We demonstrate that by using mixed nanoparticles unique highly-ordered patterns can be obtained by simple self-assembly from buffer onto hydrophobic surfaces from both concentrated and dilute two-component NP suspensions.⁴ The new method uses suspensions of poly(styrene) (PS) NPs of different size ($d = 500$ to 60nm) with different NP ratios and volume fractions. The ordering is independent of the NP surface chemistry (sulfated, carboxylated, or aminated PS) or zeta potential and occurs over a broad pH range (4-10). The method is demonstrated for two types of hydrophobic surfaces, a commercial adhesive carbon tape and octadecyltrichlorosilane (OTS)-modified glass where patterns of hexagonally packed large particles are inter-dispersed with smaller particles. However, very poor ordering is achieved using gold, mica and HOPG (highly oriented pyrolytic graphite) as substrates. The morphologies of the nanoparticle assemblies are characterised extensively by SEM and AFM. In addition, XPS and ToF-SIMS are used to characterise the surface chemistry of the NP surfaces, which also provides knowledge of the mechanisms of NP assembly by showing that the ordering is most likely associated with charge screening by buffer salts resulting in an entropically driven assembly process. These preliminary results indicate that use of two component NP assemblies opens up the possibilities of decorating surfaces with well-defined chemical nanopatterns capable of selective attachment of different proteins and/or protein resistant molecules.

¹I. Willner, and E. Katz, *Angew. Chem., Int. Ed.* 2000, 39, 1180.

²H. Agheli, J. Malmstrom, E.M. Larsson, M. Textor, D.S. Sutherland, *Nano Lett.* 2006, 6, 1165.

³S.N. Bhatia, U.J. Balis, M.L. Yarmush, M. Toner, *FASEB J.* 1999, 14, 1883.

⁴R. Mukhopadhyay, O. Al-Hanbali, S. Pillai, A. Gry Hemmersam, R.L. Meyer, C.A. Hunter, K.J. Rutt, F. Besenbacher, S.M. Moghimi, P. Kingshott, submitted.

Nanometer-scale Science and Technology

Room: 616 - Session NS-ThA

Nanoscale Sensors

Moderator: N.A. Burnham, Worcester Polytechnic Institute, V. Vogel, ETH Zürich, Switzerland

2:00pm **NS-ThA1 Nanomechanics in Life Science**, M. Hegner, CRANN, University of Dublin, Ireland **INVITED**

Future diagnostics will depend on fast, specific assays to allow personalized medical diagnostics. Increasing efforts in our group have therefore been put into the development of instrumental measurement- and functionalization schemes for cantilever-based sensors for the label-free detection of physical- and chemical phenomena of biological interactions. Cantilevers arrays offer an elegant approach where physiological ligand-receptor binding interactions occurring on the sensor generate nanomechanical signals like bending or a change in mass that is optically detected in-situ. This allows a comprehensive characterization of biological interactions: The measured mass gives information about the binding event whereas the measured surface stress (structural changes) gives insights in the effects of the ligand on the biological systems. We report on new styles of combined

measurements in the field of proteomics, genomics and present fast dynamic assessments of micro-organism growth on cantilever arrays.

2:40pm **NS-ThA3 Nanomechanical Resonance of Clamped Silicon Nanowires Measured by Optical Interferometry**, M. Belov, University of Alberta, Canada, N.J. Quitoriano, S. Sharma, T.I. Kamins, Hewlett-Packard Laboratories, S. Evoy, University of Alberta, Canada

Highly-sensitive transducers for the detection and assaying of molecular systems based on nanomechanical beams have been proposed. Mechanical objects with lateral dimensions reaching the sub-100 nm range, with high resonant frequencies and quality factors, are now routinely fabricated using surface micromachining. The surface machining procedures employed in NEMS fabrication are inherently slow, offer limited yield and usually employ plasma-assisted etching techniques that may introduce surface damage and significantly change the mechanical properties of the resonating element. The direct growth of cantilevered nanowires by chemical vapor deposition methods (CVD) offers, alternatively, a potent way for the efficient production of high-quality NEMS resonators, with sub-50nm diameters, circular profiles and small clamping losses. We report the synthesis and characterization of vibrating silicon nanowires grown by CVD. These highly-oriented and clamped silicon structures were laterally grown from the sides of etched silicon posts using a metal-catalyzed chemical vapor deposition process. The diameters and lengths of the structures ranged from 40 to 400 nanometers and from 2 to 20 micrometers, respectively. The substrates were mounted onto a piezoceramic disc, installed in a vacuum chamber and actuated at varying frequencies. The laser beam focused onto the vibrating structure was reflected back and the detected signal, proportional to the deflection of the beam relatively to the substrate, was processed by a spectrum analyzer. The data were acquired at temperatures ranging from 77°K up to 293°K, and at pressures ranging from atmospheric down to the low 10^{-6} Torr. Typical resonant frequencies ranged from 1 to 20 MHz, in agreement with the Euler-Bernoulli analysis of vibrating structures. The resonant frequency of the nanowires typically showed a 0.25% increase as the nanowires were cooled from $T = 293^{\circ}\text{K}$ to $T = 77^{\circ}\text{K}$ as a result of changing Young's modulus. We also measured qualities of the resonators over the same temperature range. We discuss the energy dissipation processes that dominate the performance of these devices at various temperatures and pressures. This work was partially supported by Alberta Innovation and Science and by Hewlett-Packard Laboratories.

3:00pm **NS-ThA4 Electronic and Structural Properties of Ti and Pd Decorated Carbon Nanotubes**, A. Felten, J. Ghijsen, Namur University, Belgium, W. Drube, HASYLAB, Germany, R.L. Johnson, University of Hamburg, Germany, D. Liand, G. Van Tendeloo, University of Antwerp, Belgium, M. Hecq, Mons University, Belgium, C. Bittencourt, Materianova, Belgium, J.J. Pireaux, Namur University, Belgium

The study of the electronic interaction between metal atoms and carbon nanotubes is essential in order to improve performances of devices such as nano-transistors or gas sensors, for example to achieve low-resistance electrical contacts. Palladium and titanium decorated multiwall carbon nanotubes appear to be good candidates for such applications. In this work, both high resolution transmission electron microscopy (HRTEM) and photoemission spectroscopy have been used. Different amounts of Ti and Pd were evaporated onto both pristine and oxygen plasma functionalized carbon nanotubes. HRTEM images show the evolution of the morphology of the metal overlayer onto the nanotube surface. Evaporation of Ti on pristine nanotubes leads to a continuous coverage even for a very low amount of evaporated metal. In contrast, Pd deposition is characterized by the formation of small clusters. Oxygen plasma treatment is seen to improve the Pd cluster dispersion and size distribution. Analysis of the core and valence bands in photoemission spectroscopy reveals also strong differences between the two metals. The appearance of a new peak at lower binding energy on the C 1s level for Ti decorated nanotube is associated to the formation of Ti-C bonds (high coverage), with evidence of a charge transfer from titanium atoms to the carbon nanotube at low coverage. For Pd on the contrary, the absence of new features in both Pd 3d and C 1s spectra are suggesting the absence of a mixed Pd-C phase.

This work is financially supported by the Nano2Hybrids (EC-STREP-033311) and PAI 6/1 projects, and by DESY and the EC under contract RII3-CT 2004-506008 (IASFS).

3:40pm **NS-ThA6 Albert Nerken Award Lecture - On Surface Analysis and Nanotechnology: A Personal Odyssey**, R.J. Colton*, Naval Research Laboratory **INVITED**

This Albert Nerken Award address recounts some science and technology highlights of my career in areas of surface analysis and nanoscience—a personal odyssey on SIMS, SERS, STM, AFM, nanomechanics, molecular dynamics, and single molecule biosensing. This presentation will recount

* Albert Nerken Award Winner

the early observation of cationized molecular ions, magic numbers in large inorganic ion clusters, and UHV-SERS (of pyridine on silver of course). Early STM and AFM work addressed the then mysterious graphite imaging mechanism and the usefulness (once realized) of tip-surface force interactions. Examples of just how useful these force measurements can be led to new technology for surface and molecular mechanics with the help of molecular dynamics simulation. But can you really make a single molecule biosensor? We'll see. My presentation will close with a brief overview of NRL nanoscience programs on nanomaterials, nanoelectronics and nanosensors/devices.

4:20pm NS-ThA8 Combined Scanning Tunnelling Microscopy & Stress Measurements to Elucidate the Origins of Surface Forces, D.E. Meehan, N.T. Kinahan, Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN) & Trinity College Dublin, Ireland, T. Narushima, National Institutes of Natural Sciences, Japan, J.J. Boland, Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN) & Trinity College Dublin, Ireland

The concept of surface stress has been discussed extensively in terms of its role in controlling single crystal reconstruction and the growth morphology of thin films. In contrast, much less is known about the role of surface stress in surface chemical reactions, where differences in atomic size, electronegativity, and the incorporation of surface vacancies are likely to be of great importance, particularly in the case of nanoscale systems where surface effects are expected to dominate. In order to address the role of stress in surface chemical reactivity, we have developed a novel measurement system capable of investigating the underlying origins of surface stress in the context of atomic surface structure.¹ This system combines for the first time two distinct measurement capabilities: (i) measurement of surface stress based on the displacement of a large (50x10x0.28mm) silicon cantilever sample; and (ii) atomic resolution observation of the surface structure of the same cantilever sample. The former measurement incorporates a capacitive detection method capable of detecting energy changes with meV/atom resolution, while the latter measurement incorporates a scanning tunnelling microscope (STM) capable of observing structural changes occurring on the surface of the cantilever sample. Although non-trivial, the development of this combined measurement system was accomplished through careful electrical and mechanical design, accompanied by the incorporation of a novel sample heating method permitting localized heating of the cantilever sample. The system is also equipped with a device capable of applying external mechanical stress to the cantilever sample, thus enabling investigation of the effects of artificially induced stress on surface-based chemical reactions. The combined application of these two measurement capabilities yields detailed information regarding the atomic-scale structure, dynamics and interactions of the surface under investigation, which will ultimately be used to elucidate the origins of surface forces, and contribute to a deeper understanding of atomic-scale phenomena. Here, we present an introduction to the measurement system, a discussion on the challenges encountered during the development process, followed by a demonstration of the capabilities of the system itself.

¹ T. Narushima, N. T. Kinahan, J. J. Boland, Rev. Sci. Instrum. 78, 053903 (2007).

4:40pm NS-ThA9 A Hydrogen-Sensitive Polymer Nanostructure with Reversible Conductance, A.R. Laracuate, M. Yang, W.K. Lee, L. Senapati, P.E. Sheehan, S.C. Erwin, L.J. Whitman, Naval Research Laboratory

There is considerable interest in the use of polymer nanostructures for flexible electronics and sensors. We have previously written poly(3-dodecylthiophene-2,5-diyl) (PDDT) nanostructures between gold electrodes using thermal Dip-Pen Nanolithography (tDPN). tDPN uses a heatable atomic force microscopy cantilever to directly deposit "inks" that are solid at room temperature. When a PDDT-coated tip is heated close to or above the PDDT glass transition temperature, PDDT flows from the tip to the substrate surface with molecular-scale order.¹ We have discovered a novel property of such PDDT nanostructures: their conductivity can be increased by more than five orders of magnitude (from $<10^{-4}$ S cm^{-1} to 10 S cm^{-1}) by exposure to energetic electrons (5 keV). In contrast, spin-coated polymer thin films deposited on similar gold electrodes do not show any electron-induced conductivity. Interestingly, the electron-induced conductivity of the PDDT device reverts to a semi-insulating state by exposure to H₂, with a measurable change in conductance occurring following exposures as low as 6×10^{-4} Torr-s. Repeated shifting between the high and low conductivity states is possible. Significantly, exposure to oxygen, argon, or ambient air does not affect the conductance, suggesting that PDDT nanostructure devices deposited by tDPN have potential as H₂ sensors. We propose a mechanism for the conductance modulation based on H desorption and re-adsorption from the side-chains of the polymer. This mechanism is supported by a two terminal response theory based on Green's-function-based Landauer-Büttiker multichannel formalism.

Thursday Afternoon, October 18, 2007

¹ Yang et al., J. Amer. Chem. Soc. 128, 6774 (2006).

5:00pm NS-ThA10 CO₂ Sensing and CO and H₂O Interactions on Mats of Gold Nanoparticle Decorated GaN Nanowires, C. Berven, S. Chava, A. Heieren, R. Abdelrahman, D. McIlroy, University of Idaho, M.G. Norton, Washington State University

We report on the use of macroscopic mats of gold-nanoparticle-decorated GaN nanowires for the detection of CO₂ and the possible generation of CO₂ along with H₂ by interactions of CO and H₂O on the surfaces of the gold nanoparticles. The sensor consisted of a mat of GaN nanowires grown on a sapphire substrate (d ~ 1 cm) using a vapor-liquid-solid growth technique.¹ The mat was ~ 20 μm thick and the nanowire diameters and lengths were ~ 200 nm and ~ 5 μm , respectively. The nanowires were decorated with gold nanoparticles using a chemical vapor deposition process resulting in a continuous layer.² The gold was reduced by selective wet etching to create a sparse coverage of nanoparticles. Current-voltage (I-V) measurements were performed when exposed to vacuum, CO, CO₂ and water vapor. All measurements were performed at 300 K and in the dark at pressures of 50 Torr to 1 atm with a maximum vacuum of 5 mTorr. When exposed to just water vapor or CO the currents were only attenuated slightly from the vacuum state. When exposed to CO₂, the current was attenuated to a much larger degree. We have previously published data and a model to explain the sensitivity of similar device to methane³ which was due to the nanowires acting like Chem-FETs and where the selectivity was attributed to the morphology of the nanoparticles. When the device was exposed to CO followed by H₂O, we saw significant reduction in the current, similar to that of just CO₂ implying that what is being sensed is CO₂ that was the by-product of the reaction of CO + H₂O occurring on the gold nanoparticles. This is not unreasonable since nanoparticle gold is known to be quite reactive.⁴ As a consequence of CO₂ being detected after the mixing of CO and H₂O on the nanoparticles, we speculate that H₂ is also being generated giving a possible new mechanism for H₂ generation for fuel cells.

¹ V. Dobrokhov, C. Berven et al., J. Appl. Phys. 99, 104302 (2006)

² A. D. LaLonde, et al., J. Mater. Res. 20, 549 (2005)

³ V. V. Dobrokhov, C. Berven et al., Nanotechnology 17, 4135-4142 (2006)

⁴ M. Haruta, Applied Catalysis A: General 222, 427 (2001).

Tribology

Room: 617 - Session TR3+NS-ThA

Nanotribology and Nanomechanics

Moderator: P.R. Norton, University of Western Ontario, Canada

2:00pm TR3+NS-ThA1 Quantitative Direct-Observation Nanomechanical Testing in the Transmission Electron Microscope, O.L. Warren, Z. Shan, S.A.S. Asif, Hysitron, Inc., E.A. Stach, Purdue University, A.M. Minor, Lawrence Berkeley National Laboratory INVITED

The increasingly strong interest in measuring and understanding the sometimes extraordinary mechanical properties of nanomaterials and individual nanostructures has encouraged us to develop the first depth-sensing indenter compatible with quantitative nanomechanical testing in the transmission electron microscope (TEM). This ambitious undertaking has encountered a number of significant technological hurdles to overcome; nevertheless, we have achieved a versatile in-situ TEM instrument that compares favorably to leading conventional nanoindenters in terms of control modes and performance specifications. Scientifically, we have exploited the unique capabilities of this novel instrument to perform direct-observation nanoindentation into thin films and monolithic materials using sharp indenters, direct-observation nanocompression onto hollow and solid nanospheres as well as onto crystalline and amorphous nanopillars using miniature flat punches fashioned with a focused ion beam (FIB), and direct-observation bending of nanowires using the aforementioned flat punches. This presentation will share the powerful nature of time correlating the often discrete features of force-displacement curves to the accompanying morphological and microstructural changes that are directly observed in the corresponding TEM movies. Our research results range from some validating current mechanistic thinking to others that are counterintuitive and therefore a challenge to conventional wisdom.

2:40pm TR3+NS-ThA3 Tribology in Full View, L.D. Marks, A. Merkle, Northwestern University INVITED

Experiments in tribology have long suffered from the inability to directly observe what takes place at a sliding contact - the classic buried interface problem. As a consequence, although many friction phenomena at the

nanoscale have identified, there can be interpretation issues resulting from indirect or ex-situ characterization of the contact surfaces or because the experimental measurements are volume averaged, rather than giving direct insight into what is taking place at a single asperity-asperity contact. We have been recently exploiting a unique instrument that allows us to simultaneously slide a tip across a surface and look at the sample using transmission electron microscopy. Using this technique, we can directly image the nanoscale processes taking place at scales from 0.2 nm to microns, as well as obtain local chemical information from techniques such as electron energy loss spectroscopy. Using this instrument we have recently observed "liquid-like" deformation where the material is solid, but behaves as if it was a liquid due to very rapid surface diffusion, similar to the classic case of liquid-like growth of gold and silver particles; the formation of a graphitic transfer layer during sliding of tungsten on graphite as well as in-situ observation of graphitization of diamond-like carbon during sliding observed by electron energy loss spectroscopy. Further results include observation of wear debris during sliding of tungsten on graphite whose size is consistent with a dislocation standoff model and a recently published dislocation model for friction at the nanoscale. These and additional results will be described.

3:40pm TR3+NS-ThA6 Atomic-scale Friction on Ultra Thin Films, T. Filleter, W. Paul, R. Bennewitz, McGill University, Canada

Friction force microscopy (FFM) provides a powerful method to study the microscopic origins of friction. FFM has previously demonstrated that a single sharp asperity scanned over an atomically flat crystalline surface can exhibit a periodic stick-slip movement following the periodicity of the underlying lattice.¹ This has been observed for a range of different crystalline surfaces, including alkali halides and metal single crystals.^{2,3} In this work we have extended the FFM technique to study atomic-scale friction on a model solid lubricant system. The system was chosen to satisfy two criteria; be composed of materials with well known bulk atomic frictional properties, and to be topographically well defined with atomic resolution. The model system, which satisfies both criteria, are ultra thin films of KBr grown on a single crystal Cu(100) substrate. Ultra thin films have been grown under ultra high vacuum conditions with a thickness of up to five monolayers of KBr on an atomically flat Cu(100) substrate. The films have first been characterized using high resolution noncontact atomic force microscopy (NC-AFM). The first and second monolayers are found to grow in a carpet-like mode overtop of the existing Cu monatomic steps. Subsequent layers grow as rectangular islands with a minimum of corner and kink sites. Atomically resolved NC-AFM topography images of the films reveal a regular superstructure in the growth which is consistent with the KBr/Cu lattice mismatch. FFM measurements show that, as expected, the KBr films do act as a solid lubricant exhibiting lower friction than the bare Cu(100) surface. It is also observed that layers with a thickness of two and greater monolayers supports stable atomic stick-slip friction. The atomic frictional properties on films as thin as two monolayers (0.66 nm) are found to be consistent with that of bulk KBr. Lateral force maps of films exhibiting a topographic superstructure do not reveal a superstructure in the lateral force. The bare Cu(100) substrate has also been found to support stable stick-slip friction which has previously not been achieved.

¹ Bennewitz, R., *Materials Today*, May 2005, p.42

² Socoliuc, A., et. al, *Phys. Rev. Lett.* 92, 13 (2004) 134301/1-4

³ Bennewitz, R., et. al, *Phys. Rev. B* 60, 16 (1999) R11301-4.

4:00pm TR3+NS-ThA7 A Scanning Tunneling Microscope and Quartz Crystal Microbalance Study of Heating and Wear at a Sliding Interface, B.D. Dawson, S.M. Lee, J. Krim, North Carolina State University

In order to probe the rise in temperature of a sliding interface, a Scanning Tunneling Microscope and Quartz Crystal Microbalance has been combined to produce a rubbing action of a tungsten tip on a copper and indium electrode, respectively. The amplitude of oscillation¹ and wear of the electrodes is observed directly with the STM. Negative frequency shifts, which are indicative of a liquid-solid interface,² were observed for tungsten on indium rubbing. The chamber was heated and negative frequencies were observed at reduced sliding speeds, implying surface melting at the indium interface. This work was funded by The National Science Foundation and the AFOSR Extreme Friction MURI.

¹B. Borovsky, B. L. Mason, and J. Krim, *J. Appl. Phys.* 88, 4017 (2000).

²C. M. Flanagan, M Desai, and K. R. Shull, *Langmuir.* 16, 9825 (2000).

4:20pm TR3+NS-ThA8 Radial Breathing Mode Frequencies of Single-Walled Carbon Nanotubes Determined by Nanoindentation with an AFM, J. Fraxedas, ICMAB-CIN2-CSIC, Spain, G. Rius, F. Pérez-Murano, IMB-CNM-CSIC, Spain, A. Verdagué, ICN-CIN2, Spain

We have experimentally determined the radial breathing mode frequency of individual single-walled carbon nanotubes with a diameter of 1.3 nm by nanoindentation measurements using an Atomic Force Microscope with

commercial microfabricated silicon cantilevers with ultrasharp tips, evidencing the sensitivity of such instruments to frequencies in the THz range, well above the resonance frequencies of the cantilevers (ca. 130 kHz).¹

¹ *Europhys. Lett.* 78 (2007) 16001.

4:40pm TR3+NS-ThA9 The Importance of Nanoscale Meniscus Formation During High-Speed Sliding Contacts, C.M. Mate, R.N. Payne, Q. Dai, Hitachi San Jose Research Center, K. Ono, Hitachi Central Research Laboratory, Japan

To help determine the nanoscale origins of friction at high-speed sliding contacts, we have developed a High Shear Rate Apparatus using technology from the disk drive industry. This technique enables us to study friction, adhesion, and wear at ultra-high sliding speeds (1 to 100 m/s) for a small pad contacting a rotating disk with an atomically smooth surface and covered with a nanometer thick lubricant film.¹ We find that the sliding characteristics are dominated by the non-equilibrium meniscus of lubricant that forms between the pad and disk surfaces and by the vibrational dynamics of the sliding interfaces. In particular, the high sliding speed results in the friction, adhesion, and bounce dynamics being asymmetric with respect to sliding direction for a pad tilted at a slight angle with respect to the rotating disk surface. These differences are attributed to the mechanical action of the lubricant layer against the converging and diverging wedges of the pad, leading to an asymmetric meniscus to form around the contact pad at high speeds. Under suitable conditions, we also find a self-excited vibration of the slider pad, a few nanometers in amplitude, which is induced by friction hysteresis coupled with adhesion hysteresis.

¹C. M. Mate, R.N. Payne, Q. Dai, and K. Ono, "Nanoscale Origins of Dynamic Friction in an Asymmetric Contact Geometry", *Phys. Rev. Lett.* 97 (2006) 216104.

5:00pm TR3+NS-ThA10 Effects of Interfacial Structure on Atomic-Scale Friction Examined using MD, J.A. Harrison, M.T. Knippenberg, J.D. Schall, G. Gao, P.T. Mikulski, United States Naval Academy

The development of micron-sized devices, such as microelectromechanical devices, for terrestrial and space applications has prompted the need for protection of the surfaces of these devices. Self-assembled monolayers (SAMs), both alkanethiols and alkylsilanes, are possible candidate for the passivation and lubrication of these devices. The fundamental problem associated with controlling friction is a lack of understanding of the underlying atomic-scale processes that govern both friction and wear. We have conducted extensive molecular dynamics (MD) simulations using our AIREBO potential aimed at understanding the atomic-scale mechanisms of friction in SAMs. We have examined the way in which the contact forces present at the interface influence friction and made direction connections between interfacial structure and friction. We have examined the effects of changing the interface structure in several ways. Some of these include changing the structure of the SAM (e.g., end-group, chemical identity, hybridization, connectivity of chains) and altering the roughness of the interface. In this talk, we will discuss our most recent findings that have examined the way in which the structure of both the SAM and the tip influence friction. ** Work supported by The Office of Naval Research and The Air Force Office of Scientific Research as part of the Extreme Friction MURI.

Nanometer-scale Science and Technology

Room: 4C - Session NS-ThP

Nanometer-Scale Science & Technology Poster Session II

NS-ThP1 Aligned Growth of Carbon Nanotube using Protein Supramolecule. *S. Kumagai*, ATRL, Matsushita Electric Industrial Co., Ltd., Japan, *T. Ono*, Tohoku University, Japan, *R. Tsukamoto*, CREST, Japan Science and Technology Agency, Japan, *S. Yoshii*, *I. Yamashita*, ATRL, Matsushita Electric Industrial Co., Ltd., Japan

Carbon nanotubes (CNTs) have remarkable electrical, mechanical and chemical properties and are expected for broad applications in nanoelectronics. For practical applications, it is desirable to be able to synthesize a CNT in a particular location. In this study, we present novel catalytic nanoparticle (NP) positioning technique for CNT growth, which is one application of the Bio Nano Process (BNP)¹. We used cage-shaped protein, apoferritin (ϕ 12nm) to synthesize homogenous catalytic ϕ 7nm Co NPs within the cavity and the negatively charged outer surface of the apoferritin was used for electrostatic placement of the inner Co NP on Si substrate. We modified Si substrate with positively charged aminosilane molecule (3-aminopropyltriethoxysilane: APTES) and made electrostatic interaction between the ferritin and a surface-modified Si substrate place the ferritins with Co core on a Si substrate. Under appropriate ionic strength around neutral pH, negatively charged ferritins were adsorbed selectively on positively charged APTES-modified area that was fabricated on negatively charged SiO₂ surface. This electrostatic adsorption method successfully worked to place the ferritins on the APTES patterns. Heat treatment under O₂ gas removed outer protein shells selectively and left only Co NPs on the substrate. The substrate with NPs placed at the designed positions was set in a DC plasma chamber and heated. Firstly, the substrate was treated by H₂ plasma to reduce the NPs. After the treatment, CNT growth was conducted under C₂H₂/H₂ plasma. The SEM observation revealed that CNTs grew not on the Si substrate surface but on the NP patterned area. This indicated that the patterned Co NPs, which were synthesized through the BNP, worked as catalyst and determined CNT growth position. Here, we demonstrated novel technique for the CNT growth at the designed positions. We also have succeeded in the single NP placement by analyzing the electrostatic interaction precisely. Individual CNT growth from arranged single NPs will be realized for nanoelectronic devices such as field emission and vertical FET. Part of the experiment was done in Micro/Nanomachining Research and Education Center, Tohoku University. This study is partially supported by Leading Project of MEXT, Japan.

¹I. Yamashita, "Bio Nano Process: Fabrication of Nanoelectronic Devices Using Protein Supramolecules" Tech. Dig. 2006 International Electron Devices Meeting p.447.

NS-ThP2 Fabrication of TiN Nanopillar Field Emitters Templated by Porous Anodic Aluminum Oxide. *T.-M. Chen*, *J.-Y. Hung*, *F.-M. Pan*, *L. Chang*, National Chiao-Tung University, Taiwan, *S.-C. Wu*, National Nano Device Laboratories, Taiwan

Anodic aluminum oxide (AAO) has been widely used as a template for fabrication of nanostructured materials. In this study, we fabricated highly ordered TiN nanopillars on the Si substrate as electron field emitters using the AAO as the template. The nanopillars showed satisfactory field emission properties because of the high aspect ratio of the nanostructure and a low work function of TiN. To prepare the AAO template, an Al film 2 μ m thick was first thermally evaporated on a sputter-deposited TiN layer of 500 nm in thickness. The Al film was anodically oxidized in an oxalic acid electrolyte at room temperature, and the as-prepared AAO pore channels had a pore diameter about 60 nm. During the preparation of the AAO pore channels, the underlying TiN layer was anodically oxidized as well in the late stage of the AAO anodization, forming titanium oxide nanodots. The TiO_x nanodots were then used as the hardmask for dry-etching the underlying TiN layer, thereby transferring the AAO hexagonal arrangement pattern to the TiN layer leading to the formation of the well-ordered TiN nanopillar array. The nanopillars were \sim 200 nm in height and \sim 50 nm in diameter. The TiN nanopillar field emitter had a turn-on voltage of $<$ 5V/ μ m, which was defined as the voltage at which the field-emission began to exhibit linear Fowler-Nordheim field emission characteristics.

NS-ThP3 Growth and Characterization of Carbon Nanotubes on Biaxially Textured Ni Alloy Metallic Substrates without Additional Catalysts. *C. Varanasi*, University of Dayton Research Institute, *J. Bulmer*, *M. Mullins*, AFRL/PRPG, WPAFB, *J. Burke*, University of Dayton Research Institute, *J. Baca*, AFRL/PRPG, WPAFB, *L. Brunke*, University of Dayton Research Institute, *K. Yost*, *P. Barnes*, AFRL/PRPG, WPAFB

One of the common methods used to grow aligned CNTs on various substrates is chemical vapor deposition (CVD) using C₂H₂ or CH₄ as precursors. In this process, the substrates are processed prior to CVD such that metallic nanoparticles such as Fe, Ni etc. are formed on the surfaces to act as catalysts during the CVD process. However, the adhesion of CNTs to the substrates has been a problem in this approach as the nanoparticles are not integrated in to the substrate. In this study, biaxially textured Ni based alloy substrates were investigated as an alternate choice of substrates where the catalyst forms an integral part of the substrate to reduce the problem of adhesion of CNTs to the substrate. A biaxially textured Ni based substrate offers a surface with a well oriented grain structure (offering uniform growth) and the defects, grain boundaries, and the precipitates of the alloying additions etc., in the materials provide the necessary nucleation sites for the CNT growth. In the present work, several biaxially textured Ni alloy based metallic substrates were investigated to grow CNTs without giving any prior catalyst treatment to the substrates. A very high density of the CNT growth was observed on these substrates when suitable conditions were used using a CVD process with C₂H₂ as a carbon source. In the present talk, the experimental details to prepare the textured metallic substrates and CVD growth conditions used to grow the CNTs will be discussed. In addition, the characterization of textured substrates and CNTs grown on these substrates by using various characterization tools such as orientation image microscopy, Raman spectroscopy, TEM, and SEM will be presented.

NS-ThP4 Synthesis and Characterization of LaPO₄:Eu Nanotubes Prepared by the Sol-Gel Template Method. *M.J. Fisher*, *W. Wang*, *P.K. Dorhout*, *E.R. Fisher*, Colorado State University

Flat electroluminescent, plasma, and field emission devices demand materials with better stability, brightness, and industrial processing ability. Lanthanide ions (e.g. Eu⁺³) have sharp and intense emission lines, and exhibit high luminescence yields. Synthesis technique, particle size and heating process strongly affect the physico-chemical properties of lanthanide ion containing oxide materials. We have synthesized pure phase LaPO₄:Eu bulk-powders and nanoparticles via the sol-gel template method, which has a high industrial processing ability for pure-phase submicron scale materials. Materials were dried at 70 °C, and sintered at 650 °C. Powder X-ray diffraction indicates that at 70 °C the bulk powder is a mix of hexagonal and monazite phases, whereas at 650 °C the bulk-powder is a pure monazite phase. SEM showed the morphology of the nanoparticles is tubular. Luminescence spectra of both the bulk-powder and the nanotubes contain the typical Eu⁺³ peaks.¹ As the nanotubes diameter decreases from 200 nm to 20 nm, the luminescence spectrum developed a broad background. The temperature and particle size are major factors in the observed phase and luminescence properties of the materials synthesized. Site-selected excitation, energy dispersive spectroscopy, and x-ray photoelectron spectroscopy results will also be discussed.

¹ J. Dexpert-Ghys, R. Maurioct, and M. D. Fauxher, Journal of Luminescence 69, 203 (1996).

NS-ThP5 Carbon Nanotubes Synthesized from Electrospun Nanofiber. *J.-Y. Hong*, *M.-H. Lee*, *W.C. Choi*, *C.-Y. Park*, Sungkyunkwan University, Korea

One-dimensional carbide materials can be synthesized using multiwalled carbon nanotubes as templates by reaction with volatile oxide and/or halide species. Nanofibers may also be used as templates to produce carbon nanotubes with catalyst by temperature reactions. Electrospinning has received steadily increasing interest due to its ability to produce nanometer-sized fibers with a high level of reinforcement. Here we introduce carbon nanotubes (CNTs) synthesized using electrospun polyacrylonitrile (PAN) nanofibers. PAN and Fe composites as a catalyst were added to dimethylformamide (DMF) and the solution was stirred magnetically until PAN was fully dissolved. The spinning dope was transferred to a glass pipette mounted vertically in the electrospinning station. A voltage of 20kV was applied to the solution to start the spinning process. And the electrospun fibers were collected in a random mat. The PAN nanofibers were stabilized for 30min at 200°C and carbonized for 1h at 700°C. Then, the nanofibers were further heated to 900°C in acetylene as the carbon source. As the results of Raman spectroscopy and HR-TEM measurements, carbon nanotubes were synthesized, at the same time, it was confirmed that the size of CNTs varies directly as that of the electrospun nanofibers. From

these results, we suggest that the size of CNTs may be controlled by the PAN concentration in the electrospun nanofibers.

NS-ThP6 Field Emission Properties of Noble-Metal Coated Carbon Nanotube-Emitters, S.Y. Lee, D.H. Ryu, J.H. Yang, W.C. Choi, C.-Y. Park, Sungkwan University, South Korea

Because of their unique geometrical structure and high aspect ratio, many researchers have studied the potential applications of carbon nanotubes (CNTs) in field emission display and high current electron source that requires low turn on voltage, high current density and emission stability. To enhance the field emission properties of CNTs, the intertube distance, densities, alignments and work function are very important factors, so which have been extensively studied in recent years.¹⁻⁴ However, as yet, the sensible solution have not been obtained. In this study, we report the field emission properties of CNT-emitters coated with noble metals (Au, Ag, etc.) and their alloy (Ag-Cu). The vertical aligned multi wall CNTs and the sequential noble metal coating are synthesized by DC-plasma chemical vapor deposition in ambient of the mixed gas (C₂H₂ and NH₃) and DC-magnetron sputtering, respectively. The results of the field emission measurements show that the field emission properties of noble metal coated CNTs have remarkably improved in the emission current density and the turn on electric field. We can find one of the reason for the enhancement in the field emission properties from SEM images obtained from the samples before and after noble metal coating. The density of emitter can be controlled by the suitable coating conditions. Also, we can enhanced the contact resistance and the emission stability under coarse condition. We suggest that the enhanced filed emission performance of the noble metal coated CNTs emitters are attributed by the reducing the emitting sites and low work function, and low contact resistance. The details will be introduced.

¹Advanced Materials 14 (20), 1464-1468 (2002)

²Applied Physics Letters 90, 013120 (2007)

³Chemical Physics Letters 434, 92-95 (2007)

⁴Applied Physics Letters 80 (13), 2392 (2002).

NS-ThP7 Synthesis and Control of Carbon Nanotubes using Diffusion Mechanism of Fe Catalyst, W. Song, C. Jeon, Y.S. Shin, W.C. Choi, C.-Y. Park, Sungkyunkwan University, Republic of Korea

Since electrical properties of single-walled carbon nanotubes (SWCNTs) are primarily determined by its diameter and chirality, control of diameter is the crucial issue for application of CNTs-based electronic device. Thus, the preparation of catalyst with small and uniform size is essential factor to grow the SWCNTs with narrow diameter distribution. In this work, we investigate the growth of SWCNTs with narrow diameter distribution using a sandwich-like structures (Al/Fe/Al) deposited on Si substrate by DC magnetron sputter. The Fe catalyst layer is 1nm and the Al top-layer has various thickness from 1 nm to 10 nm. All samples are pre-annealed at 800°C by furnace in Ar ambient. Then, CNTs are grown by thermal chemical vapor deposition with C₂H₂, H₂ at 850°C for 10 min. A sort of CNTs are determined using Raman spectroscopy, and after pre-annealing, the variety of catalyst size with the thickness of top-Al layer is checked by X-ray photoelectron spectroscopy, transmission electron microscopy and magnetic force microscopy. It shows that the density and the kind of CNTs are depend on the thickness of Al top-layer and pre-annealing conditions. From these results, we can consider the following: (1) The catalyst is out-diffused through the Al top-layer by pre-annealing process, and the exposed catalyst size will be controlled by the thickness of Al top-layer and the pre-annealing conditions. Thus, we can be control a sort of CNTs. (2) This technique can be used for the device application that employ SWCNTs.

NS-ThP8 Phosphorylation of Multiwalled Carbon Nanotubes, T.M. Ndzimandze, X.Y. Mbianda, M. Johnson, University of Johannesburg, South Africa

Carbon nanotubes are among the most exciting new materials being investigated and synthesized, owing to their outstanding mechanical, electronic and optical properties.^{1,2} For more than a decade, the translation of these properties into realistic applications has been hindered by solubility and processing difficulties.³ Recently the development of efficient methodologies for covalent chemical modifications has raised hope for the use of these materials in various fields of application such as biosensors, vaccine and drug delivery systems, medical imaging, biomaterials, water purification⁴ etc. As part of an ongoing project on the application of carbon nanotubes, we which to report here the incorporation of phosphorus moieties on the end and side walls of the multiwalled carbon nanotubes obtained through NaClO oxidation followed by condensation reactions with alkyl or aryl chlorophosphates. Characterization of the phosphorylated multiwalled carbon nanotubes has been done by transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), thermal gravimetric analysis (TGA) and Raman spectroscopy. It is anticipated that these new compounds could provide

interesting biological activity in biological systems, and properties that might allow their incorporation into both organic and inorganic polymer matrices.

¹ M.F. Yu, B.S. Files, S. Arealli and R.S. Ruoff. Phys. Rev. Lett. 84 (2000), 5552

² R. Saito, G. Dresselhaus and M.S. Dresselhaus. Physical properties of carbon nanotubes, Imperial College Press; London, 1998

³ Gabriel G. Sauthier, Fraxedas J, Moreno-Manas M, Martinez M. T, Miravittles and Casabo J. Carbon 44 (2006) 1891-1897.

⁴ Son S. J., Reichel J, He B, Schuchman M and Lee S. B. J. Am. Chem. Soc. 127 (2005) 7316-7317.

NS-ThP9 Ring-shaped Emission Patterns from Carbon Nanotube Films, M. Zumer, V. Nemanic, B. Zajec, "Jozef Stefan" Institute, Slovenia, E. Bryan, R.J. Nemanich, North Carolina State University

Field emission patterns in the shape of perfect rings were observed on the luminescent screen of a specially designed triode cell with parallel electrodes. This cell is designed for investigation of 25.5 mm diameter flat samples. During the routine I-U measurements of broad-area flat cathodes, consisting of silicon or molybdenum substrates coated with carbon nanotubes (CNTs), rings appeared sporadically as relatively stable images among other field emission patterns like lobes and daisies. Their projected size was a few mm and was thus big enough to allow providing the analysis of their details. The origin of the electrons projected onto the screen is presumably a uniformly emitting cap atop of a long single wall CNT. This is consistent with models which predict high enhancement of the electric field and a ring-shaped pattern mainly as a result of imaging on a flat screen. The macroscopic value of the electric field at which rings were recorded was between 0.7 and 2.5 V/μm. The picture brightness analysis allows estimating the current corresponding to a particular ring and its brightness profile. The current of an individual ring was in the order of 2 - 4 μA. An outstanding finding of this study is a much greater angular width of the emitted beam for most of the rings compared to those that had been observed or predicted by reported calculations. The true mechanism that causes the difference between the model and our experiment is probably related to the atomic scale phenomena not included in their calculations.

NS-ThP10 Growth of Conducting Polypyrrole on Nanometer-Scaled Holes Array by Nanosphere Lithography, K.S. Kim, H.K. Moon, B.K. Lee, N.H. Kim, Y.H. Roh, Sungkyunkwan University, Republic of Korea

Conducting polymers are attractive materials that could be used at all levels of microelectronics as alternatives for metal and semiconductors. Particularly, polypyrrole is one of the most promising conducting polymers because of its ease of synthesis, environmental stability and higher sensitivity. Additionally, through combination with nano-fabrication, this conducting polymer will provide a valuable method of large-area, easy fabrication of nanometer-scaled conducting polymer patterns that would be useful in polymer-based electronics. In this work, we have used nanosphere lithography technique using polystyrene beads and oxygen plasma ashing technique. Using nanosphere lithography, oxygen plasma ashing and chemical vapor deposition, we could fabricate the nanometer-scaled holes (< 50 nm) array on the gold coated silicon substrate. The fabricated nanometer-scaled holes are well-ordered and have high density. The polypyrrole was successfully grown on the nanometer-scaled holes by electrochemical polymerization. We confirmed that the polypyrrole was grown toward the vertical direction of the substrate by AFM and SEM. The C-V measuring of obtained polypyrrole arrays was performed. The obtained electrical and geometrical properties of polypyrrole were superior to use electrical sensors. These results will also open the possibilities to fabricate the unique tools for the highly aligned emitters, diode and vertical-type field effect transistors.

NS-ThP11 Creating a Nano-Scale Porous Network of Porphyrin Molecules, C. Urban, M. Trelka, D. Ecija, Universidad Autonoma de Madrid, Spain, P. de Mendoza, Instituto Catalan de Investigaciones Quimicas (ICIQ), Spain, J.M. Gallego, Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), Spain, R. Otero, Universidad Autonoma de Madrid, Spain, A. Echavarren, ICIQ, Spain, R. Miranda, Universidad Autonoma de Madrid, Spain

Molecular self-assembly is a very promising alternative for designing and fabricating new nano-scale materials in the so-called "bottom-up" approach. In addition, the possibility of creating patterns of molecular networks with predefined, well-controlled geometries that could be used as a sort of nanoporous molecular material is opening new ways to fields as different as catalysis, electronics, or information storage. In particular, porphyrin molecules are of special interest due to the main role they play in a wide variety of biological, and chemical processes, and also photovoltaic devices. In this work we report on the self-assembly of meso-tetrakis (2,4,6-trimethyl) phenyl porphyrin (TMsP) when vapour-deposited in UHV conditions on Cu(100). For low coverages, the porphyrins can be found isolated or forming small clusters on the surface. Intramolecular resolution allows to determine their conformation and orientation, which come dictated by the

substrate, the porphyrin main axis being parallel to the Cu[110] directions. Upon increasing the coverage, the TMsP molecules self-assemble to form a square lattice. Interestingly, our calculation reveal that the intermolecular distance and relative orientation are almost independent of the substrate, indicating that the assembly process comes mainly dictated by the intermolecular forces. An open, nano-porous, square network of TMsP can also be fabricated by depositing the molecules on Cu(100) $c(2 \times 2) / N$. This surface, formed after adsorbing < 0.5 ML of N on Cu(100) and annealing to 600 K, is composed of square N islands, ~ 5 nm wide, separated by thin Cu lines, and has been used as a template to create arrays of metallic nanostructures. When the TMsP molecules are deposited on this surface, they nucleate almost exclusively on the Cu lines, leaving empty the N islands. In this way, by carefully controlling the width of the Cu lines and the molecule coverage, a film with 5 nm wide square pores of variable density that could be use as template for the growth of other nanoparticles can be created.

NS-ThP12 Effective Model for InGaAs/GaAs Quantum Dot with Material Mixing. *I. Filikhin, M.H. Wu, V.M. Suslov, B. Vlahovic*, North Carolina Central University

We model an InGaAs/GaAs quantum dot (QD), including the height dependence of the Ga content of the QD. The effect of material mixing on the electron energy spectra is considered, using the experimentally measured height dependence of the Ga fraction from Ref.¹ Our theoretical model is based on a single sub-band approach with an energy dependent effective electron mass. We apply an approach in which the combined effect of strains, piezoelectricity and interband interactions are simulated by an effective potential². It is shown that these effects may be taken into account in an effective manner using this approach. Based on our model, we perform an analysis of the results obtained by direct treatment of strain effects in Refs.³ ("ab initio" calculations). To prove the adequacy of our model, we compare the results obtained for energy spectra of few electrons tunnelling into InAs/GaAs QDs, with experimental capacitance-gate-voltage data⁴. We find that the effective method is valid for the case of material mixing in the InGaAs/GaAs quantum dot. In the case of a linear height dependence of the Ga fraction, the strength of the effective potential must be chosen to correspond with the averaged value for the Ga distribution function. Effects of the QD cross section and the Ga fraction distribution are studied. We also compare our results with those obtained from pseudopotential calculations⁵.

This work was partly supported by the Department of Defense and NASA through Grants, W911NF-05-1-0502 and NAG3-804, respectively.

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⁵ G. Bester, A. Zunger, X. Wu, D. Vanderbilt, Phys. Rev. B 74, 081305R (2006).

NS-ThP13 Guide for Optical Observation of Quantum Confinement or Quantum Size Effects at Room Temperature. *A.C. Diebold*, University at Albany, *J. Price*, SEMATECH

Although quantum confinement effect and quantum size effects are often considered low temperature phenomena, quantum confinement has been observed by ellipsometry at room temperature. This presentation will review examples of the observation of nanoscale effects at both low and room temperature. For example, the shift in the E1 critical point of thin silicon on insulator films has been shown to be due to quantum confinement and to roughly follow a $1/L^2$ trend.¹ XPS has also observed quantum size effects for multi-monolayer Al on Si(111).² Often, effect are seen despite the shift being less than the thermal energy, KT. Despite this, attempts to observe theoretically predicted resonances in the IR region of thin, polycrystalline TiN films failed. Based on this information we will propose some guides for when these effects can be observed at room temperature.

¹ J. Price and A.C. Diebold, J. Vac. Sci. Technol. B24, (2006), pp2156 - 2159.

² Abella, et al, Phys. Rev. Lett. 87, (2001) p156801.

NS-ThP14 Observation of Si/Co/Cu/Co Surface and Interface Processes for Nanostructure Formation by Scanning High Electron Energy Diffraction. *H. Shirinzadeh*, Materials and Energy Research Center, Iran

We observe the oxidation process on clean Si surfaces using high-resolution scanning reflection electron diffraction and form nanostructures on them, through focused electron-beam (EB) induced surface reactions. Si thermal oxidation occurs layer by layer, and the interface between the oxide film (< 1.5 nm thickness) and Si substrate becomes atomically abrupt. When the sample is heated to 700-800 °C, resulting in the exposure of a clean Si substrate. The typical width of the clean Si 'open windows' is about 10 nm. Using selective reactions during heating after the deposition of Si and Co

films on the patterned samples, Si and Co nanoislands with 25 nm size are formed on Si surfaces.

Magnetic of surface and ultrathin film.

NS-ThP15 Cerium Oxide Nanoparticles: Distinguishing Influences of Size from Chemical or Environmental Effects. *S.V.N.T. Kuchibhatla, A.S. Karakoti, S. Seal*, University of Central Florida, *M.H. Engelhard, D.R. Baer, S. Thevuthasan*, Pacific Northwest National Laboratory

Quantum confinement is a frequently observed and potentially useful property of nano-sized particles. An increase in band gap with the decrease in particle size is the phenomena of quantum confinement, typically valid when the particle size is approximately the exciton radius. However, because small particles are highly dependent on their surface, sample history and the local environments may also alter their properties and produce effects that may be interpreted as quantum confinement. We show that cerium oxide (Cerium, CeO₂) is impacted by such effects. Nanoceria is a potential material for a spectrum of applications including solid oxide fuel cells, catalysis, oxygen sensors, biomedical use, and chemical mechanical planarization. The major characteristic of ceria crucial for these applications is its oxygen storage capability (OSC). The OSC is rendered to ceria by the ability to effectively switch between the 3+ and 4+ oxidation states based on ambient conditions. In the nanoscale regime, there are a number of reports that analyzed the ceria particles synthesized under different conditions. Many authors have computed the band gap and particle size by comparing the experimental UV Vis absorbance data to the effective mass approximation (EMA) theory. While some of the researchers have hypothesized that counter acting phenomena like dielectric confinement will nullify the confinement effects in ceria, others have strongly supported the quantum confinement effect. We attribute the reason for such a discrepancy in the open literature to the differences in synthesis and characterization environments along with the agglomeration of nanoparticles. We have synthesized ceria nanoparticles in different aqueous media (DI water, poly (ethylene glycol), dextran, and glucose). The optical absorbance spectra were collected as a function of time. A careful analysis of these data has clearly indicated that the ceria nanoparticles change their oxidation state in solution with time and the rate is dependent on environment. This change in chemistry denies the possibility to use the EMA theory for the particle size interpretation from the absorbance data and also raises questions about reported band gap values. Transmission electron microscopy and X-ray photo electron spectroscopy have been used to compliment the results from UV Vis analysis.

NS-ThP16 Nanofabrication of Deep Sub-wavelength Plasmonic Waveguides for Characterization. *M. Lu, L.E. Ocola, S. Gray, G. Wiederrecht*, Argonne National Laboratory

Conceptual plasmonic devices show promising potential in transmitting and processing light at deep sub-wavelength scale.¹ The design and fabrication of a 100-nm-wide hybrid light-bending waveguide structure is discussed. Numerical modelling using finite-difference time-domain (FDTD) algorithm shows the device has an efficient confinement that is capable of transmitting light around 90 degree corners with minimal loss ($< 10\%$). The waveguide core is made by electron beam lithography and reactive ion etching with a bilayer resist. Sharp inner corners, which is important for low loss light bending, are achieved by an effective proximity correction (PEC) during e-beam lithography. The 800-nm-thick metal cladding is then formed by a selective electroplating. The wave guide is designed for near-field scanning optical microscope (NSOM) characterization, by leaving open the top of the waveguide. Achievement of this waveguide will enable submicron optical devices without the need of photonic crystals.

¹T-W. Lee and S. K. Gray, Optics Express, 13, 9652-9659 (2005).

NS-ThP17 Light Emission from STM Tunneling Junction on Ag Films Grown on Si(111) Surface. *J. Woo, H. Shim, G. Lee*, Inha University, South Korea

Detection of lights emitted from the STM tunneling junction has been developed as one of the local spectroscopic method to probe optical properties of surfaces. Recently, we set up the STM with light detection apparatus which uses an optical fiber for collection of the emitted light from the tunneling junction. We obtained STM-induced light emission spectra emitted from Ag surfaces grown in two different forms on a Si(111)-7x7 surface. As characterized by STM images, films with flat terraces are grown on a 7x7 surface of Si(111), while Ag clusters with varying sizes are formed on a H/Si(111)-1x1 surface. The light emission spectra shows peaks at the energy range of 2.3~2.7 eV. The peak positions in the emission spectra remain the same for different tunneling bias voltages, indicating that the emission is induced through inelastic tunneling. The detected light emission is interpreted as due to the decay of a tip-induced plasmon (TIP) which is confined between the tip and the surface. The differences in the peak position and in the energy broadening are attributed to the difference in

roughness and in shape. Comparison of the two surfaces and discussion will be made based on the theory of light emission from TIP.

Nanometer-scale Science and Technology

Room: 616 - Session NS-FrM

Nanolithography and Nanoprocess Technology

Moderator: S. Pang, University of Michigan, L. Montelius, University of Lund, Sweden

8:00am **NS-FrM1 Stencil Lithography - Quick & Clean Surface Patterning at Mesoscopic Scales**, *J. Brugger*, Swiss Federal Institute of Technology (EPFL), Switzerland **INVITED**

Physical lithography is a surface patterning technique that relies on the local physical vapor deposition of material through miniaturized shadow mask membranes. It is extremely useful for the formation of patterns, mainly thin structured metal films, in situations where lithography equipment is not available or when the surfaces don't allow the chemical and thermal process steps typically involved in photolithography. Stencil lithography is scalable from mm to sub-100-nm sizes, which makes it very interesting as method for rapid-prototyping of nanostructures without the risk of contamination, and for laboratories without access to high-end nanolithography equipment. The major challenges in stencil lithography are following: i) low-cost fabrication of nanostencils, ii) optimized mechanical properties of thin membranes, iii) deposition of material on stencil membrane, iv) precise alignment of nanostencils, v) recycling of stencils. In collaboration with our project partners¹ we have recently progressed in several of the above mentioned challenges. Stencils fabrication can be based on a set of advanced silicon micro and nanomachining steps (including UV, DUV, EBL and FIB) and a combination of DRIE and wet etching. The mechanical stability of the ultra-thin low-stress silicon nitride membranes could be considerably improved by topographic reinforcement rims. Surface structures of metals (e.g. Al, Au, Bi, Cr, Ti, Cu) on various surfaces (e.g. Si, SiO₂, SU-8, PDMS, PMMA, SAMs, freestanding SiN cantilevers, and curved surfaces) where systematically studied in terms of patterning accuracy. Thousands of sub-micrometer NEMS resonators were integrated in CMOS by stencil lithography and sacrificial etching. Variants of stencil methods include the local doping with ions, and local polymer etching using oxygen plasma. The talk will present the current state-of-the-art of nanostencil lithography, will highlight the strength of the method but will also discuss the current limits and challenges ahead to make it a truly reliable and scalable full-wafer nanofabrication method.

¹Integrated Project 'NAPA' European Commission and Swiss Federal Office OFES (Contract no. NMP3-CT-2003-500120).

8:40am **NS-FrM3 Nanopatterning of Functional Polymers by Thermal Dip-Pen Nanolithography**, *W.K. Lee, P.E. Sheehan*, U.S. Naval Research Laboratory, *W.P. King*, University of Illinois, Urbana-Champaign, *L.J. Whitman*, U.S. Naval Research Laboratory

Thermal dip-pen nanolithography (tDPN) uses a heated atomic force microscope (AFM) cantilever to deposit material that is solid at room temperature. The cantilever melts the solid ink on the tip, allowing precise control over its deposition onto the surface.¹ This method for nanolithography has proven particularly effective for depositing polymers.² Both the polymer thickness and lateral dimensions can be controlled to nanometer tolerances by controlling the tip heating power and the writing speed. Using tDPN, controlled layer-by-layer deposition of polymer has been achieved as well as molecular alignment along the writing direction of the cantilever. Many different functional polymers have been successfully deposited on silicon oxide substrates, including those that are temperature responsive, semiconducting, piezoelectric, and light-emitting, demonstrating that tDPN is a flexible nanolithography tool for polymer deposition and patterning. We will present our characterizations of the deposited polymers and report how tDPN can be used to optimize their properties. For example, poly(N-isopropylacrylamide) [pNIPAAm] nanostructures written by tDPN undergo a hydrophilic-to-hydrophobic phase transition induced by temperature that allows the structures to controllably capture and release proteins. We use carboxylic acid functionalized pNIPAAm as a tDPN "ink" that can be grafted onto an epoxy-terminated SAM substrate. We observe the temperature-dependent phase transition by monitoring the adhesion forces of the pNIPAAm with AFM. Finally, we will describe functional polymer patterns created by tDPN in ultra-high vacuum.

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

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

9:00am **NS-FrM4 Shadow Edge Lithography for Wafer-Scale Nanomanufacturing**, *J. Bai, J.-H. Chung*, University of Washington

Many upcoming applications, such as nanoelectronic circuitry, single-molecule based chips, nanofluidics, chemical sensors, and fuel cells, require large arrays of nanochannels and nanowires. The commercialization of these state-of-the-art nanostructure-based devices, which are far superior to the microdevices, is challenged by the patterning consistence, throughput, and cost. For the purpose, we propose the shadow edge lithography (SEL) as a silicon (Si) wafer-scale nanomanufacturing method. The shadow effect of "line-of-sight" in high-vacuum evaporation is theoretically analyzed to predict the geometric distributions of the nanoscale patterns. Nanoscale patterns are created by the shadow of aluminum (Al) edges that are prepatterned using a conventional microfabrication method. Feasibility of the method is demonstrated by the fabrication of nanoscale gaps, which are further used to fabricate either arrays of nanochannels or nanowires on 4-inch Si wafers. The fabricated nanogaps have widths ranging from 15 nm to 100 nm on the 4-inch Si wafers using an e-beam evaporator (NRC 3117, Varian Inc., Palo Alto, CA). Considering the virtual source during the e-beam evaporation, the experimental results agree well with the theoretical prediction. Furthermore, by using the height differences in the pre-patterned Al edges to compensate the geometric distributions of the shadow effect, it is found that the uniformity tolerance in nanogap width can be 2 nm or 5% across the entire 4-inch Si wafers at a resolution down to 20 nm. Upon the nanogap fabrication, arrays of nanochannels are fabricated by reactive ion etching (RIE) using the e-beam evaporated Al layers as the etching mask; or arrays of chromium (Cr) nanowires are fabricated by depositing 15-nm Cr layer on the nanogap patterns followed by an Al lift-off. The fabricated Cr nanowires are further used as the RIE mask to produce arrays of Si nanowires on silicon-on-insulator (SOI) wafers. Our results show that that the evaporated Al layers can be used as the RIE or lift-off mask to transfer the nanoscale patterns with clear configuration and high yield. Thus, the proposed SEL provides a robust method for wafer-scale manufacturing for sub 50-nm structures, which may exceed the performance of the other nanopatterning methods. Because of the parallel processing nature of the SEL, it has a potential to become a key technology for massive nanomanufacturing with cost effectiveness.

9:20am **NS-FrM5 Conformal Intermediate Layers for Anti-Adhesive Coatings on Metal Molds**, *H. Schiff*, Paul Scherrer Institute, Switzerland, *S. Bellini*, ETH Zürich, Switzerland, *H. Sehr*, *J. Gobrecht*, Paul Scherrer Institute, Switzerland

Stamps for nanoimprint lithography (NIL)¹ need an excellent anti-sticking surface property, which is easy to achieve with silane chemistry, if molds are made from silicon.² Other stamp materials, such as metals, need intermediate layers, preferably made from silicon oxide (SiO₂).³ Then the chlorosilane group of commercially available fluorinated silanes can react with hydroxyl groups on the oxide surface under elimination of hydrochloric acid, and covalent binding can be achieved which is durable in hot embossing and injection molding processes. Two routes were developed to achieve a thin intermediate coating of stamps, one based on the thermal evaporation of Ti/SiO₂, and the other on Plasma Enhanced Chemical Vapor Deposition (PECVD) of SiO₂. Since evaporation is directed, a full conformal coverage of the surface, particularly if high aspect ratio structures need to be coated, is often only achieved with specific mounting setups or several subsequent coating steps from different directions. This is time consuming due to the evacuation steps and only results in limited thickness homogeneity. Therefore the PECVD was developed and applied on different metals (brass, nickel, steel) without the use of the Ti adhesion promoter. The process is conformal and 20 nm thick coatings can be achieved with high homogeneity. It is more flexible and can be performed within a few minutes. The most crucial point is the adhesion of the thin interlayer to the stamp surface during the demolding process. The durability of both layers was tested using different mechanical methods and coated molds were used in hot embossing and injection molding. Several thousand injection molding cycles are possible, and to date it seems that the durability of the new PECVD coating matches that of the evaporated films. This is a further step to establish anti-sticking coating techniques in high volume manufacturing of polymer parts by replication, and to enlarge the range of stamp materials used for molding and NIL.

¹ Schiff H., Kristensen A., In *Handbook of Nanotechnology*, Vol. ed. B. Bhushan, second edition, Springer Verlag, Berlin, Germany, 239-278 (2007).

² Schiff H., Saxer S., Park S., Padeste S., Pielas U., Gobrecht J., *Nanotechnology* 16, S171-S175 (2005).

³ Park S., Schiff H., Padeste C., Schnyder B., Kötzt K., Gobrecht J., *Microelectronic Eng.* 73-74, 196-201 (2004).

9:40am **NS-FrM6 Nanoscale Electron Beam Induced Etching (EBIE)**, *M.G. Lassiter, D. Smith*, University of Tennessee, *T. Liang*, Intel Corporation, *P.D. Rack*, University of Tennessee

Traditionally, high-resolution nanomachining utilizes a gallium focused ion beam (FIB) to physically sputter away material or dissociate a precursor material to deposit material. During the process, gallium ions are implanted into the surface of the substrate and leave undesirable effects, such as reduced transmission of clear area repairs in photomasks; otherwise damaging or change the remaining material. The use of electron beam induced processes for high spatial resolution nanopatterning has recently been developed as an alternative to FIB. The electron beam induces the dissociation of a precursor gas to cause a reaction at the surface of the material. This reaction either deposits material or removes material, depending upon the precursor/substrate combination. This presentation focuses on the latter, electron beam induced etching (EBIE) of materials. Electron beam induced etching provides superior spatial resolution and can offer much better etching selectivity compared to FIB. Additionally electrons do not damage the substrate materials because of their relatively small mass compared to gallium ions. This work characterizes the process of high resolution EBIE of various relevant materials. The effects of electron beam parameters such as accelerating voltage, beam current, and the scanning parameters are investigated, as well as the relationship of the beam parameters to the gas parameters such as pressure and injection needle position. Furthermore, various precursor gases were examined, and the effects on spatial resolution, etching rate, and selectivity against other materials are determined. A 3-D Monte Carlo type simulation of the etching process has also been developed and simulation results will be compared to experimental results.

10:00am **NS-FrM7 Atomic-Scale Device Fabrication in Silicon**, *M.Y. Simmons*, University of New South Wales, Australia **INVITED**

One driving force behind the microelectronics industry is the ability to pack ever more features onto a silicon chip, by continually miniaturising the individual components. However, after 2015 there is no known technological route to reduce device sizes below 10nm. In this talk we demonstrate a complete fabrication strategy towards atomic-scale device fabrication in silicon using phosphorus as a dopant in combination with scanning probe lithography and high purity crystal growth. A key aspect of being able to build single atom devices is the ability to distinguish single atoms on and in the silicon surface. We demonstrate a detailed understanding of the surface chemistry to identify and control individual P atoms, using phosphine as a dopant source in silicon.¹ We can place individual phosphorus atoms in silicon at precise locations² and encapsulate them in epitaxial silicon with minimal diffusion and segregation of the dopants.³ Separate studies have confirmed the range of electrical transport characteristics that can be achieved using phosphorus as a planar, buried dopant in the absence of any lithographic patterning by STM.⁴ We then demonstrate that we can pattern this planar dopant layer using STM lithography and encapsulate with low temperature silicon epitaxy without lateral diffusion of the dopants out of their lithographic regions. Electrical device characteristics at low temperatures confirm the presence of the lithographic patterning as we observe a cross-over from 2D to 1D transport in the phase coherence length.⁵ Using this process we have fabricated conducting nanoscale wires with widths down to ~8nm, tunnel junctions, single electron transistors and arrays of quantum dots in silicon.⁶ We will present an overview of the devices that have been made with this technology and highlight some of the challenges to achieving atomically precise devices.

¹ H.F. Wilson et al., Physical Review Letters 93, 226102 (2004).

² S. R. Schofield et al., Physical Review Letters 91, 136104 (2003).

³ K.E.J. Goh et al., Applied Physics Letters 85, 4953-4955 (2004).

⁴ K.E.J. Goh et al., Phys. Rev. B 73, 03541 (2006).

⁵ F.J. Rueß et al., Nano Letters 4, 1969 (2004).

⁶ F.J. Rueß et al., Small 3, 567 (2007); Nanotechnology 18, 044023 (2007); Phys. Rev. B Rapid 85, 121303 (2007).

10:40am **NS-FrM9 Advances in Atom Beam Nanolithography: A New Exposure Tool, Masks, and Resists**, *B. Craver, H. Guo, A. Roy*, University of Houston, *J. Strahan*, University of Texas, *J. Reynolds, H. Nounu*, University of Houston, *C.G. Willson*, University of Texas, *J.C. Wolfe*, University of Houston

Atom beam lithography (ABL) is a proximity printing technique where a broad beam of energetic neutral atoms floods a stencil mask and transmitted beamlets transfer the mask pattern to resist on a substrate. ABL exposures are equivalent to those formed by ions in every respect (mass, energy, angular distribution, diffraction, scattering within the mask, resist, and wafer) except for the charge of the lithography particles. ABL images, being formed by electrically neutral particles, are completely free of charge-related artifacts that occur, often unpredictably, in ion printing due to ambient electromagnetic fields and the buildup of electrostatic charge on the mask and wafer. In this paper, we describe an integrated toolset for

fabricating high density arrays with an arbitrary unit cell by atom beam lithography. The 30-50 keV exposure tool incorporates a high brightness multicusp ion source and a high pressure gas cell to convert helium ions to energetic helium atoms through charge transfer scattering. A mechanical mechanism has been developed for translating the mask image over the wafer with 1 nm precision. Nano-arrays can, thus, be fabricated using a large-area template mask consisting of a silicon membrane with a periodic array of circular openings. The mask image is translated over the wafer to create, simultaneously, an array of identical unit cells, each corresponding to an individual mask opening. Silicon stencil masks, up to 700 nm thick, are fabricated with ~50 nm openings using a magnetically enhanced, molecular bromine plasma. A plasma-deposited coating of poly(methylmethacrylate) protects the silicon membrane from ion implantation damage and thickens the mask to enhance lithographic contrast. The mask can be coated with sputtered gold to shrink the mask openings as needed for the particular application. Pattern shifts during exposure are imperceptible at the nanometer-scale. Linewidths of 25 nm have been achieved and we anticipate reporting sub-20 nm linewidths at the conference. High resolution resists with optimized sensitivity, currently under development, will be reported at the conference. Potential applications in rapid prototyping and imprint lithography template fabrication will be discussed.

11:00am **NS-FrM10 Resonances in Secondary Electron Yields from Capped Multilayer Mirrors**, *E. Loginova, B. Yakshinskiy*, Rutgers University, *S. Yulin, T. Feigel*, Fraunhofer Institut (IOF), Germany, *J. Keister*, Brookhaven National Laboratory, *T. Lucatorto, C. Tarrío, S. Hill*, National Institute of Standards and Technology, *O. Dulub, U. Diebold*, Tulane University, *M. Chandok, M. Fang*, Intel Corporation, *T.E. Madey*, Rutgers University

The magnitude of secondary electron yield (SEY) at EUV wavelengths is a major factor in determining contamination rates of multilayer mirrors (MLMs) in EUV projection optics, and we have found striking resonance effects in measurements of SEY from MLMs. Low energy secondary electrons (0 to ~20 eV) can cause dissociation of adsorbed hydrocarbons from the background gas, and lead to carbon film growth on MLM surfaces. SEY data (electrons/photon) were measured using synchrotron radiation over the range 40 eV to 180 eV for TiO₂ and Ru single crystals (clean, O-covered, C-covered, air exposed) and compared with measurements for Mo/Si multilayer films capped by Ru, TiO₂, and RuO₂. For photon beams incident at 45 degrees, the shapes of the curves for Ru multilayers, especially the maxima at ~65 eV due to the Ru 4p excitation, are very similar to the data for pure Ru; such similarities are found also for a TiO₂ crystal and TiO₂-capped MLMs. Thus, the cap layer properties dominate the SEY characteristics: this agrees with theory, which predicts that a film several nm thick contributes ~90% to the SEY characteristics of the mirrors. For incidence angles close to the surface normal, and for photon energies near 92 eV (13.5 nm), dramatic energy- and angle-dependent resonances in SEY are observed for the capped MLMs, with SEYs 2 to 3 times higher than off-resonance. Calculations show excellent correlations between the photon electric field strength in the cap layers and the angular-dependent SEYs.

11:20am **NS-FrM11 Miniature Machines for Nano-Scale Research and Manufacturing: A New Model for Equipment and Instrumentation**, *M.L. Culpepper*, Massachusetts Institute of Technology **INVITED**

Advances in nanopositioning technology make it possible to (a) increase the pace of discoveries (via instruments) and (b) improve the pace with which discoveries are manufactured and commercialized. There are a growing number of instrument/equipment applications wherein small-scale (meso- and micro-scale) nanopositioners are needed in order to achieve commercially viable speeds (kHz), resolution (Angstroms), cost (\$100s) and thermal stability (Angstroms/min). New small-scale nanopositioners are emerging to meet these requirements, however there are a few technological issues that must be addressed. The purpose of this talk is to cover (i) the fundamental reasons that will compel the creation of these nanopositioners, (ii) the economic and performance benefits that they will enable and (iii) how partnerships can help to overcome the few remaining technical/scientific issues. The import of partnerships between machine design researchers, nanofabrication process researchers, and manufacturers will be stressed as well as a plan that is focused upon creating these partnerships. The talk ends with a vision for a new class of small-scale, low-cost instrument/equipment platforms to support a new model for nano-scale research and manufacturing.

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McChesney, J.L.: EM+NS-TuA11, 10
McIlroy, D.: NS-ThA10, 32
McLachlan, J.: AS+BI+NS-WeA2, 21
Meehan, D.E.: NS-ThA8, 32
Merkle, A.: TR3+NS-ThA3, 32
Meyer III, H.M.: NS1+BI-WeA8, 23; TR2+BI+NS+MN-ThM2, 27
Meyer, R.L.: BI+AS+NS-ThA9, 31
Michel, R.: AS+BI+NS-TuM3, 6
Mikulski, P.T.: TR3+NS-ThA10, 33
Miller, B.P.: TR2+BI+NS+MN-ThM9, 28
Miller, W.: NS-ThM4, 26
Minor, A.M.: TR3+NS-ThA1, 32
Minowa, H.: AS+BI+NS-WeA3, 21
Miranda, R.: NS-MoM1, 1; NS-ThP11, 35
Moeller, J.: BI+AS+NS-ThA6, 30

Moellers, R.: AS+BI+NS-TuM12, 7
Mokaberi, B.: NS-MoA6, 5
Moon, D.W.: AS+BI+NS-TuM1, 6
Moon, H.K.: NS-ThP10, 35
Moore, J.C.: NS-TuM11, 9
Morales, J.: NS-TuM4, 8
Morkoc, H.: NS-TuM11, 9
Moulder, J.: AS+BI+NS-WeA1, 21
Mullen, T.J.: NS-MoM8, 2
Mullins, M.: NS-ThP3, 34
Munro, A.M.: EM+NS-TuA10, 10
Murduck, J.M.: NS-ThM4, 26
Murray, A.J.: NS-TuP14, 15
Murray, P.T.: PS1+NS-WeM1, 18

— N —

Nakamura, J.: NS-ThM7, 27
Nakano, R.: NS-TuP12, 15
Nakata, Y.: AS+BI+NS-TuM13, 7
Nanba, N.: NS-TuP11, 14; NS-TuP12, 15
Narushima, T.: NS-ThA8, 32
Nasrullah, A.: PS1+NS-WeM10, 20
Ndzimandze, T.M.: NS-ThP8, 35
Nealey, P.F.: PS1+NS-WeM12, 20
Nelson, M.: NS1+BI-WeA1, 22; NS-MoA9, 5
Nemanic, V.: NS-ThP9, 35
Nemanich, R.J.: NS-ThP9, 35; TR2+BI+NS+MN-ThM9, 28
Niehuis, E.: AS+BI+NS-TuM12, 7
Nigra, M.M.: EM+NS-TuA4, 10
Nihonyanagi, S.: AS+BI+NS-WeA3, 21
Ninomiya, S.: AS+BI+NS-TuM13, 7
Niraj, N.P.P.: NS-ThM6, 27
Nishikawa, O.: NS+MS-TuA10, 12; NS-TuP11, 14
Nishioka, K.: PS1+NS-WeM9, 19
Nogami, J.: NS2+EM-WeA3, 24
Noguchi, H.: AS+BI+NS-WeA3, 21
Norton, M.G.: NS-ThA10, 32
Norton, P.R.: AS+BI+NS-WeA2, 21
Notte, J.: NS+MS-TuA8, 11
Nounu, H.: NS-FrM9, 39

— O —

Ocola, L.E.: NS-ThP16, 36
Ogletree, D.F.: NS+EM-WeM11, 18
Oh, Y.-J.: NS1+BI-WeA5, 23
Ohlhausen, J.A.: AS+BI+NS-WeA10, 22
Ohta, T.: EM+NS-TuA11, 10
Ohuchi, F.S.: NS-TuM4, 8
Okita, A.: NS-ThM7, 27
Okumura, D.: NS-TuP12, 15
Olmstead, M.A.: NS-TuM4, 8
Oncins, G.: TR2+BI+NS+MN-ThM7, 28
Ono, K.: TR3+NS-ThA9, 33
Ono, T.: NS-ThP1, 34
Oohara, W.: PS1+NS-WeM3, 19
Osgood, R.M.: NS-TuP5, 13
Otero, R.: NS-MoM1, 1; NS-ThP11, 35

— P —

Pachuta, S.J.: AS+BI+NS-WeA9, 22
Palmer, J.S.: NS-MoM2, 1
Pan, F.-M.: NS-ThP2, 34
Pang, S.W.: NS1+BI-WeA9, 23
Park, B.-J.: AS+BI+NS-TuM5, 6
Park, C.G.: NS-TuM3, 8
Park, C.-Y.: NS-ThP5, 34; NS-ThP6, 35; NS-ThP7, 35
Park, J.-W.: NS-TuP9, 14
Park, K.S.: NS-TuM3, 8
Park, S.-M.: PS1+NS-WeM12, 20
Parpia, M.: NS-MoA9, 5
Passacantando, M.: NS-MoA4, 5
Patrino, N.: AS+BI+NS-WeA2, 21
Paul, W.: TR3+NS-ThA6, 33

Payne, R.N.: TR3+NS-ThA9, 33
Pearton, S.J.: EM+NS-MoA7, 4
Pérez-Murano, F.: TR3+NS-ThA8, 33
Pesetski, A.A.: NS-ThM4, 26
Petsev, D.N.: NS1+BI-WeA5, 23
Petuskey, W.T.: NS+EM-WeM6, 17
Phillips, J.: AS+BI+NS-TuM9, 7
Picraux, S.T.: NS+EM-WeM2, 17; NS+EM-WeM6, 17; NS-MoA7, 5
Pihosh, Y.: NS-TuP3, 13
Pillai, S.: BI+AS+NS-ThA9, 31
Pireaux, J.J.: NS-ThA4, 31
Plumridge, J.: AS+BI+NS-TuM9, 7
Poole, P.J.: EM+NS-MoA6, 3
Potapenko, D.V.: NS-TuP5, 13
Pradhan, D.: EM+NS-TuA5, 10
Price, J.: NS-ThP13, 36
Przybysz, J.X.: NS-ThM4, 26

— Q —

Quitoriano, N.J.: NS-ThA3, 31

— R —

Rack, P.D.: NS2+EM-WeA11, 25; NS-FrM6, 39
Rading, D.: AS+BI+NS-TuM12, 7
Raes, M.: NS-TuP2, 13
Raman, S.: AS+BI+NS-WeA1, 21
Rangan, S.: EM+NS-MoA2, 3
Rangarajan, S.: BI+AS+NS-ThA6, 30
Ratna, B.R.: NS-MoM5, 1
Rauls, E.: NS-MoM12, 2
Raymond, S.: EM+NS-MoA6, 3
Reason, M.: EM+NS-MoA8, 4
Reed, J.A.: BI+AS+NS-ThA8, 30
Reinicke, M.: PS1+NS-WeM11, 20
Ren, F.: EM+NS-MoA7, 4
Reniers, F.: NS-TuP2, 13
Renner, T.: NS1+BI-WeA1, 22; NS-MoA9, 5
Requicha, A.A.G.: NS-MoA6, 5
Reshchikov, M.A.: NS-TuM11, 9
Responte, D.J.: AS+BI+NS-TuM3, 6
Reynolds, J.: NS-FrM9, 39
Ritz, C.S.: NS+EM-WeM1, 17
Rius, G.: TR3+NS-ThA8, 33
Roberts, A.: BI+AS+NS-ThA9, 31
Robertson, M.D.: EM+NS-MoA6, 3
Rodriguez, B.J.: NS2+EM-WeA11, 25; NS-TuM13, 9
Roh, Y.H.: NS-ThP10, 35; NS-TuP1, 13; NS-TuP4, 13; NS-TuP6, 13; NS-TuP9, 14
Rosenberg, R.A.: NS2+EM-WeA4, 24
Ross, F.M.: NS+EM-WeM3, 17
Rossi, F.: NS1+BI-WeA10, 23
Rotenberg, E.: EM+NS-TuA11, 10
Roy, A.: NS-FrM9, 39
Rozhok, S.: NS1+BI-WeA1, 22; NS-MoA9, 5
Rubloff, G.W.: NS1+BI-WeA4, 23
Ruchhoeft, P.: PS1+NS-WeM10, 20
Rudolph, M.: PS1+NS-WeM11, 20
Ruzycki, N.: NS-TuM4, 8
Ryan, P.M.: NS-ThM6, 27
Ryu, D.H.: NS-ThP6, 35

— S —

Saito, T.: NS-ThM7, 27; NS-TuP10, 14
Saito, Y.: NS+MS-TuA10, 12
Sakai, Y.: NS-ThM7, 27
Samukawa, S.: PS1+NS-WeM9, 19
Sanada, N.: AS+BI+NS-WeA1, 21
Sankaran, R.M.: PS1+NS-WeM5, 19
Santucci, S.: NS-MoA4, 5
Sanz, F.: TR2+BI+NS+MN-ThM7, 28
Sapsford, K.E.: NS-MoM5, 1
Schall, J.D.: TR3+NS-ThA10, 33
Schiettekatte, F.: EM+NS-MoA6, 3

Schift, H.: NS-FrM5, 38
Schmid, H.: NS-MoM10, 2
Scudiero, L.: NS-MoA3, 4
Seal, K.: NS2+EM-WeA11, 25
Seal, S.: NS-ThP15, 36
Seebauer, E.G.: EM+NS-MoA9, 4
Sehr, H.: NS-FrM5, 38
Sekharan, A.K.: NS+EM-WeM13, 18
Seki, T.: AS+BI+NS-TuM13, 7
Senapati, L.: NS-ThA9, 32
Senevirathne, I.: NS+EM-WeM13, 18
Seyller, T.: EM+NS-TuA11, 10
Sham, T.K.: NS2+EM-WeA4, 24
Shan, Z.: TR3+NS-ThA1, 32
Sharma, S.: NS-ThA3, 31
Sheehan, P.E.: NS-FrM3, 38; NS-ThA9, 32
Shenoy, G.K.: NS2+EM-WeA4, 24
Shim, H.: NS-ThP17, 36
Shin, E.: PS1+NS-WeM1, 18
Shin, H.-J.: NS-ThM3, 26
Shin, Y.S.: NS-ThP7, 35
Shirinzadeh, H.: NS-ThP14, 36
Shtinkov, N.: EM+NS-MoA6, 3
Shukla, N.: EM+NS-TuA4, 10
Shuster, M.J.: NS-MoM8, 2
Simmons, M.Y.: NS-FrM7, 39
Singh, G.: BI+AS+NS-ThA9, 31
Smith, D.: NS-FrM6, 39
Sobe, J.: PS1+NS-WeM11, 20
Song, W.: NS-ThP7, 35
Song, Y.J.: NS-TuP18, 15
Soto, C.M.: NS-MoM5, 1
Spencer, N.D.: NS-MoM10, 2; TR2+BI+NS+MN-ThM3, 28
Sprunger, P.T.: NS+EM-WeM13, 18
Srinivasan, C.: NS-MoM8, 2
Stach, E.A.: TR3+NS-ThA1, 32
Stafford, L.: EM+NS-MoA7, 4
Stafström, S.: NS2+EM-WeA2, 24
Steinbach, A.: PS1+NS-WeM11, 20
Stern, L.A.: NS+MS-TuA8, 11
Strahan, J.: NS-FrM9, 39
Striccoli, M.: NS-MoM6, 2
Strobel, M.A.: AS+BI+NS-WeA9, 22
Stroscio, J.A.: NS-TuP18, 15
Stuchinsky, V.A.: NS-TuP13, 15
Suda, Y.: NS-ThM7, 27
Sugawara, H.: NS-ThM7, 27
Sugiyama, T.: NS-TuP11, 14; NS-TuP12, 15
Sun, C.-L.: NS+MS-TuA1, 11
Sun, Q.: EM+NS-TuA8, 10
Sun, T.: NS2+EM-WeA1, 24
Suslov, V.M.: NS-ThP12, 36
Suzuki, M.: AS+BI+NS-WeA1, 21
Swaminathan, P.: NS-MoM2, 1
Swaraj, S.: AS+BI+NS-WeA11, 22

— T —

Tadayyon, S.: AS+BI+NS-WeA2, 21
Takarai, Y.: NS-TuP11, 14
Takayama, J.: NS-ThM7, 27
Takeguchi, M.: PS1+NS-WeM9, 19
Takemura, S.: NS-TuP11, 14; NS-TuP12, 15
Talin, A.A.: EM+NS-TuA1, 10
Tam, E.: NS-TuP16, 15
Tani, Y.: EM+NS-MoA4, 3
Taniguchi, M.: NS+MS-TuA10, 12; NS-TuP11, 14
Taoda, H.: NS-TuP10, 14
Tarrío, C.: NS-FrM10, 39
Taylor, M.: AS+BI+NS-TuM4, 6
Tegenfeldt, J.: NS-TuP8, 14
Tersoff, J.: EM+NS-TuA2, 10
Tevaarwerk, E.R.: NS-MoA9, 5
Thevuthasan, S.: NS-ThP15, 36
Thornton, K.: NS2+EM-WeA1, 24

Thundat, T.G.: NS1+BI-WeA8, 23; NS-TuP19, 16;
TR2+BI+NS+MN-ThM2, 27
Ting, Y.-H.: PS1+NS-WeM12, 20
Torrent-Burgues, J.: TR2+BI+NS+MN-ThM7, 28
Tosa, M.: NS-TuP3, 13
Trelka, M.: NS-MoM1, 1; NS-ThP11, 35
Tsai, C.-H.: PS1+NS-WeM6, 19
Tsukamoto, R.: NS-ThP1, 34
Turner, K.: NS+EM-WeM1, 17
Tyler, B.J.: BI+AS+NS-ThA6, 30

— U —

Uder, B.: NS-TuM6, 8
Unger, W.E.S.: AS+BI+NS-WeA11, 22
Uosaki, K.: AS+BI+NS-WeA3, 21
Uraoka, Y.: PS1+NS-WeM9, 19
Urban, C.: NS-MoM1, 1; NS-ThP11, 35
Uritsky, Y.: NS-TuM5, 8
Urquhart, A.J.: AS+BI+NS-TuM4, 6
Ushirozawa, M.: NS+MS-TuA10, 12

— V —

Vaidyanathan, R.: EM+NS-MoA9, 4
Valla, T.: NS-TuP5, 13
Valesia, A.: NS1+BI-WeA10, 23
Van Tendeloo, G.: NS-ThA4, 31
Varanasi, C.: NS-ThP3, 34
Verdager, A.: TR3+NS-ThA8, 33
Vereecken, J.: NS-TuP2, 13
Villagran, F.: NS-MoA9, 5
Vlahovic, B.: NS-ThP12, 36
Voevodin, A.A.: PS1+NS-WeM1, 18
Vogel, V.: NS1+BI-WeA2, 22
Voss, L.F.: EM+NS-MoA7, 4

— W —

Waggoner, P.S.: TR2+BI+NS+MN-ThM1, 27
Wahl, K.J.: TR2+BI+NS+MN-ThM9, 28
Waite, A.R.: PS1+NS-WeM1, 18

Wang, A.: EM+NS-TuA8, 10
Wang, C.C.: NS-TuM5, 8
Wang, H.T.: EM+NS-MoA7, 4
Wang, H.-W.: NS+MS-TuA1, 11
Wang, P.: AS+BI+NS-WeA8, 21
Wang, S.: NS-TuP5, 13
Wang, W.: NS-ThP4, 34
Wang, Z.T.: NS-ThM6, 27
Ward, B.: NS+MS-TuA8, 11
Warren, O.L.: TR3+NS-ThA1, 32
Watanabe, D.: PS1+NS-WeM13, 20
Watanabe, Y.: NS-TuP11, 14; NS-TuP12, 15
Watson, B.M.: NS+EM-WeM13, 18
Weaver, J.H.: NS-MoM2, 1
Wege, S.: PS1+NS-WeM11, 20
Weiss, D.N.: NS-MoA8, 5
Weiss, G.A.: NS-ThM2, 26
Weiss, P.S.: NS-MoM8, 2
Weissmueller, J.: NS-TuP20, 16
Wells, D.: AS+BI+NS-TuM10, 7
Wendt, A.E.: PS1+NS-WeM12, 20
Weng, C.-H.: PS1+NS-WeM6, 19
Wenig, G.: PS1+NS-WeM11, 20
Whitaker, K.M.: EM+NS-MoA3, 3
White, R.G.: TR2+BI+NS+MN-ThM2, 27
Whitley, J.L.: NS-MoM5, 1
Whitman, L.J.: NS-FrM3, 38; NS-ThA9, 32
Wiederrecht, G.: NS-ThP16, 36
Willson, C.G.: NS-FrM9, 39
Wilson, C.D.: NS-MoM5, 1
Wittstock, A.: NS-TuP20, 16
Wolf, H.: NS-MoM10, 2; NS-MoM6, 2
Wolfe, J.C.: NS-FrM9, 39
Woo, J.: NS-ThP17, 36
Woo, R.L.: NS+EM-WeM5, 17
Wu, J.H.: NS2+EM-WeA1, 24
Wu, M.H.: NS-ThP12, 36
Wu, P.: EM+NS-MoA2, 3
Wu, S.-C.: NS-ThP2, 34

— X —

Xie, J.: NS-TuM11, 9
Xu, J.: EM+NS-TuA8, 10
Xu, L.: PS1+NS-WeM10, 20
Xu, W.: NS-MoM12, 2

— Y —

Yakshinskiy, B.: NS-FrM10, 39
Yamamoto, R.: AS+BI+NS-WeA3, 21
Yamashita, I.: NS-ThP1, 34; PS1+NS-WeM9, 19
Yang, G.: NS-TuM1, 8
Yang, J.H.: NS-ThP6, 35
Yang, J.-L.: NS-ThM9, 27
Yang, M.: NS-ThA9, 32
Ye, G.: NS2+EM-WeA3, 24
Ye, W.: NS2+EM-WeA1, 24
Yegen, E.: AS+BI+NS-WeA11, 22
Yi, D.: NS-TuP19, 16
Yilmaz, M.: NS-TuP5, 13
Yitamben, E.N.: NS-TuM4, 8
Yoo, J.W.: NS-TuP7, 14
Yoo, W.J.: NS2+EM-WeA5, 24
Yoshii, S.: NS-ThP1, 34
Yost, K.: NS-ThP3, 34
Yulin, S.: NS-FrM10, 39
Yun, J.: NS-MoA6, 5

— Z —

Zajec, B.: NS-ThP9, 35
Zaki, N.: NS-TuP5, 13
Zauscher, S.: TR2+BI+NS+MN-ThM5, 28
Zhang, G.: NS2+EM-WeA5, 24
Zhang, H.: NS-ThM4, 26
Zhao, W.: NS+EM-WeM13, 18
Zhu, T.: EM+NS-TuA8, 10
Zhu, Z.: AS+BI+NS-TuM11, 7
Zielasek, V.: NS-TuP20, 16
Zumer, M.: NS-ThP9, 35