

Graphene Topical Conference

Room: 306 - Session GR+TF+NC-MoM

Graphene and 2-D Carbon Nanostructures

Moderator: B.C. Holloway, Luna Innovations Incorporated, M.Y. Zhu, College of William and Mary

8:20am **GR+TF+NC-MoM1 Electrical Transport Properties of Two-Dimensional Carbon Nanostructures**, *Y. Wu*, National University of Singapore, *H. Wang*, National University of Singapore and Data Storage Institute, Singapore, *S.S. Kushvaha*, National University of Singapore, *S.Y.H. Lua*, National University of Singapore and Data Storage Institute, Singapore

INVITED

Recently 2D carbon nanostructures have attracted great interest due to their peculiar structural and electronic properties, especially after the successful mechanical exfoliation of single and few layer graphene from bulk graphite and epitaxial growth of graphene on SiC. We have reported previously the growth of well-aligned 2D carbon nanostructures – carbon nanowalls(CNWs), using MPECVD. Although the CNWs are structurally not as perfect as graphene sheets obtained by other techniques, its free-standing structure makes it an excellent candidate for studying electrical transport properties of 2D carbon nanostructures using end-point contacts of various types of materials including normal metal, semiconductor and superconductors. In this talk, we will present our results on (1) lateral electrical transport measurements using end-point Ti and Nb electrodes with a gap length in the range of 200 nm – 3000 nm (2) vertical transport measurements using nanopores in a UHV system. In (1) we focus on conductance fluctuation and proximity effect and in (2) we investigate the contact resistance between 2D carbon and different types of materials. In lateral transport measurements using Ti electrodes, excess conductance fluctuations with peculiar temperature-dependence from 1.4 to 250 K were observed with an electrode gap length of 300 and 450 nm, whereas the conductance fluctuation is greatly suppressed above 4.2 K when the electrode gap length increases to 800 and 1000 nm. The former is discussed in the context of the presence of both a small energy bandgap, while the latter is attributed to the crossover from mesoscopic to diffusive transport regime. On the other hand, in the case of Nb electrodes, we have observed proximity effect in samples with an electrode gap length of 200 – 500 nm and a reentrant behavior for samples with smaller gap length. Strong conductance oscillation was observed in samples using four-point probes which is attributed to the formation of SNS structures in CNW. In the vertical transport measurement using nanopores, it was found that the end-point contact resistance of carbon nanowalls on stainless steel is the lowest, followed by graphite, Si, Cu, Au (100 nm) / Ta (1 nm) / Si and Au wire. Both the contact resistance and I-V characteristics are in good agreement with the results of first principles calculations reported in the literature. The results may serve as the guides for selecting metal contacts in graphene-based devices.

9:00am **GR+TF+NC-MoM3 Characterization of Functionalized Carbon Nanosheets as a Step Towards the Development of Advanced Graphene Devices**, *R.A. Quinlan*, College of William and Mary, *E. Widenkvist*, Uppsala U., Sweden, *J. Groff*, College of William and Mary, *M. Rooth*, Uppsala U., Sweden, *M. Kelly*, Stanford U., *R.A. Outlaw*, College of William and Mary, *V. Coleman*, *O. Karis*, *B. Sanyal*, *O. Eriksson*, *H. Grenberg*, Uppsala U., Sweden, *B.C. Holloway*, Luna Innovations, Inc., *U. Jansson*, Uppsala U., Sweden

Carbon nanosheets (CNSs) are novel free-standing carbon nanostructures, composed of horizontal basal planes and vertical sheets which are made up of 1-7 graphene layers.¹ Previous work described the successful creation of defects in the graphene lattice via an acid-treatment and the characterization of these defects with x-ray absorption near-edge spectroscopy (XANES). The presence of a peak in the carbon K-edge spectra at 287eV was assigned to a C-O σ^* resonance. Theoretical modeling of a di-vacancy in a graphene bilayer system reproduced the spectra and predicts metallic conductivity of the states surrounding the defect.² Here we report the further characterization of functionalized carbon nanosheets (f-CNSs) via high resolution x-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy (TDS). Measurements were made at room temperature up to 700K with as-deposited, water- and acid-treated CNSs. XPS measurements indicate an increase in the oxygen content of the nanostructures from 1-2% in as-deposited up to 3-4% in the acid-treated samples. The decrease of sub-peak areas in the C1s and O1s spectra with heating correlates well with the decrease in atomic oxygen content. The partial pressures of H₂, O₂, CO₂, CO and H₂O measured desorbing from the f-CNSs support the model of

oxygen and hydrogen decorated defects in the graphene system. The XPS and TDS results support XANES measurements of similar samples. These results support the use of a non-oxidizing acid-treatment for controlled defect formation in a graphene system, a first step towards the development of graphene based devices.

¹ Wang et al., Free-standing subnanometer graphite sheets. *Applied Physics Letters*, 2004, 85(7): p. 1265-1267

² Coleman et al., Defect formation in graphene nanosheets by acid treatment: an x-ray absorption spectroscopy and density functional theory study. *Journal of Physics D: Applied Physics*, 2008(6): p. 062001.

9:20am **GR+TF+NC-MoM4 Application of Carbon Nanowalls to Negative Electrode in Lithium-Ion Battery for High-Rate Use**, *N. Kitada*, *H. Yoshimura*, Yokohama City University, Japan, *O. Tanaike*, Advanced Industrial Science and Technology, Japan, *K. Kojima*, *M. Tachibana*, Yokohama City University, Japan

Recent design and fabrication of electrode in Lithium-ion battery have been focused for the high rate use since rapid charge and discharge of the battery with high power density are usually required for quick start and stop of electric vehicle or hybrid electric vehicle in next generation. One of the ways to develop the electrode for high rate use is to use nano-sized active materials since the diffusion distance of lithium ions in the solid during charge and discharge is decreased by using them. Here, we reports a new nano-sized and graphitized carbon material, two-dimensional carbon nanostructures called carbon nanowalls (CNWs) [1-5], as a promising one for negative electrode material of lithium ion battery in high rate use. CNWs were synthesized at very low temperature of 973K by a dc plasma-enhanced chemical vapor deposition. They were mixed with binder Polyvinylidene fluoride in N-methylpyrrolidone, pressed and then dried to produce carbon sample electrodes. Conventional three electrodes test cells were constructed for electrochemical measurements by carbon sample as a working electrode and two lithium foils as counter and reference ones. Lithium insertion properties were studied using these test cells by cyclic voltammetry (CV) and charge/discharge measurements. CNWs is found to be an interesting graphitic active material for negative electrode of lithium ion battery having reversible capacity of more than 200 mAh/g with relatively stable charge/discharge potential which is very similar to the properties of graphite, even though CNWs are synthesized at very low temperature of 973K without any graphitization process at high temperature. These CNWs are well layered particles in nano scale having large exposure surface of graphene edge, which is expected to be suitable for lithium insertion at high rate charge/discharge, and present results of CVs and charge/discharge tests support it. [1] Y. Wu et al., *Adv. Matter.* 14, 64(2002). [2] M. Zhu et al., *Carbon*, 42, 2867(2004). [1] S. Kurita et al., *J. Appl. Phys.* 97, 104320 (2005). [2] K. Kobayashi et al., *J. Appl. Phys.* 101, 094306 (2007). [3] I. Kinoshita et al., *Chem. Phys. Lett.* 450, 360 (2008).

9:40am **GR+TF+NC-MoM5 Carbon Nanosheets: Novel Two-Dimensional Materials**, *A. Beyer*, *C.T. Nottbohm*, *X. Zhang*, *A. Turchanin*, Universität Bielefeld, Germany, *A. Sologubenko*, *J. Mayer*, RWTH Aachen, Germany, *A. Götzhäuser*, Universität Bielefeld, Germany

1 nm thick, mechanically and thermally stable carbon nanosheets are fabricated by combining molecular self-assembly with lithography. Self-assembled monolayers of aromatic molecules are cross-linked via electron or EUV irradiation. The cross-linked monolayers are released from the substrate, resulting in “free-standing carbon nanosheets” with the thickness of a single molecule.¹ We show that the nanosheets can be transferred onto arbitrary surfaces and we determine their elastic constants by AFM. We have found that nanosheets possess an extraordinarily high mechanical and thermal stability.² Carbon nanosheets can be used as ultrathin sample supports for transmission electron microscopy (TEM). Free-standing nanosheets were transferred onto TEM grids and nanoparticles were deposited onto them. When imaged by high-resolution TEM, the nanoparticles show a much higher contrast than those made with a conventional carbon film.³

¹ W. Eck, A. Küller, M. Grunze, B. Völkel, A. Götzhäuser: Free-standing nanosheets from cross-linked biphenyl self-assembled monolayers, *Adv. Mat.*, 17, 2583-2587, (2005)

² A. Turchanin, M. El-Desawy, A. Götzhäuser: High thermal stability of cross-linked aromatic self-assembled monolayers: Nanopatterning via selective thermal desorption. *Appl. Phys. Lett.*, 90, 053102 (2007)

³ C. T. Nottbohm, A. Beyer, A. S. Sologubenko, I. Ennen, A. Hütten, H. Rösner, W. Eck, J. Mayer, A. Götzhäuser: Novel carbon nanosheets as support for ultrahigh resolution structural analysis of nanoparticles. *Ultramicroscopy*, in press.

10:20am **GR+TF+NC-MoM7 Enhanced Field Emission of Vertical Aligned Carbon Nanosheets**, *M.Y. Zhu*, *R.A. Outlaw*, *H. Chen*, *M. Bagge-Hansen*, *D.M. Manos*, College of William and Mary

Field emissions from two-dimensional free-standing carbon nanosheets with ultra-thin edges synthesized in radio frequency (RF) plasma enhanced

chemical vapor deposition from CH₄/H₂ gas mixture have been previously reported. When C₂H₂/H₂ gas mixture was used, the growth temperature was lowered by 100-150 °C and well aligned vertical sheets with uniform height distribution were obtained. Typical C₂H₂ nanosheets were deposited on Si substrates using 80% C₂H₂ diluted in H₂ gas (5 sccm total gas flow rate) at 600 °C substrate temperature and 35 mTorr total pressure with 1000 W RF power for 10 min. The growth rate of the nanosheets measured from cross-sectional scanning electron microscopic images was 10.8 μm/hr. In this report, field emission measurements were taken from nanosheet samples 1.8 μm in height. Custom LabView software controlled automatic diode I-V measurements of C₂H₂ nanosheets yielded a threshold field, for an emission current density of 10 μA/cm², of ~3 V/μm, which was ~2 V/μm lower than CH₄ nanosheets. At an applied field of 5.3 V/μm, the current density was 1.1 mA/cm² compared to the CH₄ nanosheets of ~0.007 mA/cm². Calculations from the Fowler-Nordheim plots and their linear fits indicated that the effective emission area of C₂H₂ nanosheets was ~15 times that of CH₄ nanosheets and the β factor of C₂H₂ nanosheets was ~26% higher than CH₄ nanosheets. The results are consistent with the morphology differences between the two kinds of nanosheets. The lifetime tests of C₂H₂ nanosheets conducted in a DC mode with a base pressure lower than 5×10⁻⁹ Torr showed a conditioning from an emission current of ~1.1 mA to a current level of 0.65 mA after 200 hour operation without any drop-outs or arcing failure. These tests were conducted with minimal anode cooling, which may account for the decay of the current on this timescale. The vacuum pressure of the testing system was recorded along with the emission current, and found to be closely correlated to the emission current.

10:40am **GR+TF+NC-MoM8 Control of Structures and Electrical Properties of Carbon Nanowalls Using Plasma Enhanced CVD Employing N₂/O₂ Addition to C₂F₆/H₂ Gases, W. Takeuchi**, Nagoya University, Japan, *M. Hiramatsu*, Meiji University, Japan, *Y. Tokuda*, Aichi Institute of Technology, Japan, *H. Kano*, NU Eco-Engineering Co., Ltd., Japan, *M. Hori*, Nagoya University, Japan

Carbon nanowalls (CNWs), that is two-dimensional carbon nanostructure of freestanding vertically oriented graphitic sheets, attract great attentions because of several applications such as electrical devices. Recently, it was reported that the 2-D multilayer graphene sheet devices offer the high mobility and the huge sustainable currents. Therefore, CNW films would have high performances of electric devices, since the CNWs basically consist of graphene sheets. In order to realize the CNW devices, it is necessary to control structures and properties. In this study, we have successfully controlled structures and electric properties of CNWs. CNWs were fabricated on the quartz substrate by plasma enhanced CVD (PECVD) employing C₂F₆ gas with H radical injection. The influences of N₂ and N₂/O₂ addition to C₂F₆/H₂ gas mixtures on structures and electric properties of CNWs were investigated. The cross-sectional scanning electron microscopy (SEM), Hall measurement and secondary ion mass spectrometry (SIMS) were used to evaluate structures, electric properties and atomic compositions of CNWs, respectively. The SEM image of the CNWs film synthesizes by N₂/O₂ mixture gas addition indicated that the size of the individual graphene of CNWs increased with less branching. The Hall coefficient indicated the positive value for the CNW film synthesized without N₂ addition. In the case of N₂ addition, it displayed the negative one. The positive or negative value means p- or n-type conduction, respectively. CNW films doped with N atoms were characterized by SIMS to investigate the effect of the N₂ addition on the atomic composition of CNWs. The carrier and N concentration in the CNW films formed by N₂/O₂ mixture gas addition were almost the same as those in the CNW film by N₂ addition. It is considered that the N atom in the CNWs act as a donor and the electrical property of N-doped CNWs can be controlled by N atom concentration. These results will be crucial to fabricate the electrical devices of CNWs without deteriorating crystallinity.

11:00am **GR+TF+NC-MoM9 Wafer-Scale Synthesis and Electrochemical Property of Graphene Formed by Microwave Plasma Enhanced Chemical Vapor Deposition, L.C. Chen**, National Taiwan University **INVITED**

The recent experimental breakthroughs on graphene-based nanoelectronics have triggered enormous academic activities. Among the production methods of graphene, mechanical exfoliation of graphite and surface evaporation of SiC are widely used. Despite the successful fabrication in surface evaporation of SiC, process integration of graphene into the well-established Si-based technology remains a challenging task. In view of this, it is also desirable to develop a reliable and large-scale (or wafer-based) production of graphene for practical applications. In this presentation, we will demonstrate a novel synthetic route for graphene growth on silicon substrate by microwave plasma enhanced chemical vapor deposition (MPECVD). The resultant nanoarchitecture exhibits a wall-like morphology with a high density of sharp edges. Structure wise, each nanowall is composed of SiC decorated by a few layer of graphene (i.e. concrete paint

on concrete wall). Moreover, direct deposition of Pt nanostructures onto these graphene samples is also performed to explore their potentials for electrochemical energy applications. Preliminary cyclic voltammetry studies for electro-oxidation of methanol show a high ratio of forward anodic peak current to reverse peak current, suggesting an efficient oxidation of methanol to CO₂ on the Pt/graphene electrode. The effective suppression in the reverse cathodic peak current probably suggests a selective growth of Pt on graphene. Other electrochemical properties (such as electron-transfer kinetics and chemical reactivity) of MPECVD-grown graphene will also be addressed in this presentation. Our synthetic approach offers an alternative route toward wafer-scale fabrication of graphene for fundamental research and opens up various potential applications in nanoelectronics, sensing, catalysis, and energy production.

11:40am **GR+TF+NC-MoM11 Growth and Structures of Carbon Nanowalls during Plasma-Enhanced Chemical Vapor Deposition, H. Yoshimura, N. Kitada, K. Kojima, M. Tachibana**, Yokohama City University, Japan

Recently two-dimensional carbon nanostructures called carbon nanowalls (CNWs) have been fabricated by plasma-enhanced chemical vapor deposition.¹ The CNWs are vertically grown on the substrate. According to our previous studies of Raman spectroscopy² and transmission electric microscopy (TEM),³ and Ultraviolet photoelectron spectroscopy,⁴ CNWs are composed of small crystallites with a high degree of graphitization. And these small crystallites so-called "nano-graphite domains" were slightly rotated each other. Such shapes and structures of CNWs may provide us with various applications, such as gas storage, membranes for electrochemical energy storage, and field emitters. The understanding of growth process and structures in CNWs is required for the practical applications. In this paper, we report the detail of growth process and structures of CNWs. CNWs were grown by using a dc plasma-enhanced chemical vapor deposition method with a gas mixture of CH₄, H₂, Ar. Typical flow rate of CH₄, H₂ and Ar were 10, 10, and 80 sccm (standard cubic centimeters per minutes at standard temperature and pressure). To investigate the growth process, specimens were prepared for plasma reaction times of 1, 2, 3, 4, 5, 7 and 15 minutes. The shapes and structures of the specimens were investigated by means of atomic force microscopy (AFM), grazing incidence X-ray diffraction (GIXD), and Raman spectroscopy. In addition, the change in the size and quality of crystallites was observed. As reported previously,⁵ it was observed that CNWs changes from parallel to perpendicular to the substrate with deposition time. In addition, the transition structure from parallel to perpendicular was clearly observed. From these results, the growth process of CNWs will be discussed.

¹Y. Wu, et al., Adv. Matter. 14, 64 (2002)

²S. Kurita, et al., J. Appl. Phys. 97, 104320 (2005)

³K. Kobayashi, et al., J. Appl. Phys. 101, 094306 (2007)

⁴I. Kinoshita, et al., Chem. Phys. Lett. 450, 360 (2007)

⁵B. L. French, et al., Thin Solid. Film, 494, 105, (2006).

Manufacturing Science and Technology Room: 311 - Session MS+NC-MoM

CMOS Extension and Metrology Moderator: V. Ku, TSMC

8:20am **MS+NC-MoM1 A Metal Hardmask Approach for the Contact Patterning of a 0.186 μm² SRAM Cell Exposed with EUV Lithography, J.-F. de Marneffe, D. Goossens, A. Vandervorst, S. Demuyneck, A.M. Goethals, J. Hermans, F. Van Roey, B. Baudemprez, S. Brus, C. Vrancken**, IMEC, Belgium

In order to overcome patterning challenges brought by dimensional scaling and aggressive pitches, extreme ultra-violet (EUV) lithography has been recently pushed forward as a possible solution for IC manufacturing, allowing extended exposure latitude at sub-50nm dimensions. This work address the technological solutions used for contact holes patterning by means of EUV lithography. A 0.186 μm² SRAM cell has been used as a test-vehicle, showing down to 55nm circular and boomerang-shaped contacts.¹ A metal hard-mask (MHM) approach has been selected, in order to combine the etch of high-aspect ratio features with thin EUV photoresist. The pre-metal dielectric stack covering the active fins was composed of 15nm Si₃N₄ as an etch-stop liner, covered by 240nm SiO₂. The MHM was made of a 30nm TiN film on top of which was spun 20nm of organic underlayer and 100nm of EUV photoresist. This paper will describe in details the various patterning steps (lithography, MHM opening and ash, SiO₂ followed by Si₃N₄ etch, residue cleaning) leading to the successful patterning of small contacts by EUV lithography.

8:40am MS+NC-MoM2 Improved Mechanistic Understanding of Millisecond Annealing Techniques for Ultrashallow Junction Formation, Y.V. Kondratenko, C.T.M. Kwok, E.G. Seebauer, University of Illinois, Urbana-Champaign

Formation of pn junctions in advanced Si-based transistors employs rapid annealing techniques after ion-implantation in order to increase the electrical activation of dopants while minimizing their diffusion. Over the past decade, these techniques have evolved from rapid thermal processing, with time scales of about 1 s, to millisecond methods accomplished by flashlamps or lasers. Although the dopant behavior in terms of diffusion and electrical activation clearly improves as a result of the shortened time scale, the technology transition has taken place on a largely phenomenological basis with little understanding of the physical mechanism for the improvement. The present work provides the key elements of that understanding and explains nonthermal contribution of illumination on the diffusion of dopants. Continuum-based simulations were used to model experimental data in order to obtain mechanistic picture of improvement in dopant diffusion and activation during millisecond annealing. The same method was applied to explain photostimulated effects on dopant diffusion during soak annealing. The simulations solve the partial differential equations for diffusion and reaction of interstitial atoms, with activation energies for elementary diffusion and reaction steps computed by Maximum a Posteriori parameter estimation. The fundamental reason for improvements of diffusion and electrical activation in the millisecond regime is that the short time scale promotes exchange of dopant interstitial atoms with the lattice in preference to exchange with interstitial clusters. Photostimulated diffusion of dopants, however, exhibited more complicated features. Depending on annealing temperature and time, boron diffusion in silicon could be either enhanced or inhibited. Dopant activation was similarly affected. Simulations using continuum equations for the reaction and diffusion of defects were used to determine whether illumination affects cluster dynamics or steady state boron diffusion.

9:00am MS+NC-MoM3 Challenges and Opportunities for 32nm Node CMOS and Beyond, B. Doris, IBM Research at Albany Nanotech INVITED

Future CMOS technologies require significantly more transistors per unit area with improved transistor performance. Gate-length, spacer, and contact scaling are the enablers for increasing transistor density. Scaling these features for future technology nodes is a significant challenge and new processes, materials and integration schemes will be needed. Ultimately new device architectures may be needed to achieve increased density or enhanced performance. Fully depleted SOI devices like Extremely Thin Silicon on Insulator (ETSOI) and FinFETs are the possible choices for alternate architectures. Either option would be a major shift for the semiconductor industry and would pose new challenges compared to conventional planar CMOS. Performance enhancement beyond previous technologies will be needed regardless of the particular device architecture choice. Recent experiments and simulation have shown that as the transistor density increases it is even more challenging to achieve similar performance. Specifically, recent technologies have relied on local mechanical stress techniques to enhance channel mobility and thereby improve performance. As the transistor density increases, the size of features and the distance between features decreases. This situation limits the ability of stress enhancement techniques to have impact on channel mobility. Thus, new performance elements are also needed for future technology nodes. This presentation highlights the opportunities and challenges for 32nm Node CMOS and beyond.

10:20am MS+NC-MoM7 Multi Level "Air Gap" Integration for Advanced Technology Nodes, F. Gaillard, D. Bouchu, CEA-Leti-MINATEC, France, R. Gras, STMicroelectronics, France, S. Moreau, CEA-Leti-MINATEC, France, G. Passernard, J. Torres, STMicroelectronics, France

In order to extend device's performance and more particularly to improve interconnects RC delay, crosstalk and power consumption, continuous and innovative materials development have been realised over the twenty five past years to decrease dielectric constant. After the use of fluoride doped silicon oxide, low-k and later on porous ultra low k materials have emerged as serious candidates to isolate copper lines for the 90 - 32 nm nodes. Nowadays, "air cavities" introduction also named "Air Gap" represents the ultimate solution in this classical dielectric material evolution and is an attractive solution to meet the ITRS performance for advanced interconnects (22 nm technology node and below). We present an architecture where a sacrificial SiO₂ material deposited on few metal levels (two or more) is further removed by a hydrofluorhydric (HF) chemical etching agent. This HF chemistry diffuses through out patterned apertures

localized in a silicon carbide (SiCN) capping layer deposited at the end of the multi level scheme. Thus, full air gaps realization is performed when possible, but SiO₂ pillars are still needed on long metal lines patterns to avoid any collapse when complete air cavities are made underneath. This global approach allows air cavities localization, keeps mechanical integrity and avoids any via misalignment issues, as air cavities are introduced at the end of the integration. In this work, we will present a three metal level interconnect realization achieved at 65 nm design rules on a 300 mm diameter wafer; air cavities will be integrated on two metal levels and further completed up to pads realizations. Associated morphological and electrical results will be discussed. Based on simulation data and supported with experimental results, we have also predicted and demonstrated that an adequate stack composed of different doped or undoped SiO₂ materials deposited on the different metal levels can be useful to optimise the SiO₂ pillar shape. It consequently improves the coupling capacitance gain on both metal levels, which is directly linked to the air cavities volume. Indeed, if the initial stack is composed of the same SiO₂ material, the air cavities present a spherical profile because the HF chemistry removes isotropically the SiO₂ layers through the specific apertures. These encouraging "Air Gap" results could represent a promising and low cost solution to move towards the next technology nodes.

10:40am MS+NC-MoM8 Chemical Vapor Deposition of Manganese Self-Aligned Diffusion Barriers for Copper Interconnections in Microelectronics, H. Kim, Y. Au, H. Wang, H. Bhandari, Y. Liu, Harvard University, D.K. Lee, Samsung, Y. Lin, R.G. Gordon, Harvard University

Barriers to prevent diffusion of copper (Cu) and oxygen were formed by chemical vapor deposition (CVD) using a manganese (Mn) precursor vapor that reacts with silica-containing surfaces of low-k dielectrics. The manganese metal penetrates a few nanometers into the silica surface to make highly conformal, amorphous and insulating manganese silicate (MnSi_xO_y) layers on the walls of trenches and vias in interconnects. These MnSi_xO_y layers were found to be excellent barriers to diffusion of Cu, oxygen and water. The adhesion of Cu to MnSi_xO_y was also found to be sufficiently strong to satisfy the semiconductor industry requirements. The MnSi_xO_y barrier/adhesion layers become part of the insulator structure, so that they maximize the space available for Cu in the trenches and vias. Thus MnSi_xO_y is a "zero-thickness" barrier that exceeds the ITRS requirements for interconnections in future microelectronic devices. The same Mn CVD process can be applied to cap interconnect structures after chemical-mechanical polishing (CMP). On the tops of Cu wires exposed by CMP, the CVD process forms Mn that is initially dissolved in the Cu near its upper surface. During subsequent deposition of an insulator on the Cu, Mn diffuses back to the upper surface of the Cu where it forms a MnSi_xO_y layer that is strongly adherent to the Cu. These capping MnSi_xO_y layers can increase the lifetime of interconnects against failure by electromigration.

11:00am MS+NC-MoM9 What Photoemission Can Tell Us About High-K Dielectrics, R.L. Opila, G. Liu, University of Delaware INVITED

Angle-resolved photoelectron spectroscopy is an ideal probe films of candidate high dielectric constant films because the thickness of these very smooth films is comparable to the escape depth of the photoelectrons. We have successfully analyzed silicon oxynitride films of the range of thickness of 1 to 4 nm. From the N 1s spectrum we were able to identify four different binding states for N in these films: N bonded to three atoms: three silicon, two silicon and one oxygen atom, and one silicon and two oxygen atoms. In addition we identified a binding state corresponding to N bound to two silicon atoms with one unsatisfied, dangling bond. We also showed that converting the angle resolved data to a compositional depth profile could be done effectively using the maximum entropy algorithm. Recently we have been studying nitrided (HfO₂)_x(SiO₂)_{1-x} films. The breadth observed in the N1s peak can be attributed to N binding to varying amounts of Si and the relatively electropositive Hf. There appears to be a tendency for N to preferentially bind to Hf in these films. We used the maximum entropy algorithm to analyze these films. Nitridation at successively higher temperatures results in more incorporation of N into these films, and more of this N is incorporated near the oxide/Si interface. Using maximum entropy we were able to convert the angle resolved data to compositional depth profile that had adventitious oxide on the surface, preferential oxidation at the outer surface and the oxide/silicon interface, and otherwise relatively smooth composition of Si⁴⁺ and Hf⁴⁺ through the film. These results were confirmed qualitatively by medium energy scattering.

11:40am MS+NC-MoM11 Influence of Room Temperature Control System on AFM Imaging, J. Fu, National Institute of Standards and Technology, W. Chu, Harbin Institute of Technology, China, T. Vorburger, National Institute of Standards and Technology

As the technology progresses, the control of the thermal and vibrational environment for experiments is also becoming more sophisticated. In particular, temperature control to within ± 0.25° C for a general purpose lab

is fairly common place. However, even with such a stringent temperature control specification, the variation of temperature can be observed in the AFM (atomic force microscopy) images of a straight edge. In this paper we show the correlation between edge distortion of a semiconductor linewidth standard and the thermal recycling in the lab imposed by a two-level infrastructural temperature control system. A Fast Fourier Transform (FFT) analysis of the AFM images of the line links the frequency of the waviness at the line edge to the damper and reheating coil of the air conditioning feedback system. The unique frequency components present in all three axes of AFM images lead us to conclude that the temperature variation affected the PZT scanner which affected the measurements.

Surface Science

Room: 208 - Session SS+NC-MoM

Catalysis and Alloy Formation

Moderator: G.B. Fisher, Delphi Research Laboratories

8:20am **SS+NC-MoM1 Surface Structural Investigation of Ultra-Thin Films of Pd Deposited on Au(111)**, *P.A.P. Nascente*, Federal University of Sao Carlos, Brazil, *A. Pancotti, M.F. Carazzolle, A. de Siervo*, State University of Campinas, Brazil, *D.A. Tallarico*, Federal University of Sao Carlos, Brazil, *R. Landers, G.G. Kleiman*, State University of Campinas, Brazil

Bimetallic surfaces have attracted considerable interest due to their catalytic, electronic, electrochemical, and magnetic properties. The deposition of an ultra-thin metal film on a single crystal metal substrate can produce a bimetallic surface. The interfacial interactions between the two metals can lead to preferential surface orientation, surface relaxation, surface reconstruction, order/disordered effects, and surface alloying. In this work, ultra-thin films (1 and 3 monolayers) of Pd were deposited on the Au(111) surface and then characterized by X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), and X-ray photoelectron diffraction (XPD). We have considered three models: Pd overlayers on the Au(111) substrate, Pd islands covering the Au(111) surface, and a random AuPd_{1-x} alloy. The reliability of the theoretical simulations as compared to the experimental XPD data was measured through the R-factor analysis. The comparison between experimental and theoretical XPD results indicated that, for the 1 ML film annealed at 450 C, Pd diffused into the Au bulk, causing alloy formation, and for the thicker film, the Pd islands were, at most, 3 ML thick.

8:40am **SS+NC-MoM2 Epitaxial Growth Ag Films on Al Surfaces: Strain Relief Mechanisms**, *R.J. Smith, N.R. Shivaparan, M.A. Teter, W. Priyantha, M. Koczyk, M. Lerch, C. Pint*, Montana State University, *G. Bozzolo*, Ohio Aerospace Institute

We report the results of a characterization of 0-6 nm thick Ag films, deposited onto Al(001) and Al(110) surfaces at room temperature, using high energy ion backscattering and channeling, x-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), and BFS model calculations. For the Al(001) surface, measurements of the backscattered ion yields from Al and Ag atoms show that the Ag atoms occupy fcc lattice sites and shadow Al substrate atoms. However, the ion scattering yields and photopeak intensities do not follow layer-by-layer model growth curves. Together with the evolution of the Ag 3d core level binding energies and the valence band shape as a function of Ag coverage, these results support a model of Ag-Al interface alloy formation as a mechanism for strain relief in this system with ~1% lattice mismatch. For the Al(110) surface the observations are closer to those expected for layer-by-layer growth, but still show evidence of some Al diffusion into the well-ordered Ag overlayer.

9:00am **SS+NC-MoM3 Growth of Ag Islands on a Twofold Surface of a Decagonal Al-Cu-Co Quasicrystal**, *B. Unal*, Ames Laboratory and Iowa State University, *T. Duguet*, Ecole des Mines, France, *D. Jing*, Ames Laboratory and Iowa State University, *C.J. Jenks*, Ames Laboratory, *P.C. Canfield*, Iowa State University, *V. Fournée*, Ecole des Mines, France, *P.A. Thiel*, Ames Laboratory and Iowa State University

Quasicrystals are well ordered, but not periodic solid materials which have peculiar surface properties such as low friction and high oxidation resistance. Using a variable temperature scanning tunneling microscope (VT-STM), for the first time, we have studied the (0001) clean twofold surface of a decagonal Al-Cu-Co quasicrystal. Our STM studies have showed that annealing at ca.1000K causes the formation of two different surface phases one of which has a periodic structure while the other is aperiodic. At room temperature, we have also investigated the growth of Ag on these two different surface domains. In the aperiodic one, Ag prefers to

segregate into highly anisotropic islands whose longer edges are parallel to the periodic axis (i.e. the tenfold axis). As the total coverage increases, Ag islands grow vertically while preserving their highly anisotropic shape. In the other (periodic) domain, we observe smoother, more conventional growth. These two different growth behaviors strongly indicate that the aperiodic nature of the surface has a strong effect on the growth kinetics.

9:20am **SS+NC-MoM4 Collective Migration of Cu Nanostructures on Ag(111)**, *A.W. Signor, H.H. Wu, D.R. Trinkle, J.H. Weaver*, University of Illinois at Urbana-Champaign

Experimental studies of island migration, an important process in crystal growth and nanostructure synthesis, have largely been limited to homoepitaxial systems. In these systems, either diffusion or evaporation and condensation of adatoms at the island edge gives rise to a Brownian-like motion of the center of mass with size-independent barriers, and diffusivities that smoothly decrease with size according to an inverse power-law relationship. The present work with Cu-Ag(111), a lattice-mismatched system, provides compelling evidence for a strain-driven collective mechanism involving nucleation and glide of misfit dislocations. With this mechanism, the entire structure is moved by one Burger's vector as a dislocation nucleates and glides through the island and the shape is retained as the structure moves from one site to another. Quantitative analysis of island trajectories in scanning tunneling microscopy movies at multiple temperatures yields activation barriers ranging from 0.14-0.39 eV with prefactors ranging from 10^5 - 10^{18} s⁻¹ for islands containing 5-30 atoms. Significantly, the barriers are very sensitive to island size and shape, and hence island diffusivities do not scale with size in the ways predicted for traditional atomistic mechanisms, greatly affecting the overall coarsening kinetics. Temperature-accelerated dynamics simulations corroborate experimental findings, showing that collective motion of sub-units within the island, due to strain effects, result in misfit dislocation nucleation and glide, with barriers that are very sensitive to size and shape.

9:40am **SS+NC-MoM5 Step Structure and Motion on an icosahedral AlPdMn Quasicrystal**, *Y. Sato*, Lawrence Berkeley National Laboratory, *B. Unal*, Iowa State University, *K.F. McCarty, N.C. Bartelt*, Sandia National Laboratories, *A.K. Schmid, T. Duden*, Lawrence Berkeley National Laboratory, *K. Pussi*, Lappeenranta University of Technology, Finland, *T.A. Lograsso, C.J. Jenks*, Ames Laboratory, *P.A. Thiel*, Iowa State University

We have used LEEM and STM to characterize step structure and motion on a well-ordered, aperiodic icosahedral-AlPdMn quasicrystal surface. Real-time imaging capability of LEEM allows us to understand how the room temperature quasicrystal surface develops following high temperature annealing up to 910K. The way steps move on this surface at high temperature is remarkable. Two types of steps move with different velocities and cross each other. What is more, the two steps form a chicken wire-like hexagonal and rhombohedral mesh structure, as the steady-state surface morphology. From the STM step height measurement, the two steps are identified to be L and (L+M) steps, with different step heights. (L(6.8Å) and M(4.2Å) steps are two steps known to occur on this surface.¹) When the surface is cooled, extensive mass flow from the surface into the bulk has large consequences upon the step motion dynamics and resultant step structure at room temperature. M steps hidden in the step crossings of chicken wire step-networks open up and extend, as it allows a new surface layer to be exposed, and thereby forming the brick-like step structure observed at room temperature, composed of L, M, and (L+M) steps. An obvious question is how one might understand the presence of periodic step arrays at the surface of quasicrystalline samples. One would expect the stacking of the two step heights to follow the Fibonacci sequence of the bulk quasiperiodic order.¹ By permitting localized regions of the surface where the topmost plane trades position with the near-surface plane directly underneath, we propose a construction scheme that allows a step network consistent with experimental observations. Specific planar defects observed in icosahedral AlPdMn could enable such mechanism.² We discuss possible ways for this "carpet" of surface layers to be connected with the underlying bulk aperiodicity.

¹ T.M. Schaub, D.E. Beurgle, and H.-J. Guntherodt, 1994 Phys.Rev.Lett. 73, 1255.

² M. Feuerbacher, M. Heggen, and K. Urban, 2004 Mat.Sci.and Eng. A 375-377, 84.

10:20am **SS+NC-MoM7 Reactivity Trends in CO Oxidation from UHV to Elevated Pressures: Never Mind the Gap**, *D.W. Goodman*, Texas A&M University

CO oxidation on Ru, Pd, Rh, and Pt surfaces has been investigated between 10^{-8} – 10 Torr and for a variety of temperatures and O₂/CO ratios. Polarization modulation reflectance absorption infrared spectroscopy (PM-RAIRS) was used to identify the CO coverage as a function of the reaction rate for a variety of conditions up to 10 Torr. For reaction pressures less than 10^{-6} Torr, X-ray photoelectron spectroscopy (XPS) was used to measure the surface coverages of CO and O_{ads}. A clear continuum with respect to reaction rates, surface composition, and overall mechanism is

apparent over the entire pressure range investigated, i.e. there is no evidence of a pressure gap.

11:00am **SS+NC-MoM9 Structural Evolution of Platinum Catalyst in Different Pressure of CO: A Study of High Pressure STM and High Pressure XPS**, *F. Tao, Z. Liu, C.Y. Chung, D. Butcher, Y.W. Zhang, M. Grass, M. Salmeron, G.A. Somorjai*, Lawrence Berkeley National Laboratory

Bridging pressure gap of catalytic model studies is one of the most challenging issues to be addressed for elucidating mechanism of heterogeneous catalysis. A new high pressure STM was homebuilt for this purpose. CO adsorption and oxidation on a stepped platinum single crystal was selected as a model to study in a wide range of CO pressure from 10⁻⁹ to 1000 Torr as the adsorption and surface structure of CO on noble metals under a realistic catalytic condition is an important topic for pollution control. STM study revealed a significant pressure dependence of surface structure of CO adsorption. The clean platinum single crystal surface prepared in UHV progressively reconstruct by adsorbing CO at step sites and breaking the step edge at low pressure. At high pressure the surface reconstructs into clusters with a size of 1-3 nm. The dramatic structural evolution from low pressure to high pressure is reversible. The reversibility is confirmed with a synchrotron-based high pressure XPS. A model rationalizing the pressure dependence of CO adsorption on this catalyst is suggested.

11:20am **SS+NC-MoM10 From Near-surface to Surface CuPt Alloy: Cu Surface Segregation Induced by CO Adsorption**, *K. Andersson, F. Calle, J. Rossmelst, I. Chorkendorff*, Technical University of Denmark

Bimetallic alloys offer a way of tuning electronic structure and hence also surface catalytic properties. For example, a CuPt near-surface alloy¹ has recently been suggested as a promising catalyst for the water-gas shift (WGS) reaction, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$. Crucial to the catalytic performance of such alloys is the surface composition and structure under reaction conditions. Examples of segregation of one component to form a surface oxide in oxidizing environments are many. However, largely unexplored are the effects of molecular adsorbates. Using a combination of XPS, in-situ and ex-situ IR, LEED, ISS and TPD, we have studied reversible surface changes induced by elevated CO pressures and sample temperatures for surfaces with varying Cu concentrations (up to 3 ML) in the near-surface region of Pt(111). We show that at sample temperatures high enough to overcome Cu diffusion barriers (~470 K),² a CO pressure of 2 mbar is sufficient to induce segregation of Cu to the topmost surface layer, switching a CuPt near-surface alloy to a novel well-ordered CuPt surface alloy with very different properties. The thermodynamic driving force behind the surface changes is rationalized on the basis of the much greater bondstrength of CO to Pt surface atoms in the presence of Cu atoms in the topmost surface layer. This is observed experimentally as large, well-defined and high temperature CO desorption peaks (up to 580 K). The so-called "d-band model"³ explains our findings.

¹ J. Knudsen et al., *J. Am. Chem. Soc.* 129 (2007) 6485.

² N. Schumacher et al., *Surf. Sci.* 602 (2008) 702.

³ J. Greeley, J.K. Norskov, M. Mavrikakis, *Annu. Rev. Phys. Chem.* 53 (2002) 319, and references therein.

11:40am **SS+NC-MoM11 CO Adsorption on Ru(0001) and PtRu/Ru(0001) Near Surface Alloys Using Ambient Pressure Photoemission Spectroscopy**, *D.E. Starr*, Brookhaven National Laboratory, *H. Bluhm*, Lawrence Berkeley National Laboratory

Carbon supported PtRu alloy particles are currently used as the anode catalyst in proton exchange membrane fuel cells. Small amounts of CO, in the ppm concentration range, present in the H₂ fuel are known to poison the catalyst. The role of Ru is to increase the CO tolerance of the catalyst. Since both Pt and Ru are expensive metals, understanding the catalyst's susceptibility to CO poisoning and the function of Ru in reducing this susceptibility are important aspects for cost reduction of proton exchange membrane fuel cells. The increased CO tolerance of these catalysts has been attributed either to CO oxidation by adsorbed OH groups on Ru or by weaker adsorption of CO on the alloy surface than either of the pure metals leading to a decrease in the steady-state coverage of CO. Direct proof of the mechanism for the alloy's increased CO tolerance requires detailed knowledge of the surface composition under reaction conditions. As a first step towards gaining this knowledge, we have used the Ambient Pressure Photoemission Spectroscopy experiment at Beamline 11.0.2 of the Advanced Light Source to study the adsorption of CO onto Ru(0001) and PtRu near surface alloys on Ru(0001) at 300 K and pressures up to 0.5 torr. The results of this study show that at 300 K the coverage of CO on the Ru(0001) surface saturates at ~1x10⁻⁶ torr and remains constant up to 0.5 torr. At pressures greater than 10⁻² torr a second peak appears in the O1s spectra indicating the presence of a second CO species. Comparison of

these results to those obtained with a PtRu surface alloy formed on the Ru(0001) surface will be presented.

Thin Film

Room: 302 - Session TF+NC-MoM

ALD of Hybrid Materials and ALD on 3D Nanostructures

Moderator: S.M. Rossnagel, IBM T. J. Watson Research Center

8:20am **TF+NC-MoM1 Interfacial Organic Layers: Tailored Nucleation and Growth of Inorganic Thin Films for Applications in Molecular Electronics and Barrier Layers**, *J.R. Engstrom*, Cornell University **INVITED**

Interfacial organic layers, including self-assembled monolayers, have long been recognized for their potential to modify the chemical and physical properties of surfaces. One particularly exciting concept is to use interfacial organic layers to promote thin film deposition of inorganic materials, particularly in situations where nucleation is problematic. Another interesting concept involves making use of the organic layer itself as an active component in molecular-based electronics. Here, a challenge is to make electrical (top) contact with the organic layer, whilst not degrading its properties, nor forming electrical shorts due to penetration of the organic layer. Key to the realization of both of these concepts is developing an understanding of the interactions between thin film precursors, and interfacial organic layers possessing a variety of terminal organic functional groups and also microstructures. In this talk we will summarize our work in this area concerning: (i) the formation of the interfacial organic layers and their characterization; (ii) the reactions of these layers with Ti- and Ta-amido coordination complexes; and (iii) the formation of inorganic thin films on these layers using atomic layer deposition. Here we make use of supersonic molecular beam scattering techniques, atomic force microscopy, scanning transmission electron microscopy, and x-ray photoelectron spectroscopy. We will find that (undesired) penetration of the organic layers by the coordination complexes can be avoided and/or minimized by proper design of the organic layer. Concerning growth on the layers using atomic layer deposition, we find that the chemical termination and microstructure of the organic layers play an important role in terms of the kinetics of nucleation and growth, and the evolution of thin film morphology.

9:00am **TF+NC-MoM3 New Approaches to Molecular Layer Deposition Using Ring-Opening and Heterobifunctional Reactants**, *D. Seghete, B. Yoon, A.S. Cavanagh, S.M. George*, University of Colorado at Boulder

Molecular layer deposition (MLD) can produce organic or hybrid organic-inorganic films. Current MLD schemes usually employ two homobifunctional monomers as reactants. This approach presents practical difficulties because the homobifunctional monomer can react with two chemical functional groups on the surface. These "double" reactions can remove the active surface species and reduce the MLD growth rate. Homobifunctional reactants can be avoided by using ring-opening and heterobifunctional reactants. The ring-opening reactants prevent double reactions by containing a concealed functionality that only expresses itself upon reaction. The heterobifunctional reactants have two chemical functional groups that are different. These precursors react only monofunctionally with the surface to avert double reactions and growth termination. In this study, we report a three-step MLD process that involves trimethylaluminum (an inorganic trifunctional reactant), ethanolamine (a heterobifunctional reactant), and maleic anhydride (a ring-opening reactant). The extension to three-step ABC MLD processes expands the variety of reactants and compositional diversity that can be achieved for MLD. In this three-step process, trimethylaluminum (TMA) reacts with carboxylic acid species (-COOH) to deposit -AlCH₃ species. The -AlCH₃ species then react preferentially with the hydroxyl end of ethanolamine (EA) to form a surface terminated with -NH₂ species. Maleic anhydride (MA) then reacts with these amine species and undergoes a ring-opening reaction to produce carboxylic acid (-COOH) species. The TMA can then react again with the carboxylic acid species to repeat the ABC cycle. In situ Fourier transform infrared spectroscopy and quartz crystal microbalance measurements were employed to monitor the surface reactions and measure the mass changes at temperatures from 80-150 °C. Ex situ x-ray reflectivity (XRR) confirmed the linear growth of the MLD films versus number of ABC cycles. The growth rates decreased with increasing temperature from 23 Å per ABC cycle at 90 °C to 8 Å per ABC cycle at 150 °C. The XRR scans also established the low surface roughness, uniform composition and low density of the MLD films.

9:20am **TF+NC-MoM4 Molecular Layer Deposition of Hybrid Organic-Inorganic Polymers Based on Metal Alkyl and Diol Reactants**, *B. Yoon, J.L. O'Pachen, S.D. Davidson, D. Seghete, A.S. Cavanagh, S.M. George*, University of Colorado at Boulder

Hybrid organic-inorganic polymers can be deposited by molecular layer deposition (MLD) using metal alkyl and diol reactants. Our earlier work studied the deposition of alucone MLD films using trimethyl aluminum (TMA) and ethylene glycol (EG). In this work, we extend the possible metal alkyl reactants to diethyl zinc (DEZ) and the diols to 1,4-butanediol (BD), and 1,4-hydroquinone (HQ). Our studies were performed using in situ Fourier transform infrared (FTIR) spectroscopy to identify the surface species, in situ quartz crystal microbalance (QCM) measurements to quantify the mass gains with each surface reaction, x-ray reflectivity (XRR) studies to measure the film thicknesses and densities and transmission electron microscopy (TEM) to image the MLD films on nanoparticles. The reaction of TMA and EG results in a poly(aluminum ethylene glycol) film that can be described approximately as $(\text{Al-O-CH}_2\text{CH}_2\text{-O})_n$. These $(\text{Al-O-R-O})_n$ polymer films are known as alucones. The reaction of DEZ with organic diols produces zinc-containing $(\text{Zn-O-R-O})_n$ polymer films that can be called "zincones". FTIR spectroscopy studies revealed that the surface chemistry for zincone MLD was similar to alucone MLD. QCM measurements showed linear growth for zincone MLD versus number of reaction cycles. Corresponding XRR and TEM studies revealed zincone MLD growth rates of 2.0 Å per AB reaction cycle. Different organic constituents can be incorporated into alucone MLD films using other organic diols. Alucone MLD was studied using TMA + BD and TMA + HQ. QCM measurements showed linear growth with total mass gains of 30 ng/cm^2 for TMA + BD and 89 ng/cm^2 . Using film densities obtained from XRR studies, these total mass gains represent growth rates of 2.3 Å and 5.4 Å per AB reaction cycle for TMA + BD and TMA + HQ, respectively. The larger growth rates for TMA + HQ may be explained by the greater rigidity of HQ that could prevent "double" reactions from reducing the number of active surface sites and lowering the growth rate per AB reaction cycle.

9:40am **TF+NC-MoM5 Infrared Analysis of Conformality of Al_2O_3 and ZnO Atomic Layer Deposition on 3D Fibrous Structures**, *G. Scarel, G.K. Hyde, J.C. Spagnola, J.-S. Na, B. Gong, Q. Peng, G.N. Parsons*, North Carolina State University

Conformally coated 3D natural fibers are becoming important in various areas of catalysis, bio-scaffolds, drug delivery, energy storage and conversion applications. In this work we report on growth and characterization of inorganic coatings (Al_2O_3 and ZnO) on fibers including cotton and polypropylene. The coatings were prepared using low temperature (about 100 degree centigrade) ALD. We used tri-methyl aluminum and H_2O for Al_2O_3 and di-ethyl zinc and H_2O for ZnO. ALD is well known to produce conformal coatings on planar surfaces and deep trenches. However it is more difficult to establish and to characterize linear growth and conformality in complex 3D fibrous systems. We have developed a new method to evaluate linear growth and conformality on complex nano- and micro 3D structures. The method uses infrared spectroscopy to detect longitudinal optical (LO) modes in off-normal configurations (Berreman effect). These features pertain to ionic oxides and are sensitive to film thickness because they are generated by vibrations normal to the ionic oxide layer surface. We show that the height of a peak related to an LO mode grows linearly with the number of ALD cycles and that this linear behavior is related to the linearity of the growth on a planar $\text{Si}(100)$ substrate. In addition, the angular behavior of the height of peaks related to LO modes in transmission infrared spectra can be related to the degree of coating conformality. In addition the data show that on 3D structures, especially on fibers, the number of incubation cycles needed before linear growth starts is even higher than on planar substrates. We investigate this phenomenon considering the structural, compositional, and the surface energy properties of the coated structures. The method we propose offers an easy non-local method to ascertain linear growth and conformality on complex 3D samples coated using ALD.

10:20am **TF+NC-MoM7 Ferromagnetic Nanostructures by Atomic Layer Deposition: From Thin Films to Ferrofluids and Core-Shell Nanotubes**, *K. Nielsch*, Hamburg University, Germany, *J. Bachmann*, Hamburg University and Max Planck Institute of Microstructure Physics, Germany

INVITED

Magnetic nanostructures have a broad range of applications, most prominently in the areas of data storage, microelectronics, biosensing, and cell separation. For the preparation of such structures, we use atomic layer deposition (ALD), a thin film technique with the unique ability to coat pore structures of high aspect ratio conformally and uniformly while accurately tuning the layer thickness. We approach the preparation of the magnetic materials Fe_3O_4 , Co, and Ni in two steps. ALD is first used to deposit Fe_2O_3 ,¹ CoO or NiO,² either from the reaction of the corresponding metallocene with ozone or from that between the metal alkoxide and water.

The oxide is subsequently reduced to the desired ferromagnetic phase by hydrogen gas. By conformal coating of self-ordered porous anodic alumina membranes, arrays of magnetic nanotubes with diameters down to 20 nm and wall thicknesses of less than 5 nm have been achieved. The magnetic properties of the nanotube arrays, studied by SQUID magnetometry, strongly depend on the geometric parameters. The effects of tube wall thickness and tube diameter have been studied systematically,¹ and the experimental data match the results of our theoretical simulations.³ Dissolution of the alumina matrix yields ferrofluidic suspensions, made out of widely tunable magnetic particles. Finally, ALD also enables us to create core-shell nanoobjects combining different magnetic materials in various, accurately controlled geometries.

¹ J. Bachmann, J. Jing, M. Knez, S. Barth, H. Shen, S. Mathur, U. Gösele, K. Nielsch, J. Am. Chem. Soc. 2007, 129, 9554-9555.

² M. Daub, M. Knez, U. Gösele, K. Nielsch, J. Appl. Phys. 2007, 101, 09J111.

³ J. Eserig, J. Bachmann, J. Jing, M. Daub, K. Nielsch, D. Altirb, Phys. Rev. B 2008, accepted.

11:00am **TF+NC-MoM9 Tube-in-Tube Nanostructures Formed from the Kirkendall Effect using Atomic Layer Deposition on Three Dimensional Electrospun Fiber Templates**, *Q. Peng, X.Y. Sun, J.C. Spagnola, R.J. Spontak, C. Saquing, S.A. Khan, G.N. Parsons*, North Carolina State University

Three-dimensional (3D) macrostructures consisting of well-defined nanoscale elements with controlled properties have attracted significant interest for a range of fields. To date, large-scale fabrication of these 3D macrostructures remains an important outstanding challenge. We are currently exploring atomic layer deposition on a variety of nano- and micro-scale fiber systems for fabrication of macro size 3D structures with molecular-scale control. Recently, we have applied low temperature (< 80 degree C) Al_2O_3 and ZnO ALD processes onto 3D polyvinyl alcohol electrospun fiber matrix templates to form Al_2O_3 , ZnO and $\text{Al}_2\text{O}_3/\text{ZnO}/\text{Al}_2\text{O}_3$ multilayer nanotubes with controlled tube wall thickness. SEM, TEM and XRD have been used to probe the structure and crystal structure of the materials as a function of deposition parameters and post-deposition calcination and annealing. We find that upon annealing at 700 degree C, the ZnO and Al_2O_3 layers in the $\text{Al}_2\text{O}_3/\text{ZnO}/\text{Al}_2\text{O}_3$ coaxial structures can react with each other, due to the solid-state reaction and diffusion process between ZnO/ Al_2O_3 (Kirkendall effect), to form pairs of coaxial ZnAl_2O_4 hollow nanotubes separated by a nanoscale gap. Moreover, by controlling the thickness of the individual Al_2O_3 and ZnO layers and the ZnO/ Al_2O_3 thickness ratio, the final thickness of the nanotubes and the separation nanogap can be tuned to form a variety of well-defined tube-in-tube nanosystems. Under some conditions, unreacted ZnO layers can remain after annealing, resulting in multi-compositional structures with segregated voids. These results show the feasibility of extending reactivity of ALD thin films and Kirkendall effect to form a range of quasi-one-dimensional nanostructures for a variety of potential applications.

11:20am **TF+NC-MoM10 Structured Photoanodes for Enhanced Electron Transport in Dye Sensitized Solar Cells (DSSC) with Atomic Layer Deposition (ALD) Functionalization**, *M.J. Pellin, A.B.F. Martinson, J.W. Elam*, Argonne National Laboratory, *J.T. Hupp*, Northwestern University

INVITED

Inexpensive, efficient solar energy conversion requires synthetic methodology capable of creating structures that resolve the conflict between the long lengths required for efficient photon absorption with the short photoelectron diffusion lengths found for all but the most perfect crystalline materials. DSSC's photoanodes utilize titania nanocrystals sensitized with monolayers of dye to achieve efficient photon absorption. However, DSSC conversion efficiencies have been limited to ~10% by a charge collection time of milliseconds at the maximum power point. Thus efficient charge extraction is only possible with an iodide/triiodide (I^-/I_3^-) redox shuttle with both the high driving force needed to regenerate dyes at acceptable rates (and the consequent >500 mV energy cost/photon) and a remarkably inefficient I_3^- electron interception rate. We have been addressing this problem using the ability of ALD to conformally grow nm thick, pin-hole free layers on nanoporous, high surface area supports. The charge collection times can be improved either by reducing the dimensionality of the photoanode or by reducing the electron collection distances. We address the former with precision films grown on nanoporous substrates such as anodic aluminum oxide (AAO) or silica aerogel supports. The AAO, for instance, has a regular array of 200 nm straight channels that traverse its 60 @smicron@ thick membrane. ALD is used to conformally coat with either ZnO or TiO_2 (achieving peak efficiencies at ~ 4-5 nm thickness) the membrane channels. One side of the membrane is coated with a thick transparent conducting oxide such as ITO. The pore walls are then sensitized with a dye and the resulting photoanode is assembled into a photocell. The linear tubes thus created form a one-dimensional network of 60 μm long tubes with excellent charge collection times. Dramatically reduced electron collection distances can be tested with a more complex

structure grown by first coating the AAO substrate with a transparent conducting oxide such as ITO, then adding a wide band gap oxide (TiO_2), before completing the cell with dye attachment and assembly. In these cells, electron diffusion occurs radially through the thin (~5 nm) TiO_2 layer into the TCO, rather than along the pore. Again the electron diffusion times are dramatically reduced. The wide palette, precision composition, and conformal nature of ALD synthesized films enable the exploration of these complex structures improving our understanding of the factors limiting solar energy conversion. *The work at Northwestern is supported by the U.S. Department of Energy, Basic Energy Sciences Program, under Grant DE-FG02-87ER13808. Work at Argonne is supported by the U.S. Department of Energy, BES-Materials Sciences under Contract W-31-109-ENG-38.

Monday Afternoon, October 20, 2008

Applied Surface Science

Room: 207 - Session AS-MoA

Electron Spectroscopies

Moderator: A. Herrera-Gomez, Cinvestav-Unidad Queretaro, Mexico

2:00pm **AS-MoA1 Probing the Interfacial Chemistry of Polymer-Metal Systems with Electron Spectroscopy**, *J.F. Watts*, University of Surrey, UK **INVITED**

The nature of the interface between a polymer phase and a metallic substrate is crucial in many important technological endeavours, for example; adhesive bonding, organic coatings for corrosion protection and sealants. XPS has been used for many years for the forensic analysis of failed interfaces, and in some cases the analysis of interfacial failure surfaces may provide a means to understanding adhesion, and perhaps even identifying certain species that are responsible for compromising performance. However in most cases it is necessary to resort to specimen preparation strategies that allow the surface chemical analysis of the necessarily thin layer responsible for adhesion between the two phases in order to investigate the interfacial chemistry of adhesion. Two methods developed in the author's laboratory, which allow access to the interfacial region, will be described. The deposition of a very thin layer ($< 2\text{nm}$) of organic material, either a component of an adhesive or coating or a dilute solution of the fully formulated system itself, provides a route to probing the interfacial chemistry directly using XPS and ToF-SIMS. The C1s XPS data provides information regarding the changes in carbon chemistry occurring at the interface and fine structure in cationic spectra provide indications of bond formation between organic layer and substrate. This may lead to the conclusion of the existence of specific interactions across the interface and the presence of these can often be confirmed with ToF-SIMS. An alternative approach is to section a polymer/metal system to expose the interface for analysis. The use of ultra-low angle microtomy (ULAM) cut at angle in the range of $0.003 - 2$ degrees relative to the interface has been shown to be extremely effective. Once prepared small area XPS can be used to profile across the interface and in the best cases a depth resolution of $< 20\text{ nm}$ can be achieved. Using this approach it has been possible to establish the interdiffusion of active components in a paint system and the aggregation of adhesion promoter molecules, incorporated in an adhesive formulation, at the interface of aluminium bonded with a commercial epoxy adhesive.

2:40pm **AS-MoA3 2-Dimensional X-Ray Photoelectron Spectroscopy for Composite Surface Analysis**, *S. Suzer*, Bilkent University, Turkey

We describe a method for obtaining 2-Dimensional X-Ray Photoelectron Spectroscopic data derived from the frequency dependence of the XPS peaks recorded under electrical square-wave pulses, which control and affect the binding energy positions via the electrical potentials developed as a result of charging. By using the frequency dependence of the peaks and their cross-correlations, our technique enables us to elucidate electrical characteristics of surface structures of composite samples and bring out various correlations between hidden/overlapping peaks. Application of this technique to various composite surface structures will be presented, and discussed.

3:00pm **AS-MoA4 Evaluation of Uncertainties in X-ray Photoelectron Spectroscopy Intensities Associated with Different Methods and Procedures for Background Subtraction**, *C.J. Powell, J.M. Conny*, National Institute of Standards and Technology

We report uncertainties in X-ray photoelectron spectroscopy (XPS) intensities arising from commonly used methods and procedures for subtraction of the spectral background. These uncertainties were determined from a comparison of XPS intensities reported by volunteer analysts from 28 institutions and the corresponding intensities expected for a set of simulated XPS spectra. We analyzed peak intensities from 32 sets of data for a group of twelve spectra that had been simulated for a monochromatized Al K α source. Each reported intensity was compared with an expected intensity for the particular integration limits chosen by each analyst and known from the simulation design. We present ratios of the reported intensities to the expected intensities for the background-subtraction methods chosen by the analysts. These ratios were close to unity in most cases, as expected, but deviations were found in the results from some analysts, particularly if the main peak was asymmetrical or if shakeup was present. We showed that better results for the Shirley, Tougaard, and linear backgrounds were obtained when analysts determined peak

intensities over certain energy ranges or integration limits. We will present recommended integration limits for the three backgrounds that should be useful in the determination of peak intensities for other XPS spectra.

3:20pm **AS-MoA5 Investigation of Shallow Buried Interfaces by Photoelectron Spectroscopy and its Application to Protective Films on Metals**, *Y. Wang, P.M.A. Sherwood*, Oklahoma State University

It is generally very important to understand the chemical interactions that may occur at a buried interface in order to evaluate the choice of surface coatings that might be used in many practical applications. In order to make such a study it is generally possible to produce a very thin film of surface coating that is sufficiently thin to allow photoelectron spectroscopic data to be obtained from the interfacial region. The use of core and valence band photoemission to probe shallow buried interfaces will be illustrated using a number of examples of thin films on metals and carbon fibers. In particular the presentation will illustrate how thin oxide-free films of phosphate on steel surfaces can be studied, and their interaction with polymer films investigated. The effect of corrosive environments using water and saline solutions on these surfaces will be reported. It will be seen that the oxide-free phosphate films provide corrosion protection for the steel, and that the corrosion behavior is impacted by the addition of thin polymer films. The surface chemistry can be determined by using difference spectra, and by interpreting the valence band data by comparison with calculated spectra obtained from band-structure and other calculations.

4:00pm **AS-MoA7 Looking Beneath the Surface: Electron Spectroscopy with X-ray Standing Waves and Hard X-rays**, *C.S. Fadley*, University of California, Davis and Lawrence Berkeley National Laboratory **INVITED**

I will discuss two relatively new developments in photoemission: the use of nanometer-scale standing-wave (SW) excitation so as to selectively look at different depths below the surface¹⁻³ and the use of harder x-ray excitation in the multi-keV range so as to probe more deeply below the surface, in what has been termed HAXPES or HXPS.⁴ Both of these approaches have the potential for enhancing the sensitivity of photoemission to both bulk and buried interface properties, while at the same time permitting the study of near-surface phenomena. After a brief overview of basic concepts, I will discuss several recent applications of these methods, separately and in concert. These will include: variable-temperature HXPS measurements at the ESRF on fractured cubic and cleaved bilayer lanthanum strontium manganite samples,^{5,6} SW HXPS measurements at both BESSY⁷ and SPring8⁸ on systems of relevance to spintronic and semiconductor IC applications, the possibility of doing angle-resolved HXPS so as to carry out band mapping,⁹ and the possible benefits of photoelectron diffraction in the hard x-ray regime for local structure determinations.¹⁰

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¹S.-H. Yang, B.S. Mun et al., *J. Phys. Cond. Matt.* 14, L406 (2002).

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4:40pm **AS-MoA9 Methods for X-ray Photoelectron Spectromicroscopy**, *C.J. Blomfield, A.J. Roberts, S.J. Hutton*, Kratos Analytical Ltd, UK, *N. Fairley*, Casa XPS Ltd, UK

Fast parallel XPS imaging of surfaces has been commercially available for more than a decade. During this time numerous examples of both elemental and chemical state images have been published. X-ray photoelectron imaging has become a routine technique for the determination of lateral distribution of elements and chemical species at the surface and capable of a lateral resolution of $< 3\mu\text{m}$ over areas of several millimetres. More recently the spherical mirror analyser (SMA), used for energy selection in XPS imaging applications, has been combined with the delay line detector (DLD), a two-dimensional, pulse counting electron detector. This detector has allowed the realisation of quantitative surface chemical state microscopy by XPS. To generate such information requires the acquisition of a several images, or a series of images, incremented in energy so that each pixel contains photoelectron intensity information as a function of photoelectron energy. Fast counting electronics enable the detector to collect over 65,500 pixels per image. The different methods of collecting

the necessary data and the application of multivariate analysis to analyse the information content of the data and as a tool for noise reduction in individual images or spectra will be described. Methods for obtaining the maximum information from the minimum acquisition time will also be discussed. The application of the various approaches to a variety of diverse samples will be presented.

5:00pm **AS-MoA10 Structural Properties of Epitaxial SrHfO₃ Thin Films on Si(100)**, *M. Sawkar-Mathur*, University of California, Los Angeles, *C. Marchiori, J. Pompeyrine*, IBM Zurich Research Laboratory, *J. Bargar, M. Toney*, Stanford Synchrotron Radiation Laboratory, *J.P. Chang*, University of California, Los Angeles

Hafnium based amorphous oxides are currently being implemented to enable the 45-nm and 32-nm technology nodes of metal oxide semiconductor field effect transistors (MOSFETs). However, the interfacial issues arising at the amorphous oxide/crystalline Si interface justify the exploration of a lattice-matched crystalline oxide on Si to achieve an atomically sharp interface, thereby improving the device reliability. In this work, SrHfO₃, a perovskite oxide, was grown on silicon using molecular beam epitaxy (MBE). In-depth structural analysis using synchrotron techniques including XRD with a four circle diffractometer and grazing incidence EXAFS was performed to determine the crystalline quality and short range chemical bonding and order in these ultra-thin SrHfO₃ films. Nearly epitaxial growth of SrHfO₃ on Si was observed with good crystalline quality and some misalignment of grains. From the in-plane diffraction pattern, the SrHfO₃ (100) plane was found to be parallel to the Si(110) plane, yielding a 6% lattice mismatch. The d spacing of the SrHfO₃ (300) plane was found to be 1.37 Å which corresponds well with the literature reported value of 1.36 Å, suggesting no significant strain in the film. Phi scans of the SrHfO₃ (200) peak showed the four-fold symmetry expected for that plane, with no twinning, further substantiating the lack of significant strain in the film. The atomic planes were found to be highly parallel, as evidenced by the presence of interference fringes around the SrHfO₃ (001) plane. Cluster models with a radial distance of 4 Å were constructed using the perovskite crystal structure of SrHfO₃ to model the scattering amplitudes of the absorption spectra and quantify the nearest and second nearest neighbors surrounding the center absorbing Hf atom. A low level of disorder and minimal defects were observed. Based on the complementary analyses of synchrotron GI-EXAFS and XRD, MBE grown SrHfO₃ on Si has the potential to be a crystalline metal oxide for implementation in CMOS devices.

5:20pm **AS-MoA11 Improved Depth Resolution for Scanning Auger Analysis Using a Novel Sample Preparation**, *W. Liu, S. Schauer, D. Theodore, H. Ramirez*, Freescale Semiconductor Inc.

Auger depth profile analysis can be impeded by the roughening during ion sputtering. This is especially noticeable when analyzing semiconductor devices, because of the variety of materials that are susceptible to roughening, and the importance of very thin interfaces. A novel technique is presented in this paper, which combines scanning Auger analysis with FIB thinning, for analysis of single via interfacial structures in failure analysis of ICs devices. After a failing structure was identified by electrical fault isolation techniques, FIB sample preparation removes all the materials from top of the device including polyimide, passivation, metal layers, dielectric layers (ILD) until reaching about 200 Angstroms above the via interface in tungsten plug. Then a PHI SMART 200 scanning Auger instrument with a Physical Electronics model 06-350 ion gun was used for Auger depth profiling of this single via. A thin oxidized interface was observed between TiN glue layer and TiN ARC (anti-reflection coating) which resulted in the via failure. This layer would have been impossible to detect using conventional sputter depth profiling techniques. It was concluded from the following investigation and experiments that this interfacial material was caused by the "backsputtering" of ARC TiN during via etch and RF sputtering before TiN glue deposition.

Biomaterial Interfaces

Room: 202 - Session BI+SS+NC-MoA

Honorary Session for Bengt Kasemo

Moderator: M. Textor, ETH Zürich, Switzerland

2:00pm **BI+SS+NC-MoA1 Self-Assembly of Organic Molecules on Surfaces Studied by STM: Dynamics, Chirality and Self-Organization**, *F. Besenbacher*, University of Aarhus, Denmark **INVITED**

Adsorption and organization of organic molecules on solid surfaces is central to self-assembly and bottom-up fabrication within nanoscience and technology. The Scanning Tunneling Microscope allows exploration of

atomic-scale phenomena occurring on surfaces: Dynamic processes can be followed by fast-scanning STM, and from data acquired at a range of temperatures; detailed information on kinetic parameters can be extracted. In the talk, a number of studies investigating dynamics and organization of organic molecules on metal surfaces will be described, addressing surface diffusion, chiral recognition chiral switching and also the interaction of molecules with chiral sites on a metal surface¹⁻⁵. Finally, the self-assembly of Nucleic Acid (NA) base molecules on solid surfaces has been investigated. I will discuss the fact that Guanine molecules form the so-called G-quartet structure on Au(111) that is stabilized by cooperative hydrogen bonds⁶. Interestingly, cytosine molecules only form disordered structures by quenching the sample to low temperatures, which can be described as the formation of a 2D organic glass on Au(111)⁷. Molecular recognition between complementary nucleic acid (NA) bases is vital for the replication and transcription of genetic information, both in the modern cell as well as under prebiotic conditions, when a dedicated molecular machinery of evolved living organisms had not yet been developed. By means of variable-temperature Scanning Tunneling Microscopy (VT-STM) we show that on a flat metal surface, formation of complementary NA bases pairs is favoured. The C+G mixture resilience to heating is due to the formation of G-C Watson-Crick base pairs. The observation that not the oligonucleotide backbone, but a flat metal surface may be instrumental for specific WC base pairing has interesting implications for the proposed scenarios of the emergence of life.

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2:40pm **BI+SS+NC-MoA3 Interaction of AH Amphipathic Peptide with Lipid Bilayers and Application to the Understanding of Hepatitis C Viral Infection via QCM-D Measurements**, *C.W. Frank, N.J. Cho*, Stanford University, *K.H. Cheong*, Samsung Advanced Institute of Technology, Korea, *J.S. Glenn*, Stanford University **INVITED**

Membrane association of the hepatitis C virus NS5A protein is required for viral replication. This association is dependent on an N-terminal amphipathic helix (AH) within NS5A and is restricted to a subset of host cell intramolecular membranes. The mechanism underlying this specificity is unknown, but it may suggest a novel strategy for developing specific antiviral therapy. Here we probe the mechanistic details of NS5A amphipathic helix-mediated binding to both cellular-derived and model membranes using biochemical membrane flotation and quartz crystal microbalance with dissipation. In both assays, we observed AH-mediated binding to model lipid bilayers. When cellular-derived membranes were coated on the quartz nano-sensor, however, significantly more binding was detected. Biochemical flotation assays performed with trypsin-treated cellular-derived membranes exhibited reduced amphipathic helix-mediated membrane binding, while membrane binding of control Cytochrome b5 remained unaffected. Similarly, trypsin treatment of the nano-sensor coated with cellular membranes eliminated amphipathic helix binding to the cellular membranes while that of a control lipid-binding protein remained intact. These results, therefore, suggest the effect of a protein in mediating and stabilizing the binding of NS5A's amphipathic helix to its target membrane. These results also demonstrate the successful development of a new nano-sensor technology ideal for both studying the interaction between a protein and its target membrane, and for developing inhibitors of that interaction.

3:20pm **BI+SS+NC-MoA5 Tethered Biomolecular Lipid Membranes - a Membrane Mimetic Sensor Platform**, *W. Knoll, I. Köper, R. Naumann, E.-K. Sinner*, Max-Planck-Institute for Polymer Research, Germany

This contribution summarizes some of our efforts in designing, synthesizing, assembling, and characterizing functional tethered lipid bilayer membranes (tBLMs) as a novel platform for biophysical studies of and with artificial membranes or for sensor development, employing, e.g., membrane integral receptor proteins. Chemical coupling schemes based on thiol groups for Au substrates or silanes used in the case of oxide surfaces allow for the covalent and, hence, chemically and mechanically robust attachment of anchor lipids to the solid support, stabilizing the proximal layer of a tethered membrane on the transducer surface. Surface plasmon optics, the quartz crystal microbalance, fluorescence- and IR spectroscopies, and electrochemical techniques are used to characterize these complex supramolecular interfacial architectures with respect to their assembly, their structure and function. We demonstrate, in particular, that these bilayers show the fluid character of a liquid-crystalline membrane with a specific electrical resistance of better than 10 MΩcm². Then a totally novel approach for the functional incorporation of membrane proteins, i.e., by their cell-free expression and in vitro reconstitution in the presence of

tBLMs is demonstrated. We focus on the yeast expression system for the synthesis of the olfactory receptor species OR5 from *Rattus norvegicus*. By the combination of the corresponding coding DNA with the protein synthesis machinery of a cell-extract (in vitro transcription and translation) we observe spontaneous and vectorial insertion of an interesting example for a membrane protein into a tethered bimolecular lipid membrane: the OR5 receptor as a family member of the G-protein coupled receptors.

4:00pm **BI+SS+NC-MoA7 Tethered Biomolecular Lipid Membranes - a Membrane Mimetic Sensor Pattern II**, *E.-K. Sinner*, Max-Planck-Institute for Polymer Research, Germany

4:20pm **BI+SS+NC-MoA8 2D Self-Assembly of Annexin-A5 on Lipid Surfaces: Biological Function, Mechanism of Assembly and Biotechnological Applications**, *A.R. Brisson, N. Arraud, R. Bérat, A. Bouter, B. Garnier, C. Gounou, J. Lai-Kee-Him, S. Tan*, CNRS-University of Bordeaux, France

INVITED

The self-assembly of proteins in 2D arrays at membrane surfaces is a generic strategy used by the cell for the construction of functional supramolecular edifices, e.g. bacterial S-layers, inter-membrane cadherin junctions, etc.. Annexin-A5 (Anx5) is the prototype member of the annexins, a superfamily proteins which share the properties of binding to negatively charged phospholipids in the presence of Ca²⁺ ions and forming various types of 2D ordered arrays at membrane surfaces. A detailed model of the structure and mechanism of formation of Anx5 2D arrays has been elaborated from EM, AFM and physico-chemical studies on various types of model membranes – liposomes in solution, lipid monolayers at the air-water interface, supported lipid bilayers.¹⁻⁴ The long-debated question of the functional role of Anx5 and annexins starts to be elucidated. The unique properties of binding and 2D self-assembly of Anx5 were exploited to develop various types of molecular tools for nanobiotechnological applications in proteomics, diagnosis or drug delivery. Chimerical proteins made of Anx5 fused to an antibody-binding moiety or linked to cell-adhesion peptides allow the construction of 2D platforms for anchoring antibodies, proteins or cells in a controlled orientation and density.⁵ Gold particles functionalized with oriented Anx5 or Anx5-fusion proteins are used for labelling membrane fragments exposing phosphatidylserine molecules, such as apoptotic membranes or plasmatic microparticles, opening novel strategies for the separation and the analysis of circulating cell membrane fragments.

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5:00pm **BI+SS+NC-MoA10 From Surface Science to Biointerfaces to Nanoscience**, *B. Kasemo*, Chalmers University of Technology, Sweden

INVITED

The development of surface science can, depending on ones background and focus, be regarded as a bottom up outgrowth of, e.g., solid state physics towards surfaces (structure, electron structure,...) or molecular physics towards interfaces (collision dynamics, adsorption,...), or one can alternatively see it as the result of a top down process, where technologically important areas, such as semiconductor technology, materials science, catalysis and biointerfaces [1], stimulated development of more knowledge about and better tools to study interface properties and processes. The strength of surface science originates to a large extent from the strong feed back loop between the top down and bottom up processes, connecting a manifold of interesting fundamental questions with a large diversity of applications. Historically the focus of surface science has moved from simple model systems of small molecules on metal surfaces in UHV, to more complex systems in UHV or at higher gas pressures (e.g. in catalysis), to the liquid phase (e.g. electrochemistry), and further to very complex systems (biointerfaces, tribology,...), involving also more complex materials like oxides and polymers. The evolution sketched above is here exemplified by a personal and subjective choice of examples, like surface scattering and charge transfer processes, catalysis, and biomimetic membranes. The “newest” addition on the arena is nanoscience and nanotechnology, which has connected to almost all fields of traditional surface science. Although one can claim in catalysis, and several other fields, that there has always been a “nano-“ element, the control of the latter through fabrication and characterization, is what has changed dramatically over the past decade or so. Specific examples chosen here to illustrate this latter development is taken from nanotechnology for sustainable energy [2], namely (i) so called LSPR applications for solar cells and sensing, (ii) metal hydrides, and (iii) exhaust cleaning catalysis and (iv) fuel cells.

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Graphene Topical Conference

Room: 306 - Session GR+SS+NC-MoA

Materials Issues in Graphene from SiC

Moderator: N.P. Guisinger, Argonne National Laboratory

2:00pm **GR+SS+NC-MoA1 Ultrahigh Vacuum Growth, Electrical Characterization, and Patterning of Graphene Nanostructures on Si- and C-Polar 6H-SiC Surfaces**, *A. Sandin, Z. Wang, J.L. Tedesco, J.E. Rowe*, North Carolina State University, *R.J. Nemanich*, Arizona State University

We report the growth of graphene films on both C-polar and Si-polar surfaces of 6H-SiC by thermal decomposition in an ultrahigh vacuum (UHV) chamber. Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) have been used in situ to characterize the UHV films. Following growth, focused ion beam lithography has been used to successfully etch the graphene films and control the lateral dimensions of a number of nanostructures on these graphene layers with etch rates of ~18 nm/s and lateral dimensions of ~250 to 1500 nm. Epitaxial graphene films (1-4 layers thick) have been grown on the Si face. Theoretical reports have recently addressed the bandgap engineering of graphene nanoribbons by altering the physical dimensions, edge structure, and edge atoms of the nanoribbons. However, experimental control of the growth and quality graphene nanostructures is still a challenge. Several experimental studies have shown that annealed SiC does not significantly influence the electronic quality of the epitaxial graphene overlayer. However, these studies also indicate that the thickness of graphene films can be varied by controlling the Si decomposition and carbon aggregation on the surface through control of the annealing. Graphene growth on the Si-face suffers from pit formation located at SiC atomic-height steps and the carbon nanomesh (~13x13) can be observed using LEED and STM even for our thickest Si face graphene layers. Our results for graphene film growth on the more chemically reactive C-face find more rapid growth which is difficult to control. Due to the rapid growth, graphene nucleation cannot be mapped relative to the original SiC atomic terraces on the C-face. Scanning tunneling spectroscopy (STS) current-voltage (I-V) curves have been recorded and we observe both metallic behavior and bandgap formation, as well as the local density of states in bulk graphene and etched graphene edges. Future research will be directed to experimentally observe the proposed electronic properties of smaller (<20 nm in width) graphene nanostructures using STS.

2:20pm **GR+SS+NC-MoA2 Unique Stacking of Multi-Layer Graphene on 4HSiC(000-1)**, *J. Hass, J.E. Millan-Otoya, N. Sharma, M. Sprinkle, F. Ming, W.A. de Heer, P.N. First, E.H. Conrad*, Georgia Institute of Technology

Diffraction data have shown that multilayer graphene grown on the polar (000-1) face of 4H-SiC contains large, flat domains and rotational stacking faults approximately every 2 layers.¹ Such faults are particularly interesting because it has been demonstrated that rotational faults in bi- and tri- layer graphene films decouple adjacent sheets, thereby preserving the unique lattice symmetry and linear dispersion found for a single, isolated sheet.¹⁻³ This is in contrast with few-layer graphite, which grows in a Bernal stacking arrangement on the opposite polar (0001) face. Scanning tunneling microscopy (STM) and surface X-ray diffraction (SXRD) data exhibit a number of rotational domains in registry with the SiC substrate. Data will be presented which elucidate particular stacking orientations over micron scale domains. Scanning tunneling spectroscopy (STS) results will be interpreted in the context of symmetry breaking between sheets.

¹J. Hass, F.Varchon, J. E. Millán-Otoya, M. Sprinkle, N. Sharma, W.A. de Heer, C. Berger, P.N. First, L. Magaud, E.H. Conrad, *Phys. Rev. Lett.* 100, 125504 (2008).

²J.M.B. Lopes dos Santos, N.M.R. Peres, A.H. Castro Neto, *Phys. Rev. Lett.* 99, 256802 (2007).

³S. Latil, V. Meunier, L. Henrard, *Phys. Rev. B* 76, 201402(R) (2007).

2:40pm **GR+SS+NC-MoA3 Ultrahigh Vacuum and RF Furnace Production of Graphene on SiC**, *G.G. Jernigan, B.L. VanMil, D.K. Gaskill, J.C. Culbertson, P.M. Campbell*, US Naval Research Laboratory

INVITED

The electrical, mechanical, physical, and chemical properties of graphene have the scientific community in search of large area samples for technological applications. Since deHeer's¹ initial report of graphene formation by the thermal desorption of Si from SiC, efforts have been underway to use this method to make large area sheets of graphene. Creating graphene by desorbing Si from SiC is conceptually simple, but in practice it is very challenging to produce large area, uniform, electronic grade graphene. In this presentation, I will discuss the two processes we employ, ultrahigh vacuum (UHV) annealing (~10⁻⁸ mbar) and RF furnace heating (~10⁻⁵ mbar), to create graphene in areas ranging from 200 mm² to

4000 nm² on 4H and 6H SiC and on Si-face and C-face samples. As observed by Raman spectroscopy, both processes are capable of producing graphene, because each set of samples shows the distinctive D, G, and 2D Raman lines. Each process begins with the SiC surface being hydrogen etched to remove polishing damage and to create a uniformly stepped surface. However, the resulting graphene from each process has noticeably different characteristics. UHV production allows us to probe the graphene formation in situ with LEED, XPS, and STM. The UHV method results in single layer and few layer graphene films. Van der Pauw Hall measurements indicate the films have low mobility and the predominant carriers are electrons. AFM studies show that depending on desorption conditions (heating rate, final temperature, and cooling) the surface morphology is roughened due to formation of pits and islands. We believe this roughened surface explains the low mobility. RF furnace production allows us to form graphene in the same system that hydrogen etching is performed, thereby avoiding exposure of the sample to air. Van der Pauw Hall measurements of the RF furnace samples consistently have higher mobility than the UHV samples and the predominant carriers are holes. These films are thicker than the UHV samples and consist of multiple layers of graphene. The surface morphology does not consist of pits and islands, but instead shows lines of built up carbon along step edges. In the end, we want to produce graphene having the best characteristics of the UHV and RF furnace methods with controlled thickness (< 3 layers) and high carrier mobility (> 10,000 cm²/Vs).

¹C. Berger, et al, J. Phys. Chem. B 108, 19912-19916 (2004).

3:20pm GR+SS+NC-MoA5 Microscopic and Spectroscopic Studies of the Electronic Structure of Epitaxial Graphene on SiC (0001). *N. Sharma, D. Oh, M. Sprinkle*, Georgia Institute of Technology, *C. Berger*, CNRS Grenoble, France, *W.A. deHeer, T.M. Orlando, P.N. First*, Georgia Institute of Technology

Growth of high quality epitaxial graphene (EG) films on the basal plane of hexagonal SiC has been demonstrated previously, providing a potential route to wafer-scale graphene electronics. To realize this promise requires a detailed understanding of the atomic and electronic structure of the EG/SiC interface. For typical EG samples, STM measurements indicate a reconstructed interface (layer 0) covered by a layer (layer 1) that images as graphene (a honeycomb pattern) at low bias voltages, but appears to partially hybridize with interface states. For this layer, we also observe a strong suppression of the 2D Raman peak (also known as D* or G') that is characteristic of graphene. For the second EG layer, a single Lorentzian-shape 2D peak is observed, which may indicate some isolation of layer 2 from the material below. Graphene films grown on the SiC (0001) surface are intrinsically electron doped. The screening response of the 2D electron gas in EG is expected to be unique due to the small carrier density and novel electronic structure. We use local defects and deposited metal islands to locally change the carrier density, and scanning tunneling spectroscopy to probe the screening response. This is of interest since the screening region in EG could include a transition from hole to electron doping, resulting in a surface PN junction that could influence electrical transport in this system.

4:00pm GR+SS+NC-MoA7 Structural and Electronic Properties of Epitaxial Graphene on SiC(0001). *C. Riedl, D.S. Lee, J. Smet, L. Vitali, R. Ohmann, I. Brihuega*, MPI for Solid State Research, Germany, *A. Zakharov*, Lund University, Sweden, *C. Virojanadara*, now at: Linköping University, Sweden, *K. von Klitzing, K. Kern, U. Starke*, MPI for Solid State Research, Germany

Graphene layers can be grown on a solid substrate by the controlled graphitization of SiC surfaces by high temperature annealing in ultra high vacuum (UHV). However, the exact control of the number of layers grown and their quality remains a problem. In the present work, we use angular resolved ultraviolet photoemission spectroscopy (ARUPS) from He II excitation and low energy electron diffraction (LEED) to count the number of layers continuously during the preparation procedure in the home laboratory thus avoiding laborious synchrotron experiments. The layer structure and homogeneity is further analyzed by Raman spectroscopy, core level photoemission spectroscopy (PES) and low-energy electron microscopy (LEEM) measurements. On such precisely prepared graphene samples, we investigate their electronic structure using ARUPS and scanning tunneling spectroscopy (STS). The layer dependent shifting of the energetic position of the Dirac point and the detailed structure of the π -band dispersion are analyzed both with momentum and spatial resolution.

4:20pm GR+SS+NC-MoA8 Atomic Scale Properties of Epitaxial Graphene Grown on SiC. *G.M. Rutter, P.N. First*, Georgia Institute of Technology, *J.A. Stroscio*, National Institute of Standards and Technology
Two-dimensional electron systems have been of interest to scientists for many years. From high-electron mobility transistors to novel topological quasiparticles of the fractional quantum Hall effect, the field continues to be rich in scientific possibilities and technological pay-offs. To date, most

high-mobility 2D electron systems have been created at an interface between semiconductor heterostructures, making them inaccessible to the electron spectroscopies of surface science. Here we investigate graphene, a new 2D electron system that is accessible to surface studies. Our measurements use scanning tunneling microscopy and spectroscopy to elucidate the properties of epitaxial graphene, resolving heterogeneities at the level of single atoms. In this work, epitaxial graphene is created on silicon carbide wafers by thermal annealing in vacuum. Sequential scanning tunneling microscopy (STM) and spectroscopy (STS) are performed in ultrahigh vacuum at temperatures of 4.2 K and 300 K. These atomic-scale studies address the initial growth of single-layer epitaxial graphene and the role that the interface and defects play in the electronic properties of graphene. Our work shows evidence of graphene formation by mass transfer of carbon, indicated by step edge growth and the nucleation of graphene islands. STM topographic images of single-layer graphene show the atomic structure of the graphene and the graphene/SiC interface, as well as the character of defects and adatoms within and below the graphene plane.^{1,2} STS of lattice defects on single-layer graphene show localized peaks in the spectra. The energy position of such localized states offers a clue to the defect's origin and composition and will be discussed.

¹G. M. Rutter, et al., Phys. Rev. B 76, 235416 (2007).

²G. M. Rutter, et al., J. Vac. Sci. Technol. A in press, (2008).

4:40pm GR+SS+NC-MoA9 Layer-Dependent Properties of Epitaxial Graphene on Silicon Carbide*+, P.N. First, Georgia Institute of Technology

INVITED

Epitaxial graphene grown on single-crystal silicon carbide has been proposed as a platform for graphene-based nanoelectronics.¹ This new electronic material shows great potential, but also poses a number of challenges. I will discuss results from several surface characterization techniques that determine the structure and electronic properties of this system. In particular, scanning tunneling microscopy and spectroscopy are used to study the electronic and geometric structure versus the graphene layer index for epitaxial graphene on SiC(0001).² Additional measurements show that the structure of graphene grown on SiC(000 -1) differs dramatically from that grown on SiC(0001). Finally, results that address the physics of metal contacts to graphene will be presented.

*Work supported in part by NSF, NRI-INDEX, and the W. M. Keck Foundation. +Work done in collaboration with G. M. Rutter, J. Hass, N. Sharma, T. Li, E. H. Conrad, C. Berger, and W. A. de Heer at the Georgia Institute of Technology, and J. N. Crain, N. P. Guisinger, and J. A. Stroscio at the NIST Center for Nanoscale Science and Technology

¹C. Berger et al., J. Phys. Chem. B 108, 19912 (2004).

²G. M. Rutter et al., Science 317, 219 (2007); Phys. Rev. B 76, 235416 (2007); J. Vac. Sci. Technol. A (in press).

5:20pm GR+SS+NC-MoA11 Scanning Tunneling Spectroscopy of Epitaxial Graphene on SiC(0001). *S. Nie, R. Feenstra*, Carnegie Mellon University

Over the past few years many researchers have investigated the properties of single monolayers of graphite, known as graphene. This material exhibits novel electronic properties arising from its band structure which displays linear dispersion around the band extrema, leading to high carrier mobilities and the potential for high-speed electronic devices. Using scanning tunneling spectroscopy (STS) at room temperature we have studied the electronic properties of graphene formed on the Si-face of the SiC(0001) surface. The substrate was annealed in ultra high vacuum at temperatures ranging from 1200 to 1400°C to form the graphene. With increasing temperature the surface becomes more carbon rich, showing different surface structures including 5×5, 6×6, and graphene-covered 6×6. For the highest annealing temperatures, multiple (>5) layers of graphene were formed. Low-energy electron diffraction was used to monitor the change in surface structure as a function of temperature, and scanning tunneling microscopy (STM) was used to verify the structures. Tunneling spectra were acquired on each of the 5×5, 6×6, graphene-covered 6×6, and totally graphitized surfaces. A distinct spectrum of electronic states was observed on the 5×5 and 6×6 surfaces, containing intense spectrum peaks at about -1.5, -0.5, and +0.5 relative to the Fermi-level. A conductance minimum is seen at the Fermi-level for all spectra. The observed spectra are quite similar for the 5×5 and 6×6 surfaces, indicating that the spectral peaks arise from similar surface-derived dangling bonds and/or reconstructed bonding arrangements in both cases. As graphene forms, covering the 6×6 structure, these spectral peaks diminish in intensity and their energies shift slightly. In particular, near the Fermi-level, a region of minimum intensity forms extending about 0.6 to 0.8 eV below the Fermi-level. We tentatively associate this region with the 0.8 eV band gap that is known to form for bilayer graphene, with the Fermi-level located at the top of this gap. In any case, even with this evolution in the spectra, the overall position of spectral peaks is quite close for the graphene-covered surface as compared to the 5×5 and 6×6 surfaces. We therefore interpret the features observed in the graphene spectra as primarily arising from the electronic structure at the

interface between the graphene and the SiC. This work was supported the National Science Foundation, grant DMR-0503748.

MEMS and NEMS

Room: 206 - Session MN+NC-MoA

Fabrication at the Micro- and Nano- Scales for MEMS/NEMS

Moderator: A.V. Sumant, Argonne National Laboratory

2:00pm MN+NC-MoA1 Large Area Nanofabrication for MEMS Applications, L.E. Ocola, A. Imre, Argonne National Laboratory INVITED

As microelectromechanical systems (MEMS) shrink towards nano scale dimensions (or NEMS) the need for novel fabrication techniques increases. In this paper we revisit the use of two well-known techniques and propose new ways they can contribute toward the fabrication of next generation NEMS devices. The two techniques are super-high aspect ratio patterning using high-voltage electron beam lithography, and large area nanofabrication using a focused ion beam tool (FIB). In this paper we report on hydrogen silsequioxane HSQ nanopatterned into super-high aspect ratio structures (aspect ratio > 10) using 100 KV e-beam lithography, along with development in aqueous TMAH solution and DI water rinse, both performed at elevated temperatures (60 °C). Hot development allows for the rapid removal of low molar mass uncrosslinked molecules from the exposed regions while preserving the mechanical integrity of the nanopatterned structures. Raising the water rinse temperature to 60 °C also has the benefit of reducing the water surface tension by about 10%. Preliminary results of 90 nm structures using 1.2 micron thick HSQ, i.e. aspect ratios of 12, have been obtained. Such structures have immediate application in MEMS, Fresnel zone plate fabrication, and nanophotonics among others. We also have explored the use of focused ion beam (FIB) lithography in similar fashion to that of electron beam lithography. Although FIB has been employed extensively as a single write-field exposure tool for small device tailoring, mask repair, and sample characterization, it is rarely used for nanoscale patterning on a large area. This requires a high precision stage, and additional lithography software to handle complex and large pattern designs. In general, neither the hardware nor the software of FIB instruments is prepared for this task. We configured an FEI Nova 600 Nanolab Dual Beam FIB system with a 100 nm resolution X-Y stage, a Raith Elphy Lithography software interface and a Raith 16-bit DAC pattern generator for the X and Y deflectors. This provides us with the capability to expose more than 65,000 pixels/axis in one write-field, and allows us reading layout designs from files in GDSII format. Both capabilities are typical and standard in any medium-level e-beam lithography tool, but not found until recently in FIB systems. We present various large-area patterns milled in silicon and diamond thin films, and evaluated for stitching accuracy.

2:40pm MN+NC-MoA3 Large-scale Fabrication of Silicon Nanowire NEMS Devices Using a Top-down Approach, C.S. Roper, University of California, Berkeley, R.T. Howe, Stanford University, R. Maboudian, University of California, Berkeley

While bottom-up nanofabrication techniques, including vapor-liquid-solid (VLS) growth, can create single crystalline nanostructures,¹ the integration of a single nanowire into a functioning, addressable device is an extremely difficult task, and problematic on a large scale, owing to the stochastic nature of the growth process. The primary barriers to bottom-up integration are manifold. First, nanowire placement and alignment are difficult to control. VLS nanowire growth is catalyzed by molten eutectic alloy nanoclusters that wander erratically on the substrate upon heating, and often coalesce with one another, rendering even size control unacceptably loose. Furthermore, transmission of signals to and from a nanostructure is problematic due to difficulty forming either directly contacted or capacitively coupled electrodes. Electron-beam lithography can be used to pattern electrodes on a bottom-up grown nanostructure to create a device,² but its high cost and serial nature make it ineffectual for the realization of large arrays of interconnected devices. Unlike bottom-up techniques, top-down microfabrication techniques, including projection lithography, oxidation of silicon, chemical vapor deposition (CVD) of thin films, and plasma etching, readily lend themselves to precise placement, alignment, and ultra large scale integration. However, the minimum feature size and alignment error limitations of optical lithography preclude the direct patterning of nanoscale devices. We present a manufacturable fabrication process to realize large arrays of individually addressable silicon nanowire resonators using an entirely top-down approach that relies on optical projection lithography and multiple steps of controlled oxidation. Our fabrication process uses novel and elegant mask and process design to

overcome the limitations of traditional top-down processes, yielding arrays of precisely positioned, vertically aligned, and electrically connected silicon nanowires with diameters as small as 30 nm. With the aim of creating ultra-sensitive mass sensors, devices with a single vertically aligned silicon nanowire as the resonant mass and multiple electrodes spaced hundreds of nanometers from the nanowire are also fabricated with the top-down process.

¹J. Westwater et al., J. Vac. Sci. Technol. B., 15 (3) 554-557, 1997.

²H. T. Soh, et al. Appl. Phys. Lett. 75, 627-629, 1999.

3:00pm MN+NC-MoA4 Fabrication of Nanopore and Nanochannel Structures through E-Beam Lithography and Atomic Layer Deposition Processes, S.W. Nam, IBM T.J. Watson Research Center & Seoul National University, Korea, M.J. Rooks, R. Sirdeshmukh, IBM T.J. Watson Research Center, K.B. Kim, IBM T.J. Watson Research Center & Seoul National University, Korea, S.M. Rossnagel, IBM T.J. Watson Research Center

The reliable and reproducible fabrication of nanopore and nanochannel structures is essential for building nano-fluidic systems, such as a device to control bio-molecules or DNA. Here, we report on CMOS-compatible fabrication methods to generate electrode-embedded nanopore and nanochannel structures as small as 10 nm feature size. To fabricate a small size fluidic channel, we adopt a combined process of e-beam lithography and atomic layer deposition (ALD). E-beam lithography is used for generating few tens of nanometer sized hole and line structures and ALD is employed for further shrinking down the features less than 10 nm. In the case of a pore fabrication, we used a membrane of SiO₂ (100 nm)/Si₃N₄ (20 nm)/TiN (30 nm)/Si₃N₄ (20 nm) on Si wafer. PMMA (300 nm thickness) hole structures on top of the membrane were patterned by e-beam lithography, which were then transferred to the membrane layers through two-step RIE process, consisting of sequential CHF₃+O₂ and CH₄ steps to remove SiO₂ and Si₃N₄/TiN/Si₃N₄, respectively. This drilling process formed 50-80 nm diameter pore structures on membrane. In a parallel way, we fabricated trench structures by using a stack of Si₃N₄ (5 nm)/a-Si (20 nm)/SiO₂ (100 nm) films on a bulk Si substrate. PMMA (200 nm thickness) line patterns fabricated by e-beam lithography were transferred to the Si₃N₄, a-Si and SiO₂ layers through a multi-step RIE process, which generated ~50 nm width and ~60 nm depth trench structures. Then, a selective isotropic etching of SiO₂ by a dilute HF(1:500) induced a round-shaped etch profile along the trench line. Alternatively, the a-Si layer could be oxidized by furnace oxidation to partially close the trench. For both pore (70-80 nm diameter) and trench (~50 nm width) structures, we used an amorphous, conformal ALD TiO₂ film to reduce the pore or trench dimensions down to less than 10 nm. ALD film provided a self-limiting process by remaining void along the pore and the trench, which will serve as fluidic channels less than 10 nm.

3:20pm MN+NC-MoA5 Fabrication of Nickel-tipped Cantilevers for Magnetic Resonance Force Microscopy, S.A. Hickman, Cornell University, J. Van Delden, Eigenphase Technologies, L.E. Harrell, United States Military Academy, S.R. Garner, J.C. Ong, S. Kuenh, J.A. Marohn, Cornell University

Magnetic resonance force microscopy (MRFM) is a technique that may one day allow us to acquire magnetic resonance images of single molecules – an extremely exciting prospect. To date we have demonstrated that MRFM can achieve a sensitivity of ~10⁵ proton spins, using a custom-fabricated silicon cantilever with a hand glued, 9 μm diameter magnet tip. By making improved magnetic tips and mitigating surface dissipation, it may be possible to achieve single-proton sensitivity, leading to such exciting prospects as structural determination of large biomolecules. Achieving the attoneutron force sensitivity necessary to image single proton spins requires custom-fabricating cantilevers with extreme aspect ratios. In MRFM the force exerted on the cantilever, per spin, is proportional to the field gradient from the cantilever's magnetic tip. Achieving single proton sensitivity therefore also requires dramatically reducing magnet size. Unfortunately, all MRFM tips produced to date have been made by manually affixing magnets one-at-a-time to a cantilever. Even if the tips are ion-beam milled, it is difficult to see how they can be made small enough to detect a single proton. Likewise, ion-beam deposited tips have not yet reached the purity to produce the high magnetic field gradients desired for MRFM. We have developed an electron-beam-lithography (EBL) process for batch fabricating nanoscale tip magnets on ultrasensitive silicon cantilevers. Research by our group has shown that surface induced dissipation is a major source of noise. This surface dissipation results from charge in the cantilever interacting with electric field fluctuations in the sample. This surface dissipation can be minimized by fabricating the magnets overhanging the end of the silicon cantilever. We will present 50-600 nm wide nickel overhanging magnets fabricated by EBL and isotropic plasma etching. We will also present work on producing overhanging magnets via anisotropic potassium hydroxide etching, and by fabrication of magnets over sacrificial oxide pillars. Our current challenge appears to be preventing

the transformation of the magnet metal to metal silicide during the fabrication process. With our designed cantilever, we expect a sensitivity of better than 10^2 protons.

4:00pm MN+NC-MoA7 A Process for Control of the Support Conditions of Nanomechanical Beam Resonators, and Evaluation of the Resulting Impact on Mechanical Dissipation, R. Barton, S.S. Verbridge, B.R. Ilic, H.G. Craighead, J.M. Parpia, Cornell University

We have developed a fabrication process for suspended nanomechanical beam structures which allows precise control over the clamping conditions, particularly the extent of the overhanging support which results from the usual sacrificial release of such devices. We localize the sacrificial silicon dioxide material to specified locations using a process involving a chemical mechanical polishing step, followed by a deposition and patterning of the structural silicon nitride material. With proper alignment of the beam structures, we have succeeded in controlling or entirely eliminating the overhang which was previously thought to potentially impact the overall dissipation in these resonant systems. We will demonstrate that for a moderate overhang, on the order of ten percent of the resonator length, dissipation measured in terms of resonator quality factor, Q , is not significantly affected either in vacuum or ambient air. This finding demonstrates that neither the intrinsic material damping at low pressure, or the gas-related damping that is dominant at higher pressures are affected by the support overhang that inevitably results from typical release steps. We anticipate that the control over the clamping conditions we present could prove useful for more complex nanosystems, for example suspended fluid-containing nanochannels which integrate both optical and mechanical means of biomolecular detection.

4:20pm MN+NC-MoA8 Dynamic-Mode Multidirectional UV Lithography with Liquid State Photoresist, J.K. Kim, Y.K. Yoon, University at Buffalo

Recently an advanced ultraviolet (UV) lithography scheme, where UV is applied to liquid state photoresist, has been introduced with several advantages such as short process time with quick develop/rinse, and in-situ surface modification.¹ The container with liquid photoresist remains in a horizontal position to vertically incident light, resulting in relatively simple micro structures. In this research, a multidirectional UV lithography process has been developed with liquid state photoresist for complex three dimensional (3-D) microstructures, where the UV source and a substrate containing liquid photoresist have an arbitrary angle each other. A leak free container has been devised to hold liquid photoresist and is capped with the photomask plate. The container set is attached to a computer controlled movable stage with tilting and rotational functionality.² A liquid state negative tone photopatternable polyurethane, LF55GN has been utilized for test since it shows fast realization of thick structures with high aspect ratio.³ While the liquid state photoresist is exposed to UV, the stage is dynamically tilted and rotated in slow speed, at which the friction force should be greater than the inertia effect for the given viscosity of the photoresist and therefore the container and the enclosed liquid move as a single body in a quasi-static mode. This developed scheme provides all advantages of both the high aspect ratio complex 3-D micropatterning of multidirectional UV lithography with SU-8² and the rapid process time of UV lithography with liquid state photoresist.¹ As the height of the container determines the height of the structure, several thousand micro meter thick film can be easily realized unlike the spin coating approach where the thickness is limited to several hundred micrometers. Thus complex 3-D structures which are more than 1000 micrometers tall structures have been successfully demonstrated in 30 minutes. Ray tracing with regard to the stage movement has been simulated. The shapes of the fabricated structures show good agreement with those of the simulated structures. A single vertical triangular slab and an array have been demonstrated as test structures.

¹A. Sayah et al JMEMS 2007, vol.16, no.3, pp.564-570, June

²J.K. Kim et al MEMS 2008. Conference, vol., no., pp.399-402, Jan.

4:40pm MN+NC-MoA9 Development of High Rate Etching for Deep Si Etching in Advanced NLD Plasma, T. Murayama, T. Morikawa, K. Suu, ULVAC, Inc., Japan

In Si etching such as wafer level packaging technology for MEMS and the formation vertical interconnection of three-dimensional integration LSI, to establish high rate is important problem. Especially under 10um space pattern on 200-mm-diam wafer, it is desired to etch Si at high rates achieving anisotropic features. Commonly, it is essential to produce huge amount of F radicals in Si etching mainly dominated by radical reaction in Si surface, ion assist effect is important to achieve anisotropic feature.¹ Our experiments are conducted using NLD-Si etcher which we introduced sputtering system for sidewall passivation to NLD (magnetic Neutral Loop Discharge) etcher for quartz deep etching.^{2,3} In this study, we tried to improve etching rate using a novel antenna [Multi-Slits rf Antenna] for controlling both ion and F radical density. This antenna consisted of grid

type structure in which several slits are set perpendicularly in same direction to RF current. In experiments we used 3 parallel slit antenna in other words 4 parallel current paths structure, expecting high-density plasma is generated because of ion and radical generation area extending in space compared with simple single-turn antenna. Next, for control anisotropic feature, we investigated the dependence of bias rf frequency in high-density NLD plasma using this multi slit rf antenna. We used SF6 as process gas. Consequently, this antenna improved in etching rate more than two times compared with our conventional antenna. However etching feature shifted bowing. We considered that this result is caused by not only F radical increase but also sheath impedance decrease by high-density plasma. To overcome this sheath impedance decrease, we changed bias rf frequency to 2 MHz from 13.56 MHz. In low bias frequency we etched 4 um space pattern, then high rate and anisotropic feature were achieved etching rate is 10.5 um/min, selectivity (Si/SiO2) is 60 over. It is considered that for high rate and high quality Si etching it is very important that the control of incident ion energy distribution in addition to high-density radical produce.

¹ J. W. Coburn and H. F. Winters; J. Appl. Phys. 50 (1979) 3189.

² W. Chen, et al.; J. Vac. Sci. Technol., A 19 (2001) 2936.

³ Y. Morikawa, et al.; Thin Solid Films 515 (2007) 4918.

5:00pm MN+NC-MoA10 XeF2 Etching of Si and Mo for MEMS Manufacturing, J.-F. Veyan, Y.J. Chabal, University of Texas at Dallas, X.-M. Yan, A. Londergan, E. Gousev, Qualcomm

XeF₂ is a widely used isotropic etchant in MEMS and NEMS fabrication because it selectively removes a large variety of pure compounds (e.g. Si, Ge, Mo, W) but not their stoichiometric oxides. Understanding the etching mechanisms is crucial to achieve highly selective etching. We have studied and compared the XeF₂ etching of Silicon oxide-Silicon and Molybdenum Oxide -Molybdenum systems, under typical pressure conditions used in industry (~ few Torr). Using in-situ Infrared Absorption Spectroscopy (IRAS) we have investigated the reaction kinetics and characterized the gas phase, surface and subsurface species after and during the etching process. To reduce side effects due to reaction with the reactor walls and sample holders, an all aluminum chamber has been designed, with Teflon gasket and Kalrez O-ring for sealing. The length of stainless steel tubing for gas transport has also been reduced. To minimize reactions with contaminants such as water and hydrocarbon, the reactor is pumped to 10⁻⁵ Torr prior any XeF₂ introduction. The sample temperature prior and during XeF₂ exposure is controlled by heaters made with Ta filaments inserted in a ceramic frame imbedded inside the sample holders. A chromel-alumel thermocouple is placed directly in contact with the sample surface. With the sample out of the IR beam path the reaction products are monitored during and after etching process. Transmission is used to probe SiO₂/Si, and grazing angle reflection to probe MoO₃/Mo, and surface and subsurface species are detected/identified during and after etch reactions. XeF₂ induces a strongly exothermal reaction with both Si and Mo, producing gaseous SiF₄ (1030 cm⁻¹) and MoF₆ (741 cm⁻¹), and incorporating Fluorine species into the subsurface region. No reactions have been observed with stoichiometric Silicon Oxide and Molybdenum Oxide, but both oxides are completely removed when overlaying the pure material. The removal of the oxide overlayers is believed to be due to fluorine migration through the oxide and reaction with the elemental Si or Mo at the oxide-element interfaces.

5:20pm MN+NC-MoA11 A Versatile, Bilayer Resist Method for Creating Silica Microstructures, B.R. Cipriany, B.R. Ilic, H.G. Craighead, Cornell University

The rapid and widespread acceptance of polydimethylsiloxane (PDMS) in the microfabrication community illustrates the growing importance of versatile, simple, and inexpensive fabrication techniques, particularly for lab-on-a-chip applications. In this context, we demonstrate a new method for creating silica microfluidic networks over nanophotonic structures using a bilayer resist process involving Hydrogen silsesquioxane (HSQ) and a single photolithographic step. Ridge waveguides 180nm tall were formed in silicon nitride using electron beam lithography (JEOL9300FS) and reactive ion etching. A 630nm thick layer of HSQ was spun conformally over the structures and then exposed to oxygen plasma to cross-link a 10nm thin barrier layer. This barrier was robust against photoresist solvents, allowing a bilayer stack to be formed without altering the underlying HSQ bulk. Photoresist was then spun, patterned with optical lithography, and used as a mask layer. An HF based chemical etch was used to transfer the pattern into the barrier layer, followed by development to isotropically dissolve the HSQ bulk. Microfluidic networks formed with this developer-based transfer were self-terminated on the photonic structures without inducing structural damage. We studied the formation of HSQ channels with widths of 1.5-3.1 micrometers and heights of 80-520nm, respectively. Cross-sectional electron micrographs of these channels revealed a sponge-like film composition, which was compacted into a dense, amorphous silica film during a subsequent high-temperature anneal. Post-anneal measurements with a variable-angle spectroscopic ellipsometer reveal a 17% reduction in

film thickness and a negligible complex refractive index over the entire visible spectrum, relative to non-annealed films. Using an inverted microscope with photon counting modules, laser-induced autofluorescence of annealed HSQ was found to be over an order of magnitude less than PDMS, suitable for ultra-sensitive fluorescence spectroscopy. Unlike PDMS, annealed HSQ demonstrated chemical resistance in both aqueous solutions and common solvents. Within our sealed waveguide-microfluidics network, we directly observed flow of fluorophore-labeled deoxyribonucleic-acid (DNA) using fluorescence videomicroscopy. Future applications of this fabrication method include microfluidics integration with MEMS/NEMS, nanowire sensors, or other integrated optical elements.

Surface Science

Room: 208 - Session SS+NC-MoA

Reactivity at Oxide Surfaces

Moderator: S. Chiang, University of California Davis

2:00pm SS+NC-MoA1 Surface Structure and Chemistry of β -Ga₂O₃ Nanoribbons, V.M. Bermudez, S.M. Prokes, Naval Research Laboratory

β -Ga₂O₃ is an important material with applications as a catalyst support, as a transparent conducting oxide and as a critical component in chemical sensors. Much work has been done on high-surface-area powders and on polycrystalline thin films, but little is known about the surface properties of single crystals. We have carried out a series¹⁻³ of computational and experimental studies of β -Ga₂O₃ nanoribbons (NRs) which are single crystals with the (100) plane as the broad face. Ab-initio periodic slab calculations verify that the (100) surface is the lowest in energy and identify which of the two possible terminations ("A" or "B") is more stable. The (100)-B is very stable, and physisorption of molecular water, methanol or formic acid on this surface is found, computationally, to be energetically favored over dissociative adsorption. On the less stable (100)-A surface, physisorption of H₂O and CH₃OH is still somewhat more favorable than chemisorption, but formation of a bridging formate species is favored for HCO₂H. Infrared (IR) spectroscopy has been used to characterize the NRs and the interface with a gold substrate. The transmission spectrum of a thin layer of NRs shows an array of randomly-oriented single crystals. IR reflection-absorption spectra (IRRAS) suggest a reaction at the oxide/Au interface during annealing. IRRAS data for the adsorption of pyridine or 1-octanol are generally consistent with the computational results. Physisorption is the dominant effect; although, some chemisorption is also observed. This could indicate the presence of defects on the (100)-B surface or the co-existence of (100)-B and -A regions. For acetic or pentanoic acid, IRRAS clearly shows the formation of stable bridging carboxylate species which suggests that organic acids may be useful for functionalizing β -Ga₂O₃.

¹ V.M. Bermudez, Chem. Phys. 323 (2006) 193.

² V.M. Bermudez and S.M. Prokes, Langmuir 23 (2007) 12566.

³ V.M. Bermudez, in preparation.

2:20pm SS+NC-MoA2 Formaldehyde Reactions Over Rutile TiO₂(110) Single Crystal, H. Qiu, Y. Wang, Ruhr-University Bochum, Germany, P. McGill, H. Idriss, University of Auckland, New Zealand, C. Woell, Ruhr-University Bochum, Germany

The reaction of CH₂O with perfect and defective TiO₂(110) surfaces (produced by over-annealing and Ar ion sputtering methods) was studied by thermal desorption spectroscopy (TDS), high resolution electron energy loss spectroscopy (HREELS) and DFT calculations. Exposing the perfect TiO₂(110) surface to CH₂O at 100 K leads to the formation of physisorbed CH₂O and paraformaldehyde. The latter decomposes to CH₂O that desorbs at about 270 K. On the defective TiO₂(110) surface CH₂O adsorbs more strongly on oxygen vacancy sites ultimately forming a diolate (-OCH₂CH₂O-) species, as demonstrated by HREELS. Upon heating to higher temperatures this species undergoes deoxygenation resulting in ethylene formation via a reductive coupling mechanism.

2:40pm SS+NC-MoA3 Reactivity Studies on Oxide Supported Metal Nanoparticles, H.-J. Freund, Fritz-Haber-Institut, Germany INVITED

Metal nanoparticles supported on thin oxide films may be characterized at the atomic level. Typically it is assumed that reactions proceed on the surface of those particles. We report on results of hydrogenation and oxidation reactions where the interior as well as the metal-oxide interface participate. Several examples will be discussed on the basis of results on model systems characterized via STM, TPD, IRAS, r-NRA, molecular beam as well as high pressure studies.

3:20pm SS+NC-MoA5 Transient Mobility of Oxygen Adatoms Resulting from O₂ Dissociation at Oxygen Vacancies of TiO₂(110), Y. Du, Z. Dohnalek, I. Lyubnitsky, Pacific Northwest National Laboratory

The interaction of molecular oxygen with TiO₂-based materials affects many chemical and photochemical processes. We will present our recent discoveries in studying O₂ interaction with reduced TiO₂(110) surface by scanning tunneling microscopy at 300K. By tracking the same surface area before and after O₂ exposure, we confirm the known O₂ dissociation channel occurring at the bridging oxygen vacancy (O_{vac}) sites, with one O atom healing an O_{vac} and other O bonding at the neighboring Ti site as an adatom (O_a). In addition, the lateral distribution and diffusion of O_a are studied. It is revealed that there are three possible configurations for the O_a in regarding to the position of the original O_{vac} site, which can not be explained by thermal diffusion. Through detailed study, we conclude that observed distribution of the O adatoms is attained through a nonthermal, transient mobility from the energy release during dissociation. Unlike for other known cases of the dissociation of diatomic molecules where both "hot" adatoms accommodate at equivalent sites, in this study, the O atoms filling the vacancies are locked into the bridging oxygen rows and only the O adatoms are relatively free to move. The transient motion of the hyperthermal O adatoms might bring an enhanced reactivity, thus affect surface chemistry.

4:00pm SS+NC-MoA7 Direct Observation of O₂ Dissociation on Ti rows of Reduced TiO₂(110), Y. Du, Z. Zhang, Z. Dohnalek, I. Lyubnitsky, Pacific Northwest National Laboratory

The interaction of molecular oxygen with TiO₂ plays a critical role in catalytic activity of TiO₂-based materials. It is generally agreed that reactivity of TiO₂, partially reduced by a vacuum annealing, is greatly influenced by surface oxygen vacancy defects. In particular, at room temperature, oxygen molecules were believed to dissociate only at vacancy sites with one O atom filling an oxygen vacancy and the other O atom residing at the neighboring Ti site as an adatom. In this talk, we will show that the oxygen dissociation process is much more complicated from our scanning tunneling microscopy studies. We will demonstrate that O vacancies are not the only sites to dissociate O₂ and reveal another O₂ dissociation channel, where an oxygen molecule dissociates on rows of five-fold coordinated Ti atoms to form an oxygen adatom pair with two lattice constants spacing. We believe the discovery of the additional O₂ dissociation channel could have a considerable impact on the TiO₂ surface chemistry. It also calls for a partial reevaluation and/or reinterpretation some of the published experimental and theoretical results.

4:20pm SS+NC-MoA8 Reactivity of Epitaxial Vanadia on TiO₂: Are Support Interactions Required for Reactivity?, M. Li, E.I. Altman, Yale University

The reactivities of vanadium oxide epitaxial thin films were studied using temperature programmed desorption (TPD). The vanadia films were grown on rutile TiO₂(110) using oxygen plasma-assisted molecular beam epitaxy (OPA-MBE) and were shown to exhibit the (1x1) rutile structure using reflection high energy electron diffraction (RHEED), low energy electron diffraction (LEED) while X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) showed that monolayer films contained V⁵⁺ while V⁴⁺ predominated in the bulk of multilayer films. Two reaction channels at 400 K and above 500 K were detected for submonolayer coverages for 1-propanol oxidation to form propionaldehyde. The reaction channel at 400 K persists through multilayer films and thus is designated to the deprotonation of alkoxide intermediates attached to V⁵⁺ surface cations; meanwhile, a comparison of the vanadia coverage and the branching ratio between these two reaction channels suggests that the reaction above 500 K might involve alkoxides atop both V⁵⁺ and Ti⁴⁺. It is also found that the activation energy of the lower temperature channel is stable on the submonolayer film, independent of reduction and reoxidation, while the activation energy starts to increase for the higher temperature channel upon reduction. The same lower temperature reaction channel at 400 K exists throughout multilayer films where the titania support is absent, indicating that multilayer epitaxial films retain reactivity, in contrast to prior studies where disordered vanadia films were reported to be unreactive. Comparing the branching ratio of aldehyde desorption vs. alcohol desorption on films from submonolayer to multilayer, the fraction of the alcohol that dehydrogenates is higher for the submonolayer films. Together the results indicate that the TiO₂ support increases the reactivity of vanadia by structural promotion and by aiding the initial deprotonation of adsorbed alcohols.

4:40pm SS+NC-MoA9 The Chemistry of Volatile Organic Compounds on TiO₂(110) and the Influence of Defects and Coadsorbed Species, L. Benz, J. Haubrich, R.G. Quiller, C.M. Friend, Harvard University

Surprisingly high reactivity has been observed over the most stable (110) surface of TiO₂ in the reactions of volatile organic compounds, in particular, in molecules containing O moieties. Ultra-high vacuum techniques such as

temperature programmed reaction spectroscopy and scanning tunneling microscopy were employed in researching the fundamental underpinnings of this reactivity, including the dependence of reactivity on the presence of intrinsic surface defects. Specifically, carbon-carbon bond formation was observed, and the effect of environmentally relevant species such as water and oxygen on these reactions was examined. These reactions are of general interest in both environmental and catalytic processes.

5:00pm SS+NC-MoA10 Tetraoxygen on Reduced TiO₂(110): Oxygen Adsorption and Reactions with Oxygen Vacancies, G.A. Kimmel, N.G. Petrik, Pacific Northwest National Laboratory

The interaction of oxygen with TiO₂ is critical for a variety of applications including the photooxidation of organic materials, purification of water and air, and (potentially) photocatalytic water splitting. In this paper, oxygen adsorption on reduced TiO₂(110) is investigated using temperature programmed desorption and electron-stimulated desorption.¹ At low temperatures, two O₂ molecules can be chemisorbed in each oxygen vacancy. These molecules do not desorb upon annealing to 700 K. Instead for 200 K < T < 400 K, the two O₂ convert to another species which has four oxygen atoms, i.e. tetraoxygen, that decomposes at higher temperatures. In contrast when only 1 O₂ is adsorbed in an oxygen vacancy, the molecule dissociates upon annealing above ~150 K to heal the vacancy in agreement with previous results. These experimental results, which provide a new model for the interaction of oxygen with TiO₂(110), are consistent with the recent prediction that O₄²⁻ is the most stable form of oxygen in bridging oxygen vacancies.²

¹ G.A. Kimmel and N.G. Petrik, PRL 100, 196102 (2008).

² D. Pillay, Y. Wang, and G. S. Hwang, J. Am. Chem. Soc. 128, 14000 (2006).

5:20pm SS+NC-MoA11 Decomposition of Dimethyl Methylphosphonate on Ceria Thin Films, D.A. Chen, J.S. Ratliff, University of South Carolina, D.R. Mullins, S.D. Senanayake, Oak Ridge National Laboratory, X. Hu, University of South Carolina

The decomposition of dimethyl methylphosphonate (DMMP) on ceria thin films has been investigated by temperature programmed desorption and high resolution X-ray photoelectron spectroscopy. Ordered ceria films with different levels of oxidation were grown on Ru(0001), and DMMP was used as a simulant molecule for understanding the chemistry of the organophosphorus nerve agents. Methanol and formaldehyde were the major gaseous products detected from initial DMMP decomposition on the fully oxidized ceria thin films, and PO_x as well as a small amount of atomic carbon or CH_x remained on the surface after heating to 800 K. On reduced ceria, CO and hydrogen were the main desorption products with methanol and formaldehyde as minor products. DMMP chemistry on ceria was unusual because activity increased with each adsorption-reaction cycle even though phosphorus did not desorb from the surface. This increase in activity appears to be caused by the reduction of cerium oxide by DMMP itself; one possible mechanism for the redox reaction involves the formation of cerium phosphate. The chemistry of DMMP on ceria is compared with that on single-crystal TiO₂(110) surfaces. Gaseous methyl and methane were the primary products from DMMP decomposition on titania. In contrast to the ceria surfaces, titania was poisoned by the byproducts of DMMP reaction and exhibited less sustained activity for DMMP decomposition after multiple adsorption-reaction cycles.

Thin Film

Room: 302 - Session TF-MoA

ALD: Functionalization and Surface Chemistry

Moderator: R.G. Gordon, Harvard University

2:00pm TF-MoA1 Atomic Layer Deposition of Platinum on Strontium Titanate Surfaces, J.W. Elam, Argonne National Lab., S.T. Christensen, F.A. Rabuffetti, Northwestern U., W. Setthapun, B. Lee, Argonne National Lab., Z. Feng, Northwestern U., P.C. Stair, Argonne National Lab. & Northwestern U., C.L. Marshall, Argonne National Lab., K.R. Poeppelmeier, Northwestern U., M.J. Bedzyk, Argonne National Lab. & Northwestern U., M.C. Hersam, Northwestern U.

Platinum supported on metal oxide surfaces has important technological applications in oxidative dehydrogenation catalysis, photocatalysis, and in catalytic converters. The atomic layer deposition (ALD) of Pt on oxide surfaces is unusual because it proceeds via nucleation, growth and coalescence of islands in contrast to the layer-by-layer behavior typically observed during the ALD of metal oxides. This natural tendency towards agglomeration combined with the ability to infiltrate porous materials makes ALD Pt an attractive method for preparing catalysts on high surface area supports. In this presentation, I will describe our recent work exploring

Pt ALD on strontium titanate (STO) surfaces including both single crystal STO(001) substrates as well as novel STO nanocubes prepared by hydrothermal methods. We use a broad variety of methods to characterize these samples including atomic force microscopy, scanning- and transmission-electron microscopy, grazing incidence small angle X-ray scattering, X-ray reflectivity, X-ray fluorescence, and extended X-ray absorption fine structure measurements. These ex situ measurements are complemented by in situ quartz crystal microbalance and quadrupole mass spectrometer studies examining the mechanism of Pt ALD. These measurements clearly reveal the nucleation and growth of nm-sized Pt clusters on the STO surfaces where the Pt cluster size is controlled by the number of Pt ALD cycles. These Pt clusters are remarkably active for catalyzing the oxidation of hydrocarbons as demonstrated by propane light-off studies. The Pt clusters are very stable on the STO surfaces at temperatures up to 400-500°C, but sinter when heated to 800°C in vacuum.

2:20pm TF-MoA2 Remote Plasma and Thermal ALD of Platinum and Platinum Oxide Films, W.M.M. Kessels, H.C.M. Knoops, A.J.M. Mackus, S.A.F. Dielissen, M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands

Due to its chemical stability and excellent electrical properties platinum has wide application prospects in catalysis and microelectronics. Recently the deposition of Pt films in complex 3D structures by ALD has gained interest for catalyst applications in fuel cells and as a current collector layer in Si-integrated solid-state thin film Li-ion batteries. In this contribution we report on thermal and remote plasma ALD of Pt films using MeCpPtMe₃ precursor combined with O₂ gas and O₂ plasma, respectively. For the thermal process the results obtained by Aaltonen et al.¹ were reproduced (growth per cycle is 0.045±0.005 nm) and special attention was given in characterizing the growth incubation period on Si with thermal and native oxide by using in situ spectroscopic ellipsometry. With the new remote plasma ALD process (growth per cycle is 0.047±0.005 nm) the growth incubation could be reduced to a few cycles yielding the possibility to initialize Pt growth by depositing a remote plasma ALD "seed layer" and thickening the film by thermal ALD. A short plasma exposure (0.5 s) was necessary to deposit Pt films with no detectable amount of oxygen while a long O₂ plasma exposure (5 s) resulted in platinum dioxide (PtO_{2.2}, growth per cycle is 0.048±0.004 nm). Pt films were deposited with a mass density of 20.8 g/cm³ and an electrical resistivity of 14 μΩ cm, both close to the bulk values of 21.4 g/cm³ and 10.8 μΩ cm. The platinum oxide films had a mass density of 8.9 g/cm³ and they showed a semi-conductive behavior (resistivity of >100 Ω cm, bandgap 0.85 eV). In addition to ex situ film analysis, several in situ diagnostics have been employed. With spectroscopic ellipsometry the film thickness and (optical) film properties were monitored as a function of the number of cycles. From the Drude parameters in the Drude-Lorentz optical parameterization of the platinum, information about mass density and electrical resistivity was extracted. With infrared transmission spectroscopy the consumption of MeCpPtMe₃ precursor was measured while currently also the reaction products generated during the surface reactions are being investigated.

¹ T. Aaltonen, M. Ritala, T. Sajavaara, J. Keinonen, and M. Leskela, Chem. Mater. 15, 1924 (2003).

2:40pm TF-MoA3 Growth Kinetics and Mechanism of Rapid SiO₂ ALD Using Tris(tert-Pentoxo)Silanol, S.M. George, B.B. Burton, University of Colorado

Rapid SiO₂ ALD can deposit very thick, ~100 Å, conformal SiO₂ films by exposure of various silanol precursors to surfaces covered with Al-catalysts. Rapid SiO₂ ALD with tris(tert-butoxy)silanol (TBS) was reported at temperatures from 200–300°C and deposited SiO₂ film thicknesses as large as 120 Å [R.G. Gordon and coworkers (Science 298, 402 (2002))]. In this study, we have explored the growth of rapid SiO₂ ALD films using liquid tris(tert-pentoxo)silanol (TPS). TPS can deposit even thicker SiO₂ films at lower temperatures. The rapid SiO₂ ALD growth is believed to result from the growth of siloxane polymer chains at Al-catalytic sites and the cross-linking of these polymer chains to form a dense SiO₂ film. The SiO₂ film thicknesses deposited during one silanol exposure are dependent on the temperature, silanol pressure, and silanol exposure time. SiO₂ film thicknesses were determined using quartz crystal microbalance and x-ray reflectivity measurements. For TPS exposures of 1 second, the SiO₂ ALD growth rate was larger at lower temperatures and larger TPS pressures. SiO₂ ALD thicknesses of 125–140 Å were observed at the highest TPS pressures of ~1 Torr at the lower temperatures. These results indicated that higher TPS fluxes increase the siloxane polymerization rates. Likewise, the lower temperatures reduce the cross-linking rates between the siloxane polymers that self-limits the SiO₂ deposition. To explore the rate of cross-linking between the siloxane polymers, experiments were conducted where small TPS micropulses were employed with different delay times between the micropulses. The final limiting SiO₂ ALD mass gains decreased with increasing delay times. This behavior suggested that the longer delay times produced more cross-linking that self-limits the SiO₂ deposition. Other

experiments showed that higher temperatures produced faster nucleation of the rapid SiO₂ ALD. The nucleation was nearly immediate at the higher temperatures and could be as long as 10 seconds at the lower temperatures. The growth kinetics of rapid SiO₂ ALD can be understood in terms of the temperature dependence of nucleation and cross-linking and the pressure dependence of the siloxane polymerization rate.

3:00pm TF-MoA4 Atomic Layer Deposition of Titanium Dioxide: Reaction Mechanism Studies using In Situ Attenuated Total Reflection Fourier Transform Infrared Spectroscopy, V.R. Rai, S. Agarwal, Colorado School of Mines

The authors have investigated the surface reaction mechanism during the atomic layer deposition (ALD) of TiO₂ using titanium tetraisopropoxide (TTIP) as the metal precursor and O₃, atomic O, and H₂O as the oxidizers. The surface species during each half-reaction cycle were detected using in situ, real-time attenuated total reflection Fourier-transform infrared spectroscopy. Sub-monolayer sensitivity was obtained by multiple internal reflections through the ZnSe internal reflection crystal, which has a refractive index that is closely matched to that of amorphous TiO₂. We find that the surface reaction mechanism is very different for O₃- and H₂O-based ALD. Surface hydroxyl groups are generally the reactive sites for the metal precursors in a H₂O-based ALD process. In contrast, we do not detect any hydroxyl groups on the surface after the O₃ cycle. Our data shows that the reactive sites for the adsorption of TTIP after O₃ exposure of the surface are carbonate groups with symmetric and anti-symmetric stretching absorptions in the 1400 – 1700 cm⁻¹ region. These surface carbonates can be present as mono-, bi-, or poly-dentates. Due to their thermal stability at the growth temperature, all three types of carbonates are present simultaneously resulting in several overlapping absorption bands in the 1400 – 1700 cm⁻¹ region, which could not be deconvoluted. We hypothesize that during O₃ exposure, CO₂ and H₂O are formed due to the combustion of isopropoxy ligands and a small fraction of these molecules react with the TiO₂ surface producing these surface carbonates. CO₂ was in fact detected as one of the reaction products in the gas-phase by the IR beam passing through the chamber. When the isopropoxy ligands react with the surface, CO₂ from the carbonates was released into the gas phase and was again detected by the IR beam. Using O₃ as the oxidizer, relatively contaminant-free TiO₂ films were deposited at 150 °C: this is nearly 100 °C lower than the widely-accepted minimum temperature for the TTIP-H₂O ALD window. Ex situ spectroscopic ellipsometry data shows a refractive index of ~2.2 and a nearly constant growth rate of ~0.52 Å/cycle over the temperature range of 150-250 °C.

3:20pm TF-MoA5 Surface Preparation and Interface Cleaning during HfO₂ ALD on GaAs, T. Gougousi, J.C. Hackley, UMBC, J.D. Demaree, Army Research Laboratory

The atomic layer deposition of HfO₂ thin films is studied on GaAs(100) surfaces. The films are grown using tetrakis(dimethyl)amino hafnium (TDMAH) and H₂O precursors at a deposition temperature of 275°C. Several GaAs starting surfaces are investigated, including native oxide and both HF and NH₄OH-treated substrates. Wet chemical etching in either HF or NH₄OH solutions are shown to remove most of the Ga and As native oxides. Spectroscopic ellipsometry (SE) confirms linear growth rates of ~1.0 Å/cycle for all surfaces. Rutherford backscattering spectrometry (RBS) shows that steady-state growth of 2.6×10¹⁴ Hf/cm²/cycle is reached after 10 ALD cycles for the HF-etched GaAs surface while much smoother growth is observed for the native oxide surface (~2.9×10¹⁴ Hf/cm²/cycle). The interface of HfO₂ films deposited on GaAs surfaces is probed by X-ray photoelectron spectroscopy. Both the HF and NH₄OH treatments passivate the surface and prevent the oxidation of the interface during the deposition of coalesced HfO₂ films (> 15 ALD cycles). Deposition of HfO₂ films on the native oxide GaAs surfaces show gradual consumption of the native oxides during the process, indicating the presence of an “interfacial cleaning” mechanism comparable to that observed for other metal oxide ALD processes on GaAs and InGaAs substrates.^{1,2,3,4} The As-oxide and most of the Ga-oxide is removed after 20 ALD cycles. The presence of As oxides is not detected for films as thick as ~100Å (100 cycles) deposited on native oxide substrates.

¹ M.M. Frank, G.D. Wilk, D. Starodub, T. Gustafsson, E. Garfunkel, Y.J. Chabal, J. Grazul, D.A. Muller, Appl. Phys. Lett. 86, 152904 (2005)

² M.L. Huang, Y.C. Chang, C.H. Chang, Y.J. Lee, P. Chang, J. Kwo, T.B. Wu, M. Hong, Appl. Phys. Lett. 87, 252104 (2005)

³ C.-H. Chang, Y.-K. Chiou, Y.-C. Chang, K.-Y. Lee, T.-D. Lin, T.-B. Wu, M. Hong, J. Kwo, Appl. Phys. Lett. 89, 242911 (2006)

⁴ D. Shahjerdi, E. Tutuc, S.K. Banerjee, Appl. Phys. Lett. 91, 063501 (2007).

4:00pm TF-MoA7 New Barium, Strontium, and Titanium Precursors for the Deposition of Barium/Strontium-containing and Titanium Nitride Thin Films, Q.M. Wang, D.V. Shenai, Rohm and Haas Electronic Materials LLC, R.G. Gordon, Harvard University

Atomic Layer Deposition (ALD) is a technology gaining recognition in the semiconductor industry because of its exceptional benefits: an extremely precise thickness control, a very good composition control, an excellent conformality over aggressive geometries, and a wide deposition temperature window. As a result, numerous ALD-based processes are currently being developed for depositing a wide variety of metals and dielectrics for high-k gate dielectrics, metal gate/capacitor electrodes, barrier metals, seed layers, and ferroelectric films. Identification of suitable precursors has often been one of the challenges and critical success factors in ALD process development. The thermal stability and vapor pressure of the sources play a significant role in the stringent selection criteria along with a high reactivity with the second reactant in a wide temperature window, an acceptable shelf-life, and an ultra-high purity. For the ALD of high-k dielectrics, metal halides were adopted early on as the precursors of choice, which were later replaced by metalorganic sources with metal-nitrogen bonds such as metal dialkylamides and more recently developed metal amidinates. The metal amidinate sources have produced excellent results in the deposition of many thin film materials. In this study, we report the synthesis of new dialkylamidinate precursors for barium, strontium and titanium. These amidinate complexes display high thermal stabilities, acceptable vapor pressures and promise to be superior sources for deposition of barium/strontium-containing titanate, niobate, or tantalate thin films, as well as titanium nitride films by ALD. Volatility and thermal stability data for the barium, strontium and titanium amidinate complexes will be discussed. The barium and strontium amidinates are dimeric crystalline materials. The new titanium(III) amidinate is a low-melting material that greatly facilitates its handling in bubblers, while the titanium(IV) amidinate is a dimeric crystalline material. Data showing the high purity of the amidinate sources will be demonstrated by ICP-MS and FT-NMR analysis, and data characterizing their thermal stabilities will be provided from TGA/DSC and FT-NMR analysis. Preliminary deposition results of barium titanate, strontium titanate, and barium-strontium titanate thin films with these amidinate precursors will be provided.

4:20pm TF-MoA8 Ab Initio and FTIR Study of TDMAH and HTB Adsorption and Reaction on Hydrogen-terminated Si Surfaces, K. Li, N. Li, H.C. Turner, T.M. Klein, University of Alabama

An ab initio study of the reaction pathway and energetics of HfO₂ deposition from tetrakisdimethylamido hafnium (TDMAH) and hafnium tert-butoxide (HTB) onto hydrogen terminated Si(111) and Si(100) is compared with ATR-FTIR experimental data between 330K and 520K. HF-OH stretching modes are evident at low temperatures for the HTB reaction while Hf-H stretching modes are predominant for TDMAH chemisorbed layers. A mechanism involving silyl radicals for the later is proposed. The results are important towards understanding the limitations of atomic layer deposition during the initial growth phase. Factors influencing the interface bonding and coverage limitation will be discussed.

4:40pm TF-MoA9 In-situ Quadrupole Mass Spectroscopy Analysis of Low Temperature Cobalt Deposition Reactions using Co₂(CO)₈ and Co(C₂H₅)(CO)₂ in Atomic Layer Deposition Process Sequencing, S.J. Oh, G.N. Parsons, North Carolina State University

Cobalt is of interest as a catalyst in Fisher-Tropsch synthesis, in the Pauson-Khand reaction and for carbon nanotube growth. Cobalt's high magnetic permittivity also makes it valuable for data storage applications. Cobalt thin films are widely deposited by thermal and plasma ALD and CVD at temperatures between 200 and 400 °C. Lower temperature deposition processes are beginning to open new applications, including coating of temperature sensitive polymers and templating of biological materials. However, processes for conformal metal film deposition at less than 150 °C are not widely available. Previous studies of CVD Co from Co₂(CO)₈ show a transition in reaction kinetics at temperatures near 100 - 150 °C, consistent with a thermally activated increase in gas phase interactions between precursor molecules resulting in a decrease in deposition rate with increasing temperature. For this work, we undertook a study of low temperature cobalt thin film deposition using ALD process sequencing under the hypothesis that avoiding precursor interactions may produce a viable low temperature ALD process. Film growth was studied between 30 and 130 °C using Co₂(CO)₈ and H₂ gases using on-line quadrupole mass spectrometry and Auger electron spectroscopy. Similar experiments using cobalt cyclopentadienyl dicarbonyl and H₂ reactants were also performed between 140 and 350 °C. For the dicobalt octacarbonyl precursor, film deposition rate and in-situ quadrupole mass spectroscopy results demonstrate that for all gas pulse times studied, film growth proceeds continuously at temperature as low as 60 °C, with no indication for self-limiting precursor adsorption. The observed continuous film growth

with the $\text{Co}_2(\text{CO})_8$ is related to the zero-valent metal center, where no reduction step is required to produce a reactive surface for adsorption. The cyclopentadienyl dicarbonyl precursor showed evidence for carbonyl cleavage and volatile $\text{Co}(\text{cyclopentadienyl})$, without film growth at less than 300 °C. In addition, the mass spectroscopy results show evidence for CH_4 and C_2H_6 production during Co film nucleation, with no hydrocarbons present during subsequent processing. This is consistent with an interesting self-catalytic effect of the cobalt nuclei that decreased upon continuous film formation.

5:00pm TF-MoA10 Reaction Mechanism Studies on ALD and CVD of Cobalt from Dicobalt Hexacarbonyl Tert-Butylacetylene, T.Y. Park, K.W. Lee, J.S. Lee, D.O. Kim, J.S. Lee, H.T. Jeon, Y.D. Won, Hanyang University, Korea Republic

Atomic layer deposition (ALD) and chemical vapor deposition (CVD) have been widely used to deposit many different materials in many different applications in the fields of semiconductors, and displays, recently. Generally, in these deposition methods they use MO precursors because of its high reactivity, liquid source and easy to control. In this study we tried to deposit Co film with MO precursor with two different deposition methods. There is very few precursors are available as a Co source and we chose CCTBA (dicobalt hexacarbonyl tert-butylacetylene) as Co source and hydrogen as a reactant gas. Reaction mechanism in both ALD and CVD was studied in the deposition system equipped with quadrupole mass spectrometer(QMS) and Auger electron spectroscopy (AES). And we compared results with CVD and ALD. In this particular precursor CVD method give low impurity concentration and high growth rate compared to ALD grown films. This difference of impurity contents of cobalt films is due to their different reaction mechanism during deposition. In case of ALD, we think some of the ligands in a precursor were not broken completely and then incorporated into cobalt film during deposition. But for CVD, there was under 3% of carbon that was detected by AES (with RBS calibration). Therefore we will present the reaction mechanism of CCTBA precursor for depositing cobalt film by ALD & CVD method and the results that we analyzed this with in-situ QMS and AES.

5:20pm TF-MoA11 Excellent Si Surface Passivation Properties of ALD Al_2O_3 Films Studied by Optical Second-Harmonic Generation, J.J.H. Gielis, B. Hoex, N.M. Terlinden, M.C.M. van de Sanden, W.M.M. Kessels, Eindhoven University of Technology, The Netherlands

Thin films of Al_2O_3 synthesized by (plasma-assisted) atomic layer deposition (ALD) provide an excellent level of surface passivation of c-Si and III-IV compound semiconductors, which is vital for the performance of devices such as nanocrystal or wafer-based light emitting diodes, photodetectors, and high-efficiency solar cells. Recently, it was demonstrated that the surface passivation properties of Al_2O_3 thin films arise after a postdeposition anneal.¹ In general, surface passivation can be achieved by a reduction of surface defects or by electrostatic shielding of charge carriers by internal electric fields (i.e., field-effect passivation). In this contribution the nonlinear optical technique of second-harmonic generation (SHG) has been applied to study Al_2O_3 thin films on c-Si substrates with interfacial SiO_2 layers, both before and after anneal. SHG is a surface and interface specific technique that is extremely sensitive to internal electric fields. Spectroscopic SHG, carried out with a femtosecond Ti:sapphire laser tunable in the 2.66-3.50 eV SHG photon energy range, has revealed the presence of negative fixed charge in the Al_2O_3 . For as-deposited Al_2O_3 films the negative fixed charge density was found to be on the order of 10^{11} cm^{-2} , which increased to 10^{12} - 10^{13} cm^{-2} after anneal. The corresponding internal electric field most likely accounts for the surface passivation properties of Al_2O_3 thin films after anneal. The important role of the negative fixed charge density in the passivation properties of Al_2O_3 was confirmed by carrier lifetime spectroscopy and capacitance-voltage measurements. In addition, real-time SHG experiments causing multiple-photon-induced charge trapping suggest a reduction of recombination channels after anneal, which could play an additional role in the surface passivation mechanism by Al_2O_3 . It is straightforward to extend the approach discussed in this contribution to enable contactless characterization of charge and charging dynamics in c-Si/high- κ dielectric structures in situ and during processing, which provides not only relevant information on field-effect passivation but also for nonvolatile memory and CMOS transistor applications.

¹ B. Hoex et al. Appl. Phys. Lett. 89, 042112 (2006); Appl. Phys. Lett. 91, 112107 (2007).

Tuesday Morning, October 21, 2008

Energy Science and Technology Focus Topic

Room: 203 - Session EN+BI+SS+SE-TuM

Catalysis for Energy Sustainability

Moderator: D.E. Ramaker, George Washington University

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

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

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

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

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

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

Non-stoichiometric mixed phase titania composites were deposited by reactive DC magnetron sputtering. Previously we¹⁻³ demonstrated that there are solid-solid interfaces with highly reactive interfacial sites created within mixed phase titania thin films, and we observed by EPR measurement that the bulk composition of the films was not fully stoichiometric. The objective of this study is to explore the role of non-stoichiometry in mixed phase titania in terms of photoresponse and photocatalytic performance in reducing CO₂ to methane. The control of oxygen partial pressure during film deposition yielded different levels of non-stoichiometry in films deposited mostly in the transition mode. Trace amounts of nitrogen were introduced during the sputtering process to stabilize the reactive sputtering

process at the turning point of the transition mode and metallic mode and without incorporation in the films. The photocatalytic results showed that there was an optimal non-stoichiometry of titania films in terms of methane yield from CO₂ reduction. Under UV illumination, the best CO₂ conversion percentage was around 22%. In addition, both from reaction tests under visible light and the optical measurements, we determined that non-stoichiometric mixed phase titania films showed a strong light absorption shift into the visible range compared to commercial standard Degussa P25, which has a similar phase composition. SEM and TEM results showed film morphology with a high density of solid-solid interfaces developed in the films. Both EELS and XPS results identified the Ti³⁺ species in addition to Ti⁴⁺. Most of the Ti³⁺ species were located at the interfaces of titania columns, where they might serve as the reactive interfacial sites for visible light harvesting or electron trapping.

¹L. Chen, et al., Photoreduction of CO₂ by TiO₂ Nanocomposites Synthesized through Reactive DC Magnetron Sputter Deposition. Thin Solid Films, 2008. in review.

²L. Chen, et al., Fabricating Highly Active Mixed Phase TiO₂ Photocatalysts by Reactive DC Magnetron Sputter Deposition. Thin Solid Films, 2006. 515(3): p. 1176-1181.

³Hurum, D.C., et al., Probing reaction mechanisms in mixed phase TiO₂ by EPR. Journal of Electron Spectroscopy and Related Phenomena, 2006. 150: p. 155-163.

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

Metal-ligand effects on Pt are commonly utilized to decrease the CO poisoning of the anode in methanol as well as to increase the activity for oxygen reduction at the cathode. However, these effects are not clearly understood because of the general lack of information on the particle morphology (M island size, homogeneity, etc.) and CO or OH adsorbate coverages. In this work, in situ X-Ray Absorption Spectroscopy (XAS) measurements, in the near edge and extended regions (XANES and EXAFS) at the Pt L₃ edge, were carried out on three different carbon-supported electrocatalysts (Pt₃Mo, Pt₄Mo, and PtSn) in an electrochemical cell in 1 M HClO₄ along with 0.3 M methanol. The CO, OH, O, and H_{upd} relative adsorbate coverages on Pt are determined as a function of the applied potential via the ΔXANES technique and compared with comparable data reported for three different PtRu electrocatalysts (PtRu Etek, PtRu Watanabe, and Pt₃Ru) reported previously¹. The average particle morphology of each catalyst is determined from EXAFS coordination numbers and a modeling technique.¹ The onset of the n-fold O atom coverage between 0.5 and 0.9 V (RHE) tracks essentially with the particle size. The more reactive Sn and Mo atoms interact more strongly with Pt, and hence the ligand effect for the M and MO_n islands are comparable, in contrast to that for Ru vs. RuO_n. Our results are correlated with the extensive electrochemical results found in the literature on similar Pt_nM catalysts. The results suggest that the strength of the ligand effect increases in the order Ru < Mo, MoO_n < Sn, SnO_n ≤ RuO_n, where the relative Pt-CO bond strength is found to decrease and the Pt-OH bond strength increases with ligand effect. In the Sn and Mo bimetallics, the ligand effect is found to be sufficiently strong to allow CO replacement by H₂ at low currents.

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

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

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

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

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

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

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

The water-gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$) is a critical process in providing pure hydrogen for fuel cells and other applications. However, current industrial catalysts (Fe-Cr or Zn-Al-Cu oxides) are pyrophoric and require complex activation steps before usage. A fascinating puzzle has recently emerged: Au/CeO₂ and Au/TiO₂ nanomaterials show high activity for WGS catalysis. This is remarkable since in bulk form Au, ceria and titania are not known as WGS catalysts. The nature of the active phase(s) in these metal-oxide nanocatalysts is unclear at the present time, which impedes the design and optimization of WGS catalysts. We have carried out coordinated experimental and theoretical studies to address this problem. The experiments show that the model catalysts, Au/CeO₂(111) or TiO₂(110) and inverse CeO₂ or TiO₂/Au(111), display activities comparable to good WGS catalysts (i.e., Cu(100) and Cu(111)). Theoretical calculations based on density functional theory (DFT) are also carried out to understand the active sites in the oxide-gold catalysts, by probing reaction scenarios on Au, titania, and Au-TiO₂ (Au/TiO₂ and TiO₂/Au(111)) catalyst model structure. In accordance with experiments, our calculations show a very high barrier for the dissociation of water on Au and the formation of very stable formate species on titania that prevents the production of H₂ and CO₂. The model Au-TiO₂ catalyst overcomes these bottlenecks: the moderate chemical activity of gold is coupled to the more reactive oxide. The dissociation of water takes place on the oxide easily, a reaction that extended surfaces and nanoparticles of Au cannot perform. CO adsorbs on gold sites located nearby (bifunctional catalyst). Then all the subsequent steps occur at the oxide-metal interface at a reasonable speed. Our results imply that the high activities of Au/CeO₂ and Au/TiO₂ nanocatalysts in the WGS reaction depend heavily on the direct participation of oxide-metal interface. The diversity of nanoparticle structures and the interplay with the support highlight the importance of identifying critical structural motifs to model catalyst function. This research was carried out at Brookhaven National Laboratory and supported by the US Department of Energy (Chemical Sciences Division, DE-AC02-98CH10886).

Graphene Topical Conference

Room: 306 - Session GR+EM+NC-TuM

Graphene and Carbon Electronics

Moderator: B.D. Schultz, International Technology Center

8:00am **GR+EM+NC-TuM1 Two Dimensional Plasmon Behavior in Graphene Sheets on SiC(0001)**, *Y. Liu*, The Pennsylvania State University, *K.V. Emtsev, Th. Seyller*, University Erlangen-Nurnberg, Germany, *R.F. Willis*, The Pennsylvania State University

Using High Resolution Energy Loss Spectroscopy (HREELS), we compare experimental results for the wavevector-dependent behavior of plasmons in a graphene sheet on SiC(0001), with that due to a filled band of surface states on semiconducting silicon. There are significant differences in behavior between the two systems, and the behavior predicted for a classical two-dimensional sheet of electrons. In particular, the damping increases with wavevector beyond the critical momentum for Landau damping by electron-hole pairs. This unusual behavior is compared with that due to the filling of two dimensional surface states on a metallized silicon surface. The graphene results are a consequence of the unusual collective behavior of

Dirac fermions. The effect of adding additional graphene layers is discussed.

8:20am **GR+EM+NC-TuM2 Furnace Growth of High Quality Epitaxial Graphene on 4H-SiC(000-1)**, *M. Sprinkle, F. Ming*, Georgia Institute of Technology, *D. Martinotti*, CEA Saclay, France, *P.G. Soukiassian*, Université de Paris-Sud/Orsay and CEA Saclay, France, *C. Berger, E.H. Conrad, W.A. de Heer*, Georgia Institute of Technology

Multi-layer graphene grown epitaxially on the C-terminated (000-1) surface of 4H-SiC in a high vacuum (~10⁻⁵ Torr), high temperature (~1420 °C) induction furnace environment has been shown to be of extremely high quality^{1,2} and mobility.^{3,4} Though multi-layered, the material exhibits electronic properties similar to those of isolated graphene.^{1,3,4,5} Here, we characterize the material by atomic force microscopy (AFM), low energy electron microscopy (LEEM), and ellipsometry, and gain insight into growth mechanisms, highlighting growth on 4H-SiC(000-1) in comparison to 4H-SiC(0001), 6H-SiC(000-1), and 6H-SiC(0001). AFM and LEEM images demonstrate μm-scale graphene terraces. Ellipsometry and LEEM data show that graphene thickness is quite uniform over mm and μm scales.

¹ J. Hass et al., Phys. Rev. Lett. 100, 125504 (2008).

² J. Hass et al., J. Phys. Cond. Matt. 80, (in press)

³ C. Berger et al., Science 3012, 1191 (2006).

⁴ W. A. de Heer et al., Solid State Comm. 143, 92-100 (2007).

⁵ M. Sadowski et al., Phys. Rev. Lett. 97, 266405 (2006).

8:40am **GR+EM+NC-TuM3 Toward Carbon Based Electronics**, *K. Bolotin*, Columbia University **INVITED**

Carbon based graphitic nanomaterials such as carbon nanotubes and graphene have been provided us opportunities to explore exotic transport effect in low-energy condensed matter systems and the potential of carbon based novel device applications. The unique electronic band structure of graphene lattice provides a linear dispersion relation where the Fermi velocity replaces the role of the speed of light in usual Dirac Fermion spectrum. In this presentation I will discuss experimental consequence of charged Dirac Fermion spectrum in two representative low dimensional graphitic carbon systems: 1-dimensional carbon nanotubes and 2-dimensional graphene. Combined with semiconductor device fabrication techniques and the development of new methods of nanoscaled material synthesis/manipulation enables us to investigate mesoscopic transport phenomena in these materials. The exotic quantum transport behavior discovered in these materials, such as ballistic charge transport and unusual half-integer quantum Hall effect both of which appear even at room temperature. In addition, I will discuss electronic transport measurements in patterned locally gated graphene nanoconstrictions with tunable transmission and bipolar heterojunctions. We observe various unusual transport phenomena, such as energy gap formation in confined graphene structures which promise novel electronic device applications based on graphitic carbon nanostructures.

9:20am **GR+EM+NC-TuM5 Spectro-Microscopy of Single and Multi-Layer Graphene Supported by a Weakly Interacting Substrate**, *K.R. Knox, S. Wang*, Columbia University, *A. Morgante, D. Cvetko*, Laboratorio TASC-INFN, Italy, *A. Locatelli, T.O. Menten, M.A. Niño*, Elettra - Sincrotrone Trieste S.C.p.A., Italy, *P. Kim, R.M. Osgood*, Columbia University

While graphene's distinctive Dirac-cone electronic structure and simple 2D atomic structure have attracted major interest in the physics community, inherent limitations in the size of available exfoliated graphene samples have made it difficult to study this system with conventional UHV probes such as photoemission and low energy electron diffraction (LEED). Thus, previous photoemission and LEED studies of graphene have probed films grown on SiC.^{1,2,3} While graphene grown on SiC can form large area sheets, exfoliated graphene on SiO₂ continues to be the system of choice for transport experiments as it is relatively easy to gate and has shown the most interesting and impressive electrical properties.^{4,5} Using the high spatial resolution of the Nanospectroscopy beamline at the Elettra synchrotron light source, we have overcome these size limitations by utilizing micro-spot low energy electron diffraction (μLEED) and micro-spot angle resolved photoemission (μARPES) to study exfoliated graphene. In this talk, we will discuss our measurements of the electronic structure and surface morphology of exfoliated graphene using low energy electron microscopy (LEEM), μLEED and μARPES. Our LEEM data can be used to unambiguously determine the film thickness of graphene sheets by means of a quantum size contrast effect; a well understood effect in which modulations in the electron reflectivity arise due to quantum well resonances above the vacuum level.⁶ Our diffraction measurements provide information about the surface morphology of monolayer and multilayer graphene sheets, which are not atomically flat, but microscopically corrugated. This corrugation increases with decreasing film thickness, reaching a maximum for monolayer graphene. Our photoemission

measurements probe the unique massless fermionic dispersion of monolayer graphene, to confirm that the electronic structure of the valence band is well described by the one-orbital tight binding model.

¹ T. Ohta et al., *Science* 313, 951 (2006).

² A. Bostwick et al., *Nature Phys.* 3, 36 (2007).

³ S.Y. Zhou et al., *Nature Phys.* 2, 595 (2006).

⁴ K.S. Novoselov et al., *Science* 306, 666 (2004).

⁵ Y.B. Zhang et al., *Nature* 438, 201 (2005).

⁶ M.S. Altman, et al. *App. Surf. Sci.* 169, 82 (2001).

9:40am GR+EM+NC-TuM6 Intercalation and Ultrasonic Treatment of Graphite – a New Synthetic Route to Graphene, E. Widenkvist, Uppsala University, Sweden, R.A. Quinlan, The College of William and Mary, S. Akhtar, S. Rubino, Uppsala University, Sweden, D.W. Boukhvalov, M.I. Katsnelson, Radboud University of Nijmegen, the Netherlands, B. Sanyal, O. Eriksson, K. Leifer, H. Grennberg, U. Jansson, Uppsala University, Sweden

We will demonstrate that ultrasonic treatment of a graphite crystal in water can lead to the formation of small graphene-like flakes in solution. The delamination of the graphite can be increased dramatically by intercalation of bromine from a Br₂-saturated water solution. After ultrasonic treatment, large amounts of graphene-like flakes with varying thickness are observed in SEM and TEM. They can be adsorbed onto a surface of a suitable substrate by a simple dipping technique. The effect of polar and non-polar solvents as well as adsorption of the graphene on hydrophobic and hydrophilic substrates will be demonstrated and compared. DFT calculations of the intercalation process have been carried out using the SIESTA package and the effect of bromine intercalation on cohesive energy and electronic structure will be discussed and compared with experimental data. Finally, the general approach of using ultrasonic treatment and intercalation as a facile route to graphene synthesis compared to other methods will be discussed.

10:40am GR+EM+NC-TuM9 Graphene: Exploring Carbon Flatland, E.W. Hill, A.K. Geim, University of Manchester, UK INVITED

Graphene is now a bright and still rapidly rising star on the horizon of materials science and condensed matter physics, revealing a cornucopia of new physics and potential applications. We will overview our experimental work on graphene concentrating on its exotic electronic properties and speculate about potential applications.

11:20am GR+EM+NC-TuM11 The Mechanism of Graphene Growth on Metal Surfaces, E. Loginova, N.C. Bartelt, K.F. McCarty, P.J. Feibelman, Sandia National Laboratories

The structure and defects of graphene sheets have been characterized on many different surfaces, but the mechanisms of graphene growth largely remain unknown. Although simulations have been reported, how carbon atoms attach to the edge of a graphene sheet has not been experimentally determined, owing to limitations of the available experimental techniques. We have used low-energy electron microscopy (LEEM) to study the epitaxial growth of graphene on a representative metal, Ru(0001). The unique capabilities of LEEM allow us to measure simultaneously the growth rate of individual graphene islands and of the local, absolute concentration of vapor-deposited, mobile carbon adatoms. Combining this information, we have learned what controls the nucleation and growth rate of graphene on Ru(0001), and what species transport carbon over the metal surface. Graphene growth differs strikingly from the well-studied case of metal epitaxy: 1) the growth rate is limited by C-atom attachment, not by C-atom diffusion, and 2) the absolute value of the supersaturation required for appreciable growth rates is comparable to that required to nucleate new islands. Thus, a large barrier must exist for monomers to attach to the graphene step edge. We have also discovered that the growth rate as a function of supersaturation is highly nonlinear. Such behavior can be explained if carbon clusters must form, as precursors to carbon attachment. As experiment and theory reveal, this could arise from strong bonding of individual monomers to the metal substrate. We will discuss a model that explains all these observations, and thus provides insight into the molecular processes by which graphene grows. Lastly, we will show that our understanding and ability to monitor the carbon supersaturation allow the shape and position of the growing graphene sheets to be controlled. This research is supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U. S. Department of Energy under Contract No. DE-AC04-94AL85000.

11:40am GR+EM+NC-TuM12 Conformal Dielectric Layers Deposited by ALD (Atomic Layer Deposition) for Graphene-based Nanoelectronics, B. Lee, S.Y. Park, H.Y. Kim, K.J. Cho, E.M. Vogel, M.J. Kim, R.M. Wallace, J. Kim, The University of Texas at Dallas

To make use of top-gated graphene devices, uniform and thin dielectrics on top of graphene is required. However, the chemically inert nature of

graphene basal planes inhibits deposition of high quality and atomically uniform gate dielectric films. Here, we present characteristics of dielectrics employed by atomic layer deposition on top of a highly oriented pyrolytic graphite (HOPG) surface for localized gate applications. It was found that TMA/H₂O process shows selective deposition of Al₂O₃ only along with step edges which have high chemical reactivity. Therefore, it is critical to provide uniform and dense nucleation sites on the basal plane in order to achieve conformal deposition of dielectric. In this presentation, we will demonstrate a facile route providing atomically smooth and uniform Al₂O₃ layers on top of a HOPG by atomic layer deposition (ALD). The physical properties of the deposited Al₂O₃ layer will be also studied using various characterization techniques including HR-TEM, XPS, and AFM. Acknowledgements: We acknowledge financial supports by KETI through the international collaboration program of COSAR (funded by MKE in Korea) and the SWAN program funded by the GRC-NRI.

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

The Frontiers of Nanoscience

Moderator: M.C. Hersam, Northwestern University

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

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

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

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

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

Self assembly is a powerful strategy that utilizes chemical and physical forces to fabricate ensembles of nanostructures. The ultimate goal for some device strategies is to co assemble a variety of nanostructures with differing properties in arbitrary but pre defined configurations. Chemical self assembly alone presents serious challenges in this regard since it operates on one type of nanostructure: a layer of molecules, a lattice of particles, templated wires, etc. Ferroelectric Nanolithography is a directed assembly approach that positions nanostructures of various compounds into predefined functional configurations. The process relies on domain specific surface electronic structure and consequent reactivity. Starting from an understanding of the atomic structures of ferroelectric oxide surfaces, the origin of domain specific chemical reactivity will be illustrated with in situ thermal and optical SPM observations and with the deposition of metal and oxide nanoparticles. The use of electron beams and local electrodes to pattern ferroelectric substrates will be explained in terms of relevant

electron/solid interactions. A critical aspect of both understanding assembly processes and characterizing device behavior is the ability to probe local electric, dielectric and ferroelectric properties. Scanning probe based techniques that access the frequency dependence of local properties will be described. Finally the lithographic approach will be illustrated with the fabrication of a molecular opto-electronic device made of 3nm – 50 nm metal particles, optically active porphyrins, and functionalized peptide tetramers on an oxide substrate. The generalization of the approach to include, for example, integration in hybrid systems and applications in flexible electronics will be summarized.

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

Within the recent years spin-polarized scanning tunneling microscopy has become a mature tool for high spatial resolution studies of spin structures down to the atomic scale. Together with its high surface sensitivity this makes SP-STM particularly suited for the investigation of complex antiferromagnetic or superparamagnetic surfaces which—because of the lack of macroscopic magnetization—could only be studied in some rare cases with very moderate spatial resolution in the past. One particularly graphic example is the two-dimensional atomic-scale antiferromagnetic (AFM) structure observed within a Mn monolayer on tungsten (110).¹ On the atomic scale SP-STM data reveal periodic stripes running along the [001] direction with an inter-stripe distance of 0.47 ± 0.03 nm, indicating row-wise AFM order. Large scale images reveal, however, that the magnetic amplitude is not constant but is modulated with a period of about 12 nm. Magnetic field-dependent experiments show that this modulation is caused by an AFM spin spiral. First-principles calculations identify a cycloidal spin spiral which is caused by the Dzyaloshinskii-Moriya (DM) interaction as the driving mechanism for this complex magnetic order. Due to thermal excitations this spin structure becomes unstable in nano-scale islands. Switching the magnetization of a magnetic bit by injection of a spin-polarized current offers the possibility for the development of innovative high-density data storage technologies. We show how individual superparamagnetic iron nanoislands with typical sizes of 100 atoms can be addressed and locally switched using a magnetic scanning probe tip, thus demonstrating current-induced magnetization reversal across a vacuum barrier combined with the ultimate resolution of spin-polarized scanning tunneling microscopy.² Our technique allows us to separate and quantify three fundamental contributions involved in magnetization switching (i.e., current-induced spin torque, heating the island by the tunneling current, and Oersted field effects), thereby providing an improved understanding of the switching mechanism.

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

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

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

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

¹Y. Sugimoto et al. "Real topography, atomic relaxations, and short-range chemical interactions in atomic force microscopy: The case of the Sn/Si(111)-(r3x3)R30 surface". Phys. Rev. B 73 (2006) 205329.

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

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

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

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

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

* Albert Nerken Award Winner

Plasma Science and Technology
Room: 304 - Session PS-TuM

Advanced Gate Etching

Moderator: Y. Zhang, IBM

8:00am PS-TuM1 High Density Plasma Etching of Titanium Nitride Metal Gate Electrodes for FDSOI Sub-Threshold Transistor Integration, S.A. Vitale, J. Kedzierski, N. Checka, C.L. Keast, MIT Lincoln Laboratory

Dual work function band-edge metal gate electrode materials are replacing polysilicon gates at the 45nm technology node for high performance CMOS logic production. At the same time, mid-gap metal gate electrodes are being considered to replace polysilicon gates in novel fully depleted silicon-on-insulator (FDSOI) ultra-low power CMOS devices. A discussion of the physical and electrical requirements of the gate materials for these two technologies will be presented, along with an introduction to the "gate first" vs. "gate last" integration approaches. Titanium nitride metal-gated capacitors and transistors have been successfully fabricated, on a conventional SiO₂ gate dielectric. C-V curves have been measured and fit to a quantum-corrected model, with a measured workfunction of 4.55eV. Gate oxide breakdown data reveals a charge-to-breakdown approximately 10x lower than that of conventional polysilicon/SiO₂ gates, and a discussion of how this may be improved using a HfO₂ high-k gate dielectric will be presented. A key challenge of integrating metal gates is the plasma etching of the gate stack. Conventional etching of a polysilicon layer above the TiN results in a large foot at the base of the polysilicon, due to the presence of the conducting TiN film. TiN etch selectivity over SiO₂ in excess of 40:1 is achieved by measuring and exploiting the difference in ion enhanced etching threshold energy between these films. TiN is shown to etch spontaneously in HBr plasmas due to the thermodynamically favorable Ti + Br reaction, but is strongly inhibited in the presence of oxygen. TiN etching in high density plasmas exhibits a strong aspect ratio dependent etching (ARDE) effect, which can be minimized by using a two-step etch process, with different neutral-to-ion flux ratios. *This work was sponsored by the Air Force under contract #FA8721-05-C-0002. Opinions, interpretations, conclusions, and recommendations are those of the author and are not necessarily endorsed by the United States Government.

8:20am PS-TuM2 TaN Etch Mechanisms in BCl₃-based Plasmas, D. Shamiry, IMEC, Belgium, A. Danila, Moscow Institute of Electronic Technology, Russia, V. Paraschiv, M.R. Baklanov, W. Boullart, IMEC, Belgium

TaN is a potential candidate for metal gates. BCl₃ plasma is used to pattern metal gates as it has high selectivity over Si substrate and etches metal oxides (native oxides on metal gates and high-k dielectrics). During metal gate etch in inductively coupled plasma reactor, we found that TaN gate profile depends on the composition of BCl₃-based plasma. Pure BCl₃ results in an undercut of TaN. The undercut can be avoided by addition of 5% O₂, further increase of O₂ concentration (till 10%) does not change the TaN profile. When N₂ is added to BCl₃ plasma, first the undercut disappears (at about 6% of N₂) and then a slope appears as N₂ concentration increases further (toward 10%). To clarify the etch mechanisms, we studied etching of blanket TaN wafers (30 nm film deposited by PVD). To avoid ion bombardment and simulate conditions on the sidewalls of a gate, the substrate bias was set to zero. Etch rate of TaN was measured by spectroscopic ellipsometry; surface composition was examined by XPS. In the case of pure BCl₃ plasma a thick film (deposition rate of 20 nm/min) is formed. The film consists of B (50%), Cl (30%) and O (20%). The oxygen probably comes from the oxidation on air between the etching and the XPS measurements. When 5% of O₂ is added, no film is observed, the surface composition is close to as-deposited TaN (with some B added). We observed strong peaks in emission spectra of BCl₃/O₂ plasma, attributed to BO_x. When 5% N₂ is added to the BCl₃ plasma, a film of the same thickness as for pure BCl₃ is observed, but it contains less Cl (15%). We propose the following etch mechanism. In pure BCl₃ plasma a Cl-containing film is deposited on the sidewalls of the gate. Cl from the film reacts with TaN producing an undercut. When O₂ is added, no film is formed and the TaN profile is straight as B apparently reacts with O in the gas phase, forming volatile BO_x radicals. Further increase of O₂ content does not change the profile as no film is formed (until O₂ concentration reaches 50% when B₂O₃ film is deposited). When N₂ is added to BCl₃, a film is formed but in this case N₂ replaces Cl and the film becomes passivating leading to a straight TaN profile. As more N₂ added, the film passivates TaN more efficiently leading to a sloped profile.

8:40am **PS-TuM3 Etching Profile Simulation of Metal/High-k Dielectric HfO₂ in Chlorine Based Chemistry**, *T. Yagisawa, T. Makabe*, Keio University, Japan

With continuous downscaling of complementary CMOS devices, the physical thickness of SiO₂ gate dielectric is requested to be reduced to sub-micrometer regime. When the thickness is less than 1 nm, gate dielectric cannot satisfy the requirement of the low standby power CMOS devices beyond 32 nm technology node in 2013, due to the increase of gate leakage current, poly-Si gate depletion, and dopant penetration into the channel region. In order to overcome these issues, extensive studies to replace conventional poly-Si/SiO₂ with metal/high-k gate stack have been carried out. Among several candidates, HfO₂ attracts considerable attention because of its thermal stability at the interface with Si. It is well known, chlorine based chemistry is more suitable for the plasma etching of high-k dielectric HfO₂ than fluorine chemistry due to the high volatility of the etched by-products. One of the most promising procedures to etch metal/HfO₂ gate stack is Cl₂/O₂ plasma where high selectivity can be obtained over underlying Si and SiO₂. In addition, the etching residues made of Hf chloride may not be volatile in a low temperature condition. This leads to a significant adsorption at the sidewall, resulting in a variation of surface roughness (LWR: line width roughness). Thus, the etching profile of high-k material has strong dependence on substrate temperature. In this paper, the etching profile of high-k HfO₂ film is numerically predicted in the chlorine based chemistry in a two-frequency capacitively coupled plasma. Dependence of LWR on the substrate temperature will be mainly discussed by considering the redeposition of etched by-products (HfCl_xO_y) inside the pattern. Emphasis will also be given on the selectivity of HfO₂ etching over Si and SiO₂.

9:00am **PS-TuM4 Reaction Mechanisms in Patterning Hafnium-Based High-k Thin Films**, *R.M. Martin, J.P. Chang*, University of California, Los Angeles

As hafnium-based oxides are being implemented into sub-45nm CMOS devices, the corresponding development of an enabling plasma etching chemistry is necessary for patterning these new gate dielectric materials. In this work, an electron cyclotron resonance high density plasma reactor was used to study the etching of hafnium aluminates and nitrated hafnium silicates with varying compositions in chlorine-based chemistries. In general, the measured etch rate for these materials scaled with the square root of ion energy at high ion energies (> 50 eV), however the etch rates in BCl₃ was 4 to 7 times that in Cl₂, due to the change in the dominant ion from Cl₂⁺ to BCl₂⁺. The composite oxides were found to etch faster than the simple oxides, and had roughly 2 eV lower etching threshold energies. The etching threshold energy can be tuned by the film composition, making it possible to maximize the etching selectivity with respect to the gate and substrate materials. A generalized etch rate model was formulated based on the competing etching and depositing mechanisms involved in complex plasma chemistries, as determined from analysis of the experimental data, while the etch rate dependencies on neutral-to-ion flux ratio and ion energy were correctly represented. This surface site balance based approach accounts for competition between depositing and etching species with a steady-state overlayer, and employs proper assumptions for different chemistries at various energy regimes. The model fitted well to the experimental data under various ion energy and chemistry conditions, specifically, it was able to account for the transition between physical- and ion-enhanced etching in Cl₂ plasmas and the transition between deposition and etching in BCl₃ plasmas, as the ion energy increased. As quantitative information pertaining to high-k etching behavior can be extracted from this model, it is possible to extend its applicability to predict the etching characteristics of new materials in related plasma chemistries.

9:20am **PS-TuM5 Etch Challenges at the 22nm Node and Beyond**, *R. Turkot*, Intel Corporation **INVITED**

As semiconductor manufacturing marches along according to its roadmap, the challenges of plasma etch at and around the transistor continue to increase. The last few generations have shown continued success to scale transistor gate lengths and simultaneously introduce novel transistor architectures with existing plasma etch technologies. Increasing numbers of new materials and continued scaling of material thicknesses and CDs promise to keep the pressure on plasma etch to deliver innovative solutions. Selectivities to multiple novel, thinner materials will be required. Etch tool environments may experience dramatic changes from traditional silicon or oxide etches and require "re-learning" of proper cleaning and conditioning. Even analysis of the structures being created becomes increasingly difficult as we march forward. Continued vigilance to the understanding of plasma etch and early identification of novel innovations to pattern, analyze and sustain integrated solutions across research, development and manufacturing is paramount to the success of plasma etch at the 22nm node and beyond.

10:40am **PS-TuM9 Etch Mechanisms of Silicon Gate Structures Patterned in SF₆/CH₂F₂ Inductively Coupled Plasmas**, *O. Luere*, Freescale Semiconductors, France, *L. Vallier, E. Pargon, O. Joubert*, LTM-CNRS, France

Patterning sub-40 nm gates presents several challenges among which maintaining a tight CD control is one of the most challenging. To succeed, understanding the etching mechanisms in gate patterning processes is one of the challenge. In this work we have investigated the different physical phenomena involved during the patterning of silicon structures in SF₆/CH₂F₂ based plasmas. The experimental work has been carried using a 200 mm etch platform connected, under vacuum, to an x-ray photoelectron spectroscopy surface analysis system. We have studied the impact of the SF₆/CH₂F₂ ratio on the silicon etch rate, thickness and composition of the reactive layer formed on the bottom silicon surfaces of the etched structures, thickness and composition of the sidewall passivation layer formed on the silicon sidewalls and silicon profiles. Our results demonstrate that there are very good correlations between the silicon etch rates and reactive layers formed on the bottom silicon surfaces. Contrary to previous studies performed using HBr/Cl₂/O₂ chemistries our results indicate that there is no simple correlation between the thickness of the CF_x passivation layer formed on the sidewalls and the final slope obtained in silicon. Our results demonstrate on the contrary, that even if very thin CF_x based passivation layers are formed on the silicon sidewalls, significant slopes can be generated in silicon. Other experimental results will be shown to elucidate the etch mechanism driving the silicon gate etch profiles during SF₆/CH₂F₂ plasma etching.

11:00am **PS-TuM10 Reduction of Si Recess during Gate Etching with RLSA Microwave Plasma Source**, *T. Mori, M. Sasaki, T. Nishizuka, T. Nozawa*, Tokyo Electron Technology Development Institute, INC., Japan

As the design rule of ULSI devices continue to be scaled down, the critical dimension (CD) and reduction of silicon recess will need to be precisely controlled.¹ In this study, poly gate etching was evaluated to reduce silicon recess with RLSA (Radial Line Slot Antenna) microwave plasma source. RLSA generates plasma just below top dielectric plate, and as the plasma diffuses forward the wafer, its density and electron temperature become low immediately. The gate stack which was used for experiments consisted of SiN/Poly/Gate-Ox (2nm)/Si. First, it was etched with Vdc=-150V and Si recess was observed with TEM by changing over etching percent 50%, 100%, and 150%. The profile of gate stack was getting straight as increasing over etching percent and Si recess was less than 1.1nm. Second, by optimizing etching condition with lower Vdc=-135V, Si recess was 0.8nm and the profile kept straight. We suppose not only Vdc but also plasma potential Vp are effective factor to reduce silicon recess since the maximum ion energy can be estimated by adding plasma potential and Vdc. Comparing Vp under the same bias power between RLSA and RF plasma by ion energy analyzer on the chamber wall, it was found that RLSA plasma had lower Vp than RF one. RLSA can provide low Vdc and Vp condition keeping gate stack straight. This unique plasma characteristics will be able to use post 22 nm node Si etch like 3D gate that needs less etching damage on Si surface.

¹ S. A. Vitale and B. A. Smith, J. Vac. Sci. Technol. B 21, 2205 (2003).

11:20am **PS-TuM11 Effect of Inductively and Capacitively Coupled Plasma Pulsing on Charging of Features in Plasma Etching**, *A. Agarwal, P.J. Stout, S. Banna, S. Rauf, K. Collins*, Applied Materials Inc.

Plasma charging damage presents challenges to maintaining critical dimensions during plasma etching of high aspect ratio (HAR) features (aspect ratio > 50). In one form of process induced charging damage, charge retention at the bottom of trenches can lead to breakdown as the accumulated charge stresses the material and creates a weak path for the injected current.¹ Charging damage occasionally manifests itself as tapering and twisting of HAR features, where the via or trench turns from the vertical to oblique direction.² This behavior is erratic in nature due to the randomness of the ion and radical flux composition as the feature dimensions approach only a few tens of nm. Polymer deposition on the sidewalls during dielectric etching can trap charge, which leads to less than ideal profiles. Neutral beam etching³ (decreased interaction of charged particles with feature) and UV photon bombardment⁴ (which increases surface current and conductivity allowing charge to drain through) have been suggested as useful techniques to mitigate charging damage. Pulsed plasma operation of an inductively or capacitively coupled plasma reactor may also allow for control of charging damage if negatively charged species can be extracted from the plasma. In this paper, pulsed and continuous plasma operations will be compared for etching in electronegative plasmas using results from a computational investigation. A 2-dimensional plasma equipment model (HPEM)^{2,4} has been linked to a Monte Carlo feature profile model⁵ to assess the consequences of pulsed plasma operation on charging of features. Results will be discussed for source and bias pulsing in an ICP reactor for poly-silicon etching and for pulsing of dual frequency

CCP reactor for dielectric etching. Pulsed plasma operation allows for reduced interaction of charged species and depending on the mode of operation may allow for electrons to overcome the sheath potential thus neutralizing the accumulated charge. Sustaining a steady pulsed plasma can however be complicated in strongly electronegative gas mixtures as the plasma may not reignite after power is turned off.

¹ T. Ohmori and T. Makabe, Appl. Surf. Sci. 254, 3696 (2008).

² A. Agarwal, M.M. Wang, and M.J. Kushner, 54th AVS Symposium 2007.

³ D.J. Economou, J. Phys. D 41, 024001 (2008).

⁴ K. Rajaraman, Ph.D. Thesis, Univ. of Illinois (2005).

⁵ P. Stout, 60th Gaseous Electronics Conference 2007.

Synchrotron-based Spectroscopy and Spectro-Microscopy Topical Conference

Room: 310 - Session SY+SS+BI-TuM

Synchrotron-based Spectroscopy and Spectro-Microscopy

Moderator: M. Grunze, University of Heidelberg, Germany

8:00am **SY+SS+BI-TuM1 X-ray Studies of Hydrogen Bonding in Water; the Liquid Phase and on Surfaces, A.R. Nilsson**, SSRL/Stanford University and Stockholm University, Sweden **INVITED**

Water and its ability to form Hydrogen bonding (H-bonding) is the basis for all life on the planet earth. The understanding of water adsorption, wetting and reactions at solid surfaces is of importance for many different areas of science such as biomaterials, catalysis, electrochemistry, corrosion, environmental science and technologies related to hydrogen as a future energy carrier. There are recent experiments that have raised the question whether we really understand the nature of H-bonding and the structure of liquid water. We have recently devoted a major effort to the development of x-ray spectroscopy measurements of water in the different aggregation forms and adsorbed on surfaces. Using x-ray absorption spectroscopy (XAS), x-ray Raman scattering (XRS), x-ray emission spectroscopy (XES), small angle x-ray scattering (SAXS) and x-ray diffraction together with density functional theory (DFT) calculations we have demonstrated the appearance of specific spectral features that can be related to two different types of water species in the liquid, tetrahedral water and asymmetric H-bond configurations. The latter species dominates the liquid. I will address fundamental questions regarding geometric structure, electronic structure, nature of surface chemical and hydrogen bonding and reactivity of water on surfaces. The connection between studies performed at both UHV and ambient conditions will be emphasized. Several examples of different water adsorption system will be illustrated such as Pt(111), Ru(001), Cu(110), Cu(111), TiO₂, Fe₂O₃ and MgO.

8:40am **SY+SS+BI-TuM3 Soft X-ray Spectroscopy of Liquids and Liquid-Solid Interfaces, C. Heske**, University of Nevada Las Vegas **INVITED**

With the advent of high-brightness synchrotron radiation in the soft x-ray regime it has become possible to investigate vacuum-incompatible sample systems such as liquids using suitably designed in-situ cells. In such cells, thin membranes (e.g., made of SiC, SiN_x, or polyimide) separate non-vacuum sample environments from the ultra-high vacuum necessary for soft x-ray synchrotron beamlines. If the membranes are thin (e.g., on the order of 100 nanometer to 1 micrometer), it is possible to transmit soft x-rays with sufficient intensity for spectroscopic experiments. Two experimental techniques are of particular interest, namely x-ray absorption spectroscopy (XAS) to study unoccupied electronic states and x-ray emission spectroscopy (XES) to investigate the occupied electronic levels. The combination of the two approaches, i.e., the collection of XES spectra at variable resonant excitation (resonant inelastic soft x-ray scattering - RIXS), gives unprecedented insight into the electronic structure of hitherto inaccessible samples, such as liquids and liquid-solid interfaces. In this presentation, the experimental requirements for such studies will be discussed and it will be demonstrated how XAS, XES, and RIXS can give unique insights into the electronic, chemical, and dynamic properties of liquids (in particular water) and liquid-solid interfaces.

9:20am **SY+SS+BI-TuM5 High-Resolution X-Ray Photoelectron Spectroscopy as a Versatile Tool for the Characterization of Monomolecular Self-Assembled Films, M. Zharnikov**, Universität Heidelberg, Germany **INVITED**

Self-assembled monolayers (SAMs) have recently attracted considerable interest in physics, chemistry and biology due to their ability to control wetting, adhesion, lubrication and corrosion on surfaces and interfaces and their capability to become building blocks of future electronic devices. All

the above applications rely on deep understanding of properties of these systems and precise knowledge of their structure. We will review recent progress in characterization of SAMs with a chalcogen headgroup on coinage metal and semiconductor substrates by high-resolution X-ray photoelectron spectroscopy (HRXPS). As compared to conventional XPS with a laboratory X-ray source, HRXPS, which usually takes advantage of both ultimate energy resolution and tunable photon energy (synchrotron), is capable to deliver additional information on the objects of interest, including screening phenomena, homogeneity of the bonding configurations, charge transfer upon the headgroup-substrate bond formation, etc. Also, this technique is very useful when dealing with systems exhibiting a large diversity of chemical species such as, e.g., SAMs on GaAs substrates. A variety of examples will be provided. Further, it will be shown that photoemission in SAMs cannot always be described within the standard theoretical framework, which have important implications for both understanding of the XPS/HRXPS spectra of the relevant SAM-derived systems and practical applications.

10:40am **SY+SS+BI-TuM9 Chemical Imaging and Spectroscopy at Sufficiently High Spatial Resolution to Uncover Functions of Nanoscale Phenomena, M. Kiskinova**, Sincrotrone Trieste, Italy **INVITED**

The complementary capabilities of different microscopy approaches in terms of imaging, spectroscopy, spatial and time resolution are strongly requested by the multi-disciplinary research programs at the synchrotron facilities and have motivated continuous investments in development of instrumentation for imaging with spectroscopic analysis. The major part of the lecture will be focused on the potential of modern x-ray photoelectron microscopes in chemical imaging and micro-spot photoelectron spectroscopy.¹ Among the selected research topics, as representative examples are (i) addressing the surface properties of the individual C and oxide nanostructures and supported catalyst micro and nano-particles (ii) mass transport driven self-reorganization processes which can introduce lateral heterogeneity in the composition and reactive properties of surfaces (iii) quantum-size effects on the local chemical reactivity measured for ultrathin films with spatially varying thickness. The final part of the lecture will briefly illustrate the most recent achievements in combining the potential of soft x-ray transmission microscopy with multiple contrast approaches and fluorescence analysis.

Günther, S., Kaulich B., Gregoratti L., Kiskinova, M.: Prog. Surf. Sci. 70, 187, 2002.

11:20am **SY+SS+BI-TuM11 Hard X-ray Photoelectron Spectroscopy up to 15 keV: State-of-the-Art and Recent Results, M. Merkel**, FOCUS GmbH, Germany, **J. Rubio-Zuazo**, **G.R. Castro**, SpLine Spanish CRG Beamline at the European Synchrotron Radiation Facility, France, **M. Escher**, FOCUS GmbH, Germany

Hard X-ray photoelectron spectroscopy (HAXPES) gains momentum as a new non-destructive nanoanalytical method more and more. On one hand the request for non destructive and bulk sensitive analysis methods is highly visible. On the other hand the availability of a number of suitable high energy synchrotron beam lines allows for the realization of such dedicated instrumentations. A new electron analyzer that fulfills the requirements imposed by the XRD and HAXPES techniques is presented. The analyzer of the cylindrical sector type¹ in use (FOCUS HV CSA) is a very compact and at the same time highly efficient approach for this kind of electron spectroscopy. It is capable to handle kinetic energies up to 15 keV down to a few eV with the same analyzer setup and power supply.² The recent implementation of a 2D event counting detector for parallel data acquisition will be described also. By means of this detector the measurement speed is increased to overcome the restrictions imposed by the reduced sample cross sections and analyser transmission at high kinetic energies. Buried layers, as they are common for a number of nanotechnological applications, are invisible with most of the known non destructive analytical methods. To demonstrate the potential of electron spectroscopy at really high kinetic energies we used thin Au layers deposited onto a Cu substrate as a model system for bulk sensitive photoemission. The comparison of the Cu3s and Au5s peaks show the energy dependence of the depth information. It is seen that substrate properties can be probed for kinetic energies ≥ 10 keV effectively. By means of such measurements we derived the energy dependence of the effective attenuation length (EAL) for electrons in Au also. For this purpose core level spectra of different energies are taken for different film thicknesses. The extracted EAL of Au shows an energy dependence of $(E_{kin})^{0.622}$ what is in good agreement with literature data. This work was supported through the Spanish Ministry of Education and Science (MEC), grants nos. FAP-2001-2166 and MAT1999-0241-C01 and the German Ministry of Education and Research (BMBF) under grant no. FKZ 13N9033.

¹ Risley J.S, Rev. Sci. Instrum. 43 (1971) 95; Sar-El H.Z, Rev. Sci. Instrum. 38 (1967) 1210; Sar-El H.Z, Rev. Sci. Instrum. 41 (1970) 561.

² J.R.Rubio-Zuazo, M.Escher, M.Merkel and G.R.Castro, J. of Phys. Conf. Ser. 100 (2008).

11:40am SY+SS+BI-TuM12 **A Comparative Study of Interface Formation for Ca/PDHFV and Ca/PHF by Synchrotron Radiation Photoemission**, *Y.X. Guo, W. Zhao, X.F. Feng, L. Zhang, W.H. Zhang, J.F. Zhu*, University of Science and Technology of China

Interfaces of metal/polyfluorene have attracted much research interests in both technological and scientific point of view. Polyfluorene-based light emitting devices have been proved to have a high luminescence efficiency. However, the occurrence of gap states in most cases will affect the luminescence properties of organic materials. In this paper, the interface formation and energy level alignment for Ca/PDHFV and Ca/PHF have been studied by synchrotron radiation photoemission spectroscopy (SRPES) and X-ray photoelectron spectroscopy (XPS). The results imply that the chemical reaction at the interface of Ca/PDHFV is stronger than that of Ca/PHF. However, no gap states at the Ca/PDHFV interface can be observed, which is different from the observations on Ca/PHF. Both of these two interfaces display low electron injection barrier. Our findings suggest that the gap states can be removed at metal/polyfluorene interface by introducing vinylene units into polyfluorene, which may provide a new way to eliminate the gap states.

Tuesday Afternoon, October 21, 2008

Biomaterial Interfaces

Room: 202 - Session BI+NC-TuA

Protein and Cells Interactions on Micro- and Nanofabricated Substrates

Moderator: H.E. Canavan, University of New Mexico

1:40pm **BI+NC-TuA1 Exploring Single Stem Cell Biology via Microarrayed Artificial Niches**, *M.P. Lutolf*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *R. Doyonnas, H.M. Blau*, Stanford University **INVITED**

A complex mixture of extracellular cues delivered by support cells is critical for adult stem cell maintenance and regulation of self-renewal in their microenvironment, termed niche. Despite recent progress in the identification of relevant niche proteins and signaling pathways in mice, to date, hematopoietic stem cells (HSCs) cannot be efficiently cultured in vitro without rapidly differentiating. We are developing novel in vitro culture paradigms that allow fate decisions of individual stem cells to be monitored under well-controlled conditions and in real time. We have engineered microarrayed artificial niches based on a combination of biomolecular hydrogel and microfabrication technologies that allow key biochemical characteristics of adult stem cell niches to be mimicked and the physiological complexity deconstructed into a smaller, experimentally amenable number of distinct signaling interactions. Several thousand single stem cells were tracked by fluorescent time-lapse microscopy in these microarrays over a period of several days. Image analysis allowed individual cell fate changes and growth kinetics of entire populations to be statistically analyzed. Subsequent retrospective single cell RT-PCR and transplantation experiments were performed in order to correlate kinetic behavior with phenotype and function. Screening of ca. 20 putative soluble HSC regulators, including Wnt-3a and TPO, as well as surface-tethered cell-cell adhesion proteins such as N-Cadherin, allowed to identify factors that dictate distinct HSC cell cycle kinetics. Based on patterns in kinetic behavior and single cell gene expression profiles induced by stimulation with a few of these candidates, we distinguished hallmarks of self-renewal from differentiation divisions, and validated these disparate behaviors in vivo by subsequent HSC transplantation into lethally irradiated mice. Therefore, the systematic deconstruction of a stem cell niche may serve as a generalizable paradigm for defining and reconstructing artificial niches to accelerate the transition of stem cell biology to the clinic.

2:20pm **BI+NC-TuA3 Highly Ordered Protein Patterns Generated from Self-assembly of Mixed Protein Coated Nanoparticles**, *G. Singh, S. Pillai, A. Arpanaei, P. Kingshott*, University of Aarhus, Denmark

The generation of protein patterns with controllable spacing in the nanometer to micrometer range is of great interest particularly for gaining a more fundamental understanding of the molecular mechanisms associated with protein-surface interactions. Information which can provide new insights into how proteins regulate cell shape and function have great interest in many areas including medical implants, tissue engineering, sustained drug delivery devices, biofilms, and biosensors. We present here a new but simple method for generating highly ordered protein patterns that can be applied over large areas (cm²) based on the self-assembly of mixed nanoparticles of different size, from very low volume fractions. The proof concept experiments initially involve separately coating the particles with a different type of protein. The particles are then mixed at variable concentrations at low total volume fraction. Experiments are performed with fluorescently labelled proteins. For example, FITC-labelled lysozyme is adsorbed to 2µm carboxylated polystyrene particles and rhodamine-labelled BSA is adsorbed to 0.2µm aminated polystyrene particles both in PBS at pH=7.4. In separate experiments either both types of protein-coated particles are mixed in solution, or one protein coated particle is mixed with an uncoated particle. The particle suspensions are drop-cast onto the centre of a rubber ring placed on a hydrophilic Si wafer substrate. A concave shaped layer of solvent is formed allowing for long range assembly of binary colloidal particles firstly through lateral capillary forces, and later by convective flow and entropic forces. The resultant patterns consist of highly ordered hexagonal arrays of large particles as a single layer encapsulated by crystals of the smaller particles, in which single or binary proteins patterns are generated. The coverage is simply controlled by calculating the area of particles needed to fill the rubber ring, and the spacing is controlled by the appropriate ratio of starting particles. The ordered protein patterns are shown using fluorescent microscopy combined with AFM and SEM analysis. The extent of protein adsorption to the particles is determined using XPS and zeta potential measurements. The method is very simple,

fast and inexpensive and we demonstrate that the patterning of proteins covers the range for a few nanometers up to a few micrometers depending on the appropriate selection of particles.

2:40pm **BI+NC-TuA4 Laminin Functionalization onto Silicon Single Crystals and Silicon Templated in Molecule Corrals**, *S.P. Sullivan, X. Zhang, M.E. Boggs, H.P. Bui, A.V. Teplyakov, T.P. Beebe, Jr.*, University of Delaware

Biological and chemical surface modifications at the nanoscale have become a large area of research in response to the need for new and improved applications such as biochemical sensors and medical implants. The work describe here investigates the important extracellular matrix protein, Laminin onto Si(111) and templated silicon nanostructures. These substrates are being evaluated as biomaterial bridges for neuron outgrowth. The nanostructures are templated onto the surface of highly oriented pyrolytic graphite using "molecule corrals," which are nanometer-sized (1 – 100 nm diameter) structures etched into the basal plane of graphite. The initial defects from which molecule corrals originate are routinely produced using a low-energy cesium ion beam, followed by thermal oxidation at 650 °C. Using a physical vapor deposition method, silicon is then deposited onto the HOPG, leading to the formation of billions of silicon nanostructures. Previous results suggest that these structures will react similar to that of hydrogen-terminated silicon single crystal wafers. A comparison with a new protein attachment scheme, beginning with a self-assembled monolayer of 11-amino-1-undecene, was completed. XPS, TOF-SIMS, and AFM were used to characterize the substrates following each step of the reaction. To avoid deposition of physically adsorbed protein, careful rinsing and sonication procedures were optimized and used. From these results it was determined that the nanostructures react similarly to the hydrogen-terminated Si(111) surface for this covalent attachment scheme, and that protein attachment was successful on the nanostructures. To evaluate the reaction efficiency, an additional study comparing two covalent protein attachment schemes on silicon nanostructures is underway.

3:00pm **BI+NC-TuA5 Characterisation and Patterning of PEG-Supported Lipid Bilayers**, *S. Kaufmann, P. Spycher, K. Kumar*, LSST, ETH Zurich, Switzerland, *G. Papastavrou*, LCSC, University of Geneva, Switzerland, *M. Textor, E. Reimhult*, LSST, ETH Zurich, Switzerland

Supported lipid bilayers (SLB) provide a basis for biotechnological applications as they constitute a simple model of cell membranes. They are of particular interest as components of future generations of biosensors based on transmembrane proteins. Two of the current limitations of supported lipid bilayers in biosensor applications are their sensitivity to air exposure and the limited aqueous space between the sensor substrate and the membrane available for large membrane proteins. Supported membranes resting on a hydrophilic polymer spacer decouple the membrane from the surface and provide increased aqueous space, but are generally more complicated to assemble than supported lipid membranes resting on an inorganic support. Recently it has been shown that poly(ethylene glycol) (PEG) can be incorporated into the membrane of liposomes through lipid molecules end-functionalized with a PEG chain and spontaneously fused to supported PEG-lipid bilayers (PEG-SLB) on glass. These membranes have been shown to possess a remarkable stability in air and would based on the length of the PEG-chains provide enough space between the SLB and the substrate to allow incorporation of functional transmembrane proteins. However, the structure of the PEG-SLB has not been characterized and important questions like whether the PEG brush is present on both sides of the membrane, its thickness, density and the kinetics of formation of PEG-bilayers have not been addressed. We present a comparison of the kinetics of PEG-SLB formation for different PEG molecular weights and densities as well as structural information. Furthermore, patterning of PEG-SLB using microspotting in glycerol-containing buffer has been done and compared to that of phosphocholine (PC) SLBs. QCM-D and FRAP measurement indicate decreased efficiency of PEG-SLB formation with increased PEG-density. This is most apparent in the initial adsorption of PEG-liposomes suggesting that POPC lipids still drive SLB formation through a mechanism similar to pure POPC SLBs and that a higher screening of the POPC lipids by PEG chains decreases the surface interaction. Force spectroscopy measurements demonstrate the presence of PEG on both sides of the SLB. SLB formation could be facilitated in glycerol-containing buffer and spotting of PC-SLBs and PEG-SLBs obtained by hydration, but with low geometrical definition. Spotting and hydration of PEG-SLBs demonstrated a weaker adhesion of PEG-SLBs than PC-SLBs.

4:00pm **BI+NC-TuA8 Nano-Rough Surfaces Produced by Glancing Angle Deposition (GLAD) for Protein Adsorption Measurements and Cellular Assays**, *A. Dolatshahi-Pirouz*, Univ. of Aarhus, Denmark, *C.P. Pennisi*, Aalborg University, Denmark, *S. Skeldal*, *M. Foss*, *J. Chevallier*, *P. Kingshott*, Univ. of Aarhus, Denmark, *V. Zachar*, Aalborg University, Denmark, *K. Yoshida*, Indiana University and Purdue University, *F. Besenbacher*, Univ. of Aarhus, Denmark

Currently, there is a strong focus on the fabrication of nanostructured artificial surfaces in order to tailor the biological response of artificial materials. The nanostructures are mainly used for more fundamental protein and cell studies, but in some cases also for applications like implants and cell/tissue engineering. Here a simple method to generate nano-rough platinum surfaces with varying morphological characteristics and a well-controlled surface roughness has been employed. The surfaces were fabricated by glancing angle deposition (GLAD) with varying angles and deposition times. Afterwards the biological response of the characterized nanorough samples were examined by protein adsorption and cell adhesion/proliferation assays in order to evaluate their potential as biomaterials surfaces. The effect of the deposition angle, θ , and deposition time, t , on the morphological characteristics of the thin films was investigated by utilizing Atomic force microscopy (AFM) and analyzing the images in order to determine the surface roughness and the size of the nano-rough surface features. The chemical composition of the platinum coatings were examined by X-ray Photoelectron Spectroscopy (XPS). From the AFM images it is observed, that the surface nano-features residing on the substrates can be changed by varying the deposition angle: as the deposition angle approaches grazing incidence sharp columnar protrusions are grown, while more smoothly shaped surface features appear for the thin films fabricated at higher deposition angles. The surface root-mean-square roughness, w_{rms} , increased from 1.49 nm to 15.2 nm as grazing incidence was approached. The surface roughness was additionally enhanced from $w_{rms} = 6.6$ nm to 26.3 nm for films grown at $\theta = 5^\circ$ by increasing the deposition time. It is found that the blood fluid protein, fibrinogen, is influenced by the nano-rough substrates as compared to a flat control surface. Furthermore, the proliferation of primary human fibroblasts is almost completely inhibited on the nano-rough substrates. A maximum difference of almost 200% is observed between the tallest columnar surface features (44 ± 5 cells/mm²) and the flat platinum reference (125 ± 6 cells/mm²). These results show that GLAD is a versatile technique for fabrication of varying nano-rough model surface morphologies capable of influencing both the protein and cell behavior on the surface.

4:20pm **BI+NC-TuA9 HaloTag™ Protein Arrays: An Integrated Biomolecular Interaction Analysis Platform**, *N. Nath*, *R. Hurst*, *B. Hook*, *K. Zhao*, *D. Storts*, *B. Bulleit*, Promega Corporation

Protein arrays are emerging tools geared toward proteome wide detection of protein-protein, protein-drug, protein-DNA or protein-antibodies interactions. Wide application of protein array technology however faces significant challenge due to lack of high-throughput method for protein expression and purification. Here we present a new integrated approach for creating protein arrays that combines in-vitro protein expression system with HaloTag™ capture technology. The method allows for rapid and covalent capture of HaloTag™ fusion proteins in an oriented fashion directly from complex protein matrices without any prior purification. Multiple fusion proteins can be rapidly synthesized (90min) and immobilized in parallel for high throughput studies. We also demonstrate that arrayed fusion proteins are functionally active and can be used for protein-protein and protein-nucleic acid interaction studies. Furthermore, we show that by using a HaloTag-Protein G fusion we can fabricate antibody arrays directly from ascites fluid without any prior purification of antibodies. Unlike current antibody array platforms, antibodies on our platform are oriented on the surface for maximum biological activity. HaloTag™ protein arrays thus provide a single platform for multiple-biomolecular interaction studies.

4:40pm **BI+NC-TuA10 Use of Aligned Polymer Microfibres for Peripheral Nerve Repair**, *C. Murray-Dunning*, *R. McKean*, *A.J. Ryan*, *S.L. McArthur*, *J.W. Haycock*, Sheffield University, UK

Nerve guidance conduits (NGC) have considerable potential for repairing peripheral nerve gap injuries caused by trauma, with basic entubulation designs encouraging limited reinnervation of nerve fibres. Following transection injury, Schwann cells are essential for repair as they proliferate rapidly, clear debris and secrete growth factors. We have designed a closed loop bioreactor enabling us to seed Schwann cells into experimental NGCs comprised of uniaxially aligned poly-L-lactide microfibres. Cells were introduced in fibres (5-10µm diameter) varying in length from 10-80mm, contained within 1.2mm diameter silicone tubes and grown under static and flow conditions (0-5.0ml/min) for 24 - 96 hours. MTT and confocal live/dead analysis data showed that cell viability was considerably improved when given an initial 4 hour adhesion time followed by a

0.5ml/min flow rate. To optimise Schwann growth within aligned fibre scaffolds, we then investigated seeding cells onto aligned fibres which were surface modified by acrylic acid plasma deposition. Schwann cells were stained with live/dead and phalloidin-FITC fluorophores and analysed by confocal microscopy in 3D. Microfibre scaffolds revealed a high degree of uniaxial cell alignment and a 50% increase in cellular viability on acid surface treated fibres, versus uncoated PLLA fibres. In conclusion, the following NGC approach is readily adaptable for autologous and stem cell delivery methods for the pre-clinical investigation of 3D tissue models for peripheral nerve repair.

5:00pm **BI+NC-TuA11 The Synthesis of Smooth PZT Thin Films and the Effects of Self-Assembled Monolayers and Ferroelectric Polarization on Surface Properties**, *R.E. Ducker*, *A. Garcia*, *B.B. Yellen*, *S. Zauscher*, Duke University

Lead zirconium titanate (PZT) thin films have attracted a great deal of interest in recent years due to their piezoelectric and ferroelectric properties. Recent applications for these films are in microelectromechanical systems (MEMS) and ferroelectric non-volatile random access memories. Here we present the formation of self-assembled monolayers (SAMs) on thin polarizable PZT films for potential biological applications such as biosensors. PZT Pb(Zr_{0.5}Ti_{0.5})O₃ thin films were prepared by a sol-gel deposition on platinum coated silicon substrates. The surface properties of the platinum substrate were modified using SAMs and the effects on the final crystal structure was investigated. These films were characterized by X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy (XPS). We also present the formation of SAMs of alkylphosphonic acids and alkylsilanes on the surface of these PZT films. Monolayers on metal oxide surfaces are an important way of changing the surface chemistry of functional materials. The formation of SAMs on PZT is not well understood compared to other metal oxide systems. These monolayers were formed with varying surface chemistries. These were characterized by contact angle goniometry, XPS and atomic force microscopy (AFM). Thirdly we present the ferroelectric polarization of the thin PZT films. The ferroelectric domains of PZT can be polarized using a conductive AFM tip. A DC bias voltage was applied between the tip and the bottom Pt electrode on the substrate to achieve features ranging from 400nm to several microns. The characterization of the polarization was performed using scanning Kelvin probe microscopy, electric force microscopy and scanning polarization force microscopy. These techniques confirmed the presence of an out-of-plane polarization component due to the reorientation of the ferroelectric domains in the PZT. The ability to change the polarization of PZT back and forth by applying opposite polarities to the AFM tip is also demonstrated. The effect of the polarization on the monolayer is also discussed.

5:20pm **BI+NC-TuA12 Patterned Protein Gradients of Extracellular Matrix Protein Affect Cell Attachment and Axonal Outgrowth**, *W.M. Theilacker*, *A.L. Styer*, University of Delaware, *D.E. Willis*, *J.L. Twiss*, Alfred I. DuPont Hospital for Children, *M.E. Boggs*, *S.P. Sullivan*, University of Delaware, *Z. Zhang*, Spansion, Inc., *T.P. Beebe, Jr.*, University of Delaware

We have developed a method to control the local surface density of peptides and proteins that are covalently attached to various test substrates, for cell culture assays ranging from cell attachment propensity, to cell attachment density, to cellular behavior and signaling, to cell-cell interactions, for a variety of cell types and for a variety of proteins and peptides. This degree of control has recently been extended to step and continuous gradients in local protein and peptide concentrations from the micron to the centimeter length scale. Our use of these test substrates has focused mainly on neuronal cell types, for the development of new biomaterial bridging applications in brain and spinal cord injury patients, and on cell-cell interactions between osteocytes and neurons, for an understanding of "bone pain" in cancer patients. This presentation will focus on the production of these test substrates, their characterization by a variety of surface analytical and optical microscopy techniques, including XPS, TOF-SIMS, AFM, and epifluorescence microscopy with immunostaining, and the results of cell culture studies using these test substrates.

Microfluidics/Lab-on-a-Chip
Moderator: L. Rieth, University of Utah

1:40pm **BM+BI+BO+NC-TuA1 Interfacing Silicon, Biology, and Medicine at the Micro and Nanoscale: Opportunities and Prospects, R. Bashir, Y.-S. Liu, University of Illinois, Urbana-Champaign, D. Akin, Stanford University Medical School, O. Elibol, B. Reddy, University of Illinois, Urbana-Champaign, K. Park, Purdue University** **INVITED**

Nanotechnology and BioMEMS will have a significant impact on medicine and biology in the areas of single cell detection, diagnosis and combating disease, providing specificity of drug delivery for therapy, and avoiding time consuming steps to provide faster results and solutions to the patient. Integration of biology and silicon at the micro and nano scale offers tremendous opportunities for solving important problems in biology and medicine and to enable a wide range of applications in diagnostics, therapeutics, and tissue engineering. In this talk, we will present an overview of our work in Silicon-Based BioMEMS and Bionanotechnology and discuss the state of the art and the future challenges and opportunities. We will review a range of projects in our group integrating micro-systems engineering with biology, focused towards developing rapid detection of biological entities and developing point of care devices using electrical or mechanical phenomenon at the micro and nano scale. Towards this end, we will present our work on developing silicon-based petri dishes-on-a-chip, silicon based nano-pores for detection of DNA, silicon field-effect sensors for detection of DNA and proteins, and use of mechanical sensors for characterization of living cells.

2:20pm **BM+BI+BO+NC-TuA3 Chemical Imaging of Surface Immobilization Chemistry: Mapping NHS with Protein and Cell Immobilization, F. Cheng, University of Washington, H. Takahashi, University of Utah, M. Dubey, University of Washington, K. Emoto, Acclerys Technology Corporation, L.J. Gamble, University of Washington, D.W. Grainger, University of Utah, D.G. Castner, University of Washington** **INVITED**

N-hydroxysuccinimide (NHS) esters are widely used to activate covalent coupling of amine-containing biomolecules onto surfaces in academic and commercial surface immobilizations in many applications. However, their intrinsic hydrolytic instability is well-known and limits this reactive surface chemistry. No methods are known to quantify this chemistry conveniently. We have used x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) to investigate surface hydrolysis and spatial reactivity in NHS-bearing thin films.¹ Principal component analysis (PCA) of ion ToF-SIMS data correlates changes in the NHS chemistry as a function of conditions. NHS ester oligo(ethylene glycol) (NHS-OEG) monolayers on gold and commercial polymer films have been compared after surface treatments. From PCA results, multivariate peak intensity ratios were developed to assess NHS reactivity, thin film thickness and oxidation of the monolayers during surface hydrolysis. Aging in ambient air up to seven days results in some NHS hydrolysis and thiol oxidation. Overnight film immersion under water completes hydrolysis and NHS removal. The same PCA peak intensity ratios for surface coupling of amine-terminated molecules confirmed that NHS surface regeneration methods re-establish bound NHS concentrations approximately 50% of that on freshly prepared NHS-OEG monolayers. The chemometrics were then extended to commercial poly(ethylene glycol) (PEG)-based polymer film-coated glass slides.² Reactive NHS and methoxy-capped (MeO) regions (used for non-fouling) were co-patterned onto these slides using photolithographic methods. NHS patterns are easily imaged with ToF-SIMS/PCA, resolved at high sensitivity.³ NHS-specific protein coupling was imaged and correlated to NHS images by specific coupling of streptavidin on the surface through NHS chemistry. Specific NHS-mediated cell adhesion peptide (RGD) grafting could be imaged, and prompted fibroblasts in serum to attach and proliferate only on the NHS regions. Longer-term cell culture retains high cell-pattern fidelity correlating with chemical imaging of both the NHS and RGD patterns and also lack of cell adhesion to MeO regions. High cross-correlation between various ion-derived ToF-SIMS images is observed, providing sensitive chemical corroboration of pattern chemistry and biological reactivity in complex milieu. This method is unique with important practical impacts for application of new ToF-SIMS surface imaging tools to track and validate pattern fabrication and performance.

¹X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, and principal component analysis of the hydrolysis, regeneration, and reactivity of N-hydroxysuccinimide-containing organic thin films Fang Cheng, Lara J. Gamble, David W. Grainger, David G. Castner, Anal. Chem. 2007, 79, 8781-8788

²Functionalized poly(ethylene glycol)-based bioassay surface chemistry that facilitates bio-immobilization and inhibits nonspecific protein, bacterial, and mammalian cell adhesion Gregory M. Harbers, Kazunori Emoto, Charles Greef, Steven W. Metzger, Heather N. Woodward, James J. Mascali, David W. Grainger, Michael J. Lochhead, Chem. Mater. 2007, 19, 4405-4414

³Imaging surface immobilization chemistry: correlation with cell patterning on non-adhesive hydrogel thin films Hironobu Takahashi, Kazunori Emoto, Manish Dubey, David G. Castner, David W. Grainger, Adv. Funct. Mater. In press

3:00pm **BM+BI+BO+NC-TuA5 Nanoscale Determination of Conformation of a Polymeric Coating on Layered Surfaces, A. Yalcin, Boston University, F. Damin, CNR, Milan, Italy, E. Ozkumur, Boston University, G. di Carlo, CNR, Milan, Italy, B.B. Goldberg, Boston University, M. Chiari, CNR, Milan, Italy, M.S. Unlu, Boston University**

With microarrays becoming a main tool in genetics and proteomics research, advancement of microarray technology through optimization of surface chemistries and probe-target interactions has become a major research area. Ideally, surface chemistries should provide functional groups for probe attachment, minimal nonspecific adsorption, stability to environmental changes, and probe activity after immobilization for efficient target capture. Among existing surface chemistries, three-dimensional coatings are the most promising in meeting these criteria. One such 3-D polymeric coating, copoly(DMA-NAS-MAPS), has been introduced previously for use in DNA and protein microarrays. The polymer self adsorbs to the surface and forms a hydrophilic coating, where each monomer has a specific function: Dimethylacrylamide(DMA) provides self-adsorption, 3-(trimethoxysilyl)propyl methacrylate(MAPS) increases the strength of the binding through covalent attachment to the surface with silane functionalities, and acryloyloxysuccinimide(NAS) provides functional groups to covalently bind the probes. Earlier studies with copoly(DMA-NAS-MAPS) have shown an improved performance in DNA hybridization efficiency when compared to existing organosilanization-based surface chemistries. With the aim of understanding the effect of the conformation of the polymer on the obtained results, we use an interferometric technique, Spectral Self-Interference Fluorescence Microscopy (SSFM) for characterization of the conformation, specifically swelling, of the polymer on oxide surfaces. SSFM is used in combination with a standard white light reflection spectroscopy technique, which allows for measuring the average optical thickness of a biolayer on the oxide surface, as well as the axial position of fluorescent markers with sub-nanometer accuracy. In this study, we covalently attach short strands of fluorescently labeled DNA (23mers) to the functional groups of the polymer and use them to probe conformational changes. Fluorophore heights obtained at single-stranded DNA spots indicate an axial increase of 8nm upon hydration. No increase, indicating no swelling, is measured on the epoxysilanized control surface. Furthermore, we measure the swelling using different probe molecules, and report interesting results that reveal information about the size dependent probe penetration in the polymer and the dependence of hybridization efficiency to the axial position of the probes with respect to the surface.

4:00pm **BM+BI+BO+NC-TuA8 Analysis and Diagnostics based on Nanomechanics, C. Gerber, University of Basel, Switzerland** **INVITED**

In recent years we have taken AFM technology well beyond imaging, exploring new frontiers in bio analyses and diagnostics. Micro-fabricated silicon cantilevers arrays offer a novel label-free approach where ligand-receptor binding interactions occurring on the sensor generate nanomechanical signals - like bending or a change in mass - that is optically detected in-situ. We report the detection of multiple unlabelled biomolecules simultaneously down to picomolar concentrations within minutes. Differential measurements including reference cantilevers on an array of eight sensors enables sequence-specific detection of unlabelled DNA and is suitable to detect specific gene fragments within a complete genome (gene fishing). Expression of detection of inducible genes and the detection of total RNA fragments in an unspecific background will be shown. Ligand-receptor binding interactions, such as antigen recognition will be presented. Antibody activated cantilevers with sFv (single chain fragments) which bind to the indicator proteins show a significantly improved sensitivity which is comparable with the SPR (Surface Plasmon Resonance) technique. In addition, this technology offers a brought variety of receptor molecule applications such as e.g. membrane protein recognition, micro-organism detection, and enantiomeric separation. New coating procedures, enlargement of the active surface area by dendritic molecules as well as improvement of the receptor-cantilever chemical bond will be presented. These new findings may lead to a novel individual diagnostic assay in a combined label-free GENOMICs and PROTEOMIC biomarker sensor (COMBIOSENS). We foresee this novel technology being used as a tool to be applied in the upcoming field of systems biology and preventive medicine to evaluate treatment response efficacy for personalized medical diagnostics.

4:40pm **BM+BI+BO+NC-TuA10 MEMS for Implantable Medical Applications, S. Roy,** Cleveland Clinic Foundation **INVITED**

The application of MEMS technology to biomedical problems (bioMEMS) has attracted great attention over the last decade. This awareness in the potential of bioMEMS has resulted in a flurry of research activities, which, in turn, have culminated in some commercialization successes such as microarrays and lab-on-chip in vitro diagnostics. Furthermore, the feasibility of a variety of implantable bioMEMS devices for drug delivery, physiological monitoring, and tissue engineering, has been demonstrated within a research context. Unfortunately, their translation into the clinical environment has been largely limited due to technical, cultural, and economic challenges. The talk will present the state of clinical bioMEMS today, and provide examples of on-going research projects addressing unmet clinical needs, such as development of microtextured scaffolds for bone regeneration, nanoporous membranes for ultrafiltration, wireless pressure sensors for in vivo biomechanics, and microtransducers for intravascular ultrasound (IVUS) imaging.

5:20pm **BM+BI+BO+NC-TuA12 Microfabrication of MEMS-Based Neural Probes From a Bio-Inspired, Mechanically Dynamic Polymer Nanocomposite, A. Hess,** Case Western Reserve University, *J. Dunning,* Louis Stokes VA Medical Center, *J. Harris,* Case Western Reserve University, *J.R. Capadona,* Louis Stokes VA Medical Center, *K. Shanmuganathan,* *D. Tyler,* *S. Rowan,* *C. Weder,* *C.A. Zorman,* Case Western Reserve University

The development of advanced micromachining techniques for polymers has enabled the fabrication of mechanically flexible, MEMS-based neural probes from polyimide, PDMS, parylene and similar materials. The mechanical properties of these polymers can often be "tuned" during synthesis, but cannot be dynamically controlled once the material is formed. Members of our team have recently described the development of novel nanofiber-based polymer composites that exhibit reversible chemoresponsive mechanical behavior.¹ These materials consist of a low modulus polymer that is reinforced by stiff cellulose fibrils. The stiffness of the nanocomposite is dependent on the interactions between these fibrils, which can be regulated chemically. Inspiration comes from the sea cucumber, which can modify the stiffness of its dermis by chemical regulation of collagen fibers. One of these nanocomposites, a poly(vinylacetate) (PVAc), exhibits a reduction in tensile modulus from 4.2 GPa to 1.6 MPa upon exposure to water, making it particularly well suited for penetrating neural probes that must be rigid during insertion and highly compliant during deployment. This paper describes the first effort to micromachine MEMS structures from such a material. The PVAc nanocomposite consisted of a dispersion of cellulose nanofibers (~16% v/v) extracted from sea creatures known as tunicates using the process described in Ref. 1. Neural probe designs similar to the well known "Michigan Probe" were selected for the first prototypes. These probes consist of a 50 µm-thick substrate micromachined into 280 µm-wide by 3000 µm-long shanks using a 50 W CO₂ laser and a two-step process designed to minimize damage to the polymer. Both uncoated and Au-coated substrates were micromachined using this process. A process was developed to remove 300 nm of Au while only partially damaging the underlying PVAc nanocomposite, thereby enabling the fabrication of multi-electrode structures. No delamination of the Au films was observed throughout simple soak tests in PBS for 9 days. The presentation will detail the laser-based micromachining process and describe the challenges associated with PVAc micromachining, describe devices that incorporate parylene films to electrically insulate and passivate the electrodes, and review the performance of the neural probes.

¹ J. R. Capadona, K. Shanmuganathan, D.J. Tyler, S.J. Rowan, and C. Weder, *Science*, 319, 1370 (2008).

Biological, Organic, and Soft Materials Focus Topic
Room: 201 - Session BO+PS+AS+BI+SS-TuA

Plasma-deposited Polymer and Organic Surfaces in Biological Applications

Moderator: E.R. Fisher, Colorado State University

1:40pm **BO+PS+AS+BI+SS-TuA1 High Throughput Surface Chemical Analysis of Polymer Microarrays: Wettability, Protein Adsorption and Cell Response Correlations, M. Taylor, A.J. Urquhart,** The University of Nottingham, UK, *Y. Mei,* *D.G. Anderson,* *R. Langer,* MIT, *M.C. Davies,* *M.R. Alexander,* The University of Nottingham, UK **INVITED**

In the search for new and improved biomaterials, combinatorial material discovery approaches are increasingly being explored. A significant development in the production of polymer libraries by parallel synthesis was the move from preparation of macroscopic samples,¹ to on-slide

polymerisation as microarrays in nano-litre volumes.² Such microarray material libraries may readily be interrogated by automated surface analysis equipment. Recently, high throughput surface analysis of a library of 576 different acrylate copolymers in triplicate on one slide using water contact angle (WCA), XPS and ToF SIMS highlighted the difference in the bulk and surface composition of the polymer spots, and consequently the need for surface analysis data when determining structure-property relationships.³ The complexity of SIMS data, multiplied by the number of different samples necessitates the use of multivariate analytical approaches. Using partial least squares (PLS) analysis, relationships between SIMS fragments and WCA have led to identification of moieties controlling wettability across the wide range of copolymers synthesised on one microarray.⁴ Comparison of human embryonic stem cell number on the spots with SIMS spectra have identified further SIMS fragments that correlate with high or low cell-polymer affinity. Protein adsorption measurements have been undertaken in an attempt to rationalise the cell adhesion data.⁵ The correlations identified, and the information on the relationship between the surface structure and cell response or wettability will be discussed in this exploration of the high throughput approach.

¹ Brocchini S et al. Structure-property correlations in a combinatorial library of degradable biomaterials. *Journal of Biomedical Materials Research* 1998 42 66.

² Anderson DG, et al. Nanoliter-scale synthesis of arrayed biomaterials and application to human embryonic stem cells. *Nature Biotechnology* 2004 22 863.

³ Urquhart AJ, et al. High throughput surface characterisation of a combinatorial material library. *Adv Mats* 2007 19 2486.

⁴ Urquhart AJ et al. TOF-SIMS analysis of a 576 micropatterned copolymer array to reveal surface moieties that control wettability. *Anal Chem* 2008 80 135.

⁵ Taylor M et al. A Methodology for Investigating Protein Adhesion and Adsorption to Microarrayed Combinatorial Polymers. *Rapid Macromol Comm* 2008 (in press).

2:20pm **BO+PS+AS+BI+SS-TuA3 Plasma Medicine, A. Fridman,** Drexel University **INVITED**

Novel engineering and science approaches sustaining human health, such as for example radiation biology and laser medicine, represent a significant segment of technological developments around the world. Recent breakthrough discoveries of the highly energetic but non-damaging direct treatment of living tissues with non-thermal plasma enable to create new branch of the engineering medicine, PLASMA MEDICINE, which creates qualitatively new possibilities of healing, treating of previously untreated diseases, deactivation of dangerous pathogenic organisms, development of new direct methods of medical diagnostics. New types of non-thermal atmospheric plasma discharges are able to operate directly contacting human body and other living tissues, which significantly increase effectiveness of the tissue sterilization, treatment of wounds, skin and other diseases, as well as direct medical diagnostics. Obviously success of the plasma medicine depends on deep fundamental understanding of physics, chemistry and biology of the non-thermal plasma interaction with living tissues, and engineering of the relevant non-thermal plasma discharges, which is to be discussed in the presentation. Recent achievements in plasma biotechnology also address many aspects of the challenging problem of deactivation of viruses and bacteria that cannot be disinfected by traditional methods. Disinfecting large volumes of air in buildings and hospitals economically is now possible with room-temperature atmospheric pressure plasma. Similarly, atmospheric plasma technology can be employed to sterilize medical equipment, clothing, and building walls; to disinfect living tissue without side effects, and to disinfect and preserve food and water without damage. In addition, plasma technology can also be used to create innovative tools for sensing, detection and identification of dangerous pathogenic organisms as well as to characterize success of the cleansing processes. Essential advantage of the plasma biotechnology is its potential for universal availability, due to the technology's exclusive reliance on electrical power. It avoids many logistical difficulties associated with delivery, storage and disposal that typically hinder chemical and pharmaceutical approaches to sustainable health. Plasma technology can also be easily scaled from point-of-use devices to centrally operated plants capable of cleaning massive quantities of material. The key element of recent plasma technology developments is its use as a catalyst of many natural biological processes. As such, plasma can provide highly energy efficient treatment of biological materials, which is also to be discussed in the presentation.

3:00pm **BO+PS+AS+BI+SS-TuA5 Plasma Polymer Patterning of PDMS for Microfluidic Application, S. Forster, A.G. Pereira-Medrano, M. Salim, P.C. Wright, S.L. McArthur,** University of Sheffield, UK

Microfluidic systems are becoming increasingly important for a wide range of bioengineering applications including proteomics and protein separations. Polydimethylsiloxane (PDMS) has proved to be the most popular material for microfluidic device production in the laboratory due to its many advantages over traditional materials. However, PDMS has some fundamental problems, namely a lack of functionality present at the surface, high protein fouling and inability to retain stable surface modification due to its motile hydrophobic monomer. These factors can lead to the loss of

specificity and sensitivity in many bioassays. Plasma polymerisation is a method of depositing a uniform polymeric coating onto a surface, while retaining the desired functionality of the monomer. Hence, plasma polymerisation presents a versatile approach for surface modification and patterning of device channels. The wide range of monomers available for plasma polymerisation makes this approach even more suitable for use in systems where multiple surface properties within a single device are required. The aim of this work was firstly to investigate methods to produce stable plasma polymer patterns on PDMS. The coatings chosen include acrylic acid and maleic anhydride for their functional groups and tetraglyme to reduce non-specific protein adsorption. Patterning using photolithographic techniques and subsequent specific biomolecule immobilisation was achieved. Surface characterization using XPS and ToF-SIMS was used to ensure the spatial, chemical and biomolecule resolution of the device surfaces produced. This ability to combine microfluidics with spatially defined reactive regions on a 'non-fouling' background was then used in a number of applications to show the diversity and efficiency of the devices. Protein digestion by immobilized trypsin using single flow-through experiments in PDMS devices was improved using plasma polymer functionalized channels. The results achieved using mass spectrometry showed an increase in speed and sensitivity of the digestion as well as superior device reliability. Finally, plasma functionalized channels were used to investigate the effect of ampholyte adsorption onto device walls in isoelectric focusing (IEF). By coating channels with a tetraglyme plasma polymer an increase in sensitivity and reproducibility of IEF measurement was achieved. This technique can also increase the 'lifetime' of the device by ensuring channel properties were unchanged.

4:00pm **BO+PS+AS+BI+SS-TuA8 Plasma Etching for Selective Removal of PMMA from nm-scale PS/PMMA Block Copolymers for Lithographic Applications, A.E. Wendt, Y.H. Ting, C.C. Liu, X. Liu, H.Q. Jiang, F.J. Himpel, University of Wisconsin-Madison, P.F. Nealey, University of Wisconsin, Madison**

INVITED

Diblock copolymers films, in which polymer components segregate into nano-scale domains, have been shown to have tremendous potential in fabrication of nm-scale surface topographies. Applications range from microelectronics fabrication to the study of how topography affects the growth and behavior of living cells or microorganisms. Use of block copolymers as a template for pattern transfer requires selective removal of one polymer component, and has motivated our study of plasma etching of polystyrene (PS) and polymethyl-methacrylate (PMMA), the two components of the PS-PMMA diblock copolymer. To better understand the mechanisms of the etch process for these materials, we have surveyed the effects of etch gas mixture and ion bombardment energy (taking advantage of our capability to produce a narrow ion energy distribution at the substrate), in combination with chemical analysis of the resulting etched surfaces. Of particular interest are the mechanisms of surface roughening, which shows a complex dependence on plasma process conditions that is not easily explained. A review of the literature on factors contributing to surface roughness, such as intrinsic inhomogeneity in the film, local deposition/micro-masking, shadowing effects and redeposition will be presented. We ultimately propose a mechanism for roughening of PS that involves micro-masking by inhomogeneous modification of surface chemical composition (rather than deposition) in oxygen-containing plasmas. Support from the UW NSF MRSEC for Nanostructured Materials is gratefully acknowledged.

4:40pm **BO+PS+AS+BI+SS-TuA10 Correlation of Macroscopic Surface Qualities of Poly-Parylene with Plasma-Specific Parameters, G. Franz, F. Rauter, M. Häge, University of Applied Sciences, Germany**

In the course of our research how deposition conditions teleologically influence the morphology and various physical properties of the surface of various derivatives of parylene, we followed the Yasuda approach to correlate the deposition rate of polymeric films with external parameters (flow rate and power) to define three different regimes of growth.^{1,2} Since external parameters, especially the pressure, influence the polymerization in an opposite manner (rising the pressure causes an increase in the collision rate, but a decrease in electron temperature) we studied the deposition of parylene vapors with and without pulsed microwave plasmas to correlate outcome parameters such as surface energy, roughness, and deposition rate with respect to plasma density and electron temperature (Langmuir and OES) by varying the molar fraction of the monomeric species, diluted by the noble gas argon, the total pressure and the power. For this end, we determined the vapor pressure of the dimer and the chemical equilibrium between the monomer and the dimer by varying the evaporation temperature and the cracking temperature, resp., and cross-checked this equilibrium by mass spectrometry. This method has been extended to explain the onset of volume polymerization which becomes manifest by slight tarnishing of the polymer. Following Yasuda, this happens when a certain ratio of number density of the monomeric species to plasma density

is exceeded. After having established stable process windows, two further tracks have been followed, namely copolymerization with CF₄ (volume polymerization) and hydrophilic functionalization. Following Gogolides, the surface roughness has been correlated to contact angle measurements.³ The super-hydrophobic character is mainly due to surface roughening (nanotexturing) in the case of normal CVD. However, plasma treatment leads to super-hydrophobic character also for smooth surfaces. Subsequent treatment with O₂ generates long-term stable hydrophilic surfaces. To calibrate the effect of momentum transfer and to separate the chemical effect of etching, this has been compared with Ar etching.

¹ H.K. Yasuda, and Q.S. Yu; *J. Vac. Sci. Technol. A* 19, 773 (2001)

² Q. Yu, C.E. Moffitt, D.M. Wieliczka, and H. Yasuda; *J. Vac. Sci. Technol. A* 19, 2163 (2001)

³ A.D. Tseepi, M.-E. Vlachopoulou, and E. Gogolides; *Nanotechnology* 17, 3977 (2006).

5:00pm **BO+PS+AS+BI+SS-TuA11 Plasma Processing of Nanostructured Polymeric Surfaces for the Development of Immunosensors, A. Valsesia, P. Colpo, I. Mannelli, G. Ceccone, F. Rossi, European Commission Joint Research Centre, Italy**

Immunosensors play a very important role for the development of Point-of-Care analysis thanks to their rapid and sensitive detection capabilities.¹ Among others, the control of the interface between the transducer and the biological probes is a crucial issue since the bio-interface is the essential element that guaranty the bioactivity of the immobilized biological probes.² The control of the bio-interface is typically addressed by functionalizing the surface with special chemical groups. Besides, new nanobiotechnology-based tools have led to more sophisticated approaches that use for instance nanostructured surfaces. Benefits have been already shown in terms of the improvement of immunoreaction efficiency.³ In this work we propose a new method for fabricating nanostructured surfaces combining the use of colloidal masks with different plasma processes. In this method, Plasma Polymerization Processes are able to produce pinhole-free functional layers with different properties. The choice of the precursor together with the appropriate plasma processing parameter ensures the production of stable functional layers which can be used for the production of the chemically contrasted nanopatterns. Also the deposition of the colloidal mask in a controlled way is essential: for example, mass sensitive detectors (like Quartz Crystal Microbalance, QCM) require the use of very large areas in order to obtain measurable signals. Also plasma etching plays a very important role: it is important to choose the suitable processing parameters enabling the fabrication of nanostructured surface which are not limited in the patterning geometry and resolution. After the optimization of the nanofabrication process, the surfaces of immunosensors have been nanostructured. In particular we transferred the nanostructures on the crystals of QCM for on-line monitoring of the protein adhesion. The nanostructures accelerate the kinetics of absorption and increase the density of adsorbed molecules, resulting in higher bioactivity of the immobilized proteins and consequently in an improvement of the immunosensing performances.

¹ K. R. Rogers, *Applied Biochemistry and Biotechnology - Part B Molecular Biotechnology* 2000, 14, 109-129.

² B. Kasemo, *Current Opinion in Solid State and Materials Science* 1998, 3, 451-459.

³ A. Valsesia, P. Colpo, T. Meziani, P. Lisboa, M. Lejeune, and F. Rossi, *Langmuir* 2006, 22, 1763-1767.

5:20pm **BO+PS+AS+BI+SS-TuA12 Use of Multivariate Analysis Techniques to Predict Cellular Response to Plasma Polymerized pNIPAM, J.E. Fulghum, K. Artyushkova, A. Lucero, H.E. Canavan, University of New Mexico**

The primary objective of this work is to investigate the correlate structural properties of a thermoresponsive polymer, poly(N-isopropyl acrylamide) (pNIPAM), with its ability to reversibly adhere cells. pNIPAM undergoes a sharp property change in response to a moderate thermal stimulus at physiological temperatures (~32 °C). This behavior has generated great interest in the biomaterials community, and pNIPAM is being investigated as a "smart" release coating to harvest intact cell monolayers. Many techniques are used to deposit pNIPAM, including electron beam irradiation and solution deposition (e.g., silanes and self-assembled monomers). Recently, we constructed a radio frequency (rf) plasma reactor for plasma polymerization of NIPAM (ppNIPAM) from the vapor phase based on a previous design. Plasma polymerization is a sterile, solvent-free, and compatible with surfaces of any geometry or chemistry. These factors make plasma polymerization extremely useful for cell and tissue culture, which often rely on plastic tissue culture plates. Due to the inherently energetic conditions of the plasma, parameters such as maximum rf wattage, location/position of the samples in the chamber, and monomer flow have on the resulting films. In this work, pNIPAM films resulting from those varying conditions are characterized using X-ray photoelectron spectroscopy (XPS) for film composition, interferometry for film thickness, contact angles for thermoresponse, and cell detachment for cell releasing properties. Using multivariate analysis, the structural information of the films obtained at various polymerization conditions will be correlated with

their thermoresponsive and cell-releasing behavior. In this way, we will predict the conditions that will optimize film composition for bioengineering applications.

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

Photovoltaics

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

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

Solar cells, devices which can convert sunlight directly into electricity by the photovoltaic (PV) effect, is now recognized as one of the options to provide a significant fraction of the energy mix in 2050 to power the world. Presently the PV industry is booming and two important challenges lie ahead: increasing the efficiency of conversion of sunlight into electricity and obtaining the required scale in terms of the surface area produced. The latter requires high throughput processing of solar cells in all its aspects. Increasing the efficiency is scientifically attaining the most attention, but history has shown that more cost reduction can be obtained by improving processes and increasing the scale of the industry. This talk will address both challenges by discussing the role of thin film and plasma technology. Presently the solar cell market is dominated by solar cells based on crystalline silicon. In this solar cell technology, where the photo-active material is wafer based silicon, thin films still play an important role to increase efficiency by effectively passivating bulk and surface defects and enhancing light trapping in the solar cell. The high rate deposition of a-SiNx:H as passivation and anti-reflection coating, by means of the expanding thermal plasma technique, will be shortly reviewed. Possible combinations with novel concepts to convert the solar spectrum will be addressed. Recently, we also introduced plasma assisted atomic layer deposition of Al₂O₃, a high k dielectric containing a large amount of negative charge, to passivate future p-type emitters on n-type silicon based solar cells. Demonstration of improved performance of n-type solar cells using this type of passivation layer with an efficiency as high 23.2 % will be discussed. To obtain the required large scale by 2050 further improvement of thin film solar cell technology will be essential, both in terms of materials as well as in terms of processes. Apart from the need for high throughput deposition of the photo-active materials, additional thin film technologies will be needed for barrier layers on substrates to limit impurity transport, for efficient light trapping (textured surfaces and anti-reflection layers) and last but not least encapsulation layers to guarantee the lifetime of the thin film solar cell. Apart from the further development of improved materials and device concepts, process monitoring and control to improve quality and throughput becomes more and more important. I will discuss here the monitoring of high rate deposition of microcrystalline silicon by means of optical emission spectroscopy. This optical probing method also enables the in situ detection of the crystallinity of the material deposited as well as fundamental insights in the growth mechanism.

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

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

treatment. The relation between the surface morphology and the absorption factor was analyzed.

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

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

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

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

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

This thin film solar modules are expected to be the next generation of photovoltaics technologies. Their cost reduction potential has been estimated much higher than that of Si wafer technologies. Among the various thin film technologies solar cells based on chalcopyrite (CuInGaSe₂, CIGS) absorbers show the highest efficiencies, reaching 19.9% in the lab. These record solar cells are prepared by a high vacuum co-evaporation process that proceeds in three stages with different composition. A simplified two stage co-evaporation process is used in the first mass production of chalcopyrite solar modules. Further industrial processes are the sputter deposition of metallic precursors which are reacted in an annealing process to the semiconductor compound. Recently electrochemical deposition has appeared as a low cost approach to the precursor deposition. In all cases the knowledge on fundamental growth processes, nucleation behaviour and detailed reaction is limited. The details of the processes and their advantages and disadvantages for solar module production will be discussed. The afore mentioned deposition processes result in polycrystalline films with grain sizes of approximately 1 micrometer. For the investigation of the fundamental material physics it is necessary to obtain grain boundary free material. The lattice mismatch between CuInSe₂ and CuGaSe₂ on one side and GaAs on the other side is between 2.2 and -0.7% and allows epitaxy of chalcopyrite films on GaAs. Several methods for the epitaxy have been developed: metal organic vapour phase epitaxy (MOVPE), molecular beam epitaxy (MBE) and a hybrid sputter/evaporation process. The specifics of these processes will be briefly discussed and some results of epitaxial films will be presented.

4:40pm **EN+EM+NS+PS-TuA10 Influence of a Single Grain Boundary on Epitaxial CuInSe₂ Film Growth**, *A.J. Hall, D. Hebert, A. Rockett*, University of Illinois at Urbana-Champaign

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

Graphene Topical Conference

Room: 306 - Session GR+TF+NC-TuA

Graphene: Characterization, Properties, and Application

Moderator: Y.J. Chabal, University of Texas at Dallas

1:40pm **GR+TF+NC-TuA1 Computational Modeling of Graphene**, *K.J. Cho, G. Lee*, University of Texas at Dallas **INVITED**

Using the ab initio density functional theory (DFT), tight-binding (TB), and non-equilibrium Green's function (NEGF) methods, we have studied the electronic properties of graphene oxides (GOs) and graphene nanoribbons (GNRs). Dry oxidation of graphene induces epoxide groups on the basal plane, and the corresponding electronic structures of GOs show directional band gap opening. We found that GOs have small energy gaps due to the lattice distortion at low oxygen coverage θ_0 , and that they become semiconductors for $\theta_0 \geq 1/2$ with the larger gap at the higher θ_0 ($E_g = 3.3$ eV at $\theta_0 = 1$). However, for intermediate coverage, GOs become metallic along one zigzag direction while opening directional energy gaps along other zigzag directions depending on O adsorption patterns. We apply the percolation theory and NEGF method to explain the electron transport behavior of GOs. The insulating property of GOs is used to explain the inactive edge width of GNRs which are observed in GNR experimental studies. Electronic properties of GNRs are shown to have strong dependence on the edge chemistry indicating a practical challenge in graphene nanoelectronics using GNRs as channel materials.

2:20pm **GR+TF+NC-TuA3 Control of Conductivity in Graphene by Formation of Defects**, *S.H.M. Jafri, T. Blom, E. Widenqvist, K. Carva, B. Sanyal, O. Eriksson, H. Grennberg, U. Jansson*, Uppsala University, Sweden, *R.A. Quinlan*, College of William and Mary, *B.C. Holloway*, Luna Innovations Incorporated, *A. Surpi, K. Leifer*, Uppsala University, Sweden

Due to their large surface areas, the conductivity of graphene and carbon nano-sheets depends strongly on their chemical environment. This is the base for future environmental sensors containing graphene sheets. Here, ab-initio calculations propose a possibility of conductivity increase. In the experiment, a 1-2 orders of magnitude increase of the conductivity is observed experimentally on sub-nanometre carbon nano-sheets by using an in-situ nano-manipulation set-up. The conductivity of the graphene sheets was assessed from first-principle simulations. Insertion of defects in the graphene sheets can lead to a strong increase of the conductivity of single graphene sheets. To study this result experimentally, we carried out conductivity measurements on sub-nanometre graphene nano-sheets that are deposited on W-substrates by radio-frequency plasma-enhanced chemical vapour deposition. This deposition process creates free-standing micrometer-sized carbon nano-sheets with sub-nanometre thickness. These nano-sheets were exposed to an acid treatment. It has been shown recently that such acid treatment creates defects in these sheets. Using a nano-manipulator inside a scanning electron microscope, we individually contacted the nano-sheets and measured their resistance as a function of their functionalization. From more than 1000 measurements we obtain a 1-2 order of magnitude increase of conductivity in the functionalised carbon nano-sheets as compared to just water treated or untreated carbon nano-sheets. This result corresponds well to the conductivity change obtained from theory. This study makes it possible to create environmental sensors based on graphene like carbon nano-sheets.

2:40pm **GR+TF+NC-TuA4 Graphene on Graphite**, *J.W. Choi*, Kyung Hee University, South Korea

Topmost graphene layer of graphite is investigated using scanning tunneling microscopy and spectroscopy. Tunneling gap-distance, gap-voltage and bias polarity play an important role in the atomic image contrast and site-dependent tunneling spectra. The study revealed that the coupling and decoupling of the topmost graphene layer to the underlying graphite is occurred because of the weak physical interaction between graphene layers, the electronically active and mechanically soft beta-carbon atoms of graphite and the strong tip-sample interaction.

3:00pm **GR+TF+NC-TuA5 Using Templates to Assemble Graphene Oxide (GO) and Graphene Nanostructures**, *P.E. Sheehan, Z. Wei, J.T. Robinson, D.E. Barlow, E.S. Snow*, Naval Research Laboratory

Graphene and graphene oxide (GO) are new nanoscale building blocks that have generated widespread interest in both basic and applied research. The rapid, inexpensive, and reproducible generation of graphene and GO samples would expedite this work. To this end, we have directed the assembly of single-layered GO sheets using chemical templates patterned via micro contact printing.¹ Single-layer GO was inexpensively produced using the Hummer method and redispersed in water. Templates of 11-Amino-1-undecanethiol SAMS were created using microcontact printing. Unlike prior work in fullerene templating, the GO sheets could be captured electrostatically without the aid of surfactants. This process yields isolated, single-layer graphene sheets that are arbitrarily located on a patterned substrate. The electrostatic capture mechanism was verified by varying the pH to turn capture on and off. We will discuss the parameters (pH, time, etc.) that affect GO adsorption as well as the surprising resistance of the unpassivated Au substrate to adsorption of the GO sheets. Finally, the adsorbed GO and graphene were electronically and spectroscopically characterized to determine the effect of capture on the reduction process.

¹ submitted to Nano Letters.

4:00pm **GR+TF+NC-TuA8 Studies of Graphene Oxidation and Graphene Oxide Reduction by In-Situ FTIR**, *L. Goux, R. Guzman, J.-F. Veyan, Y.J. Chabal*, University of Texas at Dallas

Graphene oxide (GO) is being investigated by the graphene community because it represents one of the most promising ways to produce graphene single sheets on a large scale.^{1,2} Indeed graphene oxidation followed by exfoliation and reduction has been recently demonstrated to give single graphene layers in solution³. In addition, in any practical electronic device systems, electron transporting materials need to be controlled by insulating materials which can function as gate dielectrics or separator between device structures. Thus, the role of GO in graphene-based nanoelectronics may be comparable to that of SiO₂ in silicon-based microelectronics. We have therefore developed in-situ IR characterization to monitor graphene oxidation and GO reduction, in order to facilitate the development of graphene-based nanoelectronics. Graphene oxidation is being achieved using a remote oxygen plasma generator. We have designed a vacuum IR-cell (10⁻⁷ Torr base pressure), connected to the oxygen plasma and a Nicolet 6700 FT-IR spectrometer. Preliminary experiments have been carried out using HOPG. The GO reduction is performed in-situ by high temperature annealing in a Specac high temperature cell. In-situ FTIR studies of GO upon thermal reduction have shown a production of CO₂ gas concomitant with the disappearance of the vibrations associated to carboxyl, hydroxyl and peroxide groups in the 120°C-230°C temperature range. Interestingly the vibrational lineshape suggests that CO₂ is incorporated in GO. Around 290°C, there is a strong increase of the absorbance associated with structure changes of GO, resulting from an increase in scattering due to a higher refractive index. The change of refractive index most likely arises from an increase of electrical conductivity after reduction of GO.

¹Stankovich, S. et al. Carbon 45, 1558-1565 (2007).

²Stankovich, S. et al. J. Mater. Chem. 16, 155-158 (2006).

³Li, D. et al. Nature Nanotechnology 3, 101 - 105 (2007).

4:20pm **GR+TF+NC-TuA9 Growth of Few Layer Graphene by Microwave Plasma Enhanced CVD**, *R.G. Vitchev, A. Malesevic, A. Vanhulsel, R. Kemps, M. Mertens*, Flemish Institute for Technological Research (VITO), Belgium, *G. Van Tendeloo*, University of Antwerp, Belgium, *C. Van Haesendonck*, Catholic University of Leuven, Belgium, *R. Persoons*, Flemish Institute for Technological Research (VITO), Belgium

Graphene has recently attracted considerable attention as a potential material for nanoelectronic devices. A promising method for its mass production is microwave plasma enhanced chemical vapour deposition (MW PECVD). The main advantage of this technique is that few layer graphene (FLG) can be grown without the need of a catalyst on different substrates that can withstand high temperature (up to 700°C). However, the growth mechanism of PECVD synthesized graphene is not well understood. The aim of this work was to investigate the growth process of FLG deposited by MW PECVD on several substrates (quartz, silicon, platinum).

The resulting thin films were characterized by X-ray diffraction, scanning and transmission electron microscopy, Raman spectroscopy and angle resolved X-ray photoelectron spectroscopy (ARXPS). Three stages of film growth on silicon were identified by ARXPS: formation of a carbide layer on the substrate, deposition of an amorphous carbon layer and finally formation of a graphitic layer parallel to the substrate surface. It was established that crack edges in this graphitic layer serve as nucleation sites from which FLG flakes, only four to six atomic layers thin, grow perpendicular to the surface. This growth mechanism appears to be substrate dependent since no intermediate carbide layer was formed on both quartz and platinum surfaces. Furthermore, no amorphous carbon layer was detected on the platinum substrates, even for the shortest deposition time intervals.

4:40pm GR+TF+NC-TuA10 Uniform Transparent and Conducting Solution Processed Graphene Thin Films for Large Area Electronics, M. Chhowalla, Rutgers University **INVITED**

The integration of novel materials such as single walled carbon nanotubes and nanowires into devices has been challenging. Similarly, although fundamental research on graphene has been prolific since its discovery, reports on making it technologically feasible for integration into devices have only recently appeared. In this presentation, a solution based method which allows uniform and controllable deposition of reduced graphene oxide thin films with thicknesses ranging from a single monolayer up to several layers over large areas will be described. The opto-electronic properties can thus be tuned over several orders of magnitude, making them useful for flexible and transparent semiconductors or semi-metals. The thinnest films exhibit graphene-like ambipolar transistor characteristics while thicker films behave as graphite-like semi-metals. Controllable p-type doping via exposure to SOCl₂ vapor is also demonstrated. Cl doping leads to breakup of symmetry in ambipolar field effect characteristics, providing a route for unipolar devices. In addition, composite graphene/polymer thin film devices exhibiting on/off ratios >10 will also be reported. Collectively, our deposition method could represent a route for translating the interesting fundamental properties of graphene into technologically viable devices.

5:20pm GR+TF+NC-TuA12 Electronic Manipulation in Graphene Formed by Proton-irradiated Method, C.-H. Chuang, National Taiwan University and National Synchrotron Radiation Research Center, Taiwan, C.-H. Chen, H.-W. Shiu, National Synchrotron Radiation Research Center, Taiwan, X. Gao, M.B.H. Breese, F. Watt, S. Chen, A.T.S. Wee, National University of Singapore, M.-T. Lin, National Taiwan University, Taiwan

Graphene is referred to the honeycomb lattice of carbon atoms formed as a 2D flat single layer. It is also the building block to construct 0D fullerenes, 1D carbon nanotubes, and 3D graphite in graphitic materials. Similar to carbon-based materials, the strong C-C bonding with sp² hybridization is stable and rigid in ambient atmosphere. In this letter, we introduce the simple method to modify its electronic character and use Scanning Photoemission Microscopy (SPEM) to study its electronic structure. The previous reports about ion- or proton-irradiated graphitic materials present the new physical and magnetic property, e.g. induced ferromagnetic behavior. The reasons are mainly related to the disorder lattice, the vacancy density, or hydrogen-absorbed carbon atoms in the graphene network. However, it is necessary to provide the evidence about electronic structure after proton irradiation. SPEM provides the spatial mapping image with different element and the chemical bonding environment of XPS at the individual location. As compared with the graphite, we can know the C 1s state of graphene is similar. After the proton-irradiated impact on the graphene, the irradiated area shows the broad FWHM of C 1s state and chemical shift of 0.4 eV up to the high binding energy. Besides, we find the satellite peak with binding energy 291 eV, related to π to π^* state transition, is decreased after irradiation. The observed result in our irradiation sample may be due to the lattice reconstruction of C-C bond. Our experimental findings open up a new field in electronic manipulation in graphene-based electronics.

Magnetic Interfaces and Nanostructures

Room: 206 - Session MI+NC-TuA

Magnetic Microscopy and Magnetization Dynamics

Moderator: A.T. Hanbicki, Naval Research Laboratory

1:40pm MI+NC-TuA1 Probing Individual Magnetic Nanostructures with Spin Excitation Spectroscopy, A. Heinrich, IBM Research Division **INVITED**

Understanding and controlling the magnetic properties of nanoscale systems is crucial for the implementation of future data storage and computation

paradigms. Here we show how the magnetic properties of individual atoms can be probed with a low-temperature, high-field scanning tunneling microscope when the atom is placed on a thin insulator. We find clear evidence of magnetic anisotropy in the spin excitation spectra of individual magnetic atoms embedded in a non-magnetic surface. In extended one-dimensional spin chains, which we build one atom at a time, we find strong spin-coupling into collective quantum-spins, even for the longest chains of length 3.5nm. The spectroscopic results can be understood with the model of spin-excitations in a system with antiferromagnetic coupling, controlled on the atomic scale. High-spin atoms can show an interesting form of the Kondo effect when the magnetic anisotropy places a degenerate, low-spin Kramers-doublet in the ground-state.

2:20pm MI+NC-TuA3 Magnetic Exchange Force Microscopy with Atomic Resolution, U. Kaiser, A. Schwarz, R. Wiesendanger, University of Hamburg, Germany

Magnetic Exchange Force Microscopy (MExFM) is a novel technique that allows magnetic imaging of surfaces with atomic resolution. The set-up of this microscope resembles that of a conventional atomic force microscope, but a magnetic probe tip is used to study short-ranged magnetic exchange forces between the foremost tip atom and the underlying sample atoms. Since MExFM is sensitive to the forces between tip and sample, it is not limited to well-conducting materials like spin polarized scanning tunneling microscopy (SP-STM).¹ In our study we investigated the (001) surface of the antiferromagnetic insulator NiO with an iron-coated tip.² The microscope was operated in ultrahigh vacuum at 8 K in an externally applied magnetic field with a flux density of 5 T. All measurements were performed in the non-contact attractive force regime between tip and sample using the frequency modulation technique. At small tip sample separations we imaged the surface oxygen and nickel atoms with an additional atomic scale modulation on neighboring rows of nickel atoms. This corresponds with the antiferromagnetic arrangement of the nickel atomic magnetic moments. Since all surface nickel atoms are structurally and chemically equivalent, we can unambiguously assign the observed contrast modulation to a magnetic exchange force between tip and sample. In this talk experimental prerequisites for this new method as well as the origin of the exchange interaction are discussed.

¹ M. Bode, Rep. Prog. Phys. 66, 523 (2003)

² U. Kaiser, A. Schwarz, and R. Wiesendanger, Nature 446, 522 (2007)

2:40pm MI+NC-TuA4 Separation of Topographic Features from Magnetic Force Images using Capacitive Coupling Effect, B.I. Kim, Boise State University

Separation of topographic features from magnetic images has been an issue for the last 20 years in magnetic force microscopy (MFM). Although MFM is one of the most important imaging tools of nanoscale magnetic structures, this issue still remains largely unsolved and thus has limited the current capability of the MFM as a quantitative magnetic imaging tool. The frequent pickups of the topographic features are interpreted as transitions of the tip between bi-stable states of the tip-sample assembly in the noncontact and tapping regions in the conventional amplitude modulation MFM. The bi-stability originates from the long-range amplitude decrease due to the dc bias voltage for the uniform feedback polarity. As a method to make the amplitude increase in the noncontact region as the tip approaches the surface, an electrostatic force modulation method is introduced to utilize the capacitive coupling effect for magnetic imaging. MFM using electrostatic force modulation demonstrates the separation of the topographic features from the magnetic images with an enhanced stability. The stability is attributed to the different modulation method and servoing mechanism.

3:00pm MI+NC-TuA5 Magnetic Reconstruction of Vortexes in Co Nanocrystals, D.P. Pappas, L. Yuan, F.C.S. da Silva, A. Davydov, National Institute of Standards and Technology

Co nanocrystals were prepared and MFM measurements revealed the dependence of the magnetization on the shapes of the nano-crystals. The nanodots were formed by depositing a 10 nm film of Co onto a c-axis oriented sapphire crystal, which was then annealed to 1000 C. Nanocrystals formed with average size of about 500 nm, with a variety of shapes. From the shapes, it is apparent that some random nucleation occurred. The nanocrystals fall into two categories, hexagonal shaped and rectangular. The MFM images of the first type showed that the magnetization formed a central vortex core, with a magnetic reconstructions of either 3-fold or 6-fold symmetry around the core. The latter particles showed a maze-like magnetic configuration. These studies show that the strong uniaxial anisotropy persists in these particles, and the magnetic configuration is strongly dependent on the shape of the particles. Moreover, the circular dots have a strong tendency to form highly symmetric patterns.

4:00pm **MI+NC-TuA8 Complex Magnetic Order on the Atomic Scale Revealed by Spin-Polarized STM**, *K. von Bergmann*, University of Hamburg, Germany **INVITED**

Magnetism in low-dimensions is a fascinating topic: Even in apparently simple systems -such as homoatomic monolayers- the nearest neighbor distance, the symmetry and the hybridization with the substrate can play a crucial role for the magnetic properties. This may lead to a variety of magnetic structures, from the ferromagnetic and antiferromagnetic state to much more complex spin structures. Spin-polarized scanning tunneling microscopy (SP-STM) combines magnetic sensitivity with high lateral resolution and therefore grants access to such complex magnetic order with unit cells on the nanometer scale. Different previously inconceivable magnetic structures are observed in pseudomorphic homoatomic 3d monolayers on late 5d transition metal substrates.^{1,2} The broken inversion symmetry due to the presence of the surface can induce the formation of spin spirals, where the spin rotates from one atom to the next resulting in a nanometer sized magnetic period. The driving force for the canting of adjacent magnetic moments leading to such spirals is the Dzyaloshinskii-Moriya interaction and a unique rotational sense is found.

¹K. von Bergmann et al., Phys. Rev. Lett. 96, 167203 (2006).

²M. Bode et al., Nature 447, 190 (2007).

4:40pm **MI+NC-TuA10 Magnetization Damping in Magnetic Multilayers**, *T. Mewes*, The University of Alabama **INVITED**

For the application of magnetic multilayers in spintronic devices the magnetization relaxation is of great importance. Of particular practical interest are multilayers which include an exchange biased ferromagnet, i.e. a ferromagnet/antiferromagnet bilayer system for which the hysteresis loop of the ferromagnet can be shifted along the field axis. In comparison to bulk properties the magnetization relaxation in thin magnetic films can be enhanced for example by spin-pumping and two-magnon scattering due to local inhomogeneities. We investigated the magnetization relaxation in metallic ferromagnet/antiferromagnet based multilayer systems, using broadband ferromagnetic resonance measurements. By inserting a thin non-magnetic spacer layer, we find that spin-pumping contributes significantly to the damping in these multilayers, even for structures with no shift of the hysteresis loop. However, in exchange biased systems we observe a strong additional contribution to the magnetization relaxation.

5:20pm **MI+NC-TuA12 Perpendicular Anisotropy Graded CoPt/CoPtCr Magnetic Pillars Patterned by Nanosphere Lithography**, *X. Li, Z.R. Tadisina, A.L. Highsmith, S. Gupta, Y. Inaba, J.W. Harrell*, The University of Alabama

Patterned magnetic nanostructures such as nanodots and nanopillars are now an extremely active area of research for applications for next generation media,¹ as well as novel logic and spintronic memory devices. Bit patterned media is one of the most promising candidates to overcome the tradeoff between thermal stability and recording writability. This work will detail the deposition of perpendicular magnetic anisotropic media, a unique patterning approach using nanosphere lithography, and magnetic characterization of the patterned nanostructures. Process optimization of perpendicular magnetron sputtered CoPt and CoPtCr films of various compositions was carried out using seed layers of Ta and Ru. The anisotropy K_u ranged from 2×10^7 erg/cm³ to 2×10^6 erg/cm³ as a function of film thickness and Cr concentration. Nanosphere lithography² was used to pattern the magnetic films into nanopillars with controlled size. A self-assembled nanosphere monolayer was first prepared, tailored to a discrete dot mask by shrinking the spheres using reactive ion etching, and then transferred to hard masks and, finally, the magnetic media, by a combination of ion milling and reactive ion etching. Magnetic nanopillars with diameters ranging from 90 nm to those approaching 10 nm with correspondingly increasing pitch are obtained. The size dependence of the magnetization process, the thermal stability, and switching dynamics of the pillars are characterized in an alternating gradient magnetometer (AGM) and magneto-optic Kerr effect (MOKE) system by using angle-dependent and time-dependent remanent coercivity measurements fitted to Sharrock's equation over a wide range of timescales. A significant increase of thermal stability and coercivity was demonstrated with the decrease of pillar size. The reversal mechanism is similar to reported results of nucleation of a small reversed volume followed by rapid domain wall motion.³

¹ Robert F. Service, Science 314, 1868 (2006).

² C. L. Haynes and R. P. Van Duyne, J. Phys. Chem. B 105, 5599 (2001).

³ T. Thomson, G. Hu, and B. D. Terris, Phys. Rev. Lett. 96, 257204 (2006).

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

Nanowires and Nanosize Effects

Moderator: H. Schiff, Paul Scherrer Institut, Switzerland

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Self-assembled monolayers (SAMs) offer many potential advantages to science and industry in the form of parallel nanostructure fabrication, lubricants for MEMS, corrosion protection and sensing. As such, being able

to synthesize stable SAMs from different starting materials in a larger number of configurations will enable greater control over the systems for each of these applications. Due to the stability of metal-sulfur bonds, thiol (H-S-R) SAM formation has been studied extensively. In the case of thioethers (R-S-R), it has recently been shown that at temperatures up to 298 K in both ambient¹ and ultra-high vacuum² conditions, that the molecules still self-assemble on metal surfaces and exhibit long-range ordering, despite a weaker binding to the surface than thiols. Due to the presence of the additional hydrocarbon tail, thioethers form SAMs with a dramatically different geometry²; additionally, the weaker bonding reduces the stability of these systems relative to that of thiol SAMs. In this study it was found that in the Au(111)-(C₁₈H₃₇)₂S system, stability may be increased by elevation of the sample temperature to moderate values (400 K) during the monolayer formation. Furthermore, the gold surface reconstruction associated with increased adsorbate-substrate bond strength changes the ordering of thioether SAMs. This strong temperature dependence on the stability of the thioether SAM's structure suggests that temperature may be an easily controllable parameter in the design and tuning of self-assembled monolayers for specific applications.

¹ Jaegun Noh, Tomohide Murase, Ken Nakajima, Haiwon Lee, and Masahiko Hara, Journal of Physical Chemistry B, 2000, 104, 7411-7416;

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

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

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

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

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

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

Ceria (CeO₂) is a rare earth metal oxide known for possessing less toxicity than many other metal oxides. Although the beneficial therapeutic properties of ceria nanoparticles have been explored, poor emission properties limit its application in imaging. The continuing quest to understand the interaction of ceria nanoparticles with cell requires better luminescent property of ceria, for which a nanoscale manipulation by doping has been reported. Europium is known for its strong emission and its atomic radii being close to that of cerium favors extensive solid solubility in ceria lattice. A systematic approach has been used to optimize emission intensity by varying the dopant concentration and annealing temperature. The doped oxide particles were synthesized by room temperature chemical precipitation technique. The size and morphology of the particles were characterized by high-resolution transmission electron microscopy (HRTEM). Strain induced on doping was calculated through X-ray Diffraction (XRD) from Williamson-Hall plot and is found to increase with the amount of dopant and decreases with annealing temperature. The emission property of europium doped ceria nanoparticles were studied by photoluminescence spectra. In order to disseminate the influence of surface chemical species, oxidation state, oxygen vacancy and strain on emission, X-ray photoelectron (XPS), Raman and Infra-red (IR) spectral characterizations were carried out. XPS results indicated that the ratio of Ce³⁺/Ce⁴⁺ increases with dopant concentration and decreases with annealing temperature. Raman studies show a progressive shift to the higher

energy due to local symmetry ordering with the temperature. Emission intensity varies with the wavelength of excitation and observed transitions indicate the presence of Eu^{3+} in different symmetry environments. The photoluminescence was found to be optimum at 15mol% Eu doped ceria and gets quenched with further doping concentration. Emission spectrum of the doped cerium oxide reveals peak characteristic to energy transfer from host to Eu^{3+} and this becomes more efficient on annealing. The present results are likely to have a profound impact not only for simultaneous therapeutic and imaging, but also on using ceria as carrier under physiological conditions. The study indicates that the enhanced photoluminescence is related to the manipulation of ceria lattice at nanoscale achieved through doping of suitable element.

Surface Science

Room: 208 - Session SS1+NC-TuA

Reactions on Gold and BiMetallics

Moderator: D.A. Chen, University of South Carolina

1:40pm SS1+NC-TuA1 Surface-Mediated Partial Oxidation of Alcohols on Gold, X. Liu, C.M. Friend, Harvard University

Fundamental investigations of the chemical properties of oxygen on Au(111) will be described. These studies serve as a model for gold-based catalysis which efficiently promotes oxidation reactions of CO, alcohols, and olefins. Gold is also important in materials science more broadly because it is used for interconnects and as a substrate for self-assembled monolayers and for biological samples. Our studies of alcohol oxidation on gold single-crystal surfaces under ultra-high vacuum conditions have revealed mechanistic information for partial oxidation of alcohols that can be applied to explain the mechanism of heterogeneous catalytic processes. Furthermore, such basic knowledge is important for understanding and controlling factors that determine reaction selectivity. We have used a combination of reactivity, spectroscopic and imaging measurements in our work. These studies provide evidence that mechanistic information, established in single-crystal surface science studies, can serve as a valuable guide for understanding and designing catalytic reaction processes.

2:00pm SS1+NC-TuA2 Selective Oxidation Chemistry on Gold, J.L. Gong*, R.A. Ojifinni, N.S. Froemming, T. Yan, G. Henkelman, C.B. Mullins, University of Texas at Austin

The reactivity of atomic oxygen on Au(111) has been investigated employing molecular beam scattering and temperature programmed desorption (TPD) techniques under ultrahigh vacuum (UHV) conditions. We demonstrate that adsorbed O atoms (O_{ad}) facilitate $\text{NH}_{3,\text{ad}}$ decomposition even though ammonia does not dissociate on the clean Au(111) surface. The selectivity of the catalytic oxidation of ammonia to N_2 or to NO on Au(111) is tunable by the amount of atomic oxygen pre-covering the surface. Both N_2 and NO are formed via simple recombination reactions ($\text{N}_{\text{ad}} + \text{N}_{\text{ad}}$ and $\text{N}_{\text{ad}} + \text{O}_{\text{ad}}$). At low oxygen coverages ($\theta_{\text{O}} < 0.5$ ML), adsorbed ammonia is stripped to $\text{NH}_{x,\text{ad}}$ which decomposes to form gaseous N_2 . We also present experimental and density functional theory (DFT) calculation results of formation and decomposition of the carbonate anion ($\text{CO}_3 = \text{CO}_2 + \text{O}_{\text{ad}}$) on atomic oxygen pre-covered Au(111). A reaction probability on the order of 10^{-4} and an apparent activation energy of -0.15 eV are estimated for this reaction. The small values of reaction probability are likely part of the reason why an earlier study on Au(111) reported undetectable surface carbonate formation. Additionally, we have investigated partial oxidation of propanol on atomic oxygen covered Au(111). At reaction temperatures below 300 K, 1-propanol is oxidized to propaldehyde with 100% selectivity while acetone is the only products of 2-propanol partial oxidation. A small amount of CO_2 is formed at higher surface temperatures (i.e., above 300 K).

2:20pm SS1+NC-TuA3 Model Catalysts for Steam Reforming and Water-Gas Shift Reactions, J. Hrbek, Brookhaven National Laboratory INVITED

The molecular hydrogen used in many large scale processes in chemical industry and for operating fuel cells is produced by these catalytic reactions. Steam reforming can provide sustainable source of hydrogen when using ethanol as feedstock; water-gas shift is used to purify hydrogen by removing CO, a catalytic poison. I will describe the preparation and characterization of model catalysts, and discuss their surface interactions with reactants under vacuum and their catalytic reactivity under higher pressures. As we have shown recently (Science 318(2007)1757; Angew.

Chem. Int. Ed. 46(2007)1329)) both the model catalysts (Au or Cu on $\text{CeO}_2(111)$) and the inverse model catalysts (CeO_x or TiO_x nanoparticles supported on Au(111) or Cu(111)) have significant intrinsic activity for water-gas shift at elevated pressures. Neither Au(111) nor $\text{CeO}_2(111)$ have any activity in the WGS reaction. Our photoemission data indicate that CeO_x nanoparticles supported on the gold surface dissociate water molecules even below room temperature while the CeO_2 nanoparticles are inactive. Water dissociates on O vacancies of the oxide nanoparticle (the rate limiting step in the WGS reaction), CO adsorbs on Au site located near the oxide-metal perimeter, and subsequent reaction steps take place at the metal-oxide interface. Our ability to identify reaction intermediates under vacuum conditions and to link them with the structural characterization at the atomic level is critical for development of reaction models: specifically in the WGS process the oxide support is not a simple spectator and plays an essential role. I will also discuss experimental results obtained with the model catalysts for steam reforming of ethanol. This research was carried out at Brookhaven National Laboratory and supported by the US Department of Energy (Chemical Sciences Division, DE-AC02-98CH10886).

3:00pm SS1+NC-TuA5 Role of the Oxide Substrate on O_2 Dissociative Adsorption on Au Nanostructures: First Principle Studies, S. Stolbov, T.S. Rahman, University of Central Florida

In this work we apply the density functional theory calculations to explore the mechanism of high reactivity of Au nanoparticles on oxide substrates. We test the idea that the substrate – nanoparticle interaction makes the O_2 dissociative adsorption favorable on this system, in contrast to bulk Au, and then the O atoms, so adsorbed, are consumed by reactants for further oxidation. We exploit the observation that the 1.5-layer Au film on TiO_x displays an exceptionally high reactivity as compared to a monolayer Au film, as well as those with 2 or more layers.¹ We calculate the energetics of dissociative adsorption of O_2 on the surfaces 1.5, 2, 2.5, 3, 4.5, and 5 Au(001) layer structures in two environments: 1) free standing layers, 2) on TiO_2 fragments (modeling a substrate). For all missing row $n+0.5$ Au structures under consideration, the total energy is found to decrease upon the O_2 dissociative adsorption. However, analysis of entire pathway for this reaction suggests that the O_2 dissociative adsorption is favorable only for 1.5Au/ TiO_2 structure. This result along with the experimental finding¹ point to the O_2 dissociative adsorption as being the main mechanism for the observed reactivity of Au nanostructures. Calculated local densities of electronic states and local charges in the system will be presented for further insights into the nature of the effect.

¹M. S. Chen, D. W. Goodman, Science 306, 234 (2004). Work supported in part by DOE under grant # DE-FG02-03ER15842.

4:00pm SS1+NC-TuA8 Hydrogen Splitting on Ru and Pt Nanoparticles, E. Fiordaliso, M. Johansson, S. Murphy, R. Nielsen, I. Chorkendorff, Technical University of Denmark

Here we investigate the hydrogen splitting rate as a function of particle size for Pt and Ru by measuring the rate of the H-D exchange reaction at 1 bar. The study is mainly motivated by fuel cell applications, where highly dispersed Pt is used as the anode catalyst in the Proton Exchange Membrane (PEM) fuel cell. It was found in an earlier study that at 1 bar, Ru gives a higher rate for the H-D exchange reaction than Pt.¹ The experiments are performed in an apparatus which combines an ultra-high vacuum chamber for sample preparation and surface analysis with a high-pressure cell.² Model catalysts in the form of spots with a diameter of 1 mm are prepared by electron-beam evaporation of metal onto a sputtered highly ordered pyrolytic graphite (HOPG) substrate. The amount of metal corresponds to an average thickness between 0.2 and 50 Å. The rate of the H-D exchange reaction for each catalyst spot is measured in the high-pressure cell with the help of a combined gas dispenser and gas sampling device. The sampled gas is analyzed with mass spectrometry. Measurements were carried out at 1 bar with a gas mixture containing 1 percent D_2 in H_2 and the temperature was varied in the range 40 to 200 °C. The model catalysts were characterized with Auger Electron Spectroscopy (AES), X-Ray Photoelectron Spectroscopy (XPS) and Scanning Tunneling Microscopy (STM) before and after the high-pressure measurements. A simple model is used in order to extract the sticking probability for H_2 from data for the H-D exchange rate. Once the sticking probability has been obtained, the dissociative adsorption/desorption rate for H_2 can be calculated. The apparent desorption energy, E_{des} , for H_2 at the H coverage corresponding to 1 bar pressure is then extracted from data for the desorption rate as a function of temperature. It is found that at 0.2 Å average metal thickness, E_{des} is approximately 0.2 eV for Ru and 0.27 eV for Pt, and that the metals form particles with a mean diameter less than 10 Å. As the metal loading is increased, the particle size increases whereas E_{des} decreases. Above approximately 15 Å, an almost continuous metal film is formed and E_{des} becomes constant, 0.02 eV for Ru and 0.21 eV for Pt. Hence, the desorption energy for H_2 decreases with

* Morton S. Traum Award Finalist

increasing particle size for both Pt and Ru, but the effect is more pronounced for Ru.

¹ M. Johansson, O. Lytken, I. Chorkendorff, *J. Chem. Phys.* 128 (2008) 034706.

² M. Johansson, J. Hoffmann Jørgensen, I. Chorkendorff, *Rev. Sci. Instrum.* 75 (2004) 2082.

4:20pm SSI+NC-TuA9 Novel Pathways to Hydrogen Dissociation and Diffusion on Pd Alloys, *H.L. Tierney, A.E. Baber*, Tufts University, *J.R. Kitchin*, Carnegie Mellon, *E.C.H. Sykes*, Tufts University

Dissociation of molecular hydrogen on the surfaces of Pd-based alloys is a key step in a number of energy-related technologies, including CO₂ conversion and hydrogen separation. An understanding of the nature of H₂-surface interactions, including molecular adsorption, dissociation and surface diffusion provides a basis for the development of next-generation energy technologies. In this low-temperature scanning tunneling microscopy study we have demonstrated that individual Pd atoms in an inert Cu matrix are active for the dissociation of hydrogen and subsequent spillover onto Cu sites. The atomic-scale composition of both Pd/Cu{111} and Pd/Au{111} near-surface alloys were elucidated and H uptake was quantified. Our results indicated that H spillover was facile on Pd/Cu at 400 K but that no H was found under the same H₂ flux on a Pd/Au sample with identical atomic composition and geometry. Based on a simplistic model involving the adsorption energies of H on Pd{111}, Cu{111} and Au{111} it would appear that the barrier for H to migrate from Pd to Cu or Au is too high to occur at 400 K. DFT calculations provided insight into this unusual activity of Pd/Cu alloys for dissociation and uptake of H. The calculations revealed that the barrier for diffusion of H away from isolated Pd sites on Pd/Cu{111} alloys is lower than that of pure Pd{111}, but that this same diffusion barrier is insurmountable at 400 K on Pd/Au alloys. These results demonstrate the powerful influence an inert substrate has on the catalytic activity of Pd atoms supported in its surface.

4:40pm SSI+NC-TuA10 Alloy Nanocluster Distinct Surface Segregation Phenomena Related to the Coordination Dependence of Bond-Energies: Introduction and Application of a New Theoretical Approach, *L. Rubinchik, M. Polak*, Ben-Gurion University, Israel

This work introduces some novel aspects concerning alloy nanocluster equilibrium surface segregation phenomena and their modeling. The first involves the extraction of the Coordination dependence of Bond Energy Variations from DFT computed surface energies (the CBEV method). In particular, polynomial functions in terms of pair coordination numbers were fitted to DFT data reported recently for energies of pure Pt, Pd and Rh surfaces and small clusters. These functions yield elemental bond energy variations pertinent to any site at the cluster surface and subsurface layers. The second novel aspect, revealed when using the bond energy variations as input in statistical-mechanical computations based on the "free-energy concentration expansion method" (FCEM¹), concerns the finding that preferential pair-bond strengthening can lead to quite unique surface segregation characteristics. In particular: (i) In spite of the general tendency of Pd to segregate at Pt-Pd alloy surfaces, in cuboctahedron clusters certain (111) surface sites are populated by Pt, namely, a segregation reversal is predicted; (ii) Distinct Pd segregation profiles with maximal concentration at the subsurface layer are obtained for the Pt-Pd cluster (100) face, compared to subsurface oscillation in the Rh-Pd cluster (100) face. Further computations for Rh-Pd revealed inter-cluster separation involving "magic number" Pd segregated structures exhibiting various types of order. At higher temperatures atomic exchange among surface sites as well as surface-core desegregation processes are reflected in distinct configurational heat capacity peaks of the Schottky type.² As a test case, CBEV/FCEM computations done for the Pt-Rh(111) two-layer (oscillatory) profile show better agreement with previously reported experimental data as compared to our earlier work based on the NRL-TB/FCEM approach.³ Using the highly efficient CBEV/FCEM method enables to explore also compositional structures and properties of Rh-Pt-Pd ternary nano-clusters. Compared to current other approaches, this method is highly transparent, yielding better insight into the origin of surface segregation in bulk alloys and nanoclusters.

¹ M. Polak and L. Rubinchik, *Surf. Sci. Rep.* 38 (2000) 127.

² M. Polak and L. Rubinchik, *Phys. Rev. B* 71 (2005) 125426.

³ M. Polak and L. Rubinchik, *Phys. Rev. B* 75 (2007) 045415.

5:00pm SSI+NC-TuA11 Stability, Electronic, and Catalytic Properties of Supported Metal Clusters, *B. Roldan Cuenya*, University of Central Florida

The next generation of nanocatalysts requires detailed knowledge of the correlation between their structure and reactivity. Size- and shape-selected Au, Pt and AuFe nanoclusters with well defined intercluster distances were synthesized by diblock copolymer encapsulation. Significant changes in the electronic local density of states (LDOS) of TiC-supported Au clusters, in particular, the onset of non-metallic behavior, were observed by scanning tunneling spectroscopy with decreasing cluster size. In addition, evidence

for substrate-induced modifications in the LDOS of interfacial gold atoms was found.¹ Our temperature programmed desorption (TPD) measurements indicated a size-dependency in the catalytic activity of Au/TiC for CO oxidation.² Furthermore, interparticle interactions were found to affect the activity and life-time of our catalysts.³ The stability of oxidized gold species formed upon cluster exposure to atomic oxygen was investigated using a combination of temperature-, time- and CO dosing-dependent X-ray photoelectron spectroscopy and TPD.⁴ Our work demonstrates the formation of surface and sub-surface Au₂O₃ on Au nanoparticles. Interestingly, the stability of these species upon thermal treatment was found to depend on the reducibility of the oxide support. Finally, the formation, surface reconstruction and high-temperature mobility of size-selected bimetallic AuFe⁵ and Pt nanoclusters deposited on TiO₂(110) will be presented.

¹A. Naitabdi, L. K. Ono, B. Roldan Cuenya, *Appl. Phys. Lett.* 89, 043101 (2006)

²L. K. Ono, D. Sudfeld, B. Roldan Cuenya, *Surf. Sci.* 600, 5041 (2006)

³L. K. Ono, B. Roldan Cuenya, *Catal. Lett.* 113, 86 (2007)

⁴L. K. Ono, B. Roldan Cuenya, *J. Phys. Chem. C* 112, 4676 (2008)

⁵A. Naitabdi, B. Roldan Cuenya, *Appl. Phys. Lett.* 91, 113110 (2007).

5:20pm SSI+NC-TuA12 The Morphology and Reactivity of Metallic Nano Clusters Deposited on SiO₂ via Water Buffer Layer, *E. Gross, M. Asscher*, The Hebrew University of Jerusalem, Israel

Nanometer size gold clusters supported on metal oxide surfaces were reported as having size dependent catalytic activity. This has motivated us to prepare clusters under clean, high vacuum conditions with control over the clusters size and density. Gold nano clusters were prepared by two different growth procedures. In the first, the clusters were prepared by direct deposition (DD) of gold atoms on SiO₂/Si(100) substrates. The second growth mode is based on initial evaporation of gold atoms on top of amorphous solid water as a buffer layer at 100K which separates the small gold seed clusters from the substrate. Subsequent annealing to 300K desorbs the water molecules, resulting in aggregation and growth and (cold) deposition of nano-clusters on the substrate in a Buffer Layer Assisted Growth (BLAG) mechanism. In order to increase the BLAG clusters density we have introduced a Multi-Cycle BLAG procedure (MC-BLAG). By repeating the BLAG procedure up to seven times consecutively, the cluster density can be increased by 5 fold without affecting the clusters size. BLAG clusters are more 3D in nature, have larger height to diameter ratio than DD clusters, yet their interaction with CO is very similar to DD clusters. This is reflected by the practically identical CO stretch observed on both clusters at 2106±2cm⁻¹. UV-Visible absorption spectroscopy measurements have shown that differences in clusters morphology lead to variations in their surface plasmon resonance. The Multi-Cycle BLAG method also enables the growth of bi-metallic clusters. By modifying the preparation procedure either separated Au and Pd clusters or alloyed (Au-Pd) clusters can be prepared on the substrate. The catalytic reactivity of these bimetallic clusters is of great potential importance. We currently investigate the catalytic reactivity of bi-metallic clusters (such as gold and palladium or gold and copper) on dehydrogenation reactions. These reactions are of potential importance for various hydrogen energy applications, e.g. fuel cells.

Thin Film

Room: 302 - Session TF-TuA

Applications of ALD II

Moderator: S.M. George, University of Colorado

1:40pm TF-TuA1 ALD of High-k Gate Dielectrics on Si and Alternative Substrates, *J. Kim, H.C. Kim, B. Lee, A. Hande, E.M. Vogel, M.J. Kim, R.M. Wallace*, University of Texas at Dallas **INVITED**

For future high performance semiconductor device applications, it is critical to achieve a high quality gate dielectric with a high dielectric constant and excellent interface properties with semiconductor substrates such as GaAs, InGaAs and graphene in addition to Si. ALD has been considered as one of the most appropriate deposition techniques for high-k gate dielectrics without significant damage due to energetic particles and plasma. Due to its surface reaction nature, it is important to understand effects of reactants, such as precursors and oxidants, in conjunction with substrates on both interface and dielectric properties. Various materials characterization techniques including XPS, HRTEM, AFM, XRD, SIMS and RBS are used to investigate the physical properties of ALD derived metal oxide (Al₂O₃, HfO₂ and La₂O₃) thin films on various substrates. In particular, our in-situ XPS half-cycle study provides an insight on variation of chemical composition and binding status at the both interface and dielectric during the first few cycles.

2:20pm **TF-TuA3 ALD of High Dielectric Material LaMO₃ (M = Y, Yb, Er) Using Metal Formamidate Precursors.** *H. Li, D.V. Shenai,* Rohm and Haas Electronic Materials, *R.G. Gordon,* Harvard University

The study of ultrathin gate dielectrics has recently gained great attention due to the technological need to replace SiO₂ films in the metal-oxide-semiconductor field-effect transistors (MOSFETs).¹ According to the International Technology Roadmap for Semiconductors (ITRS),² the implementation of high-k gate dielectrics with a dielectric constant between 10 and 20 will be produced by leading manufacturers by 2008 in order to meet both low leakage current density and performance requirements. Ternary rare earth oxides are emerging as promising candidates for these applications. As shown in earlier report,³ lanthanum lutetium oxide films (LaLuO₃) obtained by pulsed laser deposition (PLD) technique showed a high dielectric constant of 32, very low leakage current density, remaining amorphous up to 1000 °C and excellent performance. Similarly atomic layer deposition (ALD) of ternary rare earth oxide films such as GdScO₃ or LaScO₃ also demonstrated the potential for substituting current high k material.⁴ However Lu and Sc elements are much less abundant in earth compared to other rare earth elements. So the precursors based on Lu or Sc can be extremely expensive to manufacture. Finding less expensive metals while maintaining those unique properties is urgent. Y, Yb and Er are three rare earth elements which are similar to Lu and Sc in ionic radii, but are much less expensive because of their natural abundance. In this presentation, we report the Y, Yb and Er precursors based on formamidate platform, which has been demonstrated to offer higher vapor pressure and higher thermal stability of the sources than commercially available conventional precursors.⁵ We will also report the ALD growth using H₂O and O₃ as co-reactants within the acceptable window of deposition temperatures. The resultant films will be characterized by AFM, XRD, and TEM.

¹Wilk et al, J. Appl. Phys. 2001, 89, 5243.

²International Technology Roadmap for Semiconductors: 2007 edition.

³(a) Lopes et al, Appl. Phys. Letts. 2006, 89, 222902.

⁴(a) Kim et al, App. Phys. Letts. 2006, 89(13), 133512/1-133512/3. (b) Wang et al, AVS 55th International Symposium, Boston, MA, 2008.

⁵Li et al, 8th International Conference on Atomic Layer Deposition, Bruges, Belgium, 2008.

2:40pm **TF-TuA4 Electrical Properties of Plasma-Enhanced Atomic Layer Deposition HfO₂/HfO₂N_x/HfO₂ Gate Oxide.** *W.J. Maeng, H. Kim,* POSTECH, Korea Republic

Nitrogen incorporation produces several benefits in the performance of high k gate oxides. However, since too much nitrogen incorporation at the interface of gate dielectric results in device degradation, the proper amount of nitrogen incorporation with precise depth profile control is desirable. In this study, the microstructure and electrical properties of plasma enhanced atomic layer deposition (PE-ALD) HfO₂ gate oxides with nitrated middle layer (HfO₂/HfO₂N_x/HfO₂) were investigated. The nitridation of the middle layer was carried out by two different in situ processes; PE-ALD using N/O mixture plasma (denoted as HfON) and PE-ALD HfN using hydrogen plasma followed by oxidation during the consequent HfO₂ deposition (denoted as HfONO). Significantly better electrical properties were obtained for HfONO than HfON in terms of hysteresis, equivalent oxide thickness, and reliability. In addition, high nitrogen incorporation up to 10 at% with improved thermal stability was achieved for HfONO sample. The experimental results will be discussed based on the atomic bonding configurations analyzed by X-ray photoemission spectroscopy.

3:00pm **TF-TuA5 Improvement of the Electrical Characteristics of Amorphous LaAlO₃ Films Made By Atomic Layer Deposition.** *Y. Liu, H. Kim, J.J. Wang, R.G. Gordon,* Harvard University, *H. Li, D.V. Shenai,* Rohm and Haas Electronic Materials

Amorphous lanthanum aluminum oxide (LaAlO₃) films were deposited on hydrogen-terminated silicon substrates by atomic layer deposition (ALD) at 300 °C. Capacitance-voltage measurements made from ALD MoN/LaAlO₃/Si stacks showed humps especially at low frequencies, indicating traps for electrons or holes. Two sources of these traps were identified: impurities and oxygen vacancies. The number of traps was cut in half by careful purification of the La precursor to remove metallic impurities to below a total of 1 ppm. The remaining traps were effectively removed by adding an oxygen (O₂) exposure either after each ALD cycle or by a post-deposition O₂ treatment at 300 °C, without affecting the dielectric constant (κ~15). The O₂ treatment also lowered the leakage current by an order of magnitude, to 1 mA cm⁻² for films with EOT = 1.3 nm.

4:00pm **TF-TuA8 In-situ Conductance Measurements during Transparent Conductive Zinc Oxide Film Growth using Low Temperature Atomic Layer Deposition.** *J.-S. Na, G.N. Parsons,* North Carolina State University

Zinc oxide has been extensively studied for applications such as solar cells, flat panel displays, gas sensors etc., and is considered as an alternative to

indium tin oxide due to its low-cost, non-toxicity, and chemical and thermal stability. For the flexible device and TFT applications, low growth temperature (<150 °C) or low carrier concentration (<10¹⁸ cm⁻³) is required. Here we report the low temperature atomic layer deposition (ALD) of zinc oxide using diethyl zinc and water as a precursor and reactant, respectively. We have developed a method to examine conductance in situ during ALD ZnO growth using two metal electrodes (Au/Cr) isolated by a thermally grown SiO₂ with a gap of 1 mm. Conductance was measured in situ during initial nucleation and steady state film growth at temperatures between 100-140 °C. The growth rate, electrical resistance, surface morphology, and crystallinity were also studied ex situ as a function of growth temperature and ALD cycles. At 120 °C the growth rate of ZnO ALD on SiO₂/Si was ~1.9 Å/cycles with ~3 cycles of incubation time and linear with the number of cycles. At 120 °C with 0.1V applied, the current was below the detection limit (<10⁻¹¹ A) for the first 42 cycles. The current increased exponentially from 10⁻¹¹ to 10⁻⁷ A between 43 and 50 cycles and followed by percolation to 10⁻⁵ A. From 70 to 200 cycles the current increased linearly from 10⁻⁵ to 5x10⁻⁴ A. Interestingly, the effect of each reactant exposure on the conductance of ZnO film during growth was quite different. Specifically at 120 °C, both DEZ and water exposure dramatically increased the conductance of ZnO film at the exponential nucleation region. Meanwhile the DEZ exposure decreased and the water exposure increased the conductance of ZnO at the ohmic linear region. This technique shows a potential for in-depth understanding of the ALD ZnO growth process in situ and also how each reactant is involved in the defect formation related to the carrier concentration within the growing ZnO film.

4:20pm **TF-TuA9 ALD Noble Metal Oxides - Film Growth and Stability Studies.** *M. Rütala, J. Hämäläinen, M. Heikkilä, K. Kukli, J. Niinistö, M. Kemell, M. Leskelä,* University of Helsinki, Finland

Noble metal oxide thin films gain interest over a broad range of application areas because of their attractive catalytic, optical, mechanical, electrical, and electrochemical properties. In integrated circuits, for example, high work function and structural similarity to high-k dielectrics make noble metal oxides potential electrode materials for capacitors and transistors. This presentation summarises our efforts in developing ozone based ALD processes for noble metal oxides. The consequences of the limited stability of noble metal oxides are also addressed using both high temperature XRD and chemical exposure experiments.

4:40pm **TF-TuA10 Increasing the Glass Cracking Resistance by Atomic Layer Deposition.** *M. Putkonen, P. Soininen, M. Rajala,* Beneq Oy, Finland, *T. Mäntylä,* Tampere University of Technology, Finland

Infrared cut-off filters are used in CCD or CMOS sensors. Typically these filters are made onto separate glass sheets placed in front of the sensor. However, recently thinner and thinner glasses are used, for example in the wafer-scale integration, which causes increasing problems due to the cracking of the substrates. Cracking of the glass due to the nanometer-scale Griffith-like flaws¹ is well known problem. These tiny flaws are usually in the range of 10-20 nm at the surface and they act as a starting point where bigger cracks start to develop. There are some available strengthening approaches, based for example on the coatings made by solution methods.² However, these relative thick coatings may require high post annealing temperatures in order to obtain desired properties without sacrificing optical properties. In this study we introduce ALD technique for improving the crack resistance of the glass. Previously ALD has been employed for example for thin film deposition onto deep microelectronic trenches as well as for coating nanometer scale features. Since ALD is highly conformal surface-controlled coating method, it is expected that the film growth will closely follow the structural flaws of the glass surface. We have utilised TMA/H₂O and SAM24/O₃ processes and studied the mechanical and optical properties of films. For example, thin films were deposited onto soda lime and D263T glass substrates measuring from 20x50 mm² to 1200x1200 mm². Typical film thicknesses were in the range of 10-30 nm, but thicker coatings were also evaluated. Batches of smaller pieces (20x50 - 100x100 mm²) were deposited in Beneq TFS 500 ALD system whereas bigger samples were evaluated in P400A, P800 and TFS 1200 systems. Depending on the sample size, glass thicknesses from 0.3 to 3 mm were evaluated. ALD processing of large area glass sheets were evaluated in terms of film uniformity and optical properties. Glass strength was evaluated against different thin film processing conditions and film thickness. According to the four point bending tests significant improvement on cracking strength were obtained by using ALD coatings.

¹ A. Griffith, The phenomena of rupture and flow in solids, Phil. Trans. Royal Soc., A221 (1920) 163.

² K. Endres et al., Enhancement of fracture strength of cutted plate glass by the application of SiO₂ sol-gel coatings, Thin Solid Films 351 (1999) 132.

5:00pm **TF-TuA11 In Situ Gas Phase Absorption Measurements During Hafnium Oxide ALD**, *J.E. Maslar, W.A. Kimes, J.T. Hodges, B. Sperling, D.R. Burgess, E.F. Moore*, National Institute of Science and Technology

In situ monitoring of atomic layer deposition (ALD) processes has the potential to yield insights that will enable improved efficiencies in film growth, in the development of deposition recipes, and in the design and qualification of reactors. In situ diagnostics potentially can be used to measure a number of parameters. Measuring precursor flux into the reactor is a relatively common application. However, such measurements are of limited value when trying to optimize deposition chemistry. Potentially more useful would be measurements of deposition precursor and product gas phase concentrations near the wafer surface. Such measurements would allow one to probe the properties of the near-surface thermal/gas velocity boundary layer that exists in many industrial ALD reactors. Since the properties of this boundary layer are strongly impacted by the state of the wafer surface, gas phase measurements in the boundary layer can provide information about the state of the wafer surface. In this work, semiconductor laser-based gas phase absorption measurements performed near the wafer surface are being investigated for use as in situ, real time diagnostics for ALD. The material system selected for investigation is hafnium oxide ALD using tetrakis(ethylmethylamino) hafnium (TEMAH) and water. Absorption measurements of water vapor were performed in the near-infrared (NIR) using a distributed-feedback (DFB) diode laser and employing a wavelength modulation detection scheme. Assuming complete reaction, the products of the TEMAH and water reaction are hafnium oxide and methyl-ethyl-amine, a volatile species under deposition conditions. Absorption measurements of methyl-ethyl-amine were performed in the NIR using an external-cavity diode laser (ECL) and employing an amplitude modulation detection scheme. In situ, time-resolved Fourier transform infrared spectroscopy measurements were used to compliment the laser-based measurements. Measurements were performed in a single-wafer, warm-wall reactor. Deposition precursor and product concentrations near the wafer surface were measured under a range of deposition conditions in an effort to correlate gas phase measurements with surface processes. The performances of the DFB laser-based and ECL-based measurement systems will be compared. In addition, efforts to model the observed concentration gradients using reactor-scale computational fluid dynamics models will be discussed.

5:20pm **TF-TuA12 Application of HRBS (High-resolution Rutherford Backscattering Spectrometry) to Elemental Depth Profiling of Advanced Gate Stack for Complementary Metal Oxide Semiconductor Devices**, *C. Ichihara*, Kobe Steel, Ltd., Japan, *S. Yasuno*, Kobelco Research Institute Inc., Japan, *H. Takeuchi*, ATDF, *A. Kobayashi*, *S. Mure*, Kobe Steel, Ltd., Japan, *K. Fujikawa*, *K. Sasakawa*, Kobelco Research Institute Inc., Japan

Hafnium-based materials with high dielectric constant have started replacing conventional SiO₂-based materials as a gate dielectric for CMOS (complementary metal oxide semiconductor) devices at production level. Much of the effort has been made to develop gate stack structures without forming bulk defects and interface states, while maintaining compatibility with CMOS thermal budgets. It is thus very important to characterize the elemental depth profile of the gate stack accurately. As compared to conventional physical analyses such as SIMS, AES, XPS, and XTEM, High-resolution RBS (HRBS) has advantages in ultra-thin film characterization as it provides non-destructive and quantitative elemental measurements with a high depth resolution (up to sub-nm) and without special sample preparations. Using HRBS, we studied the change in elemental depth profile of ultra-thin HfSiO(N) films on Si. Three different interfacial layers (HF-last pre-cleaning; ~0.8 nm chemical oxide formed by wet cleaning; and ~1.4 nm thermally-grown SiO₂ film followed by plasma nitridation) were prepared prior to the growth of ~2 nm HfSiO film by ALD. For all of the as-deposited HfSiO film experiments, Si concentration was found to be slightly higher at the top surface than in the bulk HfSiO. It was also observed that the thickness of the interfacial SiO_x layer of the HF-last sample was similar to that of the sample with chemical oxide, indicating that the Si surface was oxidized during the ALD process. The samples were, then, spike-annealed in nitrogen ambient at 1070°C. After the annealing, the accumulation of the Si at the top surface was enhanced for all the three samples, indicating the upward diffusion of Si species from the HfSiO film. The interfacial layer of the sample with chemical oxide was found to be the thickest of all the three different surface preparations after the spike annealing. Furthermore, the change in nitrogen profile was studied for the samples fabricated in two different processes (plasma-nitridation vs. NH₃ annealing) for the HfSiO films prepared on chemical oxide. The HRBS spectra revealed the difference of the nitrogen desorption during the spike-anneal between the two nitridation processes.

Biomaterial Interfaces

Room: 202 - Session BI+NC-WeM

Quantitative Nanoscale Sensing and Single Molecule Techniques

Moderator: B. Liedberg, Linköping University, Sweden

8:00am **BI+NC-WeM1 Studying Single Molecules on Living Cells. D. Klenerman**, Cambridge University, UK **INVITED**

One major challenge in biology is to understand how the individual molecules and complexes of the cell are organised and interact to form a functional living cell. To address this problem new biophysical tools are needed that are capable of studying single molecules in complexes both in the test-tube and on or in living cells. To determine the oligomerisation state of proteins we have used two colour single molecule coincidence detection based on the excitation of two distinct fluorophore labels on proteins with two lasers focussed to the same spot.¹ This method requires no prior knowledge of the structure of any complex formed or control of fluorophore position on the molecule. We show that this method can be used to characterise the protein oligomers formed during protein misfolding, ultimately resulting in amyloid fibril formation, and can distinguish between protein monomers and dimers on the cell surface.² Working together with Professor Yuri Korchev at Imperial College, we have developed a method for functional nanoscale mapping of the cell surface that is based on a scanned nanopipette. This allows high resolution, non-contact imaging of the soft and responsive cell surface using the ion current that flows between an electrode in the nanopipette and bath for distance feedback control.³ Recently we have made a major advance in the resolution of the topographic images, by scanning with fine quartz pipettes, so we can directly visualise protein complexes on the surface of live cells.⁴ The pipette can also be used to perform local nanoscale assays on the cell surface so as to perform single channel recording⁵ or apply pressure to probe the mechanical properties. We have also combined high resolution topographic imaging with simultaneous recording of the fluorescence from the cell surface.⁶ In addition the pipette can be used for controlled voltage driven delivery and deposition of biomolecules down to the single molecule level³ and this is being used to probe the structure of the cell membrane using single molecule fluorescence tracking.

References

- ¹. Anal.Chem. 78, 7707-7715 (2006).
- ². PNAS 104,17662-17667 (2007)
- ³. Phys. Chem. Chem. Phys. 7, 2859-2866 (2005)
- ⁴. Angewandte Chemie-International Edition 45, 2212-2216 (2006)
- ⁵. Biophysical Journal 83, 3296-3303 (2002).
- ⁶. PNAS 99, 16018-16023 (2002)

8:40am **BI+NC-WeM3 Theory of Single Molecule Characterization using Random Telegraph Signals. S. Vasudevan, K. Walczak, A.W. Ghosh**, University of Virginia

The future of nanoelectronics will depend not only on the capability to engineer 'smart' materials, but also on the ability to exploit new quantum phenomena that emerge at submicroscopic length scales. Molecular electronics has often been advocated as an ideal successor to silicon-based, complementary metal oxide semiconductor technology (CMOS). But its development has been thwarted by problems like poor gateability and low mobilities. Therefore we need to explore hybrid devices that do not compete with CMOS, but instead add novel functionalities by exploiting properties that are unique to molecules, such as their tendency to function as strongly correlated systems. Thus we need to account for more complex effects than usual semiclassical theory provides. In this paper we develop a theory for a new class of electronic devices that exploit correlated quantum scattering in a transistor channel. In these devices, molecules attach to the surface of a transistor channel; the chemical bonding leads to the transfer of charge and spectral weight between the molecule and the silicon surface. The overlap of molecular and silicon wavefunctions serves to passivate existing surface states as well as to create new localized molecular trap levels inside the silicon band-gap. At resonance driven by a gate, the traps are stochastically filled and emptied by the channel electrons, blocking and unblocking the channel. The resulting two-state random telegraph signal (RTS) can be used to locate the trap position both spectrally as well as spatially. This allows us to characterize and detect molecular species through unique nano-'barcodes'. The effect is enhanced in modern nanodevices as they can be fabricated practically defect free with near ballistic levels of operation. In contrast with ChemFETs, where one detects a single threshold shift for a specific molecule, here we get an entire spectral nano-'barcode' that can be compared against a compilation of theoretical responses to characterize and

sense a molecular species. Since these devices operate by modulating surface properties of transistors, we call them 'SurfFETs'. The significant advantage of such SurfFETs is their exclusive detection of only molecules that overlap significantly with the channel to cause a transfer of states. This means that this electronic detection scheme is selective and inherently avoids false positives- clearly an advantageous feature for detection of molecules.

9:00am **BI+NC-WeM4 Magnetic Tweezers Measurement of the Bond Lifetime-Force Behavior of the IgG-Protein A Specific Molecular Interaction. H. Shang**, MagSense Life Sciences, **G. Lee**, University College Dublin, Ireland

The bond lifetime-force behavior of the immunoglobulin G (IgG)-protein A interaction has been studied with magnetic tweezers to characterize the physical properties of the bond under nonequilibrium conditions. Superparamagnetic microparticles were developed that have a high and uniform magnetization to simultaneously apply a piconewton scale tensile force to many thousands of IgG-protein A bonds. A strong and a weak slip bond were detected with an effective bond length that is characteristic of short-range, stiff intermolecular interactions. These bonds are attributed to the interaction of protein A with the constant region (Fc) and heavy chain variable domain (VH) of IgG, respectively. The IgG-VH interaction appears to be one of the weakest specific molecular interactions that has been identified with a single molecule force measurement technique. This study demonstrates that magnetic tweezers can be used to rapidly characterize very weak biomolecular interactions as well as strong biomolecular interactions with a high degree of accuracy.

9:20am **BI+NC-WeM5 Elasticity Mapping of Pore Suspending Native Cell Membranes. A. Janshoff**, Institute of Physical Chemistry, Germany

The mechanics of cellular membranes is governed by a non-equilibrium composite framework composed of semiflexible filamentous cytoskeleton and extracellular matrix proteins linked to a lipid bilayer. Non-local elasticity information of native cell membranes has so far been gathered by micropipette suction and rheological whole cell experiments. Locally confined measurements were conducted by using membrane-attached beads pulled by laser tweezers and by atomic force microscopy of entire cells. As yet, local mechanical information (elasticity maps) of isolated cellular membranes, such as basolateral membranes of endo- and epithelial cells, are however, not available. Here, we introduce a novel approach that allows the mapping of mechanical properties of native freestanding cellular membranes on a nanometer length scale. Basolateral membranes of polar epithelial MDCK II cells, prepared on a highly ordered porous substrate, were locally indented with the aim to unravel how the cytoskeleton and extracellular matrix (ECM) affects the viscoelasticity of such native membranes on a predefined length scale. We found a strong relation between the density and cross-linking of actin filaments and membrane stiffness.

9:40am **BI+NC-WeM6 Size Measurement of Targeted Nanoparticle Delivery Systems. N. Farkas, J.A. Dagata, V.A. Hackley**, National Institute of Standards and Technology, **K.F. Pirolo, E.H. Chang**, Georgetown University Medical Center

The mean size and size distribution of a targeted nanoparticle delivery system (NDS) strongly influences the intrinsic stability and functionality of this molecular complex, affects its performance as a systemic drug delivery platform, and ultimately determines its efficacy towards early detection and treatment of cancer. Since its components undergo significant reorganization during multiple stages of self-assembly, it is essential to monitor size and stability of the complex throughout NDS formulation. Furthermore, reproducible and quantitative size measurement of individual entities, not only average properties of the entire population, is needed to assure potency and manufacturability of a specific formulation prior to entering clinical trials. Scanning probe microscopy (SPM) is capable of providing both high-resolution imaging of intact NDS immobilized on a substrate under fluid conditions and statistically meaningful, number-weighted averaged data for the complex. This presentation describes robust sample preparation methods and statistical image analysis of targeted liposome-based NDS with encapsulated therapeutic and diagnostic agents.¹ We present detailed examples of how variations in NDS formulation impact the size and stability of complexes with various payloads. These measurements are then compared with mean particle size distributions obtained by dynamic light scattering (DLS). SPM-based size distribution measurement technique in combination with DLS offers quantitative means of assessing size and stability, optimizing of formulation during drug development, and quality control during manufacturing of NDS.

¹ J. A. Dagata, N. Farkas, C. L. Dennis, R. D. Shull, V. A. Hackley, C. Yang, K. F. Pirolo, and E. H. Chang, Physical characterization methods for iron-oxide contrast agents encapsulated within a targeted liposome-based delivery system, Nanotechnology, in press.

10:40am **BI+NC-WeM9 Biophotonics: Resonant Detection of Single Molecules**, *A.M. Armani*, University of Southern California **INVITED**

For many biological and chemical experiments, a sensor must have high sensitivity, high specificity, and fast response time. There are many technologies which are able to achieve one or two of these three requirements, but many still face fundamental sensitivity or response limitations. Silica optical resonators are able to overcome these limitations because of the high quality factor (Q).^{1,2} In their application as a single molecule sensor, the sensitivity is derived from the long photon lifetime inside the microcavity, and the specificity is derived from functionalization of the silica surface. During the initial series of label-free detection experiments, pure Interleukin-2 (IL-2) solutions were injected into the volume surrounding the microtoroid. The microtoroid successfully detected step-like shifts in resonance wavelength from individual IL-2 molecules binding. Additional experiments have shown that even in the more complex environment of serum individual binding events of IL-2 are still resolved.³ Therefore, this single molecule sensor will enable research in new areas of biophysics and cell biology. Acknowledgements: The author would like to thank Prof. Richard Flagan, Prof. Scott Fraser, and Dr. Rajan Kulkarni at the California Institute of Technology. A.M. Armani is supported by the Provost's Initiative for Biomedical Nanoscience and the WiSE Program at the University of Southern California.

¹ A. M. Armani, D. K. Armani, B. Min, K. J. Vahala, and S. M. Spillane, Applied Physics Letters, vol. 87, pp. 151118, 2005.

² Armani, D. K., Kippenberg, T. J., Spillane, S. M. & Vahala, K. J. Ultra-high-Q toroid microcavity on a chip. Nature 421, 925-928 (2003).

³ A. M. Armani, R. P. Kulkarni, S. E. Fraser, R. C. Flagan, and K. J. Vahala, Science, vol. 317, pp. 783 (2007).

11:20am **BI+NC-WeM11 Single-Molecule Detection and Mismatch Discrimination of Unlabeled DNA Targets**, *M. Gunnarsson*, Chalmers Institute of Technology, Sweden, *P. Jönsson*, *J. Tegenfeldt*, Lund University, Sweden, *F. Höök*, Chalmers University of Technology, Sweden

Ultrasensitive biological sensors for low-abundant DNA and protein detection have emerged as an important tool for improving biomedical diagnostics, drug discovery, forensic analysis, but also advanced bioanalytical assays in fundamental research. We report on a single-molecule readout scheme based on total internal reflection fluorescence microscopy (TIRFM) demonstrating a detection limit in the low fM regime for short (30 mer) unlabeled DNA strands. Detection of DNA targets is accomplished by mediating the binding of suspended fluorescently labeled DNA-modified small unilamellar vesicles (~100 nm in diameter) to a DNA-modified substrate by unlabeled complementary single-stranded DNA. On top of rapid and sensitive detection, the technique is also shown capable of extracting kinetic data from statistics of the residence time of the binding reaction in equilibrium, i.e. without following neither the rate of binding upon injection nor release upon rinsing. The potential of this feature is demonstrated by discriminating a single mismatch from a fully complementary 30-mer DNA target.¹ The proposed detection scheme is particularly appealing due to the simplicity of the sensor, which relies on self-assembly principles and conventional TIRFM. In contrast to most other single-molecule detection schemes the imaging mode also offers possibilities for multiple spots to be measured simultaneously in an array-based design. The proposed sensor holds particular promise in cases when information about binding kinetics is valuable, such as in single nucleotide polymorphism (SNP) diagnostics.

¹ Gunnarsson, A., et al., Single-molecule detection and mismatch discrimination of unlabeled DNA targets. Nano Letters. 8(1): p. 183-188, 2008.

11:40am **BI+NC-WeM12 Optical Fiber Microarrays for Single Molecule Detection**, *H.H. Gorris*, *D.R. Walt*, Tufts University

Optical fiber microarrays have been employed for the detection of single enzyme molecules. Single enzyme molecules were enclosed with fluorogenic substrate in an array of 50,000 individually addressable microchambers etched into a glass optical fiber bundle. The large array size provided excellent statistics. The substrate turnover in the microchambers was monitored with epifluorescence microscopy. We have observed a broad distribution of discrete turnover rates of single β -galactosidase molecules that can be attributed to different enzyme conformations. When a slow-binding inhibitor was added to single β -galactosidase molecules inhibited and active states of β -galactosidase could be clearly distinguished. With a pre-steady-state experiment, we demonstrated the stochastic character of inhibitor release, which obeys first-order kinetics. Under steady-state conditions, the quantitative detection of substrate turnover changes over long time periods revealed repeated inhibitor binding and release events, which are accompanied by conformational changes of the enzyme's catalytic site. We proved that the rate constants of inhibitor release and

binding derived from stochastic changes in the substrate turnover are consistent with bulk-reaction kinetics. Furthermore, we have applied the optical fiber microarray to the detection of single horseradish peroxidase molecules. These monomeric enzyme molecules exhibit a narrower distribution of turnover rates than the tetrameric β -galactosidase, which could be explained by the number of catalytic sites involved in substrate turnover.

Biological, Organic, and Soft Materials Focus Topic

Room: 201 - Session BO+AS+BI+NC-WeM

Organized and Structured Organic Interfaces

Moderator: J.S. Shumaker-Parry, University of Utah

8:00am **BO+AS+BI+NC-WeM1 New Approaches to Chemical Lithography on the Micro- and Nanometer Length Scales**, *N. Ballav*, *S. Schilp*, Universität Heidelberg, Germany, *T. Winkler*, *H. Thomas*, *A. Terfort*, Philipps-Universität Marburg, Germany, *M. Zharnikov*, Universität Heidelberg, Germany

The development of novel approaches for the fabrication of nanostructures and, in particular, chemical and biological patterns is an important technological and scientific challenge. One of the perspective methods applies a modification of chemisorbed monomolecular films - self-assembled monolayers (SAMs), which are well-ordered 2D-assemblies of long-chain molecules attached to a suitable substrate. A flexible molecular architecture of the SAM constituents allows us to use a wide range of substrates, whereas the molecular size of these constituents makes SAMs an ideal platform for the fabrication of micro- and nanostructures. We present here two new approaches for the fabrication of chemical patterns with aliphatic SAMs as templates. Both approaches rely upon electron beam or X-ray lithography, but require much lower patterning dose as compared to already available methods as, e.g., Chemical Lithography with aromatic templates. The first technique is based on irradiation-promoted exchange reaction (IPER) between the primary SAM template and potential molecular substituent and can utilize a broad variety of commercially available molecules. The key idea of the second method is irradiation-induced activation of amino tail groups of the primary amino-terminated SAM template. Feasibility of both techniques is demonstrated by the fabrication of complex polymer micro- and nanobrushes in a broad height range and, in the case of the IPER approach, by the preparation of micron-scale gradients of protein adhesion.

8:20am **BO+AS+BI+NC-WeM2 Reversible Activation of a Polyelectrolyte Brush: Responsive Monolayers**, *R. Steitz*, Hahn-Meitner-Institut Berlin, Germany, *V. Papaefthimiou*, TU Berlin, Germany, *J.U. Günther*, *C.A. Helm*, University of Greifswald, Germany, *S. Förster*, University of Hamburg, Germany, *G.H. Findenegg*, TU Berlin, Germany

Polyelectrolytes anchored on surfaces are important in various applications and are also a challenging topic for fundamental studies. In this work, a monolayer of the PEE114-b-PSS83 [(poly(ethyl ethylene)114-b-poly(styrene sulfonic acid)83] diblock copolymer was transferred from the air/water interface to a deuterated polystyrene coated silicon (dPS/Si) surface, for evaluation as a tunable polyelectrolyte brush containing system. The grafting density of the polymer film was controlled by changing the lateral pressure during the depositions. X-ray Reflectivity and AFM measurements showed that a homogeneous layer of the block copolymer was formed, whose thickness (maximum 8 nm) increased with increasing grafting density. Neutron reflectivity studies against aqueous solutions revealed a hydrophobic PEE layer attached on the dPS/Si surface, and a carpet/brush polystyrene sulfonate (PSS) double layer in water. The effect of salt concentration on the brush nanostructure was investigated in aqueous solutions containing 0-1 M NaCl. It was found that the brush thickness decreases for salt concentrations above 0.1 M. In addition, reversible activation of the brush by changing the ionic strength of the subphase was demonstrated. These results confirm a potential use as a stimuli-responsive polymer for both fundamental studies and biological applications.

9:20am **BO+AS+BI+NC-WeM5 Phase Stability of 2D and 3D Structures of Oligopyridines on HOPG Studied by Thermal Desorption Spectroscopy and Scanning Tunneling Microscopy**, *M. Roos*, *H.E. Hoster*, *R.J. Behm*, Ulm University, Germany

Bis(terpyridine)derivatives (BTP) form highly ordered hydrogen bonded 2D networks on graphite (HOPG) at both the solid/liquid^{1,2} and the solid/gas^{3,4} interface. As found by STM at both interfaces, these adlayer structures depend on the positions of the N-atoms within the molecules, which can be varied via the synthesis process.^{1,2} Complementary to the STM studies, we have performed temperature programmed desorption experiments of two

different types of BTP molecules on HOPG. This revealed quantitative insights into phase stabilities of 2D (monolayer) and 3D (multilayer) phases. As to be expected from their large mass (618 amu) and correspondingly large moment of inertia, the translational and rotational degrees of freedom are found to play an important, even dominant role for the stability of more or less densely packed phases. This becomes apparent in strongly differing pre-exponential factors for desorption out of 2D and 3D phases. In agreement with STM observations at 300 K, the most stable phase (i.e., the one with the lowest chemical potential) for both molecules is not a close packed hydrogen bonded one, but a dilute 2D gas with facilitated translation and planar rotation. In this picture, ordered, hydrogen bonded structures observed at room temperature are only stabilized by the strong molecule-substrate interaction that allows enforcing higher coverages that go along with the more densely packed, ordered structures.

¹ C. Meier et al., *J Phys Chem B* 109 (2005) 21015

² C. Meier et al., *Angew. Chem. Int. Ed.* 47 (2008) 3821

³ H. E. Hoster et al., *Langmuir* 23 (2007) 11570

⁴ M. Roos et al., *Phys. Chem. Chem. Phys.* 9 (2007) 5672.

9:40am **BO+AS+BI+NC-WeM6 Dielectric Spectroscopy for Biological Applications**, C. Prodan, C. Bot, New Jersey Institute of Technology

Dielectric spectroscopy (DS) is a widely used technique to study the properties of cells, proteins and DNA in a fast, label free and noninvasive way. It measures the complex dielectric permittivities as a function of frequency for the given sample. Cellular membrane potential is one of the most important parameter of a living cell and represents the voltage difference between the inside and outside of a cell. Usual values of the membrane potential are in the range of 100 mV. Across a membrane of 2nm thick, this means electric fields of half million V/cm. Theoretical studies have shown that the membrane potential plays a dominant role on the dielectric permittivity of a cell suspension at low frequencies (0Hz-1kHz). Thus the membrane potential can be obtained from a simple measurement of the cell suspension dispersion curves. This talk presents the application of DS to measure and monitor the membrane potential from the low frequency dispersion curves of living cell suspensions of bacteria and mammalian cells. This technique is tested against the standard techniques for measuring the membrane potential such as patch clamping or voltage sensitive dyes.

10:40am **BO+AS+BI+NC-WeM9 True All-Organic Epitaxy in Fashionable Organic Hetero-Junctions**, G. Bussetti, C. Goletti, P. Chiaradia, Università degli Studi di Roma Tor Vergata, Italy, M. Campione, L. Raimondo, A. Sassella, A. Borghesi, Università Milano-Bicocca, Italy **INVITED**

The improvement of charge transport performances and the control of related electronic properties (a crucial step in the development of organic electronic devices) are strictly connected to the quality of the organic-organic interface, that up to now has been limited by three main problems: 1) the molecular package in organic crystals is significantly influenced by the sample size. It is a difficult task to grow a large single crystal: the substrates commonly used are often assemblies of smaller crystals with different orientations; 2) the chemical and physical properties of the substrate surface play a key role during the build-up of the organic layer. When an organic crystal is growing, significant changes (due to desorption, molecular readjustment, roughness variation, layer erosion, etc.) occur in the freshly deposited surface. Unfortunately, in-situ and real time spectroscopies are not yet commonly applied to monitor this complex phenomenology; 3) an effective thermodynamic strategy during the arrangement of the organic hetero-junction -as in inorganic Molecular Beam Epitaxy- (e.g., control of substrate temperature and sample growth rate, choice of single or multi-bunch growth, etc.) is still lacking in the deposition process. As a matter of fact, only recently a true all-organic epitaxy has been achieved. In this talk, the successful work and the most representative results we obtained in the last five years will be presented, showing that concrete possible solutions to the above mentioned points have been found. In particular, we have succeeded in growing different single organic crystals, namely α -quaterthiophene (α -4T), α -sexythiophene (α -6T), tetracene, rubrene, etc., with different shape, size (up to several square mm's) and orientation. An accurate investigation of the morphological and optical properties of the bare substrate as well as of the freshly grown ultra-thin organic layers has been performed. Our results demonstrate that the organic layer exhibits a high sensitivity to very low amount of contaminants. Moreover, we will show that is possible to tune the crystal growth from a Stransky-Krastanov to a Frank-van der Merwe mode during the layer deposition of different organic compounds [α -4T, α -6T, tetracene, rubrene, etc.] by Organic Molecular Beam Epitaxy. In conclusion, the growth of various organic heterojunctions with epitaxial quality is now a gain result.

11:20am **BO+AS+BI+NC-WeM11 Modification of Self-Assembled Monolayer Surfaces Using Hyperthermal Ion Beams**, J. Laskin, P. Wang, O. Hadjar, Pacific Northwest National Laboratory **INVITED**

Collisions of ions with surfaces play an important role in a variety of scientific disciplines including surface science, materials science, mass spectrometry, imaging and spectroscopy. This presentation will focus on phenomena that occur during collisions of complex polyatomic ions with surfaces at hyperthermal energies with specific emphasis on ion deposition, charge transfer, bond making and bond breaking processes. Because in this energy regime the initial kinetic energy of the ion is commonly sufficient for breaking chemical bonds on the surface but is too low for significant penetration of a polyatomic ion into the surface, hyperthermal collisions are well suited for chemical modification of the outer layer of the surface without substantial perturbation of the bulk substrate. In addition, careful control of the properties of the ion beam can be used for very specific surface modification. Covalent and non-covalent immobilization of peptides using soft-landing of mass-selected ions onto inert and reactive self-assembled monolayer surfaces will be discussed. Fundamental principles derived from such studies are relevant to the understanding of the transport of biomolecules through membranes in living organisms and provides a clear pathway for highly-selective preparation of biological surfaces.

Energy Science and Technology Focus Topic Room: 203 - Session EN+AS+EM+TF-WeM

Electrochemical Storage

Moderator: S. Haile, Caltech, K. Thornton, University of Michigan

8:00am **EN+AS+EM+TF-WeM1 Molybdenum Oxide Nanoparticles for Improved Lithium Ion Battery Technologies**, A.C. Dillon, National Renewable Energy Lab., S.-H. Lee, University of Colorado, Y.-H. Kim, National Renewable Energy Lab., R. Deshpande, Lam Research, P.A. Parilla, D.T. Gillaspie, E. Whimney, National Renewable Energy Lab., S.B. Zhang, Rensselaer Polytechnic Institute, A.H. Mahan, National Renewable Energy Lab. **INVITED**

Lithium-ion batteries are current power sources of choice for portable electronics. Further improvement of performance and simultaneous reduction in cost could allow for the deployment in hybrid electric vehicles or plug-in hybrid electric vehicles (PHEVs). The development of PHEVs will enable reduced oil consumption in the transportation sector. Importantly, PHEVs will also enable increased use of intermittent renewable energy resources such as solar and wind. By charging PHEVs during peak solar generation times, the load on the grid is effectively "leveled", and the average output of coal-fired power plants will be decreased. Recent efforts for electric vehicle applications are focused on new anode materials with slightly more positive insertion voltages to minimize any risks of high-surface-area Li plating while charging at high rates, a major safety concern. The state-of-the-art anode is graphite with a reversible capacity of ~ 350 mAh/g and a potential of 0.1 V relative to lithium metal. Metal oxides have long been known as Li-insertion compounds and typically operate at higher potential than graphite. Unfortunately they suffer from poor kinetics and/or capacity fade with cycling, especially at higher rates. Hot-wire chemical vapor deposition has been employed as a scalable method for the deposition of crystalline metal oxide nanoparticles at high density. Under optimal synthesis conditions, only crystalline nanostructures with a smallest dimension of ~ 10 - 40 nm are observed. Anodes fabricated from crystalline MoO₃ nanoparticles display both an unprecedented reversible capacity of ~ 630 mAh/g and durable high rate capability. Porous thin film nanoparticle anodes, deposited by a simple electrophoresis technique, show no degradation in capacity for 150 cycles when cycled at high rate (C/2 corresponding to one discharge in 2 hrs.). Micron sized MoO₃ particles are shown to fail after several cycles, under the same conditions. Both x-ray diffraction and in situ Raman spectroscopy studies reveal that upon Li-ion insertion the crystalline nanoparticles become highly disordered. Density functional theory calculations elucidate the complex Li-ion insertion process and reveal a novel mechanism confirming the nanoscale, high-rate, reversible capacity despite the loss of structural order. The synthesis of these novel nanostructured materials and their potential for improving lithium-ion battery technologies will be discussed in detail.

8:40am **EN+AS+EM+TF-WeM3 Boron Oxynitride: An Emerging Dielectric for High Temperature Capacitor Applications.** *N. Badi, S. Vijayaraghavan, A. Bensaoula*, University of Houston, *A. Tempez, P. Chapon*, Horiba Jobin Yvon, France, *N. Tuccitto, A. Licciardello*, University of Catania, Italy

Among the many technical challenges encountered in the development of high temperature electronics, the role of a passive component like capacitor is very important. Dielectric integrity at temperatures greater than 250 °C has however, up till now, been one of the major impediments to bringing out a capacitor with suitable performance characteristics at these high temperatures. In this work, we investigate applicability of boron oxynitride ($\text{BO}_x\text{N}_{1-x}$) thin films to fabricate capacitors for high temperature applications. Deposited $\text{BO}_x\text{N}_{1-x}$ layers by a filamentless ion source assisted physical vapor deposition technique show a high thermal stability up to 400 °C and a very high breakdown voltage (BDV) above 400 V/ μm . $\text{BO}_x\text{N}_{1-x}$ samples of thickness varying from 70nm – 200nm were grown in a high vacuum reactor. Prototype capacitors with boron oxynitride dielectric and titanium metal electrodes have been fabricated on 3" Si wafers followed by electrical and thermal characterization. Preliminary results indicate a very small variation (~3%) of capacitance over the frequency range of 10 KHz – 2 MHz and <10% variation in capacitance for the temperature range of 25 °C-400 °C. The device electrical characteristics studies (capacitance, leakage current, breakdown voltage), as a function of temperature and frequency for ($\text{BO}_x\text{N}_{1-x}$) dielectrics with varying oxygen to nitrogen ratio, are currently underway and their results will be presented at the conference.

This research was supported in part by USDOE grant # DE-FG02-05ER84325 to Integrated Micro Sensors, Inc.

9:00am **EN+AS+EM+TF-WeM4 Improving Efficiencies of Electrochemical Systems Through Microstructure Optimization.** *H.Y. Chen*, University of Michigan, *J.R. Wilson, P.W. Voorhees*, Northwestern University, *S.B. Adler*, University of Washington, *S.A. Barnett*, Northwestern University, *K. Thornton*, University of Michigan

The properties and performance of a wide range of materials depend on their microstructures. This is especially true in multifunctional, multiphase or composite materials in which different phases perform different functions. Therefore, controlling microstructures in these materials is one of the main routes for materials design to achieve optimal performance. Various simulation methods that can be applied to examine processing, property, and degradation during operation, including the phase-field simulations and finite element modeling, will be discussed. Through coupling of simulations of microstructural evolution and transport that use realistic microstructures, microstructural design for optimized performance is investigated. Specific examples will include microstructures found in solid oxide fuel cell electrodes and those resulting from phase separation.

9:20am **EN+AS+EM+TF-WeM5 Layer-By-Layer Approaches to Electrochemical Energy and Storage.** *P.T. Hammond*, MIT **INVITED**

New advances in multilayer assembly have involved the development of ionically conductive multilayer thin films and the introduction of electrochemical functionality. These systems have allowed the formation of a range of ultrathin electrochemical devices including electrochromic displays, proton exchange membranes in fuel cells, and the use of these multilayers in other power and micropower devices. The use of this water based electrostatic assembly method has enabled the use of simple processing conditions, such as salt content and solution pH, to act as tools for the manipulation of ion and electron transport characteristics in the film, as well as the morphology of these unique nano-assemblies. Examples of this approach include the ability to integrate highly water soluble polymers with large sulfonic acid content into mechanically stable ultrathin films has led to new membranes with ionic conductivity approaching that of Nafion, and methanol permeability two orders lower, thus lowering fuel crossover and leading to large enhancements in methanol fuel cell performance with the application of nanometer thick thin films. On the other hand, the incorporation of both organic and inorganic nanoscale objects using the electrostatic assembly approach has enabled the incorporation of genetically engineering virus biotemplates in collaborations with the Belcher research group that have resulted in new developments in battery electrodes, and the integration of titania and other materials systems for reactive electrodes. Ultimately, the use of layer-by-layer systems have led to a range of organic and inorganic materials systems that have incorporated metal oxide nanoparticles, semiconducting carbon elements, and organic polymers to yield systems of interest for solar cells, capacitor/battery and electrochemical energy electrode and separator applications.

10:40am **EN+AS+EM+TF-WeM9 Material Solutions for Solid State Energy Storage.** *L.F. Nazar*, University of Waterloo, Canada **INVITED**

The increasing demand for energy world-wide and inherent pressing environmental needs, have jump-started efforts to develop energy storage systems that can be coupled to renewable sources, and/or viable energy

conversion systems. Traditional electrode materials for lithium-ion storage cells are typically crystalline, single-phase layered structures such as metal oxides, and graphitic carbons. These materials power billions of portable electronic devices in today's society. However, large-scale, high-capacity storage devices capable of powering hybrid electric vehicles (HEV's) or their plug-in versions (PHEV's and EV's) have much more demanding requirements. This in turn, means that demands are on chemists to create novel materials, and address fundamental scientific issues relating to mass (ion) and electron transport at rapid rates. Recently, nanostructured solid state materials comprised of two more compositions, are being increasingly exploited. These can take the form of "surface modified nanocrystallites", or stuffed nanoporous materials. For example, we employ porous frameworks as electrically conductive scaffolds to encapsulate active electrode materials, where both components play a role in controlling the electrochemical performance. This presentation will provide an overview of how the nanostructured approach provides benefit over the bulk, using selected examples from a range of promising new solid state materials with targeted, and tuneable structures.

11:20am **EN+AS+EM+TF-WeM11 Platinum Nanorods as PEM Fuel Cell Electrodes.** *M. Gasda, R. Teki, T.-M. Lu, N. Koratkar, G. Eisman, D. Gall*, Rensselaer Polytechnic Institute

Platinum catalyst layers were deposited by magnetron sputtering from a variable deposition angle α onto gas diffusion layer (GDL) substrates and were tested as cathode electrodes in polymer electrolyte membrane (PEM) fuel cells. Layers deposited at normal incidence ($\alpha = 0^\circ$) are continuous, and approximately replicate the rough surface morphology of the underlying GDL. In contrast, glancing angle deposition (GLAD) with $\alpha = 85^\circ$ and continuously rotating substrates yields highly porous layers consisting of vertical Pt nanorods. At 0.40 mg/cm² total Pt loading, the rods are 100-500 nm long and ~300 nm wide, separated by 20-100 nm wide voids. The dramatic difference in microstructure is due to atomic shadowing during GLAD that causes Pt flux from highly oblique angles to preferentially deposit on surface protrusions, leading to nucleation and columnar growth on substrate mounds while surface depressions remain uncoated. Fuel cell testing at 70°C using Nafion 1135 membranes, Teflon-bonded Pt-black electrodes (TBPBE) at the anode, and atmospheric pressure hydrogen and air reactants shows a monotonic increase in performance of GLAD cathodes from 0.05 to 0.40 mg/cm² total Pt loading. Nanorod cells exhibit approximately 2x higher mass activity than continuous layers at 0.50V (corrected for iR, shorting, and gas crossover); for example, GLAD and continuous layers with approximately the same Pt loading (0.18 and 0.25 mg/cm², respectively) show 1.7 and 0.8 A/mg. In contrast, at low current density of 0.10 A/cm², the continuous layers (0.70 V with 0.25 mg/cm² Pt) outperform GLAD cells even with relatively high Pt loadings (0.65 V with 0.40 mg/cm² Pt). The GLAD cells' higher mass-specific performance at high current densities is due to their high porosity which facilitates reactant transport, while the low-current performance of the continuous layer is attributed to a higher active Pt surface area. The sputter-deposited electrodes exhibit a higher platinum utilization in comparison to TBPBE reference cathodes, with GLAD cells (1.7 A/mg) performing better than TBPBE (0.75 A/mg) at high current densities (0.50 V), while continuous layers (0.07 A/mg) outperform TBPBE (0.035 A/mg) at 0.80 V. These results indicate the promise of nanoengineering to boost catalyst utilization in PEM fuel cells.

Magnetic Interfaces and Nanostructures

Room: 206 - Session MI+NC-WeM

Magnetic Thin Films, Nanoparticles and Nanostructures

Moderator: D.P. Pappas, National Institute of Standards and Technology

8:00am **MI+NC-WeM1 Reactive Biased Target Ion Beam Deposition of AlO_x Barrier Magnetic Tunnel Junctions.** *W. Chen**, *J. Lu, K. West*, University of Virginia, *W. Egelhoff*, National Institute of Standards and Technology, *S.A. Wolf*, University of Virginia

Magnetic tunnel junctions (MTJs) with AlO_x barriers are deposited using a unique tool called Reactive Biased Target Ion Beam Deposition system (RBTIBD) utilizing low energy ion source (0-50eV) and target biasing (50eV~1200eV). The RBTIBD system applies bias voltage directly and only on the desired targets, providing sputtering energy and avoiding "overspill" contamination during film growth. The ability to control the low ion beam energy as well as the target bias, is suited for producing high

* Falicov Student Award Finalist

quality atomic scale interface for the multi-layer structures, which is the key for high tunneling magnetoresistance (TMR) performance desired for application. A typical Exchange biased MTJs stack would be Si/SiO₂/Ta/Ru/IrMn/CoFeB/AlO_x/CoFeB/Ta/Ru. The magnetic properties are measured by VSM and TMR ratio of unpatterned films is measured by CIPTech technology.

8:20am **MI+NC-WeM2 Anisotropic Competition in FM/AFM Bilayers: The Influence on Magnetic Easy Axis, FM/AFM Exchange Coupling, and Interfacial Coupled Spins.** *B.Y. Wang**, National Taiwan University and TIGP, Academia Sinica, Taiwan, *W.C. Lin*, National Taiwan Normal University, *N.Y. Jih*, *C.-H. Chuang*, *C.W. Peng*, *S.S. Wong*, National Taiwan University, *Y.L. Chan*, *D.H. Wei*, National Synchrotron Radiation Center, Taiwan, *M.-T. Lin*, National Taiwan University

We present the studies of the magnetic easy axis, ferromagnetic/antiferromagnetic exchange coupling, and interfacial spins of Fe/fcc-Mn/Cu₃Au(001) ultrathin bilayers for probing both magnetic anisotropy of ferromagnetic Fe layer and antiferromagnetic Mn layer by using magneto-optical Kerr effect (MOKE) and photoemission electron microscopy with X-ray magnetic circular dichroism (XMCD-PEEM). Combining the experimental results with the analysis from phenomenological magnetic anisotropic model, we demonstrate that the Fe and Mn layer reveals intrinsic in-plane and out-of-plane magnetic anisotropy, respectively, in which the anisotropic competition between Fe and Mn layer significantly influences the orientations of magnetic easy axis, Fe/Mn exchange coupling, and interfacial coupled spins of Fe/Mn bilayers.

8:40am **MI+NC-WeM3 Time-of-Flight Secondary Ion Mass Spectrometry Study of Manganese Diffusion in Annealed MnAs/GaAs Layered Structures.** *R.E. Goacher**, *H. Luo*, *J.A. Gardella, Jr.*, University at Buffalo

Layered structures of MnAs/GaAs grown by MBE are characterized using ToF-SIMS before and after low-temperature annealing. MnAs is studied both as a model system for investigating Mn diffusion from (GaMn)As into GaAs and as a material that may have importance for Spintronics applications in its own right.^{1,2} Two challenges that must be overcome to create practical Spintronics devices are to achieve high Curie temperatures and efficient spin injection.³ It has been shown that the Curie temperature of (GaMn)As is improved by post-growth annealing at low temperatures.⁴ However, one hypothesis regarding the failure of efficient spin injection is that the physical diffusion of spin dopant atoms (Mn) from a magnetic to a neighboring non-magnetic layer decreases the coherence of injected spin-polarized electrons. Therefore, this work investigates the extent of Mn diffusion over the relevant temperature range between the growth temperature (as low as 200 C) and approximately 400 C. The in-depth chemical profiles obtained by the ToF-SIMS analysis reveal the extent of manganese diffusion from MnAs into GaAs. Quantitative diffusion information is obtained by calibrating the Mn concentration to ion-implanted standards and the depth scale to profilometry measurements. Depth profiles obtained for samples of ~5 nm MnAs over GaAs as grown and annealed at 200, 300 and 400 C reveal the migration of Mn towards the sample surface for temperatures up to 300 C, and then significant diffusion into the bulk GaAs after annealing at 400 C. Significant Mn diffusion after annealing a thick (~150 nm) MnAs layer over GaAs at 400 C is also detected. Quantitative analysis reveals that the integrated Mn concentration decreases as the annealing temperature increases, indicating some evaporative loss of Mn during annealing. The instrumental broadening function is also measured from a delta-layer sample in order to de-convolute the broadened diffusion profiles. The application of the measured diffusion information to device design and post-growth treatment is also discussed.

¹ Ramsteiner, M. et al., Phys Rev B: Cond Matt Mat Phys, 2002, 66, (8), 081304/1-081304/4.

² Dvakanov, M. I., Los Alamos National Laboratory, Preprint Archives, Condensed Matter, 2004, 1-10.

³ Ploog, K. H., J Cryst Growth, 2004, 268, (3-4), 329-335.

⁴ Stanciu, V. et al., Phys Rev B: Cond Matt Mat Phys, 2005, 72, (12), 12534/1-12534/5.

9:00am **MI+NC-WeM4 Molecular Beam Epitaxy Integration of Barium Hexaferrite on Wide Bandgap 6H-SiC.** *Z. Cai**, *T.L. Goodrich*, *Z. Chen*, *F. Yang*, *V.G. Harris*, *K.S. Ziemer*, Northeastern University

Integration of nonreciprocal ferrite microwave devices (e.g. circulators, isolators, phase shifters, etc.) with semiconductor platforms is a necessary to meet the increasing security, usage, and portability demands of civilian and military communication systems by increasing microwave power and by reducing device volume. Barium hexaferrite (BaM, BaFe₁₂O₁₉) is ideal for microwave device applications because of its high resistivity and particularly large uniaxial magnetocrystalline anisotropy (17 kOe) with the easy direction along the c-axis. BaM films with improved ferromagnetic

resonance linewidths (< 100 Oe) have been deposited on 6H-SiC by pulsed laser deposition (PLD) through the use of a 10nm single crystalline MgO template grown by molecular beam epitaxy (MBE). Since the improvement in magnetic properties of BaM films is linked to the initial stages of BaM film growth, MBE deposition of high quality BaM has the potential to be an ideal seed layer for thick BaM film deposition by PLD or liquid phase epitaxy (LPE). BaM growth by MBE was carried out using an oxygen plasma source at pressure (<1×10⁻⁵ Torr) and solid source Ba and Fe effusion cells at substrate temperature ranging from 300~800°C. High quality film with strong c-axis aligned normal to the substrate and low coercivity (200 Oe) was achieved at 750 °C and 2×10⁻⁶ Torr with 10nm MBE-grown MgO template. In-situ x-ray photoelectron spectroscopy and reflection high-energy electron diffraction showed stoichiometric chemistry and ordered crystal structure. Ex-situ atomic force microscopy revealed a smooth surface (1.2 nm root-mean-square roughness over a 2 × 2 μm²) and x-ray diffraction patterns showed strong epitaxial growth of c-axis perpendicular to the substrate. Magnetic hysteresis loops confirmed that the easy magnetic axis of the BaM film was aligned perpendicular to the film plane. This is believed to be the first demonstration of oriented, crystalline BaM on SiC by MBE, and has the potential to be a simple and successful method to realize effective integration of BaM with SiC for next-generation microwave device application.

9:20am **MI+NC-WeM5 Exploring Complexity through Reduced Dimensionality: Novel Transport Properties of La_{5/8-x}Pr_xCa_{3/8}MnO₃ Wires.** *T.Z. Ward**, *S. Liang*, Univ. of Tennessee & Oak Ridge National Lab., *K. Fuchigami*, Univ. of Tennessee & Oak Ridge National Lab. and IHI Corp., Japan, *L.F. Yin*, Oak Ridge National Lab., *E. Dagotto*, Univ. of Tennessee & Oak Ridge National Lab., *E.W. Plummer*, Univ. of Tennessee, *J. Shen*, Univ. of Tennessee & Oak Ridge National Lab.

Currently, the condensed matter physics community is devoting a great deal of attention to complexity and the nanoscale. By combining these two areas, even well studied complex systems such as the manganites might exhibit new and unexpected phenomena. Our work shows that this is indeed the case. We employ novel lithographic techniques to spatially confine single crystal La_{5/8-x}Pr_xCa_{3/8}MnO₃ (LPCMO) thin films to the scales of the inherent electronic phase separated domains. The results of this confinement are striking differences in the electronic transport properties which allow us new insights into the underlying balance of spin-charge-lattice interactions while increasing our knowledge of the formation of and interplay between domains. We expect this technique to offer similar rewards on other phase separated materials; and with the current trend toward reduced device sizes, this type of study will be critical for future applications.

9:40am **MI+NC-WeM6 Controlling Magnetic Anisotropy in Epitaxial FePt(100) Films.** *Z. Lu**, *M.J. Walock*, *P. LeClair*, *W.H. Butler*, *G.J. Mankey*, University of Alabama

L10 FePt is a good candidate for ultrahigh density magnetic recording media because it exhibits a perpendicular anisotropy which has a very high value of K_u=7x10⁷ erg/cm³. The high anisotropy allows for a smaller thermally stable magnetic volume in the written bits. However, writing the magnetic information on a film with such a high anisotropy is a technical challenge. To solve this problem, some new multilayered media such as exchange spring, exchanged composite and anisotropy graded media have been proposed. An important technical challenge for enabling these concepts is developing an ability to control the magnetic anisotropy of each magnetic layer. For FePt films, there are two methods to control the magnetic anisotropy, either by controlling the chemical order parameter S or by varying the composition to produce Fe-rich alloys. We will report our results obtained from epitaxial films fabricated by magnetron sputtering on MgO(100) substrates with Cr and Pt as buffer layers. By varying the growth temperature, epitaxial films of Fe₅₀Pt₅₀ were prepared with order parameters ranging from 0 to 0.95 as determined by x-ray diffraction. By carefully controlling the flux of the magnetron sources, epitaxial films of Fe_{100-x}Pt_x with 25<x<50 were also produced. Results of how the anisotropy changes with the order parameter and chemical composition will be presented.

10:40am **MI+NC-WeM9 Nanopatterning with Self-assembled Nanoparticle Arrays.** *S.A. Majetich*, *C. Hogg*, *J.A. Bain*, Carnegie Mellon University

INVITED
Magnetic information storage density is quickly approaching limitations, due to the noise introduced by the grain size dispersion. The noise can be mitigated by shrinking the grain size, yielding more grains per bit, but if the grains are too small they will be superparamagnetic. This is overcome by increasing the magnetocrystalline anisotropy of the material, or by patterning the media. Self-assembled nanoparticle arrays could be useful for noise reduction in conventional media, even without perfect order. In the longer term, with ordered arrays, they could potentially be used as patterned media with very small bit size. Lithographic methods have been used to fabricate nanopatterns, but the features must be written serially, which

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would lead to high manufacturing costs. There is a great need for parallel nanopatterning approaches; many of the proposed techniques have taken advantage of self-assembly. Here we explore the limits of nanomasking on even smaller structures based on self-assembled nanoparticle arrays. Arrays of FePt nanoparticles have previously been proposed as magnetic recording media, but there have been difficulties in obtaining the desired high anisotropy phase together with regular order within the array. In addition, the particles in self-assembled nanoparticle arrays are not crystallographically oriented, and variations in the easy axis direction would be an additional source of noise. The nanomasking approach uses self-assembled nanoparticle arrays to create a template pattern that is then transferred into an underlying thin film. Ion milling is a well-known technique for patterning materials on the micron scale, but questions remain about its application to nanoscale patterning. In an ideal ion milling process, a high-energy ion strikes a surface and knocks out an atom, which is then removed by the vacuum system. One of the advantages of ion milling is its relative insensitivity to the type of atoms in the sample, in contrast to reactive ion etching, where the selective reactive chemistry of the ions provides the energy for the reaction. Reactive ion etching (RIE) is gentler, but requires that the etching products be gaseous. Here we compare the nanopatterning results using self-assembled nanoparticle array nanomasks with argon ion milling and RIE.

11:20am **MI+NC-WeM11 Functionalized Gd₂O₃ Nanoparticles to be used for MRI Contrast Enhancement**, *M. Ahren, L. Selegard, N. Abrikosova, A. Klasson, F. Soderlind, M. Engstrom, P.-O. Käll, K. Uvdal*, Linköping University, Sweden

The properties of very small particles, i.e. particles with a small volume to surface relative ratio, have been shown to clearly differ from both the atom and bulk material. Such low dimensional materials will be of main importance during material design and optimization in the future. We are now designing functionalized rare earth nanocrystals and this material is very promising as positive contrast agent in Magnetic Resonance Imaging (MRI). The core of the nanomaterial is characterized using X-ray Photoelectron Spectroscopy (XPS), Transmission Electron Microscopy (TEM) and Photo Emission Electron Microscopy (PEEM). The functionalization steps are investigated by means of XPS, Infrared (IR) Spectroscopy and Dynamic Light Scattering (DLS). The proton relaxation times were measured as a function of dialysis time and functionalization, with a MRI scanner. The relaxivity is compared to commercially available Gd based chelates (Gd-DTPA). We have shown that the core consists of pure Gd₂O₃, the particles are crystalline and in the size of about 3-5 nm. The functionalization process and dialysis procedure are shown to increase the stability of the material. A considerable relaxivity increase for functionalized and dialyzed particles compared to corresponding values for Gd-DTPA is obtained. The long term goal is to design a powerful, directed contrast agent for MRI examinations with specific targeting possibilities with strong MR- signal on the cell- and molecular level.

11:40am **MI+NC-WeM12 Interfacial Interactions of Magnetic and Nonmagnetic Spacer Layers in FeCo/Pd and FeCo/Ru Multilayer Stacks**, *M.J. Walock*, The University of Alabama, *H. Ambaye*, Oak Ridge National Laboratory, *G.J. Mankey*, The University of Alabama

Residing at the peak position on the Slater-Pauling curve, FeCo alloys are heavily used in the magnetic recording industry. However, higher magnetizations are desirable. Prior results have shown that alloying FeCo with minute amounts of 4d elements have produced materials with higher magnetizations. Another approach is the deposition of 4d elements as thin spacer layers between FeCo layers. With this tactic, we investigate the interfacial interactions between the 3d alloy and 4d elements. Among the 4d elements, Pd and Ru offer intriguing possibilities. Ru layers permit both ferromagnetic and antiferromagnetic exchange interactions, but Pd layers show only ferromagnetic coupling between the magnetic layers. A series of multilayer samples with Pd and Ru spacer layers was studied to explore these interactions. Polarized neutron reflectivity enabled the determination of the layer-specific magnetization vector distributions. The neutron experiments show that there is a small but finite magnetization of the 4d spacer layers, dependent on the distance from the interface. To confirm this observation, x-ray magnetic circular dichroism was used to probe the element-specific average atomic magnetic moments in both the 3d and 4d layers.

Nanomanufacturing Focus Topic

Room: 309 - Session NM+MS+NS+NC-WeM

Beyond CMOS

Moderator: A. Diebold, University at Albany

8:00am **NM+MS+NS+NC-WeM1 Excitronics: Excitonic Circuits for post-CMOS Electronics**, *J.-U. Lee*, University of Albany **INVITED**

In this talk, I will describe the properties of excitons in one-dimensional semiconductors that make them attractive as a post-CMOS state variable. The essential properties needed for any new state variable are: creation, transport and detection. These properties will be described for excitons created within single-walled carbon nanotube p-n diodes, one of the most fundamental of all electronic devices. The p-n diodes are formed along individual nanotubes and can show ideal diode behavior, the theoretical limit of performance for any diode. I will describe their dc, optical and the interplay between transport and optical properties. As an optical detector, these diodes are extremely sensitive and are able to probe the complete excited states of SWNTs, including the lowest exciton transition and the continuum. Based on these results, we extract properties that are meaningful for electronic applications, including exciton binding energy, transport, and optical cross section. This work was supported by the NRI/INDEX program and the University at Albany.

8:40am **NM+MS+NS+NC-WeM3 Magnetism in Mn Ion Implanted Si**, *C. Awo-Affouda*, Naval Research Laboratory, *M. Bolduc*, Tekna Plasma Systems, Inc., *V.P. LaBella*, University at Albany-SUNY **INVITED**

Magnetic semiconductors hold great potential to produced spin based devices with increased functionality and performance. Making Si ferromagnetic via ion implantation of Mn will aid in integrating such devices with conventional semiconductor manufacturing. Although observations room temperature ferromagnetic phases in Mn-doped Si have been reported by several groups, the origin of the ferromagnetism remains elusive.¹⁻³ We investigate the influence of annealing on the lattice disorder and dopant distribution of Mn ion implanted Si samples. These depth profiles reveal a strong influence of annealing temperatures on the magnetization of the samples. Specifically, above 800°C a drastic drop in the Si lattice disorder is observed which is coincident with a decrease in magnetization. Furthermore the correlation of the structural and magnetic properties suggests that the magnetization of the samples originates from Mn atoms located in the least damaged implanted region.⁴ Finally, analysis of the magnetization of the samples reveals the presence of superparamagnetic phases magnetically active at low temperatures.

¹ Bolduc et al., Phys. Rev. B, 71, p.033302 (2005)

² Yoon et al., J. Magn. Magn. Mater./331, p.693

³ Kwon et al. Solid State Commun., 136, p. 257 (2005)

⁴ Awo-Affouda et al. J. Vac. Sci. Tech. A, 25, p. 976 (2007).

9:20am **NM+MS+NS+NC-WeM5 Graphene Electronic Devices**, *A. MacDonald*, *S.K. Banerjee*, *L.F. Register*, *M. Gilbert*, *J.-J. Su*, *R. Bistritzer*, *H. Min*, University of Texas at Austin **INVITED**

Graphene is an atomically two-dimensional material which is described by ultra-relativistic quantum mechanics. I will review progress toward graphene-based electronic devices based on both conventional ideas and on the properties of novel broken symmetry states which might be realized when two graphene layers are separated by a nm scale dielectric barrier. The absence of a mass (a gap) in ultra-relativistic quantum mechanics presents a challenge in adopting conventional device physics to this material. I will discuss progress in inducing gaps by making narrow graphene ribbons or by places graphene bilayers in external electric fields. The broken symmetry which might be realized in systems with two separated graphene layers is one in which phase coherence is established spontaneously between separate layers. These states are counterflow superfluids in which current can flow in opposite directions in the two layers without dissipation. I will discuss some ideas for electronic devices based on the properties of these unusual superfluids.

10:40am **NM+MS+NS+NC-WeM9 Intrinsic and Extrinsic Limits of Charge Carrier Mobility in Graphene**, *M.S. Fuhrer*, University of Maryland **INVITED**

Graphene, a single atom-thick sheet of graphite, is a zero-gap semiconductor with an unusual linear dispersion relation (analogous to the Dirac equation for massless relativistic particles) and a density of states that vanishes at a singular point. Due to the high conductivity and charge carrier mobility, graphene is being considered for a number of applications ranging from transparent, conducting thin films to high-speed electronics. Here I will discuss experiments performed on atomically-clean graphene on SiO₂¹ in ultra-high vacuum to determine the intrinsic and extrinsic limits of

mobility in graphene,^{2,3} which point out both the promise of the material as well as the technological challenges that lie ahead in realizing better graphene samples. Intrinsic scattering by the acoustic phonons of graphene³ limits the room-temperature mobility to 200,000 cm²/Vs at a carrier density of 10¹² cm⁻², higher than any known material. However, conduction in current graphene samples is limited almost entirely by extrinsic scattering due to charged impurities in the substrate² and substrate polar optical phonons³ currently, pointing out the importance of substrate engineering for improving graphene devices.⁴ I will discuss the implications for the future of graphene technologies in terms of the manufacturing methods for large-area graphene currently being explored, such as solution processing methods, chemical vapor deposition, and epitaxial growth on metals and insulators.

¹ "Atomic Structure of Graphene on SiO₂," Masa Ishigami, J. H. Chen, W. G. Cullen, M. S. Fuhrer, and E. D. Williams, *Nano Letters* 7, 1643 (2007).

² "Charged Impurity Scattering in Graphene," J. H. Chen, C. Jang, M. S. Fuhrer, E. D. Williams, and M. Ishigami, *Nature Physics* 4, 377 (2008).

³ "Intrinsic and Extrinsic Performance Limits of Graphene Devices on SiO₂," J. H. Chen, C. Jang, S. Xiao, M. Ishigami, M. S. Fuhrer, *Nature Nanotechnology* 3, 206 (2008).

⁴ "Printed Graphene Circuits," Jian-Hao Chen, Masa Ishigami, Chaun Jang, Daniel R. Hines, Michael S. Fuhrer, and Ellen D. Williams, *Advanced Materials* 19, 3623 (2007).

11:20am NM+MS+NS+NC-WeM11 Tunneling Conductance of Molecular Wires, E. Prodan, Yeshiva University

Tunneling transport through long, insulating molecular chains is characterized by the exponential decay law $g = g_c e^{-\beta N}$, where N is the number of monomers. In the modern formulation of the tunneling transport, is determined from the complex band structure of the isolated molecular chain, a procedure that extends far beyond the limitations of simple models that approximate electron tunneling in molecular devices using square potential barriers. However, until recently, an analytic expression for the contact conductance g_c was missing. In the first part of the talk, I will review a newly formulated theory of tunneling transport in long molecular wires. This theory provides a rigorous way of computing the exponential decay constant and gives g_c as an overlap integral between three well defined and physically relevant quantities: the spectral density of the device at the Fermi level, the potential perturbation of the metallic contacts on the molecular chain, and the evanescent electron waves traversing the molecular chain.¹ The formalism will be exemplified on molecular devices made of alkyl² and phenyl chains linked to gold wires via amine groups. If the time allows, I will present the extension of the theory to the spin dependent transport, in particular to the problem of tunneling magneto-resistance.

¹E. Prodan and R. Car, DC Conductance of Molecular Wires, *Phys. Rev. B* 76, 115102 (2007).

²E. Prodan and R. Car, Tunneling conductance of amine linked alkyl chains, *Nano Letters* (in press).

Nanometer-scale Science and Technology

Room: 311 - Session NS+NC-WeM

Characterization and Imaging of Nanostructures

Moderator: R. Ruiz, Hitachi Global Storage Technologies Inc

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

The kinetics and thermodynamics of first-order phase transitions and reactions involving solids are universally controlled by defects. Examples are as diversified as nucleation centers in solid-state and electrochemical reactions, phase change and electrochemical memories, crystallization of metals, oxides, and polymers. The electronic and atomic structure of defects in solids has become accessible in exquisite detail with the advent of electron microscopy and spectroscopy techniques. In the last decade, the progress in AFM- unfolding spectroscopy and IETS has opened the pathway for probing thermodynamics and kinetics of single-molecule reactions, and vibrational modes within simple molecules. In comparison, the role of defects in solids on local phase transitions and order parameter dynamics has long remained beyond the experimental reach. In this presentation, I will summarize recent progress in spectroscopic multidimensional SPM techniques as applied for probing structure-property relationships on a single defect level using electric or thermal field confinement by an SPM tip. Ferroelectric materials provide a convenient model system in which bias-induced phase transition between two equivalent polarization states is reversible and is not associated with

diffusion, mass, or significant heat exchange and strain effects. Spatially resolved mapping of local nucleation biases allows nucleation centers to be visualized, and corresponding thermodynamic and kinetic parameters to be reconstructed. The hysteresis loop fine structure provides additional information on defect-mediated domain dynamics and defect-domain interactions. The direct imaging of a single nucleation center on sub-100 nanometer level is demonstrated. In the second part of the talk, I demonstrate the approach for dissipation probing in SPM using non-sinusoidal signals (band excitation method). In all these examples, the 3- and 4D SPM techniques enabled by the recent advances in fast data acquisition electronics are the enabling step. Finally, I discuss potential pathways for extending these concepts from observation to control and communication with the nanoscale world. Research was supported by the U.S. Department of Energy Office of Basic Energy Sciences Division of Materials Sciences and Engineering and was performed at Oak Ridge National Laboratory which is operated by UT-Battelle, LLC.

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

Quality of carbon nanotubes (CNT) strongly depends on the amount of impurities such as hydrogen, oxygen and others. However, few efforts have been paid for the quantitative evaluation of them. In order to evaluate the CNT at the atomic level point of view we mass analyzed various CNTs such as single walled CNT (SWCNT), double walled CNT (DWCNT) and multi walled CNT (MWCNT) utilizing the unique capability of the scanning atom probe (SAP).¹ In this mass analysis carbon atoms of the CNTs are field evaporated as positive ions of single atoms and clusters of few atoms. The mass to charge ratios of these ions are obtained by measuring their flight times from a specimen surface to an ion detector. One of the analyzed SWCNTs is grown by the high CO pressure process (Hipco) and other is synthesized by a direct-current arc-discharge method in He gas with Fe/Ni/S catalysis. The DWCNTs are commercially supplied. The MWCNTs are directly formed on a substrate of Ni-Cr-Fe alloy by thermal CVD at 650° using a mixture of acetylene, hydrogen and argon gases. CNTs are deposited on a W tip by silver paste. The amount of impurities is evaluated by counting the number of cluster ions forming mass peaks. For example, the numbers of C and H atoms forming the mass peak of 150 CH₃ clusters ions are 150 and 450, respectively. The number of C, H, O and other atoms are counted for all major mass peaks. The numbers of H, O and Na atoms in a Hipco SWCNT 3.7 %, 2.6 % and 0.1 % of the total number of detected atoms, respectively. Similarly, the amounts of the impurities in the CVD SWCNTs are 9 % of H, 0.7 % of O and 0.19 % of Na. The commercial DWCNTs contain fairly large amount of impurities with 20 % of H and 1.9 % of O. The MWCNT also contains a significant amount of impurities, 27 % of H, 4 % of O and 0.4 % of Na. Even if specimens are prepared by the CNT formed by an identical preparation process, most specimens show a different mass spectrum with different amount of impurities. However, many Hipco SWCNT specimens exhibit a similar mass spectrum. The binding between C atoms forming CNTs also evaluated. The mass spectrum with a large number of C²⁺ and C⁺ indicates that the C-C bonds of the CNT is strong and uniform. The relation between the binding state and the impurity content of the analyzed CNT will be discussed.

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

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

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

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

In recent years, the fabrication and characterization of nanocrystals with size-dependent properties has gained interest for both fundamental studies and technological applications ranging from magnetic storage to catalysis. Self-assembled arrays of uniform nanoclusters on the Si(111)-7x7 surface

* Peter Mark Memorial Award Winner

from In, Ga, and Al¹ have recently been observed. These nanoclusters share common characteristics: uniform atomic structure; high thermal stability; and self-assembly into well-ordered, large-area arrays. However, the electronic properties of these nanocluster arrays are not yet well understood. Experimental investigations thus far have focused on the behavior of individual nanoclusters rather than the delocalized properties of the nanocluster array as a whole. Meanwhile, a computational study of In and Al nanocluster arrays has predicted the formation of a spatially modulated 2D electron gas (2DEG) due to surface charge redistribution.² In this study, we report the observation of atomically resolved, delocalized 2D charge redistribution associated with Ga nanocluster arrays on the Si(111)-7x7 surface.³ By using ultra-high vacuum scanning tunneling microscopy and differential tunneling conductance mapping, we correlate the topography of the Ga nanocluster array with its local density of states (LDOS). In the differential tunneling conductance maps, we observe the surface charge redistribution as distinct regions of increased LDOS forming an interconnected 2D network over the Ga nanocluster array. These results indicate that a delocalized 2DEG has been induced by the Ga nanocluster array. Furthermore, the close integration of the nanoclusters with the Si substrate can be discerned from differences in the LDOS between the faulted and unfaulted unit cell halves. Interestingly, the increased LDOS disappears abruptly over clean Si(111)-7x7 unit cells, suggesting a possible route for nanopatterning of the surface electronic structure via selective masking of the Ga nanocluster formation. These atomic-scale observations are likely to impact further fundamental studies of nanocluster arrays on Si and the development of potential nanoelectronic devices.

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

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

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

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

The creation and investigation of nano-structures, molecules or atomic structures on insulating surfaces is a key approach for electronic decoupling from the substrate. It pushes AFM as an complementary imaging and spectroscopy technique to STM. Ideally, the used AFM probe should simultaneously or alternatively work in STM/STS modes without performance compromises on the latter. Based on a proven low temperature (5K) LT STM platform, we have integrated a QPlus¹ sensor, which employs a quartz tuning fork for force detection in non-contact AFM. For combined STM operation, this sensor has key advantages over conventional cantilevers: (i) a solid metal tip for optimal STM/STS and (ii) high stiffness and high stability, i.e. low vibrational noise due to small self-resonance amplitudes. For quantitative force spectroscopy on insulating thin films or semiconductors, decoupling of tunneling current and piezo-electrically induced AFM signal is important. By measurements on Si(111) and Au(111) we prove that only a dedicated pre-amplification technique can solve this problem. In addition, extremely low signals require the first amplification stage to be very close to the sensor, i.e. to be compatible with low temperatures. STS measurements using a Niobium tunneling tip reveal the superconducting gap with a FWHM of approx. 2.5 meV and prove a probe temperature of approx. 5K. The high stiffness (1800 N/m) of the sensor allows for operation with extremely small amplitudes to (i) more precisely keep the sensor with a certain force interaction regime, (ii) increase sensitivity especially for short range forces and (iii) allow for force measurements during atom manipulation experiments without disturbing the manipulation event as such.² As benchmark measurement, we present atomic resolution imaging on single crystal NaCl with oscillation amplitudes down 100pm (peak-to-peak) in constant df imaging feedback. Optimal S/N ratio is achieved with a frequency noise down to 30mHz (peak-to-peak). We also present atomic resolution measurements on MgO(100), C60 molecules on Ag(111), and first evaluation measurements of the QPlus sensor in Kelvin Probe (KPM) mode operation.

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

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

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

When considering the optical performance of thin films in the Extreme Ultraviolet (EUV), developing an accurate physical description of a thin film coating is necessary to be able to successfully model optical performance. With the short wavelengths of the EUV, film interfaces and sample roughness warrant special attention and care. The surfaces of thin film samples are routinely measured by Atomic Force Microscopy, from which roughness can be determined. However, characterizing the quality of interfaces below the surface is much more challenging. In a recent study of scandium oxide thin films, High Resolution Transmission Electron

Microscopy and Annular Dark Field Scanning Transmission Electron Microscopy (ADF STEM) were used to study the cross section of the samples. ADF STEM data analyzed along a path into the volume of the sample (normal to the interfaces) reveals information of sample density versus depth. This density-depth profile reflects the presence of subsurface film interfaces in the volume of the sample. Additionally, information from the ADF STEM profile can be used to gauge the roughness of the subsurface interfaces, which is used to refine the sample description during modeling. We believe this is the first use of ADF STEM in this capacity. This characterization technique may provide key insight to subsurface interface quality, which is particularly important when optimizing the performance of multilayer coatings in the EUV.

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

We model InGaAs/GaAs quantum heterostructured objects, such as quantum dots (QD) and quantum rings (QR), in limit of small sizes. The electronic structure of these objects is restricted to a few electron and hole levels.¹ For QDs with small sizes, the effect of non-parabolicity of the conduction band becomes very important. In our model, this effect is taken into account using the Kane formula. In this study we apply an effective approach in which the combined effect of strains, piezoelectricity and interband interactions are simulated by an effective potential.² Based on our model, we performed an analysis of capacitance-gate-voltage data¹ and photoluminescence spectra for QDs, QRs and for double concentric QRs. We show that our approach reproduces both the few electron energy level spectra and the increase of the electron effective mass relative to the bulk value due to non-parabolicity. In this case the effective mass of excited states must be energy dependent and differs from the ground state value. Also, the non-parabolic effect visibly shifts the electron energy levels in comparison with parabolic models. We include heavy holes into the model of band structure using the effective potential approach. This model allows us to reproduce measured transition energies and Coulomb shifts for excitonic complexes (X-, X+, XX).³ Ga and In material mixing in InGaAs/GaAs QD⁴ is also taken into account in this study. We compare our results with those obtained by kp-calculations⁵ and atomistic pseudopotential models.³ We note that calculations that model QDs from first principles are of fundamental interest, but our effective potential method has strong application significance, which will be appreciated by industry, due to its efficiency and accuracy in calculating physical properties. This work is supported by the DoD: W911NF-05-1-0502.

¹ B. T. Miller, et al. Phys. Rev. B 56, 6764 (1997); R.J. Warburton, et al. Phys. Rev. B 58, 16221 (1998); A. Lorke, et al. Phys. Rev. Lett. 84, 2223 (2000).

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

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

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

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

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

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

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

The characterization of nanostructured materials implies knowledge about their chemical and structural properties, leading to a growing demand for characterization methods for heterogeneous materials on the nanometer scale. However, certain properties are difficult to study with conventional characterization techniques due to either limited resolution or the inability to chemically differentiate materials without inflicting damage or using invasive techniques such as staining. By combining various analytical techniques such as Raman spectroscopy, confocal microscopy and AFM in

one instrument, the same sample area can be analyzed with all implemented methods, leading to a better understanding of nanostructured materials. Raman spectroscopy, a chemical analysis technique, combined with confocal microscopy enables the unique Raman imaging of heterogeneous materials. The power of Raman imaging stems from the high chemical information content of molecular vibrational spectra. In the Raman spectral imaging mode, a complete Raman spectrum is recorded at every image pixel, leading to a two-dimensional array consisting of ten-thousands of complete Raman spectra. From this array images are extracted by analyzing various spectral features (sum, peak position, peak width, etc). Differences in chemical composition, although completely invisible in optical images, will be apparent in the Raman image and can be analyzed with a lateral resolution down to 200 nm. If higher resolution is required, by simply turning the microscope turret, the confocal Raman microscope can be transformed in to an AFM. Using this imaging technique, structures below the diffraction limit can be visualized from the same sample area. For the analysis of various devices formed on a support, an automated sample positioner with a travel accuracy better than 5 μm is incorporated in the instrument. Special scripting functions allow the automated execution of predefined measurement sequences on any user defined selection of measurement points on the sample, guaranteeing the most comprehensive surface analysis tool for systematic and routine research tasks.

Surface Science

Room: 208 - Session SS1+NC-WeM

Surface Structure and Morphology

Moderator: A.A. Baski, Virginia Commonwealth University

8:00am **SS1+NC-WeM1 Short vs. Long-Range Interactions: Consequences of Distributions.** *T.L. Einstein*, University of Maryland, A. Pimpinelli, University Blaise-Pascal, France and University of Maryland, K. Kim, A. BHadj Hamouda, R. Sathiyarayanan, University of Maryland

In computing terrace-width distributions on vicinal surfaces, one commonly assumes a long-range repulsion between steps as the inverse square of the step separation. In many cases there may be a different short-range interaction, or the steps might be able to locally form double-height steps (inconsistent with the fermion analogy). We show that such effects can alter the apparent strength of the interaction, leading to flawed predictions of the strength of the long-range elastic repulsion while still offering a good fit by the generalized Wigner distribution. Since these are finite-size effects, we show how to deal with this problem by measuring several misorientation angles of the vicinal surface. More generally, the range of the interaction affects the form of the distribution in a remarkable way; we discuss the limiting forms and the crossover between them. We apply these ideas to other surface phenomena, such as the distribution of capture zones in island growth. Work at UMD supported by the MRSEC, NSF Grant DMR 05-20471. Visits to UMD by AP supported by a CNRS Travel Grant.

8:20am **SS1+NC-WeM2 Studies of Plasma Nitridation of Ge(100) by Scanning Tunneling Microscopy.** *J.S. Lee, E. Chagarov, A.C. Kummel*, University of California, San Diego

Several recent reports on Ge MOSFET have shown the benefit of having either GeON or GeN interfacial layer between Ge and the high-k gate oxide. We have performed scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) experiments to understand the bonding and electronic structure for Ge-O and Ge-N surface species. For Ge-O, a Ge(100) surface was exposed to O₂ and annealed to form order structures. The O₂ dosing pins the Fermi level at high local coverage. Formation of Ge-N adsorbates is more challenging since N₂ nor NH₃ readily dissociate on clean Ge(100). We performed the direct nitridation on Ge(100) using an electron cyclotron resonance plasma source, and investigated the submonolayer structures of the surface using STM. The nitrided surface was annealed between 200°C and 500°C to differentiate the various adsorbate sites. By annealing the surface above the oxygen desorption temperature but below the nitrogen desorption temperature, our preliminary data is consistent with our being able to prepare Ge-N adsorbates. We are also performing STM experiments and DFT calculation to determine the electronic structure of the Ge-N adsorbates and explain why they might be superior interfacial passivants compared to pure GeO₂.

8:40am **SS1+NC-WeM3 Atom-Wide Co Wires on Vicinal Cu(111).** *N. Zaki, D.V. Potapenko, R.M. Osgood*, Columbia University, *P.D. Johnson*, Brookhaven National Laboratory

Due to stronger electron-electron interactions, 1-D systems are predicted and, in some cases, have been shown to exhibit unique and exotic electronic

physical properties, such as spin-charge separation, spin-splitting in a nonmagnetic metal,^{1,2} and fractional-charge phase solitons.³ One route to the formation of 1-D systems is by self-assembly using low-index vicinal crystal surfaces. In this regard, we have successfully formed 1-atom wide Co wires using Cu(775), a 7-atom wide stepped array with (111) terraces. Contrary to a recently reported DFT prediction, the Co wires are not laterally encapsulated but are positioned exactly at the step edge. Furthermore, the wires can be relatively long; in one case, a wire measured 160 Co atoms. We will present STM studies of this system performed at room temperature and under UHV. While vicinal Cu(111) does exhibit "frizz" at the steps when scanning above cryogenic temperatures, the Co wires pin the edges, visually accentuating their presence under STM. Furthermore, we observe a lower density of states for the Co wires as compared with the Cu steps, which also serves to differentiate the two metals. Cu(111) possess a surface projected bandgap which may electronically decouple the wire electrons that reside in this gap. Correspondingly, STS measurements of these atom-wide wires will be discussed.

¹D. Sanchez-Portal, S. Riikonen, and R. M. Martin, PRL 93, 146803 (2004)

²I. Barke, Fan Zheng, T. K. Rugheimer, and F. J. Himpsel, PRL 97 226405 (2006)

³P.C. Snijders, S. Rogge, and H. H. Weitering, PRL 96, 076801 (2006)

9:00am **SS1+NC-WeM4 Surface Self-Diffusion and Structural Evolution of Pd/Cu(100) Surface Alloys.** *E. Bussmann, I. Ermanoski, G.L. Kellogg*, Sandia National Laboratories

Ultra-thin films of Pd on Cu(001) are of interest both as model systems for metal-metal surface alloy formation and as potential electromigration inhibitors for Cu interconnect applications.¹ To determine how alloyed Pd, residing in the atomic layer below the surface, affects Cu surface self-diffusion, we are using low energy electron microscopy (LEEM) to study the decay of 2-D Cu islands as a function of temperature and second-layer Pd concentration. These studies are enabled by previous investigations, in which the distribution of Pd in the top three Cu layers was determined from multiple-scattering-theory fits to LEEM-IV spectra.² Here, we use LEEM-IV spectra in a "fingerprinting" mode to monitor the Pd concentration during deposition and island decay. Measurements of the decay rates as a function of temperature show that the activation energy for island decay increases from 0.82±0.04 eV to 1.02±0.07 eV when 0.06±0.03 ML of Pd is alloyed into the second layer. As the Pd concentration is further increased, up to 0.5 ML, we observe a monotonic decrease in the island decay rates at temperatures less than 240°C. These measurements confirm that Pd, alloyed into the second layer, slows Cu surface transport and suggests a mechanism by which Pd could reduce the detrimental effects of electromigration. A full Arrhenius analysis was not possible at higher Pd concentrations because a significant fraction of the Pd is lost from the second layer during the measurements. We are currently using LEEM to investigate the mechanism of this Pd dissolution, which appears to involve Pd diffusion into the bulk and Cu diffusion to the surface. Work supported by the U.S. DOE, Office of BES, DMSE. Sandia is operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. DOE's NNSA under Contract No. DE-AC04-94AL85000.

¹C. K. Hu, et al., Appl. Phys. Lett. 81, 1782 (2002).

²J. B. Hannon, J. Sun, K. Pohl, and G. L. Kellogg. Phys. Rev. Lett. 96, 246103 (2006).

9:20am **SS1+NC-WeM5 Additive-Enhanced Mass Transport on Metal Surfaces: Hunting Elusive Agents of Change.** *P.A. Thiel, M. Shen, C.J. Jenks, J. Evans, D.-J. Liu*, Iowa State University

INVITED

Sulfur is well known to enhance dynamic rearrangements of single-crystal metal surfaces for the coinage metals (Ag, Cu, and Au). It has been proposed that the associated enhanced surface mass transport of metal is due to the formation and diffusion of stable metal-sulfur clusters or complexes. From scanning tunneling microscopy (STM) images of a Ag(111) surface with adsorbed sulfur below room temperature, we have been able to "see" clusters that probably contribute to enhanced transport. We propose that the imaged clusters are Ag₃S₃.¹ Our ability to see these trimeric clusters derives from the feature that they self-organize into a distinctive dot-row structure. The dot-rows are very robust, in the sense that they exist over a coverage range that spans an order of magnitude (0.03 to 0.5 monolayers). The dots are assigned as Ag₃S₃ clusters, based on DFT calculations of their energetic stability, on the calculated and measured dimensions of the dots in STM, and on experimental evidence that they incorporate Ag. We have also explored the effect of S on Ag surface dynamics by measuring the stability of Ag adatom islands produced by vapor deposition and subsequently exposed to S. By varying both surface temperature and S-coverage, we identify three regimes: At high S-coverage where a dense row-dot structure forms, the Ag islands are stable or "frozen" over long periods of time. At intermediate coverage, S serves to destabilize the Ag islands. At very low coverage (0.01 monolayer), S has no effect because it passively decorates step and island edges. Thus, S is not

universally effective in accelerating mass transport, but rather exhibits complex dependencies upon temperature and coverage.

¹ M. Shen, D.-J. Liu, C.J. Jenks, and P.A. Thiel, *J. Phys. Chem. C*, 112, in press (2008).

10:40am **SS1+NC-WeM9 Growth and Evolution of Au/Ge(111) Studied by LEEM and STM**, *J. Giacomo, S. Chiang, C. Mullet, A.M. Durand*, University of California Davis

The clean Ge(111) surface has a $c(2 \times 8)$ reconstruction at room temperature. Au growth on Ge(111) above 300°C occurs via nucleation. The first layer is an epitaxial $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase with a coverage of IML. Further Au coverage results in the formation of islands. When heated to about 620°C, the $(\sqrt{3} \times \sqrt{3})R30^\circ$ Au transitions to a disordered phase. In LEEM videos, we observed domains fluctuating between the ordered and disordered phases at the transition temperature. For 2 to 10 ML of Au coverage, we have observed three dimensional islands in the LEEM images, as expected for the Stranski-Krastanov growth mode. Surprisingly, the LEEM movies show concerted hopping of islands of approximately 100 nm diameter near 300°C. Preliminary data measured by STM show additional evidence for the Stranski-Krastanov mode.

11:00am **SS1+NC-WeM10 Si Adatoms Atop the Si(111)5x2-Au Surface Diffuse in One Dimension by a Defect-Mediated Hopover Process**, *E. Busmann*, Sandia National Laboratories, *S. Bockenbauer*, Stanford University, *F.J. Himpsel*, University of Wisconsin-Madison, *B.S. Swartzentruber*, Sandia National Laboratories

The Si(111)5x2-Au surface has provided new understanding of the properties of one-dimensional electronic states.¹ The reconstruction includes an overlayer of Si adatoms which partly determine the surface electronic properties.² The chainlike surface structure naturally confines the adatoms to tracks, similar to bits in existing digital media, and previous workers have used the individual adatoms as bits in a model atom-scale memory.³ We have characterized the thermal 1-d diffusion of the adatoms by scanning tunneling microscopy. The statistics of motion are inconsistent with diffusion by a random walk. Instead, correlations between sequential adatom jumps in both direction and time imply that the diffusion is defect-mediated. We show that the unique character of the statistics of the diffusion is consistent with a model in which each adatom diffuses by hopping over a defect localized nearby. Specifically, the measured (nonbinomial) jump length distribution, the (nonexponential) wait-time distribution, and the observed correlations are all modeled accurately over a range of temperatures (145-215° C) using a Monte Carlo implementation of our model. The effective activation barrier for adatom diffusion is found to be 1.24 ± 0.08 eV. Intuitively, defect-mediated hopover diffusion is unexpected in a strictly 1-d system, because sequential diffusion events arising from adatom jumps back-and-forth over the defect are always in opposite directions leading to zero net displacement. Work supported by the U.S. DOE, Office of BES, DMSE. Sandia is operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. DOE's NNSA under Contract No. DE-AC04-94AL85000.

¹ I. Barke, R. Bennet, J. N. Crain, S. C. Erwin, A. Kirakosian, J. L. McChesney, and F. J. Himpsel, *Solid State Comm.* 142, 617-626 (2007).

² H. S. Yoon, S. J. Park, J. E. Lee, C. N. Whang, and I.-W. Lyo, *Phys. Rev. Lett.* 92, 0986801 (2004).

³ R. Bennet, J. N. Crain, A. Kirakosian, J.-L. Lin, J. L. McChesney, D. Y. Petrovykh, and F. J. Himpsel, *Nanotechnology* 13, 499-502 (2002).

11:20am **SS1+NC-WeM11 Influence of Si Deposition on the Phase Transition Temperature of Si(111)-7x7**, *I.A. El-Kholy, H. Elsayed-Ali*, Old Dominion University

Reflection high-energy electron diffraction (RHEED) during the Si(111)-(1x1)_h to (7x7) phase transition shows that Si deposition lowers the transition temperature. A Ti-sapphire laser (100 fs, 800 nm, 1 kHz) was used to ablate a Si target on Si(111)-(1x1)_h during quenching from high temperature. To measure the transition temperature during quenching with and without Si deposition, the experiment was performed as follows: Initially, in the absence of the laser ablation plume, the Si(111) was kept at a temperature above the phase transition temperature to ensure the uniformity of the temperature throughout the surface area of the sample. The heating current was switched off and the RHEED pattern was recorded. Then, in the presence of Si laser ablation plume, the sample was kept at the same high temperature as was done without an ablation plume. The RHEED intensity was observed as the substrate was exposed to the Si plume and the Si(111) substrate was quenched at a rate of ~40°C/s. The RHEED patterns when the Si plume was present showed a shift in the transition temperature from 840°C without the plume to 820°C with the plume. We interpret this result based on the effect of adatom mobility on the nucleation of the (7x7) structure. In the vicinity of the transition temperature, the two phases coexist on the surface. When the surface temperature is lowered below the transition temperature, the reconstruction starts to grow at the step edges then expand across the terraces. Since the high temperature (1x1)_h phase has higher density than the (7x7), the excess atoms, found on large terraces after

quenching, are released when the lower density (7x7) is formed. The quenching process results in the cooling of the surface at a lower rate than the time needed for adatoms to diffuse across the terraces; consequently the adatoms are trapped on the surface forming secondary (7x7) nuclei on terraces, thus reducing the observed (1x1)_h to (7x7) transition temperature.

11:40am **SS1+NC-WeM12 Vanadium Adsorption on Si(111)-7x7 Surface: A Combined DFT and STM Investigation**, *F. Stavale*, Nat'l Inst. of Metrology & Federal U. of Rio de Janeiro, Brazil, *M.M. de Araújo*, Nat'l Inst. of Metrology, Brazil, *A.A. Leitão*, Nat'l Inst. of Metrology & Federal U. of Juiz de Fora, Brazil, *R.B. Capaz*, Nat'l Inst. of Metrology & Federal U. of Rio de Janeiro, Brazil, *H. Niehus*, Nat'l Inst. of Metrology & Humboldt-U. of Berlin, Germany, *C.A. Achete*, Nat'l Inst. of Metrology & Federal U. of Rio de Janeiro, Brazil

The development of superlattices of nanodots and nanomagnetism, metals on Si substrates are of great scientific and technological importance. Consequently metal deposition on Si(111) 7x7 has been studied intensively by the surface science community. The surface diffusion energies and diffusion pathways of the adsorbates are important subjects to understand the growth mechanism of nanostructures. In this sense the scanning tunneling microscopy (STM) appeared to be a powerful technique for the study of adatom diffusion on the Si(111) 7x7 surface. In general the transition metals expose a high reactivity usually due to the formation of silicide nanostructures. Although several reports on V-Si(111)-7x7 surface system are already available a detailed and complete study of the vanadium from the very beginning adsorption stages up to high coverage cluster and island coalescence on the Si(111)-7x7 substrate has not been yet performed. In this work, we report about an investigation from the low-coverage regime up to few monolayers of vanadium deposition on Si(111)-7x7 in the range of 100K up to 850K substrate temperature. A combination of STM, density-functional theory (DFT) adsorption energy calculations and simulated STM images has been applied. In the low coverage and temperature regime we identify the most common STM signatures in this system to be: (1) substitutional vanadium atoms at silicon adatom positions and (2) interstitial vanadium atoms between silicon adatoms and rest atoms. At higher temperatures the diffusion of adatoms and clusters promote cluster coalescence into specifically shaped nanoclusters which occupy very special unit cell positions of the substrate. Such clusters are composed by vanadium and silicon atoms into an initial silicide formation. Finally, at high coverage, depending on the initial vanadium coverage and the post-annealing temperature well shaped (faceted) VSi₂ clusters are formed. In conclusion a model for the adsorption, diffusion and reaction of vanadium on the Si(111)-7x7 surface is proposed.

Surface Science

Room: 209 - Session SS2+NC-WeM

Functional Metal Oxides and Quantum Metal Structures

Moderator: J.E. Reutt-Robey, University of Maryland, College Park

8:00am **SS2+NC-WeM1 Can Ferroelectric Polarization be Used to Manipulate Metal-Oxide Interactions?**, *Y. Yun, N. Pilet, U.D. Schwarz, E.I. Altman*, Yale University

Ferroelectric polarization creates high energy surfaces that are expected to reduce their surface energy by reconstructing or adsorbing compensating charges. Because opposite charges must be screened on opposite surfaces, different surface atomic structures and reactivities are anticipated. Since the polarization can be changed by applying an electric field, this suggests switchable surface chemical properties. We previously found that this effect can be exploited to alter how strongly polar molecules adsorb on LiNbO₃(0001) surfaces (Y. Yun and E.I. Altman, *J. Am. Chem. Soc.* 129 (2007) 15684). To determine if ferroelectric polarization can alter the catalytic properties of supported metals, the interaction of Pd with LiNbO₃(0001) was characterized using electron diffraction, photoelectron spectroscopy (XPS and UPS), ion scattering spectroscopy (ISS), atomic force microscopy, and CO temperature programmed desorption (TPD). Positively poled LiNbO₃(0001) surfaces behave like many other oxides. The Pd atoms aggregate into nanoparticles, with the smallest nanoparticles exhibiting XPS peak shifts that can be associated with a size effect. CO adsorption on these nanoparticles is largely unaffected by the size of the nanoparticles, the LiNbO₃ support, and annealing. In contrast, preliminary results suggest that Pd behaves very differently on negatively poled LiNbO₃. In this case, the Pd photoemission peak shifts persist to higher Pd coverages and annealing causes the Pd peak intensity to decrease; annealing has no effect on Pd on positively poled LiNbO₃(0001). Further, initial

findings suggest that modest heating to just 600 K severely attenuates the ability of the Pd to adsorb CO.

8:20am **SS2+NC-WeM2 Temperature Dependence of Intrinsic Nucleation in Ferroelectrics**, *P. Maksymovych, S. Jesse*, Oak Ridge National Laboratory, *M. Huijben, R. Ramesh*, University of California, Berkeley, *A. Morozovska*, National Academy of Science of Ukraine, *S. Choudhury, L.-Q. Chen*, Pennsylvania State University, *A.P. Baddorf, S.V. Kalinin*, Oak Ridge National Laboratory

Nucleation of domains is central to understanding and applying ferroelectric materials. In bulk ferroelectrics, the number of ferroelectric nuclei grows rapidly with temperature, verifying the involvement of thermal fluctuations, which are widely interpreted as a result of defect, modified local barriers. In homogeneous, low defect thin films, a local voltage source can produce intrinsic switching domain without the influence of defects. We have examined the temperature dependence of intrinsic domain nucleation for the first time using Piezoresponse Force spectroscopy of model oxide materials, BiFeO₃ and Pb(Zr_{0.2}Ti_{0.8})O₃ from 34 to 300 K. Measurements were performed in ultra high vacuum, which allowed cryogenic cooling but also precluded the presence of water known to significantly affect ferroelectric phase stability. The key finding is that the temperature dependence of ferroelectric switching initiated by a scanning probe tip is small and amounts to only a 20 percent increase in the nucleation voltage upon cooling of the films to the lowest temperature. These results are in stark contrast to previous reports for ferroelectric switching in the capacitor geometry where the coercive field increases by at least a factor of five over a similar temperature range. To complement the experimental data, a theoretical analysis was carried out based on two models, the rigid ferroelectric model and phase-field simulations. The temperature dependence predicted by the phase-field modeling is small and in good agreement with the experiments, while the rigid ferroelectric model overestimates it considerably. We conclude that the intrinsic ferroelectric switching induced by scanning probe experiments involves minimal contribution from thermal fluctuations. PM was supported as a Eugene P. Wigner Fellow at ORNL. Research was performed at the Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, and supported by the Office of Basic Energy Sciences, U.S. Department of Energy.

8:40am **SS2+NC-WeM3 Catalysis of M-YSZ(100) Model Anodes for Solid Oxide Fuel Cells**, *R.G. Green, J.B. Giorgi*, University of Ottawa, Canada

Solid oxide fuel cells (SOFC's) convert chemical energy directly into electrical energy through a reaction involving the oxidation of fuels, such as hydrogen or natural gas. The oxidation reaction occurs at the anode which is typically composed of a nickel-yttria-stabilized-zirconia (Ni-YSZ) cermet. This composition provides the active triple phase boundary where gas (fuel), the active catalyst (metal) and the oxide ion provider (YSZ) meet. We will discuss a model system of this complex catalyst which has been studied under ultrahigh vacuum. To create this model, we deposit an active transition metal (Pd, Ni, Co) in the form of nano-particles onto single crystal YSZ (100). The defective YSZ surface offers a range of meta-stable nanostructures that can interact with the metal component. Additionally, the surface shows high reactivity toward carbon at high temperature. These properties add difficulty and complexity to the model systems. Results of catalytic activity toward methane as a function of metal composition and particle size will be discussed. The catalysts have been studied in-situ using photoelectron spectroscopy, scanning probe microscopy, as well as thermal desorption spectroscopy and reaction techniques.

9:00am **SS2+NC-WeM4 Structure of Au and Ag Clusters on Al₂O₃/FeAl(110)**, *M.C. Patterson, O. Kizilkaya, R.L. Kurtz, P.T. Springer*, Louisiana State University

We present ultraviolet photoemission and STM studies of Ag and Au clusters deposited on both clean and oxidized FeAl(110). Preliminary DFT calculations indicate that deposition of Ag or Au results in the formation of bilayer islands with Ag(110) or Au(110)-like structure, due to the almost perfect match between the adsorbate and substrate lattice constants. This is concordant with studies of Ag growth on the similar intermetallic alloy NiAl(110).¹ High coverage levels of either adsorbate do not wet the FeAl surface, which can be seen by the presence of distinctive FeAl(110) valence band, Al 2p core level, and Fe 3p core level features at all levels of coverage. Angle dependent photoemission shows no dispersion in valence band features as a function of emission angle, and confirms that adsorbate, Fe, and Al are all present in the surface region. Additionally, some evidence of Al-Au alloying is observed in the Al 2p core level and Au 5p features in the Au/FeAl(110) system.

¹B. Unal, F. Qin, Y. Han, D. Liu, D. Jing, A. R. Layson, C. J. Jenks, J. W. Evans, and P. A. Thiel, Phys. Rev. B. 76, 195410 (2007).

9:20am **SS2+NC-WeM5 The Effect of Water and Surface Order on Reactivity**, *R.G. Quiller, L. Benz, T.A. Baker, M.E. Colling, C.M. Friend*, Harvard University

Understanding the effect of hydrating or hydroxylating a surface is an important aspect of interfacial chemistry. Intermolecular interactions including hydrogen bonding between water, hydroxyl groups, and oxide species play a crucial role in determining products and reaction rates in a range of heterogeneous reactions. Using surface science techniques such as temperature-programmed reaction and infrared reflection absorption spectroscopy, we studied the effects of such interactions on a number of catalytically and environmentally relevant systems on both Au and TiO₂ single crystal surfaces. We found that in addition to changes induced by water-related interactions, defects and surface ordering also played an important role in surface reactivity. Our results, therefore, emphasize the role of surface preparation and water coverage. These results help determine the role of intermolecular interactions on gas-oxide reactions and have implications in heterogeneous catalysis and environmental chemistry.

9:40am **SS2+NC-WeM6 Engineering Thin Film Superconductivity Toward Single Atomic Layer: A Scanning Tunneling Microscopy/Spectroscopy Study**, *S.Y. Qin, J.D. Kim, A.A. Khajetoorians, C.K. Shih*, University of Texas at Austin

Ultra-thin Pb films on semiconductor substrates have exhibited many intriguing phenomena manifested by the quantum confinement of electronic states. Quantum stability has been a topic of interest for many years. Recently, it was shown that quantum confinements also play an interesting role on superconductivity. Oscillations of superconductivity gap and T_c as a function of film thickness have been observed in Pb/Si(111) and Pb/Ge(111) systems. Moreover, it is found that the superconductivity remains very robust even for films as thin as 5 ML. An interesting question arises as to what extent the robustness of superconductivity remains in even thinner regime. By using a different surface template, namely Pb/Si(111) root 3 surface, we have grown uniform Pb films down to 2 ML. The film shows preferred thicknesses of 2ML and 4ML, presumably a manifestation of the quantum stability. While superconducting gap remains robust down to 4ML and shows BCS-like temperature dependence, superconductivity of 2ML Pb film exhibit several interesting features. First of all, the superconducting transition temperature is significantly lower. Moreover, we find that even with nearly perfect 2ML films, the magnitude of superconducting gap is strongly suppressed by a minute concentration of hole defects. On the contrary, the gap is not affected by distribution of small excess nano-islands.

10:40am **SS2+NC-WeM9 Effect of Quantum Well States on the Formation of MnCu c(2x2) Surface Alloy**, *W. Kim*, Korea Research Institute of Standards and Science, *I. Kim*, Chonnam National University, Republic of Korea, *C. Min*, Seoul National University, Republic of Korea, *H.-D. Kim*, Pohang Accelerator Laboratory, Republic of Korea, *C. Hwang*, Korea Research Institute of Standards and Science

The formation of quantum well states in metallic thin films under a certain boundary condition cause the sharp change in the intensity of electron density of states(DOS) at Fermi level of the thin films as the film thickness varies. This thickness dependence of DOS at Fermi level is the origin of quantum size effects found in many physical properties of the metallic thin films. In this study, we carried out the experiments to examine the effect of the quantum well states in the Cu/fcc Co(001) system on the formation of a surface alloy. It is well known that deposition of a half monolayer Mn on the Cu(001) leads to the formation of a very stable single layer MnCu c(2x2) surface alloy, and the origin of this process has been attributed to the magnetic energy of enhanced surface magnetic moment of Mn atom.¹ As the first step of the experiment, we examined the evolution of the Mn core level photoemission spectra with increasing Mn thicknesses, comparing the low energy electron diffraction(LEED) pattern for each Mn thickness. From the obtained spectra, we found out that there exist the features which are closely related to the surface alloy formation. Based on this spectroscopic evidence of surface alloying, we investigated the effect of quantum well states on the formation MnCu surface alloying. We deposited half monolayer Mn atoms on the wedge shaped Cu layers formed on the fcc Co(001) surface, and measured Mn core level photoemission spectra for the different Cu thicknesses. The observed spectra show overall correlation with the oscillating behavior of DOS at Fermi level as the thickness of Cu layers changed. Judging from the changes of Mn core level spectra, we could conclude that the lower electron density of states at Fermi level enhanced the formation of MnCu ordered surface alloy. This conclusion was also confirmed by the direct observation of the intensity of the half order spots of c(2x2) LEED pattern of MnCu surface alloy formed on the Cu/fcc Co(001) system with selected thicknesses of Cu layer. The results of our study strongly support the previous interpretation of the formation of stabilized MnCu surface alloy.

¹. M. Wuttig et al., Phys. Rev. Lett. 70, 3619 (1993).

11:00am **SS2+NC-WeM10 Adsorption of the Thiol Molecule (SCH₃)₂ on a Metallic Quantum Well System**, *L. Tskipuri, R.A. Bartynski*, Rutgers University

We have studied the bonding of the thiol molecule dimethyldisulfide (SCH₃)₂ on ultrathin Cu and Co films that exhibit metallic quantum well (MQW) states using inverse photoemission (IPE), reflection-absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD). This thiol is similar to more complex organic molecule that exhibits the self-assembled properties on metal surfaces. After a room temperature exposure of the Cu surface to the thiol molecule at a dose of ~ 2.5 L, a c(2 x 2) low energy electron diffraction (LEED) pattern confirmed that the adsorbate forms an ordered overlayer. A large sulfur signal is observed in Auger electron spectroscopy (AES) and the C-H stretch mode was observed in IR with a frequency of 2915 cm⁻¹ confirming molecular adsorption. Changes in the IPE spectrum upon adsorption are dominated by suppression of the substrate-related features, although some weak adsorbate-induced peaks are also observed. Both experimental and theoretical evidence indicates that electronic orbitals involved in molecule-surface bonding are in the same energy range as the MQW states of the substrate and the possible influence of MQW states on molecular adsorption and self-assembly of the thiol molecule will be discussed.

11:20am **SS2+NC-WeM11 Adsorbate Dynamics under Nanoscale Confinement**, *Z. Cheng, G. Pawin, D. Sun, M. Luo, D. Kim, Y. Zhu, L. Bartels*, University of California at Riverside

The diffusion of isolated adsorbates at extended low-index metal surfaces has been studied by scanning tunneling microscopy at many places, yet the behavior of isolated molecules may significantly differ from that of molecules at higher coverages and in confined structures such as nanometer-size metal clusters. We investigate the behavior of coverages of CO molecules confined to 4nm pores formed on Cu(111). While high-coverages form ordered patterns, in which vacancy diffusion and the behavior of dislocation lines can be studied, intermediate coverages aggregate to disordered islands or disperse completely across a pore, thus resembling a 2D liquid and gas, respectively. Isolated molecules show different diffusive behavior at the perimeters of the pore and at their center, revealing the importance of substrate confinement for the molecular behavior.

11:40am **SS2+NC-WeM12 Charge Carrier Separation and Transport at Organic Semiconductor Interfaces**, *X.-Y. Zhu*, University of Minnesota **INVITED**

Charge carrier generation and transport are central to the operation of all organic electronic and optoelectronic devices, such as organic light-emitting diodes (OLEDs), field effect transistors (OFETs), and photovoltaic cells (OPVs). A fundamental distinction from their inorganic counter parts is the localized nature of charge carriers and electronic excitations in organic semiconductors. Localization is a fundamental character resulting from the narrowness of the electronic band, the flexibility of the organic molecule, the deformability of the van der Waals bonded lattice, and the low dielectric constants of organic solids. This is in addition to the prevalence of structural and chemical defects that form the bulk of charge carrier traps in organic semiconductors. We study the exciton dissociation and charge carrier localization problem in organic semiconductors using femtosecond time-resolved two-photon photoemission (TR-2PPE) spectroscopy to follow the formation and decay of excitons and small polarons in organic semiconductors. These experiments are beginning to answer the following critical questions: How do charge carriers separate at organic heterojunctions in an OPV? How does an electron localize to form a small polaron?

Tribology Focus Topic

Room: 205 - Session TR+MN+NC-WeM

Surfaces and Interfaces in MEMS/NEMS

Moderator: J.A. Harrison, United States Naval Academy

8:00am **TR+MN+NC-WeM1 A Study of Au and Ru RF MEMS Contacts in Controlled Vacuum Environments**, *M. Walker*, North Carolina State University, *N. McGruer*, Northeastern University, *J. Krim*, North Carolina State University

Studies of RF MEMS switch performance under ultra clean and controlled environmental conditions have to date been extremely limited.¹ Such studies are highly valuable however, as they provide an opportunity to separately examine the impact of various factors such as contamination films, creep, deformation and stiction that plague current RF MEMS switch reliability. We have constructed a custom ultra high vacuum chamber with in situ

surface cleaning, variable temperature and gas dosing capabilities in an effort to isolate the multiple variables that impact RF MEMS contact resistance and longevity. This chamber allows us to study switches in atmosphere followed by studies performed in the cleanest environment possible. We have investigated cantilever MEMS devices with both Au on Au and Ru on Ru contacts. Au on Au switches have so far been investigated by the vast majority of studies, and provide baseline material for our studies. Ru on Ru switches are far less studied. Ru is currently our material of interest on account of its harder properties that resists creep and deformation. In atmosphere we observe the resistance of a closed switch over time then open the switch. We pump the chamber to a base pressure of 9 x 10⁻¹⁰ torr followed by measuring the resistance over time then opening the switch. Surface cleaning is performed via in situ oxygen plasma. This is followed by closing the switch and observing the resistance over time. We have observed switches that have initially had infinite resistance in both atmosphere and UHV exhibit tens of ohms contact resistance after oxygen plasma cleaning. The resistance values after oxygen cleaning are closer to the theoretical values for clean contact. We compare these resistance changes to theoretical models² that account for creep and deformation of the switch contacts. A study of contact resistance as a function of hydrocarbon uptake is in progress.³ This work was supported by the DARPA Center for RF MEMS Reliability and Design Fundamentals Grant # HR0011-06-1-0051 and the AFOSR Extreme Friction MURI Grant #FA9550-04-0381.

¹ C. Brown, A. Morris, A. Kingon, J. Krim, submitted to J. MEMS

² O. Rezvani, C. Brown, M. Zikry, A. Kingon, J. Krim, D. Irving, D. Brenner, submitted to J. Applied Physics

³ H. Koidl, W. Rieder, Q. Salzmann, vol. 22, No. 3, 1999.

8:20am **TR+MN+NC-WeM2 Bimetallic Nanoparticles as Surface Coatings in MEMS Switch Contacts**, *M.L. Jespersen*, Air Force Research Laboratories, *S.T. Patton*, University of Dayton Research Institute, *J. Slocik, R. Naik, A. Campbell, A.A. Voevodin*, Air Force Research Laboratories

Microelectromechanical systems (MEMS) switches have a broad range of applications in the aerospace, communications, and electronics industries. However, contact failure, especially during hot switching, prevents widespread implementation of the next generation MEMS devices in new technologies. Few studies have investigated physical and chemical processes that occur on modified MEMS contact interfaces, although one published study used self-assembled monolayers (SAMs) as a switch lubricant.¹ These SAMs thermally decompose in the contact.¹ We also have investigated nanoparticle liquids (NPLs) deposited onto MEMS contacts as nanomaterial-based lubricants, which improved the performance and durability of MEMS contact switches by orders of magnitude.² In this study, we investigated bimetallic (Au/Pd) nanoparticles (NPs) as surface lubricants for MEMS contact switches. Bimetallic systems offer enhanced properties for MEMS by taking advantage of the physical characteristics of the individual components. For example, Au has a low contact resistance, while Pd exhibits higher melting temperatures and lower adhesion. Performance of bimetallic NP-lubricated contact surfaces were investigated, using a micro/nano-adhesion apparatus as a MEMS switch simulator with in-situ monitoring of contact resistance and adhesion force. Ex-situ analyses of the chemical and physical processes at the contact interfaces were carried out using SEM, TEM, XPS, and scanning Auger spectroscopy. Bimetallic NPs exhibited orders of magnitude improvement in electrical performance and durability as compared to uncoated and SAM-coated contacts. The observed improvement in performance and reliability results from nanoscale surface roughness extending across multiple nanocontact regions, enhanced thermal and electrical conductivity over SAM coatings, and self-limited nanowire growth that prevents shorting failure in the contact regions, as determined from physical and chemical analyses. Based on these results, bimetallic nanoparticles are promising candidates as surface lubricants for MEMS switch contacts.

¹ S. T. Patton, K. C. Eapen, J. S. Zabinski, J. H. Sanders, and A. A. Voevodin, "Lubrication of MEMS RF switch contacts using self-assembled monolayers," J. Appl. Phys., vol. 102, pp. 024903-1 – 024903-5, 2007.

² A. A. Voevodin, et al. "Nanoparticle-Wetted Surfaces for Relays and Energy Transmission Contacts." Small, vol. 3, pp. 1957-1963, 2007.

8:40am **TR+MN+NC-WeM3 Contact Mechanics and Lubrication of MEMS Switches: Insights from Atomic and Multiscale Modeling**, *D.W. Brenner*, North Carolina State University **INVITED**

We have been using a combination of molecular modeling and continuum analysis to understand and predict a range of dynamic processes that occur during the contact of RF and capacitive MEMS switches. The results of these studies are being used in the rational design of new materials and lubrication strategies for enhancing the lifetimes of these devices. In the case of closed RF-MEMS switches, it will be shown that the time-dependent resistance is well described by a power law, and using an asperity creep model that the prefactor and exponent in the power law can be related to the surface roughness and creep coefficient, respectively. For

capacitive switches we have used molecular modeling to explore the efficacy of a “bound+mobile” lubrication scheme involving tricresylphosphate molecules diffusing on an octadecylchlorine self-assembled monolayer. Temperature-dependent diffusion coefficients calculated from the simulations have been used in a scaling relation for liquid lubrication that depends on the ratio of the contact area to the product of the lubricant diffusion coefficient and the switch cycle time. This combination of atomic modeling and multiscale analysis predicts that this molecule-surface combination will only be effective for temperatures greater than ~200K and up to ~MHz oscillation frequencies.

This work was done in collaboration with D. Irving, O. Rezvani, C. Brown, M. Zikry, A. Kingon, C. Padgett and J. Krim. This work was supported by the Extreme Friction MURI program, AFOSR grant FA9550-04-1-0381 and the Office of Naval Research.

9:20am **TR+MN+NC-WeM5 Sidewall Tribometer Study of Vapor Phase Lubricants for MEMS**, *D.A. Hook, B. Vlastakis, B.P. Miller*, North Carolina State University, *J. Rutledge*, University of California, Irvine, *M.T. Dugger*, Sandia National Laboratories, *J. Krim*, North Carolina State University

Long hydrocarbon and fluorocarbon based monolayers have been widely used in MEMS applications to prevent release related stiction and adhesion. These and similar monolayers, however, have proven ineffective as MEMS lubricants. Indeed, even the most robust of SAM layers fails to protect devices from tribological failure for either normal or sliding cyclic contact.¹ Alternate schemes, such as vapor phase lubrication, must therefore be developed if progress is to occur.² The vapor phase of pentanol has recently been reported by Seong et al to extend the lifetime of a MEMS device in a mixture of dry nitrogen and various concentrations of pentanol. Macroscale friction experiments have meanwhile shown the build up of long carbon chain reaction films in identical conditions.³ In order to probe the effectiveness of pentanol and related alcohols, we have employed a ringdown measurement technique with a specially designed MEMS sidewall tribometer to compare the coefficients of friction of a device before and after introduction of pentanol into a vacuum chamber at one monolayer of coverage. Initial measurements show no change in the coefficient of friction, but subsequent measurements show a progressive decrease. This reflects a formation of a reaction film extremely quickly upon rubbing. Lifetime measurements using the sidewall tribometer were also taken with shorter chain alcohols, namely trifluoroethanol and ethanol, at one monolayer coverage to determine whether amount of carbon present affects the lubricating properties as well as the role of methyl versus trifluoromethyl termination. It has been found that ethanol's ability to lubricate is dependant upon the initial state of the device whereas trifluoroethanol and pentanol will lubricate a device that has previously failed. Work funded by the AFOSR Extreme Friction MURI #FA9550-04-0381.

¹Hook, D.A., Timpe, S.J., Dugger, M.T., Krim, J., “Tribological Degradation of Fluorocarbon Coated Silicon Microdevice Surfaces in Normal and Sliding Contact” *Journal of Applied Physics*, in press

²Krim, J., Abdelmaksoud, M., “Nanotribology of Vapor-Phase Lubricants” *Tribology Issues and Opportunities in MEMS*, B. Bhushan, ed. 1998 pp. 273-284

³Asay, D.B., Dugger, M.T., Ohlhausen, J.A., Kim, S.H., “Macro- to Nanoscale Wear Prevention via Molecular Adsorption”, *Langmuir* 2008, 24, 155-159.

9:40am **TR+MN+NC-WeM6 Effects of Organic Vapor Adsorption on Nanoasperity Adhesion and Friction – From Fundamentals to MEMS Applications**, *S.H. Kim*, Pennsylvania State University

As the contact size involved in mechanical device operations decreases, the adsorption of gaseous molecules on the contact surface – which normally ignored in macroscopic measurements – becomes more important and dominant factors governing the contact properties such as adhesion and friction. Water adsorption can cause high adhesion and severe wear of silicon oxide surfaces. In contrast, alcohol vapor adsorption from the ambient can provide unprecedentedly efficient lubrication effects for operation of microelectromechanical systems (MEMS) with sliding contacts. Atomic force microscopy (AFM) is an ideal tool for studying the adhesion and frictional behavior of nanoscale asperity contacts. The tribological response of a silicon nanoasperity contact was studied with AFM with alcohol vapors as the VPL. Alcohol vapor adsorption on silicon oxide surface readily forms a thin organic film on the surface which mitigates the adhesion and friction forces between the AFM tip and substrate surfaces. The origin of adhesion and friction changes in the presence of alcohol vapor is elucidated through vibrational spectroscopic investigation of the thickness and structure of the adsorbed layers as well as theoretical calculations of their tribological responses.

10:40am **TR+MN+NC-WeM9 Dynamics and Spreading of Pentanol and Other Alcohols for MEMS Applications**, *B.P. Miller, J. Krim*, North Carolina State University

Microelectromechanical Systems (MEMS) have the potential to revolutionize widespread technologies, but friction and other tribological issues are currently preventing commercialization of devices that contain

surfaces in sliding contact. Self-assembled monolayers (SAMs), while highly effective against release related stiction, have proven ineffective as MEMS lubricants. Indeed, even the most robust of SAMs fail to protect devices from tribological failure for either normal or sliding cyclic contact.¹ Alternative MEMS lubrication schemes must therefore be developed if progress is to occur. Vapor phase lubrication has been proposed as a solution to the issue of tribological device failure in Micro-Electro-Mechanical Systems (MEMS) with TCP and alcohol vapors attracting much interest as candidate materials.² In an effort to understand the basic mechanisms of lubrication we have performed a quartz crystal microbalance (QCM) study of the uptake, sliding friction, and spreading rates of adsorbed ethanol, trifluoroethanol (TFE) and pentanol films on silicon, aluminum and perfluorodecyltrichlorosilane (PFTS) treated substrates.³ In response to the oscillatory motion of the QCM, pentanol, and also ethanol, exhibit viscoelasticity and/or interfacial slippage when adsorbed on silicon or PFTS, implying that enhanced tribological performance may be expected in MEMS devices. TFE exhibited slippage on silicon but not PFTS. Significantly lower mobility levels were observed for all three alcohols adsorbed on aluminum. This work is funded by AFOSR Extreme Friction MURI Grant #FA9550-04-1-0381.

¹D. A. Hook, M. T. Dugger, and J. Krim. *J. Applied Physics*, in press.

²J. Krim and M. Abdelmaksoud, in *Tribology Issues and Opportunities in MEMS*, B. Bhushan, ed. (Kluwer Academic, Dordrecht, 1998), pp. 273-284; W. Neeyakorn et al., *Trib Lett.* 27 (2007) 269-276; D. B. Asay, M. T. Dugger, S. H. Kim. *Trib Lett.* 29 (2008) 67-74.

³B.P. Miller and J. Krim, Submitted to *Langmuir*.

11:00am **TR+MN+NC-WeM10 Effect of Fluid Flow on the Sensitivity of Microcantilever Sensors**, *R. Desikan, D. RangaPrasad, A. Passian, R.H. Datar, T.G. Thundat*, Oak Ridge National Laboratory

Microcantilever arrays are emerging as an attractive platform for detection of biomolecules because of their high sensitivity, miniature size, and their ability to work under solution. Selectivity in detection is accomplished by immobilizing receptor molecules on one surface of the cantilever. Interaction of biomolecules with the immobilized receptors results in cantilever bending. In general, the cantilevers are operated under constant flow of the buffer solution. Since cantilevers are sensitive to fluid flow, the flow rate is kept constant during injection of analytes in the flowing buffer solution. In some cases, reference cantilevers are used to eliminate the effect of fluid flow rate. However, we have observed that the interaction of analytes on receptors on cantilever surface is affected by the variations in the flow rate. More analyte molecules tend to bind the receptors on cantilever surface in static condition when molecular interaction is influenced by diffusion, compared to dynamic condition where analyte molecules flow across the cantilever using a flow control system. This work addresses the issues associated with biomolecular adsorption kinetics, flow rate dependence, and cantilever geometry for increasing the sensor sensitivity.

11:20am **TR+MN+NC-WeM11 Self-Affine Fractal Analysis of MEMS Surfaces for Minimizing Adhesion**, *D.-L. Liu*, Worcester Polytechnic Institute, *J. Martin*, Analog Devices Incorporated, *N.A. Burnham*, Worcester Polytechnic Institute

Differing approaches to studies of the influence of surface roughness on adhesion have recently appeared in the literature. 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 Yet a simple continuum model predicted the qualitative behavior of adhesion as a function of root-mean-square surface roughness in the nanometer to tens-of-nanometers range.² Although a useful first-order approximation, the assumptions in the latter work were severe; a more descriptive approach is necessary in order to design surfaces that either maximize or minimize adhesion. Self-affine fractal analysis provides a reasonable framework in which to move forward. In addition to the root-mean-square (RMS) roughness, it characterizes surfaces with two more parameters, the roughness exponent and the correlation length. A high roughness exponent and a small correlation length should minimize adhesion for two rough surfaces, as predicted by Chow.³ Our adaptation of his work shows similar results for the case of a smooth tip of an atomic force microscope (AFM) and a rough surface. Specifically, the surfaces had the same RMS roughness, 0.2 μm , and the same lateral correlation length, 3.0 μm , but their roughness exponents ranged from 0.1 to 1.0. The height-height correlation functions and the height distribution functions were calculated from the surface height data, and the three fractal parameters were extracted for all the surfaces. The adhesion between a smooth AFM tip and the fractal rough surfaces were then calculated based on both the height distribution and the force-distance relationship between one molecule in the AFM tip and the fractal rough surface. The adhesion was found to decrease linearly as the roughness exponent increased. Furthermore, experimental data of the adhesion between AFM tips and MEMS surfaces as a function of the three fractal parameters will be shown and compared with the theoretical 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 D.-L. Liu, J. Martin, and N.A. Burnham, Appl. Phys. Lett. 91, 043107 (2007).

³ T.S. Chow, Phys. Rev. Lett. 79, 1086 (1997).

Wednesday Afternoon, October 22, 2008

Biological, Organic, and Soft Materials Focus Topic

Room: 201 - Session BO+AS+BI-WeA

Advances in Surface Analytical Methods for Organic and Biological Interfaces

Moderator: D.W. Grainger, University of Utah

1:40pm **BO+AS+BI-WeA1 In-situ Broadband Sum-Frequency Spectroscopy of Biomolecules at Interfaces**, *P. Koelsch, V. Kurz, R. Schmidt*, University Heidelberg, Germany, *C.L. Howell*, University of Maine, *M. Grunze*, University Heidelberg, Germany

Sum-frequency generation (SFG) spectroscopy has been employed to characterize a variety of biointerphases in extended spectral regions in aqueous environment. This contribution summarizes our recent SFG studies on DNA films, extracellular matrix compounds, switchable self assembled monolayers, and other biological molecules. Molecular level details revealed in these studies show that SFG offers the prospect of characterizing conformation, orientation and ordering of biological molecules at interfaces in situ. The technique of SFG spectroscopy is inherently surface specific having submonolayer resolution. Being an all-optical technique it can be operated in aqueous environment and even buried interfaces can be assessed. However, beside the obvious potential impact of SFG spectroscopy, to date, most studies of biological systems have only been performed in the CH and OH stretching vibration regions. This is related to the difficulties in generating tunable high energy light pulses with table top laser systems at the biologically relevant lower wavenumber region (amide and fingerprint) to gain SFG spectra with reasonable signal to noise ratios. In this contribution we show, that our broadband femtosecond SFG spectrometer provides spectral data in the amide I and fingerprint region in air and aqueous environment on a daily bases which opens the opportunity to characterize in situ orientation and conformation of a wider class of more complex biomolecules. We will summarize these biologically related SFG results and demonstrate the potential impact of this technique, also to introduce SFG spectroscopy as another method for examining biofilms ex situ and in situ.

2:00pm **BO+AS+BI-WeA2 Secondary Protein Structures in Barnacle Cement**, *D.E. Barlow*, Nova Research, *G. Dickinson, B. Orihuela, D. Rittschof*, Duke University Marine Laboratory, *K.J. Wahl*, U.S. Naval Research Laboratory

Understanding the chemistry of barnacle adhesion is of great interest in the areas of marine biofouling prevention and materials science of adhesives. While most work on the chemistry of barnacle adhesion to date has focused on identifying the protein composition of barnacle cement, relatively little has been done to directly characterize structure of barnacle cement proteins in their native states. Such studies should provide further insight into relationships between chemical structure and adhesion, as well as the types of biochemical mechanisms that may play roles in barnacle cement curing. We have used atomic force microscopy (AFM), circular dichroism (CD), and Fourier transform infrared (FTIR) spectroscopy to characterize cements deposited on quartz and CaF₂ substrates in seawater by barnacles (*Amphibalanus amphitrite*) transferred from silicone release panels. AFM imaging consistently shows that secondary cement residues left on the substrates are fibrillar. Circular dichroism spectra of cement residues on quartz showed negative peaks centered near 225 nm and positive peaks at about 195 nm, indicating that the barnacle cements are primarily helical in structure, but also contain some β -sheet components. This is further confirmed by transmission FTIR of cement residues on CaF₂, for which the amide III band is found to be composed of a broad band centered ~ 1650 cm⁻¹ consistent with α -helical structures, and components near 1685 and 1630 cm⁻¹ consistent with β -sheet structures. These results suggest that the fibrillar structures are predominantly helical in structure, in contrast with fibrillar structures like amyloids that exhibit primarily β -sheet conformations.

2:20pm **BO+AS+BI-WeA3 Analysis of Biosamples with Imaging TOF-SIMS**, *H. Nygren, P. Malmberg*, University of Gothenburg, Sweden
INVITED

Secondary ion mass spectrometry (SIMS) is based on the acceleration of primary ions onto a target. Secondary electrons, neutrals and ions are emitted from the target reflecting its chemical composition. SIMS is unique in its ability to detect simultaneously several target molecules in compound samples and to image their localization at subcellular resolution. The aim of the project is to develop the technology of imaging TOF-SIMS as a tool in biomedical research for analysis and localization of relevant target

molecules e.g. inorganic ions, lipids, drugs, carbohydrates and proteins in the same sample. Recent research in TOF-SIMS has shown the distribution of a wide variety of compounds in biological tissue. The current issues in TOF-SIMS analysis are the data interpretation and identification of all new peaks detected with this technique. Until 2004, only a few high mass peaks of biological origin were identified, which leaves us in a situation where much of the interpretation of spectra remains to be done. The aim of this presentation is to define analyte molecules by mass spectra obtained using new primary ion sources with unique fragmentation properties. The possibility to detect proteins is of special interest. It is also an aim of the project to educate students in the analysis of cells and tissue with a high technology method as the research group is presently purchasing our own TOF-SIMS instrument.

3:00pm **BO+AS+BI-WeA5 A Laser Desorption Vacuum Ultraviolet Postionization Imaging Mass Spectrometer for Biological Sample Analysis**, *J.F. Moore*, MassThink LLC, *A. Akhmetov, G.L. Gasper*, University of Illinois at Chicago, *R. Carlson*, Montana State University, *M. Blaze, L. Hanley*, University of Illinois at Chicago

Creating images with mass spectrometry (MS) at <10 micron scale resolution is a substantial challenge due to diffusion effects and low signal levels. A new instrument is described for laser desorption and in-source postionization (LDPI) imaging mass spectrometry with enhanced performance over the previous non-imaging instrument.¹ A significant fraction of the desorbed molecules are intercepted by a vacuum ultraviolet (VUV) postionizing laser, then extracted into the time-of-flight (TOF) mass analyzer. Postionization provides a higher and more consistent sensitivity than matrix-assisted laser desorption/ionization for certain analytes, thereby enhancing imaging MS on this small length scale. The instrument utilizes 349 nm laser desorption with 5 micron minimum spot size, 157 nm laser postionization and will operate at ~ 200 Hz. Samples are analyzed in microprobe mode and are imaged by rastering the x-y stage. The ion source also incorporates digital optical imaging of the sample surface, which allows for correlation of MS and optical images. The orthogonal geometry of the ion source provides for good separation of direct ion signal and postionized signal by varying the extraction delay, leading to enhanced mass resolution. Use of LDPI-MS is demonstrated for the detection of antibiotics within intact bacterial biofilms.² *Staphylococcus epidermidis* is a common Gram positive bacterium that resides on human skin and is one of the most frequent culprits behind hospital acquired biofilm infections. Treatment of biofilm infections is hindered by the limited ability of antibiotics to kill biofilm associated microbes. LDPI-MS is used to detect antibiotics within intact biofilms without significant interference from other biofilm chemical constituents. Sulfadiazine is detected these biofilms at relatively high concentrations while tetracycline is detected at near clinical concentrations. These results indicate that imaging MS of bacterial biofilms, animal tissue, or other biological samples by LDPI-MS can be applied to analysis of low ionization potential analytes such as the described antibiotics and other compounds including pharmaceuticals.

¹M. Zhou, C. Wu, A. Akhmetov, P.D. Edirisinghe, J.L. Drummond and L. Hanley, *J. Amer. Soc. Mass Spectrom.* 18, 1097 (2007).

²G.L. Gasper, R. Carlson, A. Akhmetov, J.F. Moore and L. Hanley, *Proteom.* (2008) in press.

4:00pm **BO+AS+BI-WeA8 3D Mass Spectrometric Analysis of Non-Dehydrated Biological Samples**, *H.F. Arlinghaus, J. Möller, C. Kriegeskotte, D. Lipinsky*, Westfälische Wilhelms-Universität Münster, Germany

ToF-SIMS and laser-SNMS are increasingly important tools for analyzing the elemental and molecular distribution in biological samples. However, in-vivo analyses of tissues or cell cultures are impossible because the sample must accommodate the vacuum conditions of the instrument. Thus, fixing the sample in its vital state, such as freezing, is essential. Sample preparation by cryo-fractionation or cryosectioning techniques followed by freeze-drying has been successfully used. However, these techniques exhibit several limitations. In order to overcome these limitations, a combination of a ToF-SIMS/laser-SNMS instrument and an in-vacuum cryosectioning instrument were developed for directly preparing and analyzing frozen non-dehydrated samples. The correct sample temperature after preparation and during the analysis showed to be a major factor for the quality of suitable ToF-SIMS/Laser-SNMS analyses. On the one hand, it is necessary to keep the sample cold to avoid freeze drying, on the other hand, a slight increase of the sample temperature removes adsorbates formed by residual gas in the cutting chamber and, more importantly, water resulting from the cutting process, and anticipates adsorption during the analysis. In our presentation, we will show and discuss how to optimize the sample's temperature, sample preparation techniques for analyzing various biological samples, and the possibility of obtaining 3D molecular images of frozen non-dehydrated biological samples. Our data will show that both TOF-

SIMS and Laser-SNMS are capable of imaging elements and molecules in complex biological samples and that they are very valuable tools in advancing applications in life sciences.

4:20pm BO+AS+BI-WeA9 Construction of Complex Two- and Three-Dimensional Nanostructures: Combined Time-of-Flight Secondary Ion Mass Spectrometry and Microscopy Studies, C. Zhou, P. Lu, A.V. Walker, Washington University in St. Louis

Methods for the chemically selective deposition of metals, semiconductors, biomolecules and other compounds have been studied and applied to the construction of complex multilayer structures. This work has important applications in molecular and organic electronics, sensing, biotechnology and photonics. To illustrate our approach we present two examples: the chemical bath deposition (CBD) of zinc sulfide on functionalized SAMs and the construction of three-dimensional nanostructures via layer-by-layer growth. CBD is a solution-based method for the controlled deposition of semiconductors. ZnS is a direct band-gap semiconductor used electroluminescent devices and solar cells. Two sizes of crystallites are observed to form: ~500 nm nanoflowers and ~2 μm crystallites. Nanoflowers nucleate at Zn(II)-carboxylate terminal group complexes on -COOH terminated SAMs. They grow via an ion-by-ion reaction pathway and remain chemically bound to the SAM. In contrast, the micron-sized crystallites form in solution (cluster-by-cluster growth) and are observed on all SAMs studied (-OH, -COOH and -CH₃ terminated SAMs). These crystallites can be easily removed from the surface using sonication. Thus under the appropriate experimental conditions ZnS can be selectively deposited onto -COOH terminated SAMs. We illustrate this by selectively depositing ZnS on a patterned -COOH/-CH₃ terminated SAM surface. Our approach for the construction of three-dimensional nanostructures begins with a single SAM layer deposited and UV-photopatterned using standard techniques. A second layer is then assembled by specific chemical reaction with the terminal groups of the first SAM. Additional layers are deposited using the same method. Experiments to date have focused on the specific coupling reaction of amines with carboxylic acids to form multilayer structures. Using TOF SIMS imaging we have followed each step of this reaction and have been able to demonstrate the selective formation of multilayer structures on patterned -COOH/-CH₃ surfaces. This coupling is used to make several proof-of-concept multifunctional structures.

4:40pm BO+AS+BI-WeA10 TOF-SIMS Analysis of Lipid Transfer between Vesicles and Supported Lipid Bilayers on TiO₂, P. Sjövall, SP Technical Research Institute of Sweden, A. Kunze, B. Kasemo, S. Svedhem, Chalmers University of Technology, Sweden

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) was used to investigate the electrostatically driven lipid transfer between negatively charged vesicles (POPS) and a positively charged supported lipid bilayer (POEPC) on a TiO₂ surface. Quartz crystal microbalance with dissipation (QCM-D) was used to monitor the formation of the POEPC bilayer (by vesicle adsorption and rupture), the subsequent interaction with POPS vesicles, and the resulting lipid transfer between the bilayer and the vesicles. In addition, QCM-D showed that SDS treatment of the bilayer after lipid transfer removed mass corresponding to one of the lipid leaflets (seemingly leaving a lipid monolayer), and that a bilayer could be reformed upon POEPC vesicle adsorption on this monolayer. TOF-SIMS analysis using Bi₃⁺ primary ions was used to provide quantitative estimates of the lipid composition in the different lipid layers. The lipid bilayers were prepared for TOF-SIMS analysis by plunge freezing and freeze drying(1). In order to allow for unambiguous detection of POPS in the lipid bilayers, POPS with fully deuterated palmitate fatty acid tail groups was used in the buffer vesicles. Quantitative estimates of the lipid compositions were made based on the signal intensities from the deuterated (POPS) and undeuterated (POEPC) palmitate ions, as well as from the oleate (POPS and POEPC) ion, using a simple model for the concentration-dependent TOF-SIMS signal intensities. Reference bilayers prepared with known lipid compositions were analysed in order to provide calibration points for the quantitative analysis. The results show that the POEPC bilayer after lipid transfer contains approximately 50% POPS, while the SDS-resistant monolayer contains about 70% POPS and the reformed bilayer contains 20-25% POPS. Possible asymmetries in the lipid composition of the bilayers were, however, not taken into account. A number of peaks, which can be assigned to molecular ions of POPS, were observed in the negative ion spectra of the POPS-containing lipid bilayers. Interestingly, these peaks were absent in the spectra from the SDS-resistant monolayer, although the signal from the deuterated palmitate ion indicated about 70% POPS in the monolayer. This suggests that the POPS molecular peak only shows appreciable intensity in TOF-SIMS spectra from the bilayer structure, similar to what has been observed previously for POPC.¹

¹Prinz et al., Langmuir 2007, 23, 8035-8041.

5:00pm BO+AS+BI-WeA11 Spatial Distribution Analysis of a Selenium Based Anti-Cancer Drug in Tumor Tissue Samples by ToF-SIMS, S.A. Burns, University at Buffalo, M. Khin, L. Kazim, Y. Rustum, S. Cao, F. Durrani, Roswell Park Cancer Institute, J.A. Gardella, University at Buffalo

Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has recently found new applications in the field of tissue analysis due to the advancement of cluster ion sources.¹ Bi cluster primary ion sources have been shown to produce chemical images with high spatial resolution, to ca. 100nm. The use of C60 cluster ion sources for depth profile analysis distributes the ion impact force allowing for a more specialized analysis of organic samples.² ToF-SIMS is an extremely useful application to detect low molecular weight drugs within a polymeric membrane. This study utilized this application to spatially image drug distribution of an anticancer agent in a two types of tissue samples. Nude mice implanted with human head and neck tumors were treated with methylselenocystein (MSC), a known anticarcinogen.³ MALDI imaging has been used to determine the distribution of another anti-cancer drug, CPT-11 when MSC has also been introduced.⁴ The distribution of CPT-11 was found to be more even throughout the tumor in the presence of MSC. This indicates that the MSC causes an increase the vasculature of a tumor thereby allowing other anti-cancer drugs to distribute evenly. MALDI imaging was able to show drug distribution but could not associate the fragment peak of the MSC with the vasculature of the cells due to restrictions in image resolution (100 μm). ToF-SIMS imaging has been shown to reach resolutions of 100nm allowing for this type of analysis to be performed. MSC treated tumor and liver samples were analyzed using imaging and depth profiling to determine the distribution of drug with respect to the vasculature of the tissue. The first step of this study was to determine characteristic peaks from the MSC that could be identified in the tissue samples. Analysis of the livers and tumors of the mice that had been treated with MSC had fragment peaks with isotopic distributions indicating selenium containing organic compounds not found in the control samples. These fragment peaks were used as the drug peaks whose distribution in the tissue samples were compared to fragment peaks which could be attributed directly to cell vascular structure.

¹Brunelle, A. et al. Journal of Mass Spectrometry 2005, 40, 985-999

²Fletcher, J.S. et al. Analytical Chemistry 2006, 78, 1827-31

³Azrak, R.G. et al. Biochemical Pharmacology 2007, 73, 1280-1287

⁴Prieto Conaway, M.C. et al. Thermo Scientific 2008, Application Note.

5:20pm BO+AS+BI-WeA12 Effects of Different Sample Preparation Methods for Cell Imaging using TOF-SIMS, J. Malm, SP Technical Research Institute of Sweden, D. Giannaras, University of Glasgow, UK, P. Sjövall, SP Technical Research Institute of Sweden, N. Gadegaard, M.O. Riehle, University of Glasgow, UK

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is increasingly being used for chemical imaging of cells and tissue. A concern in these studies is that the samples need to be prepared for the vacuum environment. Several sample preparation methods exist for this purpose. In this work, effects of different preparation methods on the structure and surface chemistry of human fibroblast hTert cells were studied. Two fixation protocols, using glutaraldehyde (GA, C₅H₈O₂), and osmium tetroxide (OsO₄), respectively, were compared to a non-fixing protocol where cells were washed with ammonium formate (AF, NH₄HCOO) prior to drying. Three drying techniques were compared, namely freeze-drying (FD) after rapid plunge-freezing, critical point-drying (CPD), and alcohol ladder-drying (ALD). Imaging TOF-SIMS with Bi₃ cluster primary ions was used to compare the different preparation protocols with respect to surface chemistry, and the structure of the cells after preparation was studied using scanning electron microscopy (SEM). For the AF-washed samples, changes in cell volume was followed by interference reflection microscopy (IRM). The results show that both the fixation/washing protocols as well as the drying protocols affect the chemical information obtained in TOF-SIMS analyses. For GA-fixed samples, both CPD and ALD give rise to reduced phosphocholine (PC) signal on the cell surface by two orders of magnitude, as compared to FD, while no significant differences are seen for cholesterol and amino acid fragment ions. GA-fixed samples post-fixed using OsO₄ showed PC intensities reduced by only one order of magnitude, going from FD to CPD or ALD. The cholesterol intensity was found to be higher for AF-washed cells and cells fixed with OsO₄, than for GA fixed cells. An increase in amino acid intensity going from AF to GA to OsO₄ was also observed.

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

Energy: Tools and Approaches

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

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

A continuous, in-line process suitable for high throughput manufacturing of CdS/CdTe photovoltaic devices has been demonstrated. Utilizing this process, devices with efficiencies of 13% has been fabricated with a low iron soda lime glass (3"x3") with ant-reflection coatings. The process has been extended to large area devices (16" x16" substrate size). After CdCl₂ treatment, devices showed $V_{oc} > 700$ mV and $J_{sc} > 20$ mA/cm². This performance is similar to the performance of small area devices which showed good stability. Also we have employed many methods including Spectroscopic Ellipsometry (SE) as a non-destructive tool to characterize CdS/CdTe heterojunction specifically studying the effects of processing on the optical properties of the thin-film layers.

2:20pm **EN+AS+TF+VT+NC-WeA3 Molecular Dynamics and Experimental Investigations of Reversible Absorption of H₂, CH₄, and CO₂ in Calixarenes**, *J.L. Daschbach, P.K. Thallapally, B.P. McGrail, L.X. Dang*, Pacific Northwest National Laboratory

Molecular solids based on calix[4]arenes have been shown to exhibit reversible absorption of small gas molecules, and remain stable, at temperatures above 400 K. As such, they are interesting as prototypical molecular systems for storing guests like hydrogen and methane, and potentially selectively trapping carbon dioxide in hydrocarbon based systems. We have conducted high-pressure and temperature gas absorption experiments with low density p-tert-butylcalix[4]arene (TBC4) in which calixarenes are slightly offset to form a skewed capsule with an estimated free volume of 235 Å³. Hydrogen and methane absorption near 300 K were 1.0 and 2.2 wt% respectively. Carbon dioxide is adsorbed at a 1:1 loading per TBC4 molecule at 3 atm. In recent work we have shown that the high density form of TBC4 will absorb CO₂ at 3 atm, undergoing a phase transformation in the process, and it can be reversibly cycled between these states using moderate combinations of temperature and pressure. Somewhat surprisingly, we have found that TBC4 can be loaded with up to two CO₂ per TBC4 molecule. We have used empirical molecular simulation techniques to study the dynamics of CO₂ and CH₄ in TBC4. The rattling motion of the absorbed small molecules have been characterized using velocity autocorrelation. The coupling to the host lattice is probed by temperature dependent calculations. The effects of increased loading are studied up to the 2:1 loading of CO₂, and clearly show differences in the host-guest coupling for molecules outside the cavities relative to the cage entrapped molecules. The free energy of absorption of CH₄ and CO₂ is studied under range of conditions by thermodynamic integration. These data support the experimental observations that these molecules can be reversibly adsorbed at moderate pressures and temperatures.

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

Advanced electron microscopy, using the latest aberration-corrected and monochromated (scanning) transmission electron microscopes (S/TEM) is helping to bring new scientific and technological insights that are advancing progress in areas such as health, energy and the environment. Specifically, with global energy resources under increasing pressure, great efforts are being made to develop new nanomaterials that will lead to renewable energy sources and increased efficiency, to sustain energy supplies into the long term future whilst helping to preserve and protect the Earth's environment. To get there, we are being taken to atomic realms such that, to tailor new nanomaterials for specific functions, it is essential to precisely understand, accurately control and truly visualize structure-property relations at an unprecedented level. The atomic structure of nanomaterials and the energy needed for their function can be optimized by the fundamental understanding of catalytic behavior of nanoparticles and by a better understanding of the physical properties on the atomic level of systems such as solar cells, fuel cells and light sources (LEDs). This requires advanced tools that allow us to see down to the individual atoms and sense their chemical environment. It means having the ability to perform experiments in situ, to follow specific chemical reactions and physical processes, and there is a need to be able to do this in multi-dimensions, both spatial and temporal. We discuss and demonstrate the role

of advanced electron microscopy in answering some of the most challenging and fundamental scientific questions in the field of catalysis, ranging from electron tomographic 3D reconstruction of the crystal facets of catalyst nanoparticles and aberration-corrected imaging correlated with density functional theory for elucidating precise atomic positions, to in situ studies of catalytic reactions for visualization of otherwise unseen intermediate nanostructures. These examples relate the nanostructures investigated to the property manifested by that particular structure, enabling us to gain new information about catalytic function.

3:00pm **EN+AS+TF+VT+NC-WeA5 Investigation of Low Temperature-Annealed TiO₂ Electrodes Prepared by Sol-Gel Technique for the Fabrication of Dye-Sensitized Solar Cells**, *M.F. Hossain, S. Biswas, M. Shahjahan, A. Majumder, T. Takahashi*, University of Toyama, Japan

Dye sensitized solar cells (DSCs) are considered as a low cost alternative to conventional p-n junction solar cell devices. The high light-to-energy conversion efficiencies achieved with dye sensitized solar cells (DSCs) may be attributed to the nanoporous TiO₂ electrode. Among the various techniques for the preparation of TiO₂ photo-electrode, the relatively simple sol gel method is the most widely used because of its ability to obtain films with tailored properties on large, curved substrates, and also it is a low temperature process. Crystallinity is one of the key factors behind the photovoltaic performances of TiO₂; therefore achievement of better crystallinity at relatively low temperature is an important issue. In our present study, the titanium dioxide porous films were deposited on SnO₂:F coated glass by sol-gel technique; where, an alcoholic solution of tetrabutylorthotitanate was hydrolysed in a water/alcohol/acetic acid mixture. These films were transparent and crack free. For this investigation; annealing temperature and number of coating layers were varied. All the films were annealed at different annealing temperatures, ranging from 350 to 500°C. Sufficiently good crystalline samples were obtained by annealing at 350°C. The X-ray diffraction patterns of all TiO₂ films confirmed the anatase structure. The surface morphology of the films has been observed by atomic force microscope and field emission scanning electron microscope. The morphology of TiO₂ thin films strongly depends on annealing temperatures and number of coatings. Incident photon-to-current conversion efficiency is calculated for all the solar cells with different TiO₂ thin films to evaluate the economic viability of this technique. It has been observed that the photoelectric conversion efficiency of DSCs increases with the optimization of annealing temperature as well as with the increase of the numbers of layers.

In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference
Room: 310 - Session IS+NS+TR-WeA

In Situ Microscopy and Spectroscopy – Interfacial Science and Catalysis

Moderator: I. Petrov, University of Illinois at Urbana-Champaign

1:40pm **IS+NS+TR-WeA1 Large Sample Volume, Constant Flow, High Temperature MAS Probe for Catalytic Systems**, *J.J. Ford, J.Z. Hu, J.A. Sears, J.H. Kwak, D.W. Hoyt*, Pacific Northwest National Laboratory

We have recently finished construction of a new NMR probe to study catalytic systems under conditions where the reactions actually occur. The probe uses a 9.5 mm commercially available MAS rotor system and is built to operate in a 500 MHz wide bore magnet. An integrated heater assembly is able to raise the sample temperature to 400°C while the sample is spinning up to 3.5kHz. The rotor and stator assembly have been modified to allow a continuous flow of reactants through the rotor while it is spinning and at temperature. The carrier gas of either N₂ or He can carry reactants into the probe and move products out of the probe. Inserts for the rotor diffuse the gas stream over the catalyst bed and collect it on the other side. This allows steady state NMR measurements to be made under conditions comparable to those in typical catalytic environment – high temperatures and a steady influx of reactants and exhaust of products. The high sensitivity from this larger sample volume probe allows ¹³C observation at natural abundance. Performance test results will be presented, including an investigation of the reaction mechanisms of the carbonylation of dimethyl ether to methyl acetate on mordenite. This work has been supported by an intramural capability grant from EMSL and a DOE-Catalyst grant.

2:00pm **IS+NS+TR-WeA2 Photoelectron Emission Microscopy during CO Oxidation on Non Reconstructing Noble Metal Surfaces**, S. Wehner, S. Karpitschka, Universität Bayreuth, Germany, P. Hoffmann, Hahn-Meitner-Institut Berlin, Germany, Y. Burkov, D. Schmeißer, Technische Universität Cottbus, Germany, H.R. Brand, J. Küppers, Universität Bayreuth, Germany

The catalytic CO oxidation on Iridium(111) and Palladium(111) surfaces was investigated experimentally under ultrahigh vacuum (UHV) conditions using photoelectron emission microscopy (PEEM) to visualize surface species. The underlying reaction-diffusion system based on the Langmuir-Hinshelwood mechanism was analyzed numerically. The effect of noise on this bistable surface reaction was examined for both surfaces. In a surface science experiment the effects on product formation detected by mass spectroscopy and the development of spatio-temporal patterns on the surface were explored. The influence of noise on the reaction rates and the formation of spatio-temporal patterns on the surface was analyzed by superposing noise of Gaussian white type on the feed gas composition, characterized by the molar fraction of CO Y (variance $(\Delta Y)^2$), which represents multiplicative and additive noise. CO- and oxygen-covered regions are visible in PEEM images on both surfaces as brighter resp. darker areas as a consequence of their work function contrast. In the Iridium case islands of the adsorbate, corresponding to the globally stable branch, are formed in a background of the other adsorbate. The long transient times are the result of the extremely slow domain wall motion of these islands (around $0.05 \mu\text{m s}^{-1}$). For small noise only a few islands nucleate and grow until they merge and finally fill the whole surface. With increasing noise the number of islands increases and their maximum size decreases. At constant ΔY the island wall velocity and the number of islands increases when Y approaches the hysteresis boundary. The island density increases with noise, but the wall velocity is independent of applied ΔY . In the Palladium case quasi-periodic breakdowns of the CO_2 with an interval of some thousands of seconds are recorded. These breakdowns are connected with very large patterns on the surface. Their domain wall motion is very fast (about $10 \mu\text{m s}^{-1}$). This long quasi-periodic behavior vanishes, already when small noise is superposed. For larger noise the CO oxidation reaction on both surfaces shows bursts and switching in the product CO_2 rate and the recorded PEEM images.

2:20pm **IS+NS+TR-WeA3 Catalytic Raman Spectroscopy: Structure and Activity during Reaction**, M.A. Bañares, S.J. Khatib, O. Guerrero-Pérez, M.V. Martínez-Huerta, A.E. Lewandowska, Catalytic Spectroscopy Laboratory, CSIC, Spain **INVITED**

Catalysts with large surfaces are much more complex than the model single crystals. To single out the active site under real working conditions of the catalyst is an enormous task. It requires a combination of techniques and the development or adaptation of techniques, which allow measurements under catalytic conditions (high temperatures and high pressures). This is the field of in situ spectroscopy. We have recently developed a new methodology that combines the determination of catalyst activity/selectivity and its molecular structure in a single experiment.^{1,2} We have named this methodology "operando" (Latin for "working"). The presentation will cover Raman studies to assess structure-activity relationships on supported oxides (namely V, Cr, Mo) during alkane and ammonia activation (ammoxidation). In addition, a combination of in situ Raman, XANES, and EPR spectroscopies is used to study the nature of the interaction between V and oxides supports. On most oxide supports, the redox cycle involves reversible reduction of supported vanadia sites. Ceria support behaves differently, though. Surface V^{5+} species strongly interact with ceria support promoting a reduction of surface Ce^{4+} to Ce^{3+} . Upon heating or during reaction surface vanadia reacts with ceria support forming a CeVO_4 phase. The active site appears to be $\text{V}^{5+}-\text{O}-\text{Ce}^{3+}$ for both systems. The redox cycle for oxidative dehydrogenation appears to be associated with Ce, rather than with V sites.³

ACKNOWLEDGMENT. The support of the Spanish Ministry of Education and Science (CTQ2005-02802/PPQ)

¹ "Operando Raman study of alumina-supported Sb-V-O catalyst during propane ammoxidation to acrylonitrile with on line activity measurement", M. O. Guerrero-Pérez and M. A. Bañares, Chem. Commun. 12, 1292 (2002).

² Miguel A. Bañares, Catal. Today 100, 71 (2005) (SPECIAL ISSUE NUMBER 100)

³ M.V. Martínez-Huerta, J. M. Coronado, M. Fernández-García, A. Iglesias-Juez, G. Deo, J.L.G. Fierro, M.A. Bañares, J. Catal. 225 (2004) 240-248

3:00pm **IS+NS+TR-WeA5 Understanding Nanoparticle Behavior in Solution: Combining Real-Time In Situ with Selective Ex-Situ Measurements to Study Transformations of Nanoparticulate Iron**, D.R. Baer, Pacific Northwest National Laboratory, P.G. Tratnyek, J.T. Nurmí, Oregon Health & Science University, J.E. Amonette, P. Nachimuthu, C.M. Wang, M.H. Engelhard, Pacific Northwest National Laboratory, A. Sharma, Y. Qiang, University of Idaho

In many circumstances nanoparticles are transformed by their environment. These transformations may impact particle structure, involve the formation

of surface or contamination layers or alter important particle chemical or physical properties critical for specific applications. In our studies of nanoparticulate iron in aqueous solution related to contaminant transport in the environment, we need to understand the nature of the transformations and the time frame over which they occur. We are also working to develop methods to control (increase or decrease) the rate of these changes. We find that real-time in situ measurements are essential in addition to some batch ex-situ measurements to fully characterize the transformation. Determining minimum combination of in-situ and ex-situ measurements that provides the essential information is a challenge. We have used electrochemical potential and gas production (hydrogen production) to observe the real-time dependence of particle reaction properties. These have been correlated with batch ex-situ measurements, often involving anaerobic sample handling, of surface composition (XPS), particle phase composition and structure (XRD and TEM) and reaction rates with probe molecules (carbon tetrachloride). Real time in situ measurements are increasingly important as we develop ways to alter the particles with the intent of controlling the transformation rate of particles in aqueous solution. Initial data indicates that sulfur and transition metal doping of the particles significantly alters the overall reactivity and the interaction with contaminants. We are currently examining the impact of sulfur and transition metal additions as well as changes in oxide shell thickness on the reaction lifetime of core-shell iron nanoparticles. Because of a need to provide additional types of time-dependent information we are applying microbeam XRD and TEM in closed cells to examine these particles as they change in solution. This work is supported by the US Department of Energy Offices of Basic Energy Science and Biological and Environmental Research. A portion of the work has been conducted the the EMSL, a US DOE national user facility.

4:00pm **IS+NS+TR-WeA8 Dynamics of Catalytic Nanoparticles**, A. Datye, A. Delariva, J. Gabaldon, L.M. Sanders, R. Goetze, Q. Xu, University of New Mexico, T. Hansen, University of New Mexico and Haldor Topsøe A/S, Denmark, S. Helveg, P. Hansen, B.S. Clausen, Haldor Topsøe A/S, Denmark **INVITED**

Nanometer sized particles constitute the active phase in heterogeneous catalysts, such as those used in automotive exhaust pollution control, in energy conversion and for synthesis of chemicals. The unique properties of heterogeneous catalysts, their activity and selectivity, depend on the size and composition of nanoparticles. Since catalysts are used at elevated temperatures, these nanoparticles undergo coalescence and ripening leading to particle growth. Understanding and controlling these growth processes is critical since supplies of precious metals (such as Platinum, or Gold) are limited and demand keeps increasing, for example in fuel cells. Fundamental understanding of catalyst deactivation via sintering requires careful experimental work using a combination of ex-situ and in-situ studies. Ex-situ studies allow us to map out global rates and kinetics of particle size evolution. For this purpose, we have used a combination of TEM, STEM, XRD, chemisorption and reactivity measurements. In-situ observations can reveal nanoparticle dynamics and are crucial to bridge the gaps in our understanding, often revealing unexpected events. In this presentation, we will highlight our current state of understanding of sintering phenomena in heterogeneous catalysts. This research is supported by the National Science Foundation.

4:40pm **IS+NS+TR-WeA10 In-situ Transmission Electron Microscopy of Solid-Liquid Interfaces**, H. Saka, Nagoya University, Japan **INVITED**

Most of the industrially important inorganic materials are manufactured from liquid phase. This is true for metallic materials and semiconductors (e.g. Si). Even in the case of ceramic materials, the liquid phase plays an important role in the process of sintering. The performances of the final products of these materials are controlled during the transformation from liquid to solid states. Needless to say, the reaction front of the liquid-to-solid transformation is the interface between the solid, being solidified, and the liquid phases. Thus, in order to manufacture final products with high performance, it is of great necessity to control the solidification process, and this necessitates, in turn, a detailed knowledge of the solid-liquid (S-L) interface, which controls the solidification process. Recently it has become possible to observe S-L interface by an in-situ heating experiment in a transmission electron microscope (TEM), some of which will be presented in this presentation.

Magnetic Interfaces and Nanostructures

Room: 206 - Session MI-WeA

New Directions in Spintronics

Moderator: G.J. Mankey, University of Alabama

1:40pm MI-WeA1 Spin Tunneling and Transport through Organic Semiconductors - Towards Large Spin Relaxation Length, *J. Moodera*, Massachusetts Institute of Technology **INVITED**

The emerging field of organic spintronics is merging the two hot fields - organic electronics and spintronics. Chemical tunability of electrical properties in organic semiconductors (OS) with a bottom-up approach, along with the mechanical flexibility and low-cost fabrication processes has given rise to organic-electronic devices, such as light-emitting diodes (OLED) and field effect transistors (OFET). From the spintronics viewpoint, of growing interest is the potential to transport and manipulate spin information in OSs. Spin-orbit and hyperfine interactions, the main cause of spin-decoherence, being weak in OSs, suggest a large λ_s in these materials. Electron spin polarized tunneling is explored with ultrathin layers of the molecular organic semiconductor tris(8-hydroxyquinolino)aluminum (Alq3) and Rubrene (C₄₂H₂₈). Significant tunnel magnetoresistance (TMR) was measured in magnetic tunnel junctions at room temperature, which increased when cooled to low temperatures. Spin polarization of the tunnel current through these OS layers directly measured using superconducting Al as the spin detector, shows that minimizing formation of an interfacial dipole layer between the metal electrode and organic barrier significantly enhanced elastic tunneling characteristics and greatly improves the spin transport. For example, directly measured spin diffusion length (λ_s) in amorphous rubrene by spin polarized tunneling is large in comparison to amorphous Si or Ge, where no spin-conserved transport has been reported. These results will be discussed. Based on our findings, λ_s in single crystalline OS can be expected to reach even millimeters, showing the potential for organic spintronics development. Work done in collaboration with Tiffany Santos, Jenny Shim, Karthik V. Raman and supported by KIST-MIT project fund and ONR grant.

2:20pm MI-WeA3 Magnetism and Magnetoresistance in Multilayer Thin Film Rings, *C.A. Ross*, Massachusetts Institute of Technology **INVITED**

Magnetic data storage devices, including magnetic random access memories and patterned media, are based on thin film magnetic nanostructures. Magnetic multilayer thin film rings present a particularly interesting geometry, and their rich behavior offers opportunities for development of multibit magnetic memories and programmable, non volatile logic devices. A single layer magnetic ring can adopt a variety of stable and metastable magnetic states characterized by different numbers of domain walls, and the behavior of a multilayer ring is further complicated by magnetostatic and exchange interactions between the individual magnetic layers. In this study, rings with nanoscale to micron scale dimensions are made using electron beam lithography and self-assembled block copolymer lithography. We will describe the behavior of single layer, multilayer and exchange-biased magnetic rings, including control of the chirality of the magnetization direction, and magnetotransport measurements made on electrically contacted rings that show large relative changes in resistance, and we will discuss how these structures may be used in multibit memory cells and logic devices.

4:00pm MI-WeA8 Electrical Spin Injection into Silicon: A Comparison between Fe/Schottky and Fe/Al₂O₃ Tunnel Contacts, *G. Kioseoglou, A.T. Hanbicki, C.H. Li, P.E. Thompson, O.M.J. van 't Erve, M. Holub, C. Awo-Affouda, R. Goswami, G. Spanos, B.T. Jonker*, Naval Research Laboratory

Electrical spin injection is a prerequisite for a semiconductor spintronics technology. While significant progress has been realized in GaAs, little has been made in Si, despite its overwhelming dominance of the semiconductor industry. Si is an ideal host for spin-based functionality due to its smaller spin orbit than GaAs (responsible for spin relaxation) and to its long spin lifetimes (microseconds). Recently¹ we have reported successful injection of spin-polarized electrons from an Fe film through an Al₂O₃ tunnel barrier into Si (001). The circular polarization of the electroluminescence (EL) resulting from radiative recombination in Si and in GaAs (in Si/AlGaAs/GaAs structures) tracks the Fe magnetization, confirming that these spin polarized electrons originate from the Fe contact. The polarization reflects Fe majority spin. We determined a lower bound for the Si electron spin polarization of ~30% at 5K, with significant polarization extending to at least 125K. Here we compare electrical spin injection from Fe into MBE grown Si n-i-p heterostructures using different tunnel barriers-

a reversed biased Fe/Si Schottky contact and an Fe/Al₂O₃ barrier. For both types of structures the EL spectra are dominated by transverse acoustic and optical phonon emissions in the Si and the circular polarization of the EL due to radiative recombination in the Si tracks the Fe out of plane magnetization. However, the polarization is almost 50% lower for the Fe/Si contact than that of the Fe/Al₂O₃/Si system. This could be due to different interface structure or it may result from changes in the transport mechanism involved. Systematic TEM analysis has been performed to correlate the interface structure with the observed optical polarization, and reveals some Fe/Si intermixing that is absent in the Fe/Al₂O₃/Si structure. While the zero bias resistance for the Fe/Al₂O₃/Si system shows very weak temperature dependence, the resistance for the Fe/Si system increases orders of magnitude with decreasing temperature. This implies that two different transport mechanisms may be responsible for the spin injection.

¹B.T. Jonker, G. Kioseoglou, A.T. Hanbicki, C.H. Li, and P.E. Thompson, Nature Physics 3, 542 (2007). This work was supported by ONR and core programs at NRL.

4:20pm MI-WeA9 Current Perpendicular to Plane Giant Magnetoresistance in Magnetic Multilayers*, *W.P. Pratt, Jr.*, Michigan State University **INVITED**

Giant magnetoresistance (GMR) in magnetic multilayers, consisting of alternating ferromagnetic and non-magnetic (F/N) layers, is now a major field of study in metallic magnetic materials both for fundamental physics and important sensor applications, especially read heads in computer hard drives. Until recently, applications of GMR mostly used Current-In-Plane (CIP) geometry. However, the Current-Perpendicular-to-Plane (CPP) GMR can be larger, and the CPP geometry has certain fabrication advantages. Indeed, CPP tunneling-MR read heads are now in computers, and CPP-GMR in metallic multilayers is competing for next-generation read heads. There is also great theoretical and experimental interest in the inverse phenomenon to CPP-GMR, where a high-density (~10¹⁷ A/cm²) spin-polarized CPP current exerts a large enough torque on a given nano-size F-layer to cause its magnetization to precess and then switch. Such current-induced magnetization switching (CIMS) has potential applications in magnetic random access memories. Progress in this field is tied to understanding the spin-polarized transport parameters of existing and new materials. The CPP-GMR usually gives more direct access to these fundamental parameters: F/N interface resistances, asymmetries of conduction electron scattering in the bulk of F-layers and at F/N interfaces, and the length scales for electron spin-memory loss due to spin-flip scattering. After a brief review of the CPP-GMR and CIMS phenomena, I will present examples of important CPP-transport parameters that we have quantified for a wide variety of F and N metals. I will then illustrate applications of this knowledge of the CPP parameters to CIMS in F/N/F trilayer structures.

*Work supported by US National Science Foundation, the MSU Keck Microfabrication Facility and Seagate Technology.

5:00pm MI-WeA11 Spin Transport between Spin-Polarized Sources and Drains: Advantage of Carbon Nanotubes on Semiconductors, *A. Fert*, Université Paris-Sud, France, *J.-M. George, H. Georgetaffres, R. Mattana*, CNRS, France, *L.E. Hueso, N.D. Mathur*, Oxford University, UK **INVITED**

Spin transport in a nonmagnetic lateral channel between a spin-polarized source and a spin-polarized drain is at the basis of several concepts of spin transistor. So far, the problem has been mainly studied for structures in which the nonmagnetic channel is a conventional semiconductor.¹ Spin injection into a semiconductor from a spin-polarized electrode begins to be well mastered. More difficult is the transformation of the spin information - related to the magnetic configuration of the electrodes- into a large electrical signal, ideally DV/V » 1 or larger, if V is the bias voltage and DV its variation when the magnetic configuration is changed. In experiments on structures in which the lateral channel is a semiconductor, DV/V does not generally exceed a few 1% and the electrical signal DV is only in the mV range.¹ In contrast, in the experiments on carbon nanotubes between ferromagnetic contacts we will present, high values of DV/V (above 70%) and large DV (of the order of 100 mV) can be obtained.² After a description of the theoretical background, we will discuss the origin of the difficulties for semiconductors and explain why large values of DV/V and DV can be easily obtained with carbon nanotubes. We will emphasize the potential of carbon nanotubes, graphene and other molecules for spintronics, and conclude by presenting some next challenges for molecular spintronics.

¹ Jonker, B.T. and Flatté, M.E.F. Electrical spin injection and transport in semiconductors, in Nanomagnetism (eds. Mills D.L. & Bland J.A.C.) (Elsevier, 2006).

² Hueso, L. E., Pruneda J.-M., Ferrari V., Burnell G., Valdés-Herrera J.P., Simons B.D., Littlewood P.B., Artacho E., Fert A. and Mathur N.D.. Transformation of spin information into large electrical signals via carbon nanotubes, Nature 445, 410 (2007).

Nanoscale Devices and Sensors

Moderator: S. Ewoy, University of Alberta, Canada

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

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

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

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

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

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

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

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

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

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

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

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

The electrodynamic response of semiconductor nanowires across radio- to microwave frequencies is of great interest to both nanomaterial physics and high-frequency device applications of nanowires. It is of particular interest to highlight differences between nanowire and bulk characteristics of the same nominal material. We present measurements of conductance spectra on undoped, p-type, and n-type silicon nanowire (SiNW) arrays from 0.1 to

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

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

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

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

Bacteriophages are class of viruses that infect bacteria and use them as a host for replication. These phages are highly bacterial-strain specific and thus have the potential to be used as naturally sensitive and selective probes for the detection of pathogens. We have already reported the use of the biotin-streptavidin affinity to immobilize biotinylated phages onto gold surfaces. However, the need of genetic modification limits the versatility of this approach. Thus, there is a need to develop a simple universal process to immobilize phages onto sensor surfaces. We studied different surface modification protocols for gold substrates and their efficiency to capture phages and subsequently the bacteria was analyzed by using SEM and Fluorescence Microscopy. Wild type T4 phage was chosen as the model system for the study with *E. coli* EC12 strain as the host bacteria. Control experiments were performed with 3 non-host bacterial strains (*E. coli* 6MIN1, NP 30 and NP 10) to ensure specificity and selectivity of the system. The thiol binding chemistry on gold surfaces was utilized to modify the surface by using cysteine and cysteamine. The results revealed that the gold surfaces modified with cysteine or cysteamine and further activated by treatment with glutaraldehyde enables best phages density and bacteria capture as compared to other modifications. The SEM study for phage immobilization shows that a surface density of 15 ± 3 phages/ μm^2 was obtained. In our previous work, the biotin-streptavidin interaction was used to immobilize biotin expressing genetically-engineered phages which gave us a surface density of 10 ± 5 phages/ μm^2 . Thus, the surface modification of the substrate enables a better phage density. The protocol was then duplicated on to a gold-coated cantilever surface, which again showed successful phage immobilization and subsequent bacterial capture. Microcantilever-based detection has been shown to have a mass sensitivity equivalent to that of a single bacterium. The shift in the resonance peaks of the cantilever, before and after the treatment of phage immobilized surface to bacteria, has been used as a measure to confirm bacterial capture. Thus, we illustrate a universal approach towards specific capture and detection of pathogenic bacteria, which could be potentially be employed in numerous

sensing platforms such as microresonators, surface plasmon resonance, and quartz-crystal microbalance.

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

A scanning probe microscope has been integrated into a variable-pressure scanning electron microscope for in-situ nanoscale experiments. The heart of the instrument is a self-sensing, self-actuated cantilever¹ oscillated at resonance for non-contact dynamic force or tapping mode imaging. We have employed piezoresistive readout and thermally driven bimorph actuation. The integrated Si tips have been formed at the end of the cantilever by a micro-machining process. A digitally-synthesized sine wave of variable frequency and amplitude excites the cantilever by driving an integrated resistor which generates thermal stress. Lever deflection is monitored by an integrated piezoresistive sensor, and the SEM is used to calibrate the sensor response. A commercial digital phase-lock loop controller² adjusts the drive signal to maintain a constant oscillation amplitude and fixed phase shift relative to the drive frequency. A lab-built piezo scanner including a lateral translation system and a commercial nanotranslator for the tip approach complete the system. The system performance and noise levels will be compared for operation at the first, second and third resonant modes of the cantilever sensor, and the effects of ambient gas pressure will be discussed.

¹Ivo W. Rangelow, Microelectronic Engineering 83 (2006) 1449-1455.

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

Plasma Science and Technology Room: 304 - Session PS1-WeA

Fundamentals of Plasma-Surface Interactions II Moderator: S.M. Han, University of New Mexico

1:40pm **PS1-WeA1 Adsorption and Desorption Dynamics of Atomic and Molecular Chlorine on Plasma-Conditioned Stainless Steel Surfaces**, *L. Stafford*, Université de Montréal, Canada, *R. Khare, J. Guha, V.M. Donnelly*, University of Houston, *J.S. Poirier, J. Margot*, Université de Montréal, Canada

We investigated the interactions of atomic and molecular chlorine with plasma-conditioned stainless steel surfaces through both experiments and modeling. The adsorption and desorption dynamics of Cl and Cl₂ was characterized using a rotating substrate technique in which portion of the substrate surface is periodically exposed to an inductively coupled chlorine plasma and to an Auger electron spectrometer in separate, differentially-pumped chambers. After several hours of exposure to the Cl₂ plasma, the stainless steel substrate became coated with a Si-oxychloride-based layer (Fe:Si:O:Cl = 1:7:15:6) due to chlorine adsorption and the slow erosion of the silica discharge tube. Analysis of products desorbing from this surface through measurements of pressure rises in the Auger chamber as a function of substrate rotation frequency showed significant adsorption and desorption of Cl₂ with the plasma off, with sticking coefficients comparable to those obtained previously on plasma-conditioned anodized aluminum. Desorption rates were however much higher on stainless steel, probably because of its smoother surface morphology. When the plasma was turned on, a much larger pressure rise was observed due to delayed (i.e., Langmuir-Hinshelwood) recombination of Cl atoms. Recombination coefficients, γ_{Cl} , ranged from 0.004 to 0.03 and increased with Cl-to-Cl₂ number density ratio before reaching some plateau for Cl/Cl₂ > 0.6. A similar behavior was previously observed on plasma-conditioned anodized aluminum. This set of gamma values was then applied to the modeling of high-density chlorine plasmas with large stainless steel or anodized aluminum surfaces exposed to the plasma. The model is based on fluid equations in which the particle balance equations for electrons, Cl, Cl₂, Cl⁺, Cl₂⁺, and Cl⁻ are solved together with the corresponding flux equations and the energy balance equations. Using the gamma values determined in this study as a function of Cl/Cl₂ number density ratio, model predictions of Cl and Cl₂ densities in surface-wave and inductively coupled plasma reactors with both stainless steel and anodized aluminum walls will be compared with measured Cl and Cl₂ densities.

2:00pm **PS1-WeA2 Effect of Cu Contamination on Recombination of O Atoms on Plasma Conditioned Surfaces**, *J. Guha, R. Khare, V.M. Donnelly*, University of Houston, *L. Stafford*, Université de Montreal, Canada, *S. Sirard, D. Wei, G. Delgadino, E.A. Hudson*, Lam Research Corporation

Advanced dual-damascene integration schemes require patterns to be transferred through organic masks and anti-reflection coatings as well as through inorganic dielectric materials. During plasma etching of dielectrics down to underlying Cu layers, sputtered Cu may coat the reactor walls, causing process drift. In a CCP etch reactor, it was found that the photoresist (PR) etch rate drops for an O₂-based plasma process, after the plasma reactor has been exposed to Cu-containing wafers. Also the local PR etch rate is depressed opposite a Cu coupon attached to the upper electrode. The decrease in etching rate suggests that Cu could cause a decrease in the etchant concentration in the plasma, perhaps due to an increase in the heterogeneous atom recombination rate on the chamber walls. We have therefore studied the effects of traces of Cu on O recombination on an oxygen plasma-conditioned surface, using the spinning wall technique. With this method, a cylindrical spinning substrate (in this study, stainless steel coated with oxygen, as well as silicon from etching of the discharge tube) is rotated through differentially pumped chambers, allowing the surface to be periodically exposed to a 5mTorr, 600W O₂ plasma, an Auger spectrometer, and a Cu PVD source. With no Cu on the surface, a pressure rise was observed in the Auger chamber, due to desorption of recombined O₂. This pressure rise was converted into an absolute desorption flux through calibrations and was measured as a function of substrate rotation frequency. With separate measurements of absolute O-atom impingement fluxes, a Langmuir-Hinshelwood recombination coefficient of $\gamma_0 = 0.10$ was derived for the steady-state, Cu-free surface, coated with a layer with an atomic composition of Fe:[Al+Si]:O ~ 1:2:9. This surface was then exposed to a Cu dose of $\sim 10^{11}$ cm⁻², depositing a small fraction of a monolayer ($\sim 5 \times 10^{14}$ cm⁻²), which is well below the detection limit by Auger analysis (~ 0.1 monolayers). This trace amount of Cu caused a 13% increase in γ_0 . The surface was further exposed to the Cu doses of $\sim 2, 3$, and 8×10^{11} cm⁻². Each added dose causes γ_0 to increase accordingly. At 8×10^{11} cm⁻² $\gamma_0 = 0.15$. Much larger doses ($\sim 3 \times 10^{13}$ cm⁻²) resulted in detectable Cu on the surface and a γ_0 of ~ 0.3 .

2:20pm **PS1-WeA3 Impact on Wafer to Wafer Repetability of Cleaning/Coating Strategies in a 300mm ICP Plasma Reactor**, *L. Babaud*, ST Microelectronics/CNRS-LTM France, *P. Gouraud*, ST Microelectronics France, *O. Joubert, E. Pargon*, CNRS-LTM France
Nowadays in microelectronics, work focuses on the optimization of the 32 nm technological nodes and below. One of the key challenges to achieve the desired performance is to optimize well controlled and repeatable plasma etching processes leading to critical dimension control in the nm range. In gate etching processes one of the key parameter directly driving the process repeatability is the chamber reactor conditioning. Indeed, previous studies have shown that changes in the chamber wall conditioning are identified as one of the main origin of process drift leading to variations of key process parameters (etch rate, etch profiles, selectivity, and uniformity) inducing wafer to wafer variability. In this presentation we propose to investigate different chamber wall coating strategies such as SiOCl or Carbon rich coated films in 300 mm industrial ICP reactors. Correlation between morphological results and passivation layer formation on the silicon gate etch sidewalls using both type of coatings are performed using 300 mm in-situ XPS dedicated to chemical topography analyses. In addition, we will investigate the impact of the plasma chemistry on the process repeatability by investigating more specifically the influences of the SiCl₄/O₂ ratio used for chamber wall coating and of the SF₆/CHF₃ ratio used during poly gate patterning.

2:40pm **PS1-WeA4 Synergistic Mechanisms of Plasma-Polymer Interactions**, *D.B. Graves*, University of California at Berkeley **INVITED**
Plasmas have been widely used to alter polymer surfaces and films, but relatively little is known about mechanisms. The interactions of low temperature, chemically reactive plasmas with polymers are generally more complex than interactions with inorganic materials. Polymers have macromolecular structure that is generally completely altered in the near-surface region by exposure to plasmas. Ions impacting the polymer surface with tens to thousands of eV coupled with fluxes of reactive radicals, electrons and photons create a vast range of potential alterations. These effects can be localized within nanometers of the surface with initial alterations that are completed within a picosecond, or can be extended in space (depth) and time over many orders of magnitude. In this talk, I will focus on recent results from both experimental and computational studies of plasma-polymer interactions in my laboratory. Molecular dynamics simulations of argon ions impacting simple polymer structures help interpret corresponding ion beam-polymer exposure experiments. Vacuum ultraviolet radiation from plasmas has recently been shown to play a key

role under some conditions in roughening PMMA-based 193 nm photoresist in the presence of ion bombardment and heating. We have also studied the effects of radicals and electrons as well as the role of polymer temperature in polymer degradation, etch and roughening mechanisms.

4:00pm **PS1-WeA8 Fluorination Mechanisms of Al₂O₃ and Y₂O₃ Surfaces by Irradiations of High Density CF₄/O₂ and SF₆/O₂ Plasmas**, *K. Miwa, N. Takada, K. Sasaki*, Nagoya University, Japan

Al₂O₃ is a typical wall material for plasma processing chambers. Interactions between the surface and fluorine-based plasmas would result in process drifts and/or particle generations.^{1,2,3} Recently, replacing Al₂O₃ by Y₂O₃ was tried in an etching tool.³ However, the interaction mechanisms have not been examined in detail. We studied the mechanisms and compared the robustness of Al₂O₃ and Y₂O₃ against the irradiation of high density fluorine-based plasmas excited by a helicon wave.⁴ In the experiment, an rf power at 13.56MHz (2kW, 10Hz pulse) was supplied to a helical antenna around a quartz tube of 1.6 cm inner diameter. A uniform magnetic field was applied, so that the plasma was confined radially. A sample piece (25 mm squared Al₂O₃ or Y₂O₃) was placed on the end plate of the experiment chamber. The total pressure of CF₄ (or SF₆) and O₂ was 7 mTorr. The duration of the irradiation was 2 hours. The sample surfaces were analyzed by XPS. On the Al₂O₃ surface irradiated by the CF₄/O₂ plasma column, fluorinated (AlO_xF_y and/or AlF_x) and metallic Al were detected at relative concentrations of 11 % and 1.6 %, respectively. In the outside area of the irradiation, concentrations of those were 5.7 % and 1.1 %. On the contrary, lower concentrations of those were observed by the SF₆/O₂ plasma. These results suggest that CF_x (x=1-3) radicals react with Al-O with the ion bombardment in the plasma column. The fluorination would be induced by the reaction between carbon and oxygen. In contrast, reaction probabilities between SF_x (x=1-5) radicals and Al-O would be lower than that of CF_x, since the bonding energy of S-O (549 kJ/mol) is much lower than that of C-O (1077 kJ/mol). In addition, the metallic Al might be induced from the fluoride by high-flux bombardment of low-energy ions.⁵ On the other hand, in both irradiations of CF₄/O₂ and SF₆/O₂ plasmas onto the Y₂O₃ samples, the relative concentrations of fluoride (YO_xF_y and/or YF_x) and metallic Y were much lower than the concentrations of aluminum fluoride and metallic Al on the Al₂O₃ samples. The results can be attributed to the fact that Y-O bonding energy is larger than that of Al-O (512 kJ/mol). In other words, Y₂O₃ is more robust than Al₂O₃.

¹G. Cunge, et. al., Plasma Sources Sci. Technol. 14, 599 (2005)

²K. Miwa and T. Mukai, J. Vac. Sci. Technol. B 20, 2120 (2002)

³K. Miwa, et. al., Proceedings of the IEEE. ISSM 2007, PO-O-210, 479 (2007)

⁴M. Aramaki, et. al., Jpn. J. Appl. Phys. 43, No.3, 1164 (2004)

⁵J. Roth, et. al., Nucl. Fusion, 36, No. 12, 1647 (1996)

4:20pm **PS1-WeA9 193 nm Resist Modification Induced by Ballistic Electrons in a DC+RF Hybrid Etcher**, *M. Honda*, Tokyo Electron AT Limited, Japan, *K. Yatsuda*, Tokyo Electron Limited, Japan, *L. Chen*, Tokyo Electron America Inc.

193 nm photoresist (PR) has low plasma etching tolerance. Resist bending, wiggling and poor etch resistance are serious problems in semiconductor manufacturing. The DC+RF Hybrid is a capacitively coupled plasma etcher with a superimposed DC voltage. This configuration was proven to be most effective for maintaining PR integrity during etching. A high negative DC bias is applied to the upper electrode. Secondary electrons emitted from the electrode surface under intense ion bombardment, are accelerated in the sheath and consequently injected into the bulk plasma, forming a ballistic electron beam. This paper presents an investigation of the mechanisms by which a 193 nm resist is modified as a result of exposure to the ballistic electrons. Various surface analytical techniques (SEM, FTIR, Raman, and SIMS) were employed. In addition, simulations were used to calculate the energy dependence of the penetration depth of electrons, ions and UV into the PR. There was no observed modification of the PR under plasma etching without DC bias. On the other hand, the thickness of the modified PR layer increased with increasing DC voltage. The modified depth of the PR layer was in good agreement with the electron penetration depth obtained from Monte Carlo simulations. The observed PR modification was not due the energetic ions, since the modified depth was much greater than the ion penetration depth, obtained from Monte Carlo simulations. In addition, the UV intensity did not correlate with the modified layer thickness. In conclusion, ballistic electrons play an essential role in modifying 193nm resist during etching using a Hybrid DC+RF etcher. By implementing this etcher, many of the critical issues related to the 193nm resist were eliminated.

4:40pm **PS1-WeA10 Impact of UV Plasma Light on Photoresist Pattern Linewidth Roughness during Gate Etch Processes**, *E. Pargon, M. Martin, K. Menguelti, X. Mellhaoui, A. Bazin, O. Joubert*, LTM/CNRS, France, *J. Foucher*, LETI/CEA, France

Typical Polysilicon/gate oxide transistors in integrated circuits are made using a sequence of lithography and plasma etching steps. The decrease in critical dimensions (CDs) of integrated circuits imposes incredibly stringent requirements on lithography and etching processes. According to the International Technology Roadmap for Semiconductors (ITRS 2007), the gate CD for high performance logic devices will be 13 nm for the 32 nm technological node and requirements for linewidth roughness (LWR) will be of 1 nm (3σ). Best lithographic processes result in resist LWR of 4.5 nm (3σ) (measured by CD-SEM). Furthermore, it is now demonstrated that the roughness of the resist pattern sidewalls is partially transferred into the active layers of the gate stack during gate etch processes, impacting significantly the final device performance. In this study, CD-AFM is used to investigate the LWR generated during the lithography and plasma etching steps involved in the patterning of the gate transistors. CD-AFM is a technique that can measure LWR values by scanning resist patterns in 3 dimensions while CD-SEM techniques only bring information in 2 dimensions. Using appropriate experimental protocols, LWR can be estimated at $\pm 7\%$ by CD-AFM technique. Our results demonstrate that the efforts to minimize the final gate LWR can be largely concentrated on the etching steps preceding those used to pattern the active materials of the gate stack (Polysilicon, metals, High K) and more particularly those involving the photoresist patterns. Our results demonstrate that LWR of photoresist patterns can be strongly minimized during plasma exposure. For instance, after HBr or Ar plasma cure, the resist sidewalls can be smoothed leading to a decrease in LWR roughness of about 10%, while HBr/O₂ resist trimming processes will induce a 50% decrease in LWR (initial LWR ranging from 18 to 11 nm) strongly minimizing the final LWR of the gate. Experiments using MgF₂, Sapphire and glass windows to separate the influence of plasma radiation from the impact of ions and radicals reveal that UV light emitted by the plasma plays a crucial role in the resist pattern smoothing. Since the other materials involved in the gate stack are less sensitive to UV plasma light, our results demonstrate that the decrease in LWR can be mainly monitored by working on the plasma etch steps involving the photoresist, i.e resist trimming, BARC and hard mask opening steps.

5:00pm **PS1-WeA11 Influences of UV Photon Irradiation to ArF Resist during Plasma Etching Processes**, *K. Koyama, B. Jinnai, S. Samukawa*, Tohoku University, Japan

By the downscaling of semiconductor devices, the ArF excimer laser (193 nm) lithography is now used in the fabrication of sub-100-nm devices. For the ArF lithography, chemical amplification resist is widely used. Differing from the conventional resist, the chemical amplification resist consists of photo acid generator (PAG) which generates photo-acid by UV photon irradiation. Photo acid undergoes a large number of chemical reactions through the acid-catalyzed reaction. In other words, the chemical amplification resist is very sensitive to UV photons. However, during the plasma etching process the ArF resist has serious problems, such as the low etching selectivity for underlying materials and the enhancement of line edge roughness (LER) because it is very weak against reactive plasma irradiation. In order to overcome these issues, it is essential to understand the mechanism of surface reactions for ArF resist during plasma etching processes. In this study, we investigated the effects of UV photon irradiation on the etching selectivity of ArF resist during plasma etching processes by combination of our developed neutral beam etching and conventional plasma etching. Samples were etched by chlorine atom beam (without photon irradiation) and chlorine plasma (with photon irradiation). The etching rate in the neutral beam process was much lower than that in the plasma process, and the etching selectivity of ArF resist in the neutral beam process is drastically improved, as compared with that in the plasma process. Furthermore, to clarify the effects of UV photon irradiation on the ArF resist, we investigated the changes in the chemical bonding state in ArF resist films by using FTIR spectroscopy. In the plasma processes, C-H bonds of alicyclic group and ester C=O bonds in the ArF resist film drastically decreased compared with neutral beam process. Based on these results, we found that UV photon irradiation caused breaking C-H and C=O bonds and degraded the etching selectivity of ArF resist to the etching materials.

5:20pm **PS1-WeA12 Role of Ion Bombardment Energy in Surface Roughening during Plasma Etching of Polymers and Silicon**, *Y.H. Ting, C.C. Liu, X. Liu, H.Q. Jiang, F.J. Himpel, P.F. Nealey, A.E. Wendt*, University of Wisconsin-Madison

Surface roughness in plasma etching is a critical issue for fabrication of nanoscale features. Surface roughness can degrade the electrical and optical performance of nano-devices, and can be a benefit in other applications

such as study of biomimetic cellular response to surface topography, surface-enhanced Raman spectroscopy and fabrication of super-hydrophobic surfaces. The theme of this study is the role of ion energy in roughness of polymer surfaces etched in oxygen and fluorine-based plasmas, while prior studies of roughness have included the role of ion to neutral flux ratio at the surface, passivation, pressure, gas mixture, etc. Polystyrene (PS) and polymethyl-methacrylate (PMMA) are of particular interest here for block copolymer lithography of nano-scale features using PS-b-PMMA diblock copolymers, and etching of these materials is contrasted with silicon plasma etching. An rf bias on the substrate electrode, with voltage waveform tailored to provide a narrow ion energy distribution (IED), is employed to enable precise energy selection of bombarding ions. The dependence of surface roughness on bombarding ion energy has been observed using AFM for PS and PMMA during oxygen and fluorocarbon-based plasma etching using the tailored waveform. Based on NEXAFS and XPS measurements of the chemical composition of etched surfaces, we conclude that in oxygen plasma etching, localized oxidation of the PS produces a micromask that enhances roughness, and that roughness is then amplified by shadowing of neutral etchants by the topographical features. As ion bombardment energy increases above the etch onset energy in both oxygen- and fluorocarbon-based plasmas, the thickness of the steady state passivation film, measured with XPS, has been shown to decrease, and surface roughness diminishes. At higher ion energies, the dependence of surface roughness on ion energy differs qualitatively between different materials and gas mixtures. For example, the surface roughness of PMMA increases with increasing ion energy in an oxygen plasma while silicon roughness decreases with increasing ion energy in SF₆ plasmas. Published models of etching and roughening mechanisms will be evaluated by comparison with our measurements of roughness as a function of bombarding ion energy, as well as with other published results. Support from the UW NSF MRSEC for Nanostructured Materials is gratefully acknowledged.

Advanced Surface Engineering
Room: 204 - Session SE+NC-WeA

Hard and Nanocomposite Coatings: Synthesis, Structure, and Properties II

Moderator: J. Patscheider, EMPA, Switzerland

1:40pm **SE+NC-WeA1 Structural Development and Mechanical Properties of TiN-Ni Nanocomposite Coatings**, *J.P. Riviere*, University of Poitiers, France, *A. Akbari*, Sahand University of Technology, Iran, *C. Templier*, University of Poitiers, France

INVITED

Superhard nanocomposite coatings represent an important class of new materials with enhanced mechanical properties. The synthesis of these coatings has been principally obtained by both techniques: plasma-assisted chemical vapour deposition or reactive magnetron sputtering. It appears that dual ion beam assisted deposition could be also an effective tool for tailoring the structure and properties of nanocomposite coatings because it permits independent control of the process variables such as particle nature, energy, flux. A particular important effect of the bombardment of a growing film with energetic ions is the enhanced adatom mobility which plays an important role in the renucleation of nanograins and on the formation of the percolation network of the intergranular phase. We have investigated the formation of hard nanocomposite coatings with improved toughness consisting of TiN nanograins embedded in a soft metallic intergranular phase of Ni using reactive ion beam assisted deposition. A composite Ti-Ni target was sputtered with 1.2 keV Ar⁺ ions and the growing films were simultaneously bombarded with a mixture of 50 eV Ar⁺+N₂⁺+N⁺ ions. The chemical composition was deduced from RBS analysis and a N/Ti ratio of ~ 0.85 independent of the Ni content was determined. Phases, grain size, and texture of the coatings were investigated by XRD and HRTEM. In the composition range 0-22.5 at% Ni, δ -TiN is the only crystalline phase and Ni appears as an X Ray amorphous phase. The hardness increases up to a maximum of 41 Gpa at 6 at.% Ni which corresponds to a TiN crystallite size of ~ 8 nm and a Ni intergranular phase thickness of roughly 1 monolayer. Stress analysis was performed by XRD using the crystallite group method (CGM) developed for textured materials and coatings. It is shown that the hardness enhancement in TiN-Ni nanocomposite coatings is not correlated with residual stresses, but rather with the intrinsic nanostructure. An important improvement in wear resistance is observed however the highest wear resistance is obtained for the coatings exhibiting the highest toughness and not the highest hardness. These results show the beneficial influence of the ductile metallic amorphous intergranular phase on the mechanical behaviour of nanocomposite coatings.

2:20pm **SE+NC-WeA3 Processing and Characterization of Polymer-Ceramic Nanolaminate Thin Films**, *A.R. Waite*, Air Force Research Labs/UTC, Inc./University of Dayton, *J.O. Enlow*, Air Force Research Labs/UES, Inc., *C. Muratore*, Air Force Research Labs/UTC, Inc., *J.G. Jones*, Air Force Research Labs, *H. Jiang*, Air Force Research Labs/Materials Science & Technology Applications, LLC, *T.J. Bunning*, *A.A. Voevodin*, Air Force Research Labs

Polymer-ceramic nanolaminate thin films were synthesized by coupling chemical and physical vapor deposition processes. Highly cross-linked fluoropolymer layers were deposited by room temperature plasma enhanced physical vapor deposition from octafluorocyclobutane (OFCB) precursor gas. Gas flow rates, substrate position and rf power were examined to produce a dense polymer coating with a minimum refractive index of 1.38. Magnetron sputtering processes were investigated for deposition of amorphous TiO₂ with a high refractive index. Stoichiometric TiO₂ with a refractive index >2.3 was produced via reactive sputtering and sputtering of a titania target in pure Ar, however, reactive sputtering in an oxygen atmosphere resulted in decomposition of the polymer film. Multiple polymer-ceramic film architectures were investigated, including a quarter wave stack notch filter consisting of alternating TiO₂ and fluoropolymer layers (3 and 2 layers, respectively). Analysis of nanoindentation results was used to compare the fracture toughness and other mechanical properties of multilayered and monolithic films. The combination of optical and mechanical properties for different nanolaminate architectures revealed that the coupling of polymer-ceramic thin film materials has potential for the development of useful electro-optical devices with remarkable toughness and flexibility compared to the current state of the art.

2:40pm **SE+NC-WeA4 A New Approach to the Synthesis of Adherent Hard Coatings with High Toughness**, *A.N. Ranade*, Northwestern University, *L.R. Krishna*, International Advanced Research Centre (ARCI), India, *Y.W. Chung*, Northwestern University

Traditional ceramic coatings provide abrasive wear protection because of high hardness. However, these coatings have low fracture toughness, making them susceptible to surface or internal flaws and failure under high impact loads. In addition, when deposited onto metal substrates, lower thermal expansion coefficients of ceramic coatings compared to those of metals can cause thermal stress that may result in delamination. This paper explores a new approach to the synthesis of adherent hard coatings with high toughness. The approach begins with a metal matrix identical to that of the substrate, followed by the incorporation of nanoscale hard particles to increase hardness by Orowan strengthening. Theoretical estimates indicate that incorporation of 10 vol. % of such nanoscale particles can raise the hardness by as much as 20 GPa. Since the coating matrix is identical to that of the substrate, this should result in maximum adhesion and minimum thermal stress. Furthermore, by choosing nanoscale particles whose structure is semi-coherent with the metal matrix, local stress at the particle-matrix interface may activate the motion of screw dislocations, thus preserving the high fracture toughness of the matrix. This paper will present initial results of this exploration, using Ti as the matrix and semi-coherent TiB₂ nanoparticles as the strengthening agent. Characterization tools include x-ray diffraction (structure), AFM (surface roughness), SEM/TEM (size and distribution of nanoparticles), nanoindentation (elastic modulus, hardness, and fracture toughness), and scratch testing (adhesion), as a function of nanoparticle concentration. These studies should provide a general strategy for designing adherent hard coatings with high toughness.

3:00pm **SE+NC-WeA5 Influence of Nb on Structure, Properties, and Phase Stability of Ti-Al-N Hard Coatings**, *P.H. Mayrhofer*, *R. Rachbauer*, Montanuniversität Leoben, Austria, *L. Hultman*, Linköping University, Sweden

Metastable Ti_{1-x}Al_xN thin films synthesized by plasma-assisted vapour deposition crystallize in the industrially preferred cubic NaCl (c) structure with AlN mole fractions (x) ≤ 0.7. We reveal, via X-ray diffraction (XRD) and transmission electron microscopy (TEM), that the addition of niobium to c-Ti_{1-x}Al_xN has only a minor influence on the structure and morphology of as deposited coatings. By a combination of differential scanning calorimetry, XRD, and TEM investigations we can conclude that the onset temperature for decomposition of the formed metastable phases increases with increasing Nb content. After annealing at 1450 °C the coating decomposed into c-Ti_{1-y}Nb_yN and h-AlN phases. This decomposition process is initiated via spinodally formed cubic Ti-rich and Al-rich domains. As these domains influence plastic deformation during the nanoindentation experiments an increased hardness is observed after annealing at temperatures in the range 800–1000 °C. At higher temperatures c-AlN transforms to h-AlN. Due to the reduced mechanical properties of h-AlN compared to c-AlN this transformation is accompanied by a hardness reduction. The experimentally observed results are corroborated by a combination of ab initio and continuum-mechanical calculations.

4:00pm **SE+NC-WeA8 Development of MoN-Ag-Based Nanocomposite Films for Severe Tribological Applications**, *A. Erdemir*, *O.L. Eryilmaz*, Argonne National Laboratory, *M. Urgen*, *V. Ezirmik*, *K. Kazmanli*, Istanbul Technical University, Turkey

Using the principles of a crystal-chemical model, we designed and produced novel nanocomposite coatings that are made of hard MoN_x and soft Ag phases. Because of the very high ionic potentials of the complex sulfides and phosphates that they form during lubricated sliding tests in formulated engine oils, these nanocomposite coatings are able to drastically reduce friction and at the same time increase resistance to wear and scuffing under severe boundary lubricated sliding regimes. In this paper, we will concentrate on the fundamental tribological mechanisms that control the sliding friction and wear behaviors of these nanocomposite coatings. The major implications of this study is that using such a fundamental approach one can design and manufacture coatings that are very compatible with lubricants and hence suitable for a wide range of rolling, rotating and sliding bearing applications in engines and other lubricated mechanical systems.

4:20pm **SE+NC-WeA9 Process Variables Effect of PVD Nitride Hard Coatings Deposited on Chromium-Based Tool Steel Substrates**, *A. Neira*, North Carolina State University, *F. Sequeda*, *A. Ruden*, Universidad del Valle, Colombia, *J.M. Gonzales*, Universidad Nacional, Colombia

Process variables parameters as substrate temperature, bias voltage and N₂/Ar ratio were studied during the deposition of IV, V and VI group materials in the form of nitrides, (TiAlVN, ZrN and CrN). Those coatings were deposited on chromium-based steels, like AISI H-13 and AISI-4140 commonly used for high mechanical performance even after long exposure at high working temperatures and AISI D-3 designed for high resistance to wear or to abrasion and for resistance to heavy pressure. This work was done using available coating production techniques like Plasma Assisted Physical Vapor Deposition (PAPVD) and DC-Reactive Magnetron Sputtering and physical properties resulting from modifying the process parameters like crystal structure, film texture, and mechanical properties like strain micro deformation, hardness, wear resistance friction coefficient and adhesion of the coating to the substrate were addressed in this study and conducted through film characterization techniques such as X-Ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscope (SEM), micro and nanoindentation, wear and adhesion test. An special attention was given to the deposition of TiAlVN due to the differences on bonding types between components Al and V considered as “film stabilizers” increasing the film hardness and promoting the Magneli phase formation type (V_xO_{3x-1}), offering a reduction in the friction coefficient for auto lubrication phenomena, increasing its use for tribological coating applications.

4:40pm **SE+NC-WeA10 Water Adsorption on Phosphorous-Carbide Thin Films**, *E. Broitman*, Carnegie Mellon University, *A. Furlan*, *G.K. Gueorguiev*, Linköping University, Sweden, *Zs. Czigány*, Research Institute for Technical Physics and Materials Science, Hungary, *A.J. Gellman*, Carnegie Mellon University, *S. Stafström*, *L. Hultman*, Linköping University, Sweden

Amorphous phosphorous-carbide films have been considered as a new tribological coating material with unique electrical properties. However, the coatings cannot be practically used until now because CP_x films rapidly oxidize/hydrolyze and delaminate when in contact with air. Recently we demonstrated that CP_x thin solid films with a fullerene-like structure can be deposited by magnetron sputtering. Thus, the introduction of P atoms in the graphene structure induces the formation of bent and interlinked grapheme planes.^{1,2} In this work we compare the uptake of water of amorphous phosphorous-carbide (a-CP_x) films, with fullerene-like phosphorous-carbide (FL-CP_x) and amorphous carbon (a-C) films. Films with thickness in the range 10-300 nm were deposited on quartz crystal substrates by reactive DC magnetron sputtering. The film microstructure was characterized by X-ray photoelectron spectroscopy, and transmission electron microscopy and diffraction. A quartz crystal microbalance placed in a vacuum chamber as described in³ was used to measure their water adsorption. Measurements indicate that the amount of adsorbed water is highest for the pure a-C films and that the FL-CP_x films adsorbed less water than a-CP_x. To provide additional insight into the atomic structure of defects in the FL-CP_x, a-CP_x and a-C compounds, we performed first-principles calculations within the framework of Density Functional Theory. Emphasis was put on the energy cost for formation of vacancy defects and dangling bonds in relaxed systems.⁴ Cohesive energy comparison reveals that the energy cost formation for dangling bonds in different configurations is considerable higher in FL-CP_x than for the amorphous films. These simulations thus confirm the experimental results that dangling bonds are less likely in FL-CP_x than in a-CP_x and a-C films.

¹ A. Furlan, G.K. Gueorguiev, Zs. Czigány, H. Högborg, S. Stafström, and L. Hultman, Phys. Stat. Solidi Rapid Research Letters (2008) in press

² G.K. Gueorguiev, A. Furlan, H. Högberg, S. Stafström, and, L. Hultman, Chem. Phys. Lett. 426 (2006) 374

³ E. Broitman, V.V. Pushkarev, A.J. Gellman, J. Neidhardt, A. Furlan, and L. Hultman, Thin Solid Films 515 (2006) 979

⁴ E. Broitman, G. K. Gueorguiev, A. Furlan, N. T. Son, A.J. Gellman, S. Stafstrom, and L. Hultman, ICMTF, San Diego, CA (May 2008).

5:00pm SE+NC-WeA11 Structure-Property Relationships of Galvanic Nickel-NanoDiamond Composite Coatings, D.L. Schulz, R.A. Sailer, North Dakota State University, G.E. McGuire, O. Shenderova, International Technology Center

Galvanic nickel coatings have been in use for decades and have many desirable properties including corrosion resistance and relative ease of application. Recently, work has been performed to enhance the tribological properties of nickel-based coatings by incorporation of diamond nanoparticles as a wear-resistant component of this functional coating.¹ In this previous study, detonation nanodiamonds (DNDs) produced from a mixture of carbon-containing explosives were used. The DNDs were then employed as a hard filler in nickel electroplated films giving Ni-DND composite coatings. It was found that the presence of the DNDs significantly affected the properties of the coatings in an intriguing fashion. Toward that end, Ni-DND coatings exhibited improved microhardness and wear resistance when compared to Ni-only control coatings but the latter showed better erosion resistance.¹ These observations warrant a better understanding of the structure of the Ni-DND coatings and the effect on various mechanical properties. The work presented in this paper relates to an investigation of the structure/tribological properties of Ni-DND composite coatings. Characterization data to be discussed includes wear rates, hardness profiles and composite structure as measured by pin-on-disk, nanoindentation and high resolution SEM test methods.

¹ I. Petrov, P. Detkov, A. Drovosekov, M.S. Ivanov, T. Tyler, O. Shenderova, N.P. Voznecova, Y.P. Toporova, D. Schulz, Diamond & Related Materials 15 (2006) 2035–2038.

5:20pm SE+NC-WeA12 Deposition of Various Nitride and Oxiceramic Coatings by an Industrial-Scale LAFAD Process, V. Gorokhovskiy, C. Bowman, D. VanVorous, J. Wallace, Arcocom Surface Engineering, LLC

Nearly defect-free nitride and oxiceramic coatings were deposited by the unidirectional dual large area filtered arc deposition (LAFAD) process. One LAFAD dual arc vapor plasma source was used in both gas ionization and coating deposition modes with and without vertical magnetic rastering of the plasma flow. Substrates made of different metal alloys, as well as carbide and ceramics were installed at different vertical positions on the 0.5 m diameter turntable of the industrial scale batch coating system which was rotated at 12 rpm to assess coating thickness uniformity. Targets of the same or different compositions were installed on the dual cathodic arc sources of the LAFAD plasma source to deposit a variety of coating compositions by mixing the metal vapor and reactive gaseous components in a magnetized strongly ionized plasma flow. The maximum deposition rate typically ranged from 1.5um/hr for TiCr/TiCrN to 2.5 um/hr for Ti/TiN multilayer and AlN single layer coatings, and reached up to 6 um/hr for AlCrO based oxiceramic coatings. The vertical coating thickness uniformity was +/-15% inside of the 150mm area without vertical rastering. Vertical rastering increased the uniform coating deposition area up to 250 mm. The coating thickness distribution was well-correlated with the output ion current distribution as measured by a multi-sectional ion collector probe. Coatings were characterized for thickness, surface profile, adhesion, hardness and elemental composition. Estimates of electrical resistivity indicated good dielectric properties for most of the AlCrO based oxiceramic coatings. The multi-elemental LAFAD plasma flow consisting of fully ionized metal vapor with reactive gas ionization rate in excess of 50% was found especially suitable for deposition of nanocomposite, nanostructured coatings. Potential applications of this highly productive coating deposition process are discussed.

Tribology Focus Topic

Room: 205 - Session TR+NS+EM+NC-WeA

Nanotribology and Nanomechanics

Moderator: S.J. Bull, Newcastle University, UK

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

INVITED

The condensed matter properties of conjugated organic systems are critically important to thin-film transistors for flexible electronics. As with conventional (inorganic) semiconductors, crystallinity is expected to strongly impact electronic transport. But unlike inorganic semiconductors,

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

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

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

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

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

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

Friction is of tremendous technological importance and has, consequently, been under study for centuries. This research has led to the development of classical theories of friction that have successfully solved several tribological problems. However, these classical theories do less well at describing the behavior of advanced materials that operate under extreme environments. Here, we describe integrated experimental and computational studies of atomic-scale friction and wear at solid-solid interfaces across length and time scales. The influence of molecular orientation in the case of polymer films of polytetrafluoroethylene and polyethylene, on friction and wear are discussed. In addition, the tribological behavior of polycrystalline molybdenum disulfide is elucidated in a combination of atomic-force

microscopy and classical molecular dynamics simulations. These results provide new insights into how classical theories of friction may be modified to better describe advanced materials under extreme environments. This work is supported by a MURI from the Air Force Office of Scientific Research through grant FA9550-04-1-0367.

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

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

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

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

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

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

¹ D. Eggiman, senior thesis, Physics Department, Worcester Polytechnic Institute, 2007.

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

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

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

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

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

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

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

Thursday Morning, October 23, 2008

Biomaterial Interfaces

Room: 202 - Session BI+NC-ThM

Engineering Biointerfaces

Moderator: S. Zauscher, Duke University

8:00am **BI+NC-ThM1 Engineering Membrane Physical Properties and Dynamics using Structured Interfaces.** *A.N. Parikh, B. Sani, A.M. Smith, M. Howland, A.M.A.M. Brozell*, University of California, Davis
INVITED

Interfacial organization of lipids and amphiphiles into a discrete number of molecular layers provides, arguably, one of the most pristine experimental realizations of self-organized, two-dimensional systems. It provides an experimental test-bed for the study of a rich variety of interface-dominated processes, including surface melting, low-dimensional phase transitions, surface dynamics, and phase coexistence and separation. This talk will present recent experimental evidence from our laboratories which highlight the importance of substrate structure (e.g., topography, charge, and surface energies) in engineering the physical properties, namely curvature, morphology, and lateral dynamics, in supported lipid bilayers. Applications of such engineered surfaces in examining the dependence of membrane phase separation and phase transition on bilayer curvature and morphology will be discussed.

8:40am **BI+NC-ThM3 Fluidic and Air-Stable Supported Lipid Bilayer and Cell-Mimicking Microarrays.** *X.-Y. Zhu*, University of Minnesota

As drug delivery, therapy, and medical imaging are becoming increasingly cell-specific, there is a critical need for high fidelity and high-throughput screening methods for cell surface interactions. Cell membrane-mimicking surfaces, i.e., supported lipid bilayers (SLBs), are currently not sufficiently robust to meet this need. Here we describe a method of forming fluidic and air-stable SLBs through tethered and dispersed cholesterol groups incorporated into the bottom leaflet. Achieving air-stability allows us to easily fabricate SLB microarrays from direct robotic spotting of vesicle solutions. We demonstrate their application as cell membrane-mimicking microarrays by reconstituting peripheral as well as integral membrane components that can be recognized by their respective targets. These demonstrations establish the viability of the fluidic and air-stable SLB platform for generating content microarrays in high throughput studies, e.g., the screening of drugs and nanomedicine targeting cell surface receptors.

9:00am **BI+NC-ThM4 Supported Lipid Membranes as Biomimetic Model Systems.** *S. Svedhem, A. Kunze, H. Ekstrand*, Chalmers University of Technology, Sweden, *P. Sjövall*, SP Technical Research Institute of Sweden, *R. Frost, M. Edvardsson, B. Kasemo*, Chalmers University of Technology, Sweden

Engineering of surface-supported lipid membrane model systems is currently a very active field of research. The present contribution will focus on two recent examples from our group in this area; (i) Lipid exchange between liposomes and supported lipid membranes of opposite charge, and (ii) The action of lipases on supported lipid membrane structures. These examples cover different kinds of supported lipid structures; both (planar) supported lipid bilayers and (intact) supported liposomes, as well as different kinds of biomolecular interactions associated with them. Key experimental techniques used to follow processes at these interfaces are the quartz crystal microbalance with dissipation monitoring (QCM-D), optical reflectometry, surface plasmon resonance (SPR), fluorescence microscopy, atomic force microscopy (AFM) and time-of-flight secondary ion mass spectrometry (TOF-SIMS). Our first examples deal with lipid exchange/transfer between lipid membranes, which is important for many biological functions, but which has also the potential for in situ engineering of supported membranes. To learn more about how the dynamics of such processes can be studied, we have investigated the interaction of positively and negatively charged lipid vesicles with supported lipid bilayers (SLBs) of opposite charge. In particular, it was possible to follow the different steps during such modification processes both by QCM-D and TOF-SIMS, the latter allowing direct estimation of the fraction of different lipids in the membrane. These results have also implications for studies of how nanoparticles interact with membranes. The second example covers how lipases (PLA2 and PLD) act on membranes, and in particular how lag phases for such interactions can be monitored by QCM-D. Depending on the type of lipase under study, either dissolution or membrane morphology changes were observed. In conclusion, the combination of surface-supported lipid membranes and surface-sensitive analytical techniques allows for detailed studies of processes of relevance for biological

membranes. In particular, the molecular composition can be controlled, and morphological changes of the membrane structure can be induced and visualized

9:20am **BI+NC-ThM5 Nanopatterning Proteins Over Large Areas for Biological Applications.** *J. Malmström, H. Agheli, P. Kingshott, D. Sutherland*, University of Aarhus, Denmark

The recent decade has seen a rapid expansion in the ability to create and study nanometer scale objects and these new methods are being applied to the study of biological systems. The immobilisation of bioactive molecules has long been a goal in biomaterials and tissue engineering research, for use as stimulatory cues or model systems to study biointeractions. The advent of soft lithographic routes and efficient approaches to minimise non-specific protein interactions for example through immobilised polyethylene oxide coatings has led to microscale patterns of proteins were routinely demonstrated and applied as model systems to study biological systems. While patterns at the micrometer scale of considerable interest and application, the size of and lengthscale at which proteins and other macromolecules are structured in vivo is in most cases at the nanoscale. Patterning biomolecules at the nanometer scale gives a significant potential for studying how biological systems function at the macromolecular length scale or to mimic the structure of biological interfaces with macromolecular resolution. A key requisite for the study of cellular biosystems is the ability to robustly generate large areas of patterns. In this work colloidal lithographic routes utilising electrostatic self assembly to generate dispersed monolayers of colloidal particles as masks for pattern generation have been used to generate nanostructured interfaces. Substrates with nanopatterned surface chemistry have been used as templates for generation of nanopatterns of proteins. Hydrophobically modified gold nanopatches in a silicon oxide background have been used to open up arrays of 100nm nanometer diameter regions within a protein rejecting background (based on PLL-g-PEG) and used to demonstrate nanopatterning of a number of protein systems (Laminin, Osteopontin and Ferritin). Nanostructured interfaces have also been fabricated on QCM-D sensors and used to study *in situ* protein and antibody binding at nanoscale patches while AFM microscopy of dried samples was used to quantify protein and antibody binding utilising height histograms. A combination of QCM-D, AFM and SPR derived data was used to establish the thickness and density of the adsorbed laminin layers at both nanoscale patches and homogeneous surfaces.

9:40am **BI+NC-ThM6 Fabrication and Testing of Electrospun Novel Biodegradable Polyurethane Scaffolds.** *N. Brown, C. Zhang, T. Boland*, Clemson University

Synthesis and fabrication of biomaterials that can temporarily mimic the native tissue is a lofty aim in Tissue Engineering. It is also paramount in Regenerative Medicine material research. Such a biomaterial could be formed into scaffolds and be temporary replacements of tissues or for other internal biomaterial corporal needs. Our work here is on the use of a novel biodegradable polyurethane (BPU) that was electrospun and fabricated into tubes. Once fabricated, smooth muscle cells (RASMC) were ink-jet printed onto the same scaffolds and tested for degrees of cell alignment BPU are biopolymers that are designed to mimic the elasticity and memory of native tissue. These biopolymers can be designed to fit the application. This BPU was synthesized from methylene di-p-phenyl-diisocyanate (MDI), polycaprolactone diol (PCL-diol) and N, N-bis (2-hydroxyethyl)-2-aminoethane-sulfonic acid (BES), serving as a hard segment, soft segment and chain extender respectively. The BPU was then electrospun into nanofibers and formed small diameter (4 mm) blood vessels. The blood vessels were electrospun at various extrusion rates to determine optimum pore size and fiber diameters. This was accomplished by SEM imaging. The mechanical testing included tensile and burst pressure testing to determine if the scaffold could withstand extreme physiological conditions. Burst pressure testing results were from 1600-2900 mm Hg. Fiber diameters were in the 700-1000 nm range. Pore sizes were in the 50-90 μ m range. Mechanical testing results indicated an elongation of 620 \pm 120% with memory. The mechanical testing indicated that these scaffolds could withstand extreme mechanical physiological conditions well exceeding what they would experience in vivo. The imaging indicated fiber formation that could mimic an extracellular matrix or act as an internal physical barrier. Lastly, ink-jet printing was used as a cell placement method to control the location of cells on material. Cell printing was used to determine if RASMC cell alignment was possible and to what degree patterns could be printed to conjure alignment on the fibrous scaffolds. Histological results of the RASMC patterns on the electrospun scaffolds will be presented.

10:40am **BI+NC-ThM9 Electrically Insulating Pore-Suspending Membranes on Highly Ordered Porous Alumina**, *C. Steinem*, University of Goettingen, Germany **INVITED**

In the last years, we have developed a membrane system that combines the merits of freestanding and solid supported bilayers. These membranes suspend the pores of a highly ordered porous material such as porous alumina (nano-BLMs) or porous silicon (micro-BLMs). In this talk, I will discuss the electrical properties and stability of these membranes as a function of lipid composition and under flow conditions. We were able to demonstrate that a buffer solution exchange can be readily achieved by placing the membranes in a flow system. The membranes turned out to be stable as evaluated by the changes in membrane resistance obtained from impedance analysis. The membrane resistances are sufficiently high to analyze ion channel activity on the single channel level. In particular, we have demonstrated that connexins can be inserted into nano-BLMs exhibiting full functionality.

11:20am **BI+NC-ThM11 Supported Lipid Bilayers on Nanoporous Substrates for Multi-technique Membrane Sensing**, *K. Kumar, S. Kaufmann, A.M. Tabari, M. Textor, E. Reimhult*, ETH Zürich, Switzerland

Supported lipid bilayers (SLBs) formed from the rupture of liposomes have the advantage over other planar membrane architectures in that they can be formed completely bereft of organic solvents, enabling the further incorporation of sensitive ion channels or membrane proteins.¹ Porous structures allow the use of fusogenic surfaces which enhance the formation of SLBs, while accommodating the incorporation of larger membrane proteins. By integrating these porous structures with suitable gravimetric or optical sensor surfaces that could double up as electrodes, it would be possible to conduct electrochemical measurements in tandem with, e.g., affinity measurements. For optical sensing techniques such as waveguide spectroscopy, if the pores are small enough, it would also be possible to discriminate between processes occurring on the surface and within the pores.² We have developed a process where it is possible to etch high aspect ratio pores into silicon nitride and silicon oxide with a tunable diameter between 50 nm and 150 nm using particle lithography for patterning etch masks.³ Sensor substrates for coupled plasmon waveguide resonance (CPWR) measurements, quartz crystals for quartz crystal microbalance with dissipation (QCM-D) measurements and glass slides for microscopy techniques were fabricated. The influence of nanopore density and size on the kinetics of formation of SLBs by liposome fusion was investigated by QCM-D and the structure of the lipid bilayer in the pore area was investigated by atomic force microscopy, confocal fluorescence microscopy and nanoscopy.⁴ QCM-D, microscopy and nanoscopy measurements suggest the formation of fully covering SLBs by liposome fusion on such substrates. Atomic force microscope (AFM) images and force distance measurements on individual SLBs over pores seem to indicate that the formed SLB also spans the nanopores, but are strongly deformed by the tip interaction. These results set the stage for the next phase of experiments, where electrochemical measurements can be made in situ on the waveguide or quartz crystal after the confirmed formation of a pore-spanning SLB.

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

² Lau, K.H.A., et al. J Phys Chem B, 2004. 108(30): p. 10812-10818.

³ Reimhult, E., et al. Nanotechnology, 2007. 18(27): p. 7.

⁴ Donnert, G., et al. PNAS, 2006. 103(31): p. 11440-11445.

11:40am **BI+NC-ThM12 Patterning of Plasma Polymers for Bioarray**, *G. Mishra, S.L. McArthur*, University of Sheffield, UK

The high-density, multi-analyte chips required for genomic and proteomic research can be successfully produced using a precise surface patterning methodology that allows controlled positioning of chemically distinct active areas. A major challenge with current bio-sensing devices which requires addressing is the need for surface chemistry that allows immobilised biomolecules of diverse types to retain their biological activity. Plasma polymerisation presents a versatile approach to surface modification of these devices. The range of monomers available for plasma polymerisation makes this manufacturing approach even more suitable for use in systems where multiple coatings with specific properties are required for a single device. The control offered by this surface modification technique and the ability to spatially define reactive regions to reduce non-specific background adsorption is integral to this project. This study highlights the efficacy of photolithographic plasma polymer patterning and provides a rare insight into issues associated with achievable chemical specificity and spatial resolution. A multi-technique investigation (XPS, ToF-SIMS, AFM, fluorescence microscopy) of surface chemistry and its biological response forms the focus of the study. Using ToF-SIMS data and multivariate analysis, we highlight the intricacies of pulsed plasma polymerised surface chemistry and propose a unique approach to optimising these parameters in order to maximise functional group retention. ToF-SIMS data has also been used to provide new insight into the mechanism of pulsed plasma polymerisation.

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

Semiconducting Biointerfaces and Sensors

Moderator: L.J. Brillson, Ohio State University

8:00am **BO+EM+BI+NC-ThM1 AlGaIn/GaN HEMT And ZnO Nanorod Based Sensors for Chemical and Bio Applications**, *B.S. Kang, H.T. Wang, K.C. Chen, Y.L. Wang, T. Lele, J. Lin, S.J. Pearton, F. Ren*, University of Florida

AlGaIn/GaN high electron mobility transistor based sensors are good candidates for low cost, handheld, and wireless chemical and biomedical sensor due to their excellent thermal as well as chemical stability and sensitivity to the changes of ambient. The electrons in the AlGaIn/GaN HEMT two-dimensional electron gas (2DEG) channel are induced by piezoelectric and spontaneous polarization effects and there is no dopant needed. There are positive counter charges at the AlGaIn surface layer induced by the 2DEG. Any slight changes in the ambient of the AlGaIn/GaN HEMT affect the surface charges of the AlGaIn/GaN HEMT. These changes in the surface charge are transduced into a change in the concentration of the 2DEG in the AlGaIn/GaN HEMTs. We have demonstrated AlGaIn/GaN HEMT based individual sensors for protein, DNA, kidney injury molecules, prostate cancer, pH values of the solutions, pH in the exhaled breath condensate, and mercury ions with specific surface functionalizations. We have also demonstrated ZnO nanorod based sensors to detect UV, hydrogen, carbon monoxide and ammonium. Recently, we integrated ZnO nanorods with AlGaIn/GaN HEMT to detect glucose in the breath condensate. This approach makes a possibility of integrating AlGaIn/GaN HEMT based sensors with ZnO nanorod sensors on a single "smart sensor chip" with the techniques of selective area functionalization and microfluidic device approaches. This smart sensor chip can be mounted on a handheld, portable, wireless transmitter circuit board.

8:20am **BO+EM+BI+NC-ThM2 Label-Free Dual Sensing of DNA-Molecules using GaN Nanowires**, *A. Ganguly, C.-P. Chen*, National Taiwan University, *K.H. Chen*, Academia Sinica, Taiwan, *L.C. Chen*, National Taiwan University

GaN, a leading optoelectronic material, is also known to be non-toxic and bio-compatible. Interestingly, this material in the form of nanowires (NWs), with the advantages of large surface-to-volume ratio and direct electrical-path due to surface-induced spatial-separation of charge-carriers, could possess high sensitivity to the local environment, hence to the surface-immobilized biomolecules. Here, we report the GaN NWs possess high bio-binding efficiency and provide a platform for in situ, label-free, and rapid (assay-time within 2 hours) detection of DNA-molecules with dual-sensing capability (electrochemical and optical). Both electrochemical (EC) and optical (photoluminescence, PL) measurements showed clear distinction of pristine GaN NWs with probe-DNA (pLF) immobilization, and after further hybridization, employing a popular target-DNA with anthrax lethal factor sequence (LF). In label-free condition, both EC and PL-based techniques exhibited high sensitivity, without any little effort to optimize the sensing-condition, up to nM and pM of concentrations, respectively for the recognition of LF, with very low assay-time. Furthermore, successful application for detection of "hotspot"-mutations, related to human p53 tumor-suppressor gene, revealed excellent selectivity and specificity towards the fully-complementary targets, down to pM concentration, even in presence of mutations and non-complementary strands, suggesting the potential pragmatic application in complex clinical samples. The simplicity in detection-method, without any requirement of extra step/modification in both probe and target-systems, and simultaneously, the unique label-free dual-detection capability of GaN NWs, with excellent selectivity and sensitivity, can make them a promising choice of transducers, even in clinical application.

8:40am **BO+EM+BI+NC-ThM3 GaN Field Effect Transistors for Biosensor Applications**, *W. Lu*, The Ohio State University **INVITED**

Biosensors based on electrical field effect transistors (FETs) are of great research interests due to their properties of label free, low cost, small size, and easy integration to external circuitry electronics. Such biosensors have been fabricated on many semiconductor materials including Si, silicon on oxide, carbon nanotube, ZnO, etc. Si-based such biologically FETs (bioFETs) suffer from various difficulties such as limited sensitivity and current drift caused by degradation of gate dielectrics and chemical instability. Due to the chemical inertness and the high concentration of two dimensional electron gas (2DEG) at the AlGaIn/GaN interface, AlGaIn/GaN heterojunction FETs have great potentials for detection of bioagents in biological buffers with high ionic strengths. In this paper, we will give an overview of recent research progress on GaN FET biosensors. The process

and characterization of functionalization of AlGa_N surface for biosensing applications will be discussed. The detection of streptavidin (STA) and monokine induced by interferon γ (MIG) proteins and hybridization process of single strand DNAs by AlGa_N/Ga_N HFETs will be presented. Specifically, for STA detection, at different ionic strengths, the effect of Debye length on detection sensitivity has been demonstrated. No current change is observed for fully biotinylated STA, indicating that there is no non-specific binding. Furthermore, we have used open binding pockets of specifically-bound STA on the biotinylated surface as receptors for detection of biotinylated MIG proteins. The results show that the devices are capable of detecting of biotinylated MIGs at pathological concentrations even at physiological ion strengths. In part, this is due to the superior stability of the AlGa_N/Ga_N HFET platform in buffer, which results in sensor noise being sufficiently low to allow reproducible detection of protein analyte binding. For comparison, regular unbiotinylated MIG proteins gave no current change, indicating that there is no non-specific binding and the change of current is due to the charges transferred from charged analytes.

9:20am **BO+EM+BI+NC-ThM5 Surface Functionalization of ZnO Nanoparticles and Thin Films for Sensor Applications**, *L. Selegard, C. Vahlberg, F. Söderlind, V. Khranovskii, A. Lloyd Spetz, R. Yakimova, P.-O. Käll, K. Uvdal*, Linköping University, Sweden

A new procedure has been developed for functionalization of electrochemically produced ZnO nanoparticles. The core of the particles was characterized using TEM, PEEM and LEEM. Single crystal nanoparticles, with uniform spherical morphology with a size of approximately 50Å were obtained. The first aims of ZnO nanoparticle functionalization were to make a stabilizing molecular layer at the surface and to prepare for further linking possibilities, for use in different types of sensing applications. The functionalization process was investigated and the molecular layer was verified by XPS and FT-IR. Parallel studies on biofunctionalization of plane ZnO thin films were performed to obtain a suitable reference system. One of the molecules used for functionalization of the nanoparticle surface was (3-Mercaptopropyl)triethoxysilane (MPTS) as it enables further functionalization on the thiol part and as it has the possibility to form a stable network around the particles. The MPTS linking was investigated by XPS and NEXAFS. The XPS spectra of the functionalized particles showed significant signal from both Si and S verifying the presence of MPTS. XPS core level S2p spectrum further showed presence of SH groups, indicating that thiols was available for further linking processes. Another molecule of interest for nanoparticle functionalization is oleic acid. The strategy is then to coordinate the carboxyl groups to the surface and further linking will be based on hydrophobic interactions. The TEM and PEEM results, so far, indicated that the particles were not fully dispersed but the use of oleic acid showed a much smaller extent of agglomerated particles than for example MPTS. PEEM also showed that the oleic acid capped particles was much more heat stable than MPTS capped once. ZnO nanoparticles show two emission peaks, one band gap related UV-emission and one visible emission arising from oxygen vacancies. In this work fluorescence spectroscopy was used to study the emitted, visible light of the particles as a function of different surface modifications.

9:40am **BO+EM+BI+NC-ThM6 Surface Functionalization and Micropatterning of Ta₂O₅ Films Using Organo-silane and Atom Transfer Radical Polymerization(ATRP) Methods**, *W. Kulisch, D. Gilliland, G. Ceccone, L. Sirghi, F. Rossi, H. Rauscher*, European Commission Joint Research Center, Italy

Optical waveguide biosensors frequently require the use high refractive index thin films such as tantalum pentoxide to act as both as a light guide and as a surface on which active biomolecules can be covalently immobilized. In this work, a process for the room temperature deposition of Ta₂O₅ films onto silicon/silica and thermoplast substrates by reactive ion beam sputtering from a tantalum target has been developed. The resultant high refractive index films have been chemically and optically characterized and methods examined for the wet chemical modification of the oxide film to produce either reactive amino groups or low protein fouling polyethylene glycol (PEG) layers. In both cases the first step toward the functionalization of the as-grown films used either an oxygen plasma or to an UV/O₃ treatment to produce a clean and fully oxidized surface. Using these clean, active surfaces-NH₂ terminated SAMs could be routinely produced using a conventional silanization process using 3-aminopropyl trimethoxysilane (APTMS). To produce high density, low protein binding (anti-fouling) layers a more sophisticated procedure based on surface initiated atom transfer radical polymerization (SI-ATRP) of poly(ethylenglycol)methacrylate (PEGMA) has been used. In this method the oxide surface is firstly modified using a combination of poly(glycidylmethacrylate) (PGMA) and α -bromoisobutyryl bromide (BIB) to produce a surface rich in tethered α -bromoisobutyryl groups. These BIB

groups can then used as initiation sites for the growth of dense PEG films using the copper complex catalysed ATRP of PEGMA macromonomers. To characterize the final surfaces and to assist in the optimization of process, time-of-flight secondary ion mass spectrometry (TOF-SIMS), X-ray photoelectron spectroscopy (XPS), contact angle measurements and atomic force microscopy (AFM) have been applied to samples after each step of the different processes. The effectiveness of the two processes will be demonstrated and examples given of methods by which the two methods have been combined for the production of fouling/non-fouling micropatterned surfaces.

10:40am **BO+EM+BI+NC-ThM9 Designing the Interfaces between Biomolecules and Semiconductor Substrates: From the C60 Buckyball Model System to Shape-Restricted DNA Molecules**, *X. Zhang, A.V. Telyakov*, University of Delaware

A well-characterized interface based upon covalent binding between biomolecules and semiconductor surface was designed using the functionalized self-assembled monolayers (SAM) on Si(111) surface and specific shaped-restricted DNA molecules. This type of interface can serve as a prototype for the future devices in biosensing and single molecule spectroscopy. The spectroscopic and microscopic benchmarks were initially tested using fullerene C60 as a model to understand the attachment chemistry of large molecules with amine-terminated SAM on Si(111) surface. X-ray photoelectron spectroscopy (XPS) and Infrared spectroscopic (IR) studies, supported by computational investigation, verified the covalent attachment of C60 to the amine-terminated SAM on Si(111) surface. The atomic force microscopy (AFM) revealed the topography of the C60-modified surface with molecular resolution. The biomolecule/semiconductor interface was tailored with the same amine-terminated SAM on Si(111) surface and thiol-DNA molecules, which is achieved via a sulfo-succinimidyl 4-(N-maleimidomethyl)-cyclohexane-1-carboxylate (SSMCC) crosslinker molecule. The shape-restricted thiol-DNA is anchored to the surface through the formation of covalent bonds as confirmed by XPS and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The AFM is used to visualize the well-defined and selective covalent binding of thiol-DNA molecules on SAM-covered Si(111). In addition, AFM and contact angle measurement are employed to study the change of the surface topography and the change of the surface hydrophilicity following each step of the DNA attachment chemistry on silicon.

11:00am **BO+EM+BI+NC-ThM10 The Effect of a Spacer Thiol on the Orientation and Hybridization Properties of 40mer DNA SAMs on Gold**, *L.J. Gamble, P.-C. Nguyen, T. Weidner*, University of Washington, *D.W. Grainger*, University of Utah, *D.G. Castner*, University of Washington

Methods for surface-immobilizing single-strand nucleic acids while preserving their original hybridization specificity with minimal non-specific interactions remain an important goal for improving the performance of surface bound DNA microarray and biosensor applications. Before the full potential of DNA microarrays can be realized, fundamental issues must be better understood, including how the crowding, conformation and orientation of immobilized DNA impacts DNA target hybridization efficiency. For detection of small amounts of DNA in a target solution, the coverage and orientation of DNA probes should be optimized for the capture of low concentrations of DNA via hybridization. In this study the effect of backfill of mercaptohexanol (MCH) on 40mer thiolated single stranded DNA (SH-ssDNA) sequence orientation and hybridization efficiency is studied with X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, sum frequency generation (SFG) vibrational spectroscopy, and surface plasmon resonance (SPR). While XPS and NEXAFS are both ultra-high vacuum techniques, SPR is a real-time solution based technique and SFG spectroscopy can be acquired both at the solid-air interface as well as the solid-liquid interface. While the 40mer DNA is longer and expected to be more disordered, the NEXAFS N k-edge spectra showed increased polarization dependence of the peaks at 401eV and 399eV for the 40mer sequence increased with an MCH backfill time of 1 hour. SFG spectroscopy results showed that incorporation of the MCH into the DNA monolayer resulted in an increase of the nucleotide related peaks at 2961 cm⁻¹ and 3045 cm⁻¹ which maximized at 1 hour MCH backfill. This evidence of orientation changes in the surface bound 40mer DNA will be correlated with hybridization data from SPR.

11:20am **BO+EM+BI+NC-ThM11 Anchoring and LT-STM/STS Characterization of Single Organic Molecules at Semiconducting and Insulating Surfaces**, *M. Szymonski, A. Tekiel, S. Godlewski, G. Goryl, J. Prazmner-Bechcicki, J. Budzioch*, Jagiellonian University, Poland

In recent years self-assembling of organic molecules deposited onto different surfaces have attracted considerable attention because of important applications in organic electronic technologies and prospects for

development of single molecule computing devices. In this presentation we will report on our recent studies of initial stages of growth and organization of several organic molecules on reconstructed (001) surface of InSb, (011) and (110) surfaces of TiO₂, and on ultrathin KBr layers grown epitaxially on InSb(001). Among different organic molecules the perylene derivative -3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA), often regarded as a model system for planar-stacking molecules, copper phthalocyanine (CuPc), violet landers (VL), and chiral helicene[11] molecules were studied by means of scanning tunneling microscopy (STM) at room and liquid nitrogen temperatures, nc-AFM at room temperature and low energy electron diffraction (LEED). It is shown that during initial stages of growth on InSb molecules often form chains parallel to [110] crystallographic direction of the c(8x2) reconstructed substrate. They are frequently attached to the lower terrace step edge, or some defects on the surface, indicating surprisingly weak interaction between the molecules and the substrate and their high mobility along [110] diffusion channel. Geometrical orientation of the molecules with respect to the reconstruction rows of the substrate will be discussed. We will present the images acquired with submolecular resolution, as well as images demonstrating the pinning effect of the molecular chains by surface charge density waves, and incorporation of the molecules into overall electronic structure of the system.

11:40am **BO+EM+BI+NC-ThM12 Molecular Self-Assembly of Functionalized Fullerenes on a Closed Packed Metal Surface**, *B. Diaconescu*, University of New Hampshire, *T. Yang, S. Berber*, Michigan State University, *M. Jazdzzyk, G. Miller*, University of New Hampshire, *D. Tomanek*, Michigan State University, *K. Pohl*, University of New Hampshire

Self-assembled organic thin films have a great number of practical applications, ranging from sensors and biological interfaces in medical implants to organic electronics and photovoltaics. Generally speaking, self-assembled monolayers (SAMs) form as a result of a delicate balance between competing molecule-substrate and intermolecular interactions. Therefore, to control such self-assembly processes in a useful way, it is mandatory to understand how this balance reflects onto the SAM's final structure. Here, we present a combined STM and DFT study of the self-assembly of C60 molecules functionalized with long alkane chains, F-C60, on the (111) surface of silver. We find that F-C60 molecules lay down on the Ag surface and form a complex zigzag like pattern with an oblique unit cell of 4 nm by 2.5 nm and two molecules per basis. The C60s are placed at a larger than van der Waals distance. The symmetry of the functionalized C60 self-assembled monolayer is dictated by the alkane-surface interaction while the size of the unit cell is a consequence of the in-plane intermolecular interactions. These results show that C60s can be assembled in a two-dimensional and non-compact molecular array and suggest a way to control their surface density via appropriate chemical functionalization.

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Energy Science and Technology Focus Topic

Room: 203 - Session EN+EM+NS+P+A+T+V-ThM

Energy: Tools and Approaches

Moderator: S.P. Williams, Plextronics, Inc.

8:00am **EN+EM+NS+P+A+T+V-ThM1 Nano-Structured and Micro-Structured Semiconductors for Better Efficiency of Solar Cells**, *C.-F. Lin, J.-S. Huang, S.-C. Shiu, J.-J. Chao, C.-Y. Hsiao, K.-H. Tsai*, National Taiwan University **INVITED**

The foreseeable depletion of fossil fuel and the global warming caused by the carbon dioxide had led to the increasing attention of alternative renewable energy, especially photovoltaic. Therefore, crystalline Si-PV devices are quickly spreading. Unfortunately, the large consumption of Si materials hinders their vast applications. Many efforts have been switched to developing thin-film PV devices. In this talk, we will discuss the use of nano-structured and micro-structured semiconductors that enable the fabrication of thin-film solar cells with improved efficiency. Several types of such thin-film solar cells will be discussed, including the organic-semiconductor-nanowire composite film, organic-semiconductor micro-structure composite film, nano-wire semiconductor thin film, and micro-structured semiconductor thin film. In the thin-film solar cells using organic-semiconductor-nanorod composite film, different types of semiconductor nanowires such as ZnO, Si, and GaAs nanowires are used to replace the acceptor-type organics for two purposes: increasing the electron mobility and assisting the formation of nano-morphology for better inter link between the donor organics and acceptor materials. The fabrication procedures of those nanowires as well as the formation of the organic-

semiconductor-nanowire composite film with controlled nano-morphology will be presented. For the other solar cells using nano-structured and micro-structured semiconductors, we will particularly describe the technique of nanowire/micro-structure transfer. In our approach, the nanowires and micro-structures are made from the bulk semiconductors or epitaxial semiconductors, so they will have much better crystal quality than the usual thin-film materials. In addition, after nanowires and micro-structures are transferred to other transparent substrates, the original wafer can be reused, so the material cost can be lowered considerably. In addition, it offers the advantages of the bending flexibility, not being limited by the brittle property of semiconductors. Furthermore, in comparison with current III-V tandem solar cells taken by monolithic approach, which requires lattice match and current balance, our approach enables mechanically stacking. Thus each cell could be designed individually to match the entire solar spectrum for optimal solar usage. Therefore, such new-type thin-film solar cells are expected to be potentially efficient and low cost.

8:40am **EN+EM+NS+P+A+T+V-ThM3 Endohedral Metallofullerenes as Improved Acceptor Materials for Organic Solar Cells**, *M. Drees*, Luna Innovations Incorporated, *R. Ross*, Georgetown University, *C. Cardona*, Luna Innovations Incorporated, *E. Van Keuren*, Georgetown University, *D. Guldi*, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany, *B.C. Holloway*, Luna Innovations Incorporated

Cost factors in inorganic solar cells have opened up a new path to less expensive manufacturing techniques using bulk heterojunction polymer/fullerene based solar cells. Using empty cage fullerene derivatives as the acceptor material, state-of-the-art organic photovoltaics currently display ~5% overall conversion efficiency. One of the main factors limiting the efficiency in organic solar cells is the low open circuit voltage. The open circuit voltage is governed by the molecular orbitals of the donor and acceptor material; therefore better matching of the orbitals will lead to improved voltages. Here we present a novel acceptor material based on Trimetasphe[®] carbon nanomaterials (TMS). Trimetasphe[®] are endohedral metallofullerenes that consist of a trimetal nitride cluster enclosed in a C80 cage. First-generation Trimetasphe[®] carbon nanomaterial derivatives have been synthesized and show behavior consistent with C60 but with improved molecular orbitals. Electrochemical data suggests a maximum voltage increase of up to 280 mV over C60-PCBM-based devices and photophysical characterization of shows efficient and stable charge separation. Initial bulk-heterojunction devices have been synthesized with open circuit voltages that are 280 mV higher than reference devices using C60-PCBM and conversion efficiencies exceeding 3.1%.

9:00am **EN+EM+NS+P+A+T+V-ThM4 Morphology Study of Vacuum-Deposited Pentacene:C60 Mixed Thin Films for Photovoltaic Applications**, *J. Xue, Y. Zheng, J.D. Myers, J. Ouyang*, University of Florida

The efficiency of organic photovoltaic (PV) devices has gained steady increase in past 20 years, showing a potential to provide clean and low-cost electrical energy in the near future. Bulk heterojunction (HJ) composed of nanoscale percolation of donor and acceptor phase have been demonstrated to improve the efficiency of organic PV device. Such improvement is attributed to the creation of a spatially distributed interface, which enhances exciton dissociation, and the presence of continuous conducting paths for efficient charge collection. However, ideal nanoscale percolation is not readily achievable. Therefore, understanding the morphology inside the bulk heterojunction plays an important role on achieving efficient PV device. Here, phase separation in donor-acceptor (D-A) mixture composed of pentacene:C60 and how it contributes to a percolated morphology are studied. The pentacene:C60 mixed films are fabricated by co-deposition of two molecules with vacuum thermal evaporation (VTE) method. The mixing ratio of pentacene and C60 is controlled by varying the deposition rate of each species. X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM) are used to characterize the vacuum deposited pentacene:C60 mixed film. XRD patterns of pentacene:C60 mixed films indicate phase separation inside the mixture, which is reflected by appearance of characteristic diffraction peaks of thin film phase pentacene. SEM and AFM images reveal the change of surface morphology of the mixed films with varied mixing ratio and deposition rate, suggesting different degree of phase separation inside. Base on this information, PV devices are fabricated and their performance is investigated. It is found that by suppressing the phase separation between pentacene and C60 to nanoscale the PV performance is improved significantly. The open circuit voltage (Voc) and short circuit current (Jsc) increase from 0.45 V and 9.7 μ A/cm² in pentacene:C60 = 1:1 (by weight) device to 0.58 V and 1.3 mA/cm² in pentacene:C60 = 1:5.5. All these suggest that degree of phase separation of molecular mixtures can be controlled by varying the process conditions, which may lead to new

pathways to generate nanoscale percolation for application in efficient organic PV devices.

9:20am **EN+EM+NS+P+A+T+V-ThM5 Tailoring the Morphology of Organic Solar Cells with Surface Templates**, *S. O'Donnell*, University of Virginia and The MITRE Corporation, *P. Reinke*, University of Virginia

One of the most important applications of fullerenes is their incorporation in organic solar cells, where they function as an electron acceptor in conjunction with photoactive molecules such as porphyrin. The photoyield is intimately linked to the morphology, which determines the efficiency of exciton diffusion and separation, and the effectiveness of charge transport to the electrodes. Control of the morphology across lengthscales, spanning the range from the molecule to the several hundred nm, is critical to optimization of solar cell functionality. We control the morphology by using tailored substrate templates on which we assemble ultrathin films with well-defined regions of acceptor and photoabsorber molecules. This approach enables us to measure the morphology and interface structure with atomic resolution with scanning probe methods, and to subsequently investigate the photocurrent distribution. A pattern with variable geometry is written on the surface of highly oriented pyrolytic graphite (HOPG), our model surface, with a focussed ion beam (Ga⁺, 30 keV ion energy), which creates regions with a high density of surface defects interspaced with largely undamaged graphite surface. The surface defect structure, its extension and density within the pattern is characterized prior to molecule deposition. Surface defects interact strongly with the fullerene molecules, and thus provide nucleation centers for the formation of fullerene islands whose position is in registry with the artificial pattern. The boundary of the ion damaged region serves as the primary nucleation center for the formation of C60 islands, whose shape is controlled by the pattern geometry and the diffusion length of the molecules. We will describe how the artificial pattern can be used to tailor the morphology across lengthscales and discuss the extension of this method to other, technically relevant surfaces such as quartz which possesses a natural patterning in the form of ledges. The complete 2D nanostructure can be built by deposition of fullerene on the templated HOPG, and the remaining "empty" graphite surface is then filled with photoabsorber molecules. We will show the movement of porphyrin molecules into the pattern, and how the interfacial region between fullerenes and porphyrins evolves, and discuss the resultant morphologies. This hierarchical assembly of organic solar cells will enable us to tailor morphologies and link them uniquely to the photophysical processes.

9:40am **EN+EM+NS+P+A+T+V-ThM6 Photoemission Studies of Lead Sulfide Nanocrystals in Organic Films**, *A.T. Wroble*, *D.J. Asunskis*, *A.M. Zachary*, *I.L. Bolotin*, University of Illinois at Chicago, *D.J. Wallace*, *M. Severson*, University of Wisconsin-Madison, *L. Hanley*, University of Illinois at Chicago

Lead sulfide (PbS) nanocrystals have shown potential for use in optoelectronic applications including photovoltaics. PbS nanocrystals are grown directly into polymers or organic oligomer matrices to control the size and surface chemistry of the resulting nanocrystals. Transmission electron microscopy is used to determine the size distribution of PbS nanocrystals in organic films grown by either colloidal synthesis in polymer solutions or gaseous deposition using a cluster beam deposition source. Both the colloidal and cluster beam deposition methods are described in detail. Various techniques in photoemission spectroscopy are then applied to these PbS nanocrystal-organic films. X-ray photoelectron spectroscopy (XPS) confirms that PbS nanocrystals are present. Soft-XPS using 200 eV photon energies available at a synchrotron radiation source provides surface sensitivity to observe the interaction of the PbS nanocrystal surface with the organic matrix and is compared to XPS results obtained using 1487 eV photon energy. Little or no bonding between the PbS nanocrystals and the organic phase is observed. The core of the nanocrystals are found to be 1:1 Pb:S, but their surfaces are enriched in Pb. Finally, core level binding energy shifts in XPS under simulated solar irradiation are used for contact-free evaluation of element-specific photovoltaic electrical response of these PbS nanocrystal-organic thin films.

10:40am **EN+EM+NS+P+A+T+V-ThM9 Rational Design of Nanostructured Hybrid Materials for Photovoltaics**, *S.B. Darling*, *I. Botiz*, Argonne National Laboratory, *S. Tepavcevic*, *S.J. Sibener*, The University of Chicago, *T. Rajh*, *N. Dimitrijevic*, Argonne National Laboratory

Efficient conversion of photons to electricity in organic and hybrid materials depends on optimization of factors including light absorption, exciton separation, and charge carrier migration. Bulk heterojunction devices target these processes, but disorder on the nanoscale results in inefficiencies due to exciton recombination and poor mobility. By rationally designing the morphology at appropriate length scales, one can enhance the effectiveness of internal processes and, therefore, the performance of

photovoltaic devices. In this work, we have implemented this approach in two hybrid material systems—both of which may provide pathways to low-cost, large-area fabrication.¹ The first involves a rod-coil block copolymer which is used both as an optoelectronically active material and as a structure-directing agent to pattern active material into ordered nanostructures. The second system uses electrochemically prepared titania nanotube arrays in concert with in situ polymerization of electron-donating material. In both cases, the characteristic donor-acceptor length scale is controlled to be comparable to the exciton diffusion length throughout the active layer, and the domains are oriented perpendicular to the incident light direction to encourage efficient charge migration.

¹ Use of the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract #DE-AC02-06CH11357. Parts of this work were also supported by the NSF-MRSEC at the University of Chicago.

11:00am **EN+EM+NS+P+A+T+V-ThM10 Electronic Energy Level Alignment in Dye Sensitized Oxide Surfaces**, *S. Rangan*, *J.P. Theisen*, *E. Bersch*, *R.A. Bartynski*, Rutgers University

We have used direct and inverse photoemission to measure the occupied and unoccupied electronic states of N3 dye and determine their alignment with the band edges of single crystal and nanostructured TiO₂ and ZnO substrates. In dye-sensitized solar cell applications, the HOMO-LUMO gap of the dye molecule determines the useful portion of the solar spectrum, and charge transfer of photoexcited electrons to the substrate depends on the alignment of the LUMO to the substrate conduction band edge. We have compared the N3 dye properties on well characterized rutile TiO₂(110) and wurtzite ZnO single crystal surfaces to adsorption on more technologically relevant TiO₂ anatase nanoparticle and ZnO nanorod substrates. Samples were prepared and passivated with a pivalate layer in UHV, then sensitized ex-situ in a solution of N3 dye in acetonitrile. STM measurements show that the pivalic acid forms an ordered overlayer on the TiO₂(110) surface and that the N3 dye molecules can be imaged after sensitization. For N3 on TiO₂(110) as shown below, our spectroscopic measurements show that passivation significantly reduces contamination (presumably from water in the ambient) and that the N3 HOMO occurs at 0.9 eV above the TiO₂ valence band edge, while the LUMO is found 0.5 eV above the conduction band edge. On ZnO, the N3 HOMO occurs at 1.3 eV above the ZnO valence band edge but the N3 LUMO occurs 2.1 eV above the conduction band edge, much higher than what is measured on TiO₂. Comparison with experimental and theoretical values from the literature will be discussed.

11:20am **EN+EM+NS+P+A+T+V-ThM11 Preparation of Nanoporous ZnO Photoelectrode using PEG Template for the Fabrication of Dye-Sensitized Solar Cells**, *M.F. Hossain*, *S. Biswas*, *M. Shahjahan*, *T. Takahashi*, University of Toyama, Japan

Recently, great attention has been paid to dye-sensitized solar cells (DSCs) due to their low fabrication cost. The high light-to-energy conversion efficiencies achieved with dye sensitized solar cells (DSCs) may be attributed to the nanoporous TiO₂ electrode. Zinc oxide (ZnO) is a wide band gap semiconducting material with a similar band gap and electron affinity to those of TiO₂ and has been considered as an alternative material in DSCs applications. Among the various techniques for the preparation of ZnO photo-electrode, the relatively simple sol gel method is the most widely used because of its ability to obtain films with tailored properties on large, curved substrates. In our present study, the nanoporous ZnO films were deposited on SnO₂:F coated glass by sol-gel technique with polyethylene glycol (PEG) as organic template, Zn(CH₃COO)₂·2H₂O as precursor, ethanol as solvent and NH(C₂H₄OH)₂ as chelating agent. The ZnO films have been characterized by the TG-DTA, XRD, SEM AFM, FTIR and UV-VIS systems. The surface morphology of the nanoporous ZnO films strongly depend on the Zn(CH₃COO)₂ concentrations, PEG contents and number of coatings. It was revealed from optical study that the dye absorption increases with the increase of PEG concentrations. Incident photon-to-current conversion efficiency is calculated for all the solar cells with different ZnO thin films to evaluate the economic viability of this technique. The variation of photoelectric conversion efficiency of the solar cells, deposited with different Zn(CH₃COO)₂ and PEG concentrations are discussed with the analysis of different microstructure of the ZnO thin films and the corresponding dye-incorporations.

11:40am **EN+EM+NS+P+A+T+V-ThM12 Metal / Polymer Interfaces: Ca on Polyfluorenes**, *J.A. Farmer*, *J.H. Baricuauro*, University of Washington, *E. Zillner*, Universitaet Erlangen-Nuernberg, Germany, *J.F. Zhu*, University of Science and Technology of China, *C.T. Campbell*, University of Washington

Conjugated polymers are being investigated for use in organic photovoltaic devices and organic electronics due to favorable cost and ease of processing compared to devices based on inorganic materials. The synthetic tunability of polymer-based devices makes them applicable to many technological applications. The creation of cheap organic photovoltaic devices would

significantly improve our ability to harness solar energy and curb the use of fossil fuels. The development of organic LED and organic electronics may give rise to flexible computer displays and hardware that could revolutionize human interaction with computing devices. Crucial to the performance optimization of these devices is understanding the interaction between the metal electrodes and the polymer. The structure and energetics of the interface between Ca and two polyfluorenes, poly(9,9-di-n-hexylfluorenyl-2,7-diyl) (PDHF) and poly(9,9-di-n-hexylfluorenyl-2,7-vinylene) (PDHFV), were studied in ultrahigh vacuum using adsorption microcalorimetry, and low-energy ion scattering spectroscopy. The initial sticking probabilities of Ca on pristine PDHF and PDHFV at 300 K were 0.40 and 0.53, respectively. The sticking probability of Ca on PDHFV began decreasing after ~0.06 ML, and then increased toward unity after ~0.24 ML. Because no similar behavior was seen on PDHF, this decrease in the Ca sticking probability on PDHFV is tentatively ascribed to the presence of the vinyl group. At submonolayer coverages on both polymers, the integrated Ca ISS peak area increased slowly below 1 ML, with a value less than 1 % of a saturated Ca surface at 300 K. These results indicated that most of the Ca at low coverages were below the surface, and not visible to ISS. Beyond 1 ML the Ca peak area increased, and ultimately a continuous Ca film formed at ~50 ML. Based on the variation of Ca peak area with coverage, Ca grows as 3D islands on these polymer surfaces. The heat of adsorption of Ca on PDHF at 300 K was initially 240 kJ/mol and 315 kJ/mol on PDHFV. The heat of adsorption of Ca on PDHF decreased to the heat of sublimation of Ca in ~0.25 ML; the heat of sublimation was reached by ~0.50 ML for PDHFV. The interesting thermodynamic and sticking behavior below 0.50 ML, where Ca is interacting strongly with specific adsorption sites on the polymer will be discussed, and related to the use of these polyfluorenes in device applications.

In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference

Room: 310 - Session IS+NS+TR+NC-ThM

In Situ Spectroscopy – Dynamic Nanoscale Processes

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

8:00am **IS+NS+TR+NC-ThM1 Spatially-Resolved, Surface-Species Concentrations from Electron Reflectivity -- How Graphene Grows on a Metal.** *K.F. McCarty, E. Loginova, P.J. Feibelman, N.C. Bartelt*, Sandia National Laboratories

The rates of many surface processes, and notably of film growth, are governed by the concentrations of mobile adsorbed species. But, few techniques, if any, are available to measure small concentrations of adsorbed species with high spatial resolution. Therefore, the relationship between adsorbates and surface processes typically emerges from indirect observations. Motivated by this limitation, we are developing a technique based on electron reflectivity to obtain local adsorbate concentrations. We measure electron reflectivity changes from the brightness of low-energy electron microscopy (LEEM) images. They yield the local surface-species concentration with high spatial and temporal resolution. This quantitative approach offers the ability to determine the local adsorbate concentrations on heterogeneous surfaces dynamically and under in-situ conditions. We will illustrate the technique's capability with a direct determination of the relationship between mobile carbon adatoms, and the growth of graphene (i.e., of single atomic sheets of graphitic carbon) on Ru(0001), a representative metal. The carbon is supplied by segregation from the bulk metal upon cooling, or by deposition from an evaporator. We find that the reflectivity of low-energy electrons decreases in strict proportion to the concentration of adsorbed, gas-like carbon. By calibrating using known coverages, we can determine absolute adatom concentrations. The graphene growth mechanism was deciphered by simultaneously measuring the instantaneous growth rate of individual graphene islands, and the concentration of surrounding carbon adatoms. The mechanism is very striking and in sharp contrast to metal epitaxy. We found that: the graphene growth rate is limited by carbon atom attachment and not by carbon atom diffusion; the growth rate as a function of supersaturation is highly nonlinear. We will present a model that explains these observations and provides insight into the molecular processes by which graphene grows. Separately, we have determined the carbon adatom concentrations that are in equilibrium with the carbon in Ru's bulk and with graphene, respectively. This information helps understand the competition between the system's three possible carbon configurations: C in bulk Ru, C as adatoms, and C in graphene. This research was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U. S. Department of Energy under Contract No. DE-AC04-94AL85000.

8:20am **IS+NS+TR+NC-ThM2 Electron Diffraction Characterization of In Situ Deformation of Gallium Oxide Nanobelts.** *J.M. Vaughn, M.E. Kordesch*, Ohio University

A transmission electron microscope fitted with a home-built nano manipulator for in situ mechanical deformation of nanobelts is reported. Nanobelts of beta Ga₂O₃ are grown by the vapor transport method from gallium metal in an argon gas flow at 950 degrees centigrade. A single 2.5 um wide, approximately 200 nm thick and 10's of microns long belt is deformed by direct contact with the manipulator probe. Deflections of up to 180 degrees are possible without fracture of the belt. A series of TEM diffraction patterns are collected during belt deformation. The diffraction pattern is observed to distort as the belt is deformed. In addition to the distortion of the monoclinic belt diffraction pattern, additional diffraction spots are observed through belt deformation. Analysis of the additional spots and deflection in preexisting spots reveal simultaneous lengthening and contracting in measured planar spacings. This data is modeled by lattice deformations, which allows for such a large deformation of the belt. The lattice deformation model results in the lattice constant 'c' having two simultaneous values for any given diffraction pattern. The maximum simultaneous deformation in 'c' is measured to be 11.3 and 16.3 Angstroms. Lattice constant 'a' behaves similarly with values 5.1 and 7.9 Angstroms. Finally, the lattice deformation model is compared to a plane slipping model, which may also explain the additional spots and deformation.

Funded by a 2005 AVS Undergraduate Research Award.

8:40am **IS+NS+TR+NC-ThM3 Direct Observation of Carbon Nanotubes Formation from Selectively Fabricated Catalyst Particles.** *R. Sharma*, Arizona State University

INVITED

Carbon nanotubes (CNT) have many advantageous properties with potential for diverse advanced materials applications if their controlled synthesis can be optimized. For some applications, such as field-emitting displays, in-situ deposition of catalyst particles is an important step for CNT synthesis. Post synthesis characterization of CNTs is frequently performed using transmission electron microscopy (TEM) techniques. Therefore environmental scanning transmission electron microscope (ESTEM) is perfectly suited for in situ observations of nucleation and growth of CNTs. A modern ESTEM, equipped with a field-emission gun (FEG), energy filter or electron energy loss spectrometer, scanning transmission electron microscopy (STEM) coils, and bright and dark field detectors, is a versatile tool for understanding their synthesis process at nanometer level. We have employed a modified Tecnai-F20 ESTEM to understand the catalytic chemical vapor deposition process for CNT synthesis. Time, temperature and pressure resolved digital video imaging is used to determine the effect of synthesis condition on their structure and morphology. Statistical analysis of the CNTs formed under varying synthesis conditions show that 95% yield for SWCNTs can be achieved at 650oC in 1 mTorr of acetylene using Ni as catalyst. We have combined electron beam induced decomposition (EBID) of nonacarbonyl diiron (Fe₂(CO)₉) to fabricate arrays of Fe particles that are catalytically active for the thermal decomposition of acetylene to form multiwall CNTs. Atomic resolution video images are used to understand the nucleation and growth mechanism from crystalline catalyst particles. Detailed phase transformation of the catalyst particle and CNT growth mechanisms from selectively fabricated Fe particles will be presented.

9:20am **IS+NS+TR+NC-ThM5 Investigating Catalyst Behavior Prior to and during the Growth of Carbon Nanotubes with Environmental Cell TEM.** *E.A. Stach, S.M. Kim, D.N. Zakharov, P. Amama, C. Pint, R.H. Hauge, B. Maruyama*, Purdue University

INVITED

In order to understand how carbon nanotubes form, one must have a detailed understanding of the size, shape and evolution of the catalysts responsible for their nucleation and growth. In this presentation, we describe our recent studies in understanding the evolution of Fe catalysts deposited on alumina during the so-called supergrowth of carbon nanotubes. These studies rely heavily on the exploitation of the unique capabilities of environmental transmission electron microscopy to observe at the atomistic scale how catalyst nanoparticles transform under varying regimes of temperature and pressure. We will show that modifications of the substrate treatment and carrier gas atmosphere have a strong effect on catalyst coarsening. In particular, we find the presence of H₂O – the key ingredient in supergrowth – leads to a reduction in the Ostwald ripening of the Fe catalysts, thereby leading to denser nanotube carpets. Additionally, under conditions identical to those used in supergrowth, we confirm the diffusion of Fe into the Al₂O₃ supporting layer. This effect could play a significant role in the catalyst surface density during supergrowth, as well as provide another route in which carpet growth may terminate. These studies are correlated with real time TEM observations of the Ostwald ripening rate of Fe nanoparticles on different supports in H₂ and H₂ + H₂O atmospheres, and on the nucleation and growth of the tubes themselves.

10:40am **IS+NS+TR+NC-ThM9 The Large Chamber SEM: A New Tool for Non-Destructive Testing**, *M. Klein*, VisiTec Microtechnik GmbH Germany

Although conventional SEMs are limiting the size of objects or production equipment to be inspected scanning-electron-microscopes (SEM) are well known instruments for the use in nearly any micro-technology. A more flexible tool to allow a visual control of micro-mechanical manufacturing, assembling, and testing process is not yet described. Analyzing human behaviour during the visual investigation of objects and adapting this behaviour, lead to a new concept of electron microscopes called Large Chamber Scanning Electron Microscope (LC-SEM) In this case the electron optics is installed within the vacuum chamber and can be positioned freely inside this chamber. This change of kinematics combines conventional SEM's advantages of high resolution and high depth of focus with the possibility to observe and test micro-mechanical handling and assembly equipment. Using the LC-SEM allows a new understanding of these processes. The paper describes development, functionality, and applications of this LC-SEM. There are fields of application within the microtechnology and macro-technology as well. The paper is focused on the use of the LC-SEM within microtechnology, microassembly and micromechanics. For nearly any process of manufacturing in the microworld a transmission of information to the human macroworld is necessary. For this purpose especially a visual control is important. Optical microscopes are of limited use due to their small magnification and depth of focus (e.g. an optical microscope offers just a depth of focus of 2 μm at an enlargement of 100). Conventional scanning-electron-microscopes (SEM) offer a much better resolution and a better depth of focus but are limited in the size and weight of objects to be inspected because of the usually small vacuum-chambers. Conventional goniometer tables are constructed with a very high precision and for a load carrying capacity up to 20 kg. The load carrying capacity is greatly restricted in that in conventional goniometer tables it is necessary to provide numerous moving guide elements and slide carriages, which for cost reasons are only designed for a moderate load. Therefore an Large Chamber- Scanning Electron Microscope as a tool to support the investigation of microproduction has been developed which opens new fields of application to electron microscopy. Key to the functionality of this microscope is the adaption of human behaviour during the investigation of objects.

11:00am **IS+NS+TR+NC-ThM10 In-situ Electron Microscopy and Spectroscopy Studies of Interfaces in Advanced Li-ion Batteries under Dynamic Operation Conditions**, *C.M. Wang, Z.G. Yang, S. Thevuthasan, J. Liu, D.R. Baer*, Pacific Northwest National Laboratory, *N. Salmon*, Hummingbirds Scientific

Repeated charging and discharging of a Li-ion battery induces microstructural evolutions both at the interface between the electrolyte and the electrode and within the electrode (active materials) due to Li migration. Although it has been established that this structural evolution is responsible for the failure of such batteries, the mechanisms of the microstructural evolution as a function of charging/discharging are not well understood. Advanced diagnostic tools such as electron microscopy along with other surface and bulk sensitive tools, usually in ex-situ mode, have been used to probe into this scientific issue. However, it has been realized that characterizing this interface using an ex-situ capability is a challenge as the materials will be altered during sample preparation and processing and the interface will be stable only under the operating conditions. In-situ capabilities that enable the observation of the structural and chemical changes during the dynamic operation of battery are needed to address this scientific and technological challenge. We have been developing an environmental holder capability for TEM, trying to gain fundamental scientific understanding of the chemical and structural evolution at the interface between the electrolyte and the electrode as well as within the electrodes under the dynamic operation conditions of the Li battery system. In the preliminary research work, we have explored the interface change using TiO₂ nanowire as the anode material. Transmission electron microscopy (TEM) imaging, electron diffraction, and electron energy-loss spectroscopy (EELS) were used to probe into these structural evolutions during the operation of the battery.

11:20am **IS+NS+TR+NC-ThM11 The Dynamics of the Initial Oxidation Stages of Cu and Cu Alloys**, *J.C. Yang*, University of Pittsburgh **INVITED**

Surface oxidation processes play critical roles in environmental stability, high temperature corrosion, electrochemistry, catalytic reactions, gate oxides and thin film growth as well as fuel reactions. Much is known about oxygen interaction with metal surfaces and about the macroscopic growth of thermodynamically stable oxides. At present, the transient stages of oxidation – from the nucleation of the metal oxide to the formation of the thermodynamically stable oxide – represent a scientifically challenging and technologically important terra incognita. Furthermore, since environmental

stability is an essential property of most engineered materials, many theories exist to explain its mechanisms. However, nearly all classical theories assume a uniform growing film, where structural changes are not considered because of the previous lack of experimental methods to visualize this non-uniform growth under conditions that allowed for highly controlled surfaces and impurities. One can now see structural changes under controlled surface conditions, by in situ ultra-high vacuum transmission electron microscopy (UHV-TEM), and thereby challenge the commonly used assumption of a uniform oxide formation. Here, we present a systematic study of the dynamics of the initial and transient oxidation stages of a metal and alloys with in situ UHV-TEM. We have previously demonstrated that the formation of epitaxial Cu₂O islands during the transient oxidation of Cu(100), (110) and (111) films bear a striking resemblance to heteroepitaxy, where the initial stages of growth are dominated by oxygen surface diffusion and strain impacts the evolution of the oxide morphologies. We are presently investigating the early stages of oxidation of Cu-Au and Cu-Ni as a function of oxygen partial pressures, temperatures and composition. For Cu-Au oxidation, the oxidation mechanisms change due to the limited Cu around the oxide island leading to a dendritic growth of the Cu₂O islands. For Cu-Ni oxidation, the addition of Ni causes the formation Cu₂O and/or NiO where the oxide type(s) and the relative orientation with the film depend on the Ni concentration, oxygen partial pressure and temperature. This research program is funded by the National Science Foundation (DMR 0706171) and Department of Energy (DE-FG02-07ER46446).

Nanomanufacturing Focus Topic

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

Printable Lithography and Processing

Moderator: D. Janes, Purdue University

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

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

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

Nanometer scale metallic contacts which can be directly deposited on planar substrates are of growing importance in view of future applications involving the integration of molecular electronics with current silicon technology. Here, a method which may provide well defined nanogap electrodes of predetermined spacing in a reproducible manner, without the need of sequential direct writing techniques, would be highly advantageous. We present a novel technique using direct high-resolution metal nanotransfer printing and demonstrate its capability to fabricate nanogap electrodes of predetermined spacing on a solid substrate such as silicon. The one-step transfer process is economical, simple and fast, and preserves the mold for manifold transfer. Using molecular beam epitaxy (MBE) a sandwich-like structure is grown with monolayer precision, comprising few nanometer thick GaAs layers embedded in AlGaAs. This structure is cleaved atomically flat perpendicular to the <110> crystallographic direction. Subsequently, the exposed GaAs layers are wet chemically etched

thereby generating a 3D grating structure with nanometer-resolution at their edges. This structure serves as mold for nanotransfer printing: By coating the grating surface with a metallic thin film of PdAu/Ti (7/5 nm) and pressing the mold against a Si/SiO₂ substrate the patterned PdAu/Ti sandwich structure is directly transferred onto the surface. This one-step process does not require any flexible buffer layer or additional organic adhesion promoters. We report on a series of successful transfer experiments using different multi-line molds with varying aspect ratios and linewidths down to below 10 nm. In particular, we demonstrate electrically functional PdAu metal electrode pairs with separations down to 25 nm, featuring lead resistances of the order of kΩ and gap isolation in excess of 50 GΩ up to 2 Volts.

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

High quality organic & carbon-based thin-film transistors (TFT) have been successfully fabricated onto plastic substrates using transfer printing. With this printing process, each device component (conducting electrodes, polymer dielectric layer and semiconductor layer) was printed using only pressure and temperature, eliminating all chemical processing on the plastic device substrates. Pentacene (Pn), poly(3-hexylthiophene) (P3HT), carbon nanotube mats (CNTM) and graphene TFTs were all fabricated on polyethylene terephthalate (PET) substrates. Bottom gate, bottom source/drain devices yielded mobilities of 0.237 cm²/Vs for Pn and 0.04 cm²/Vs for P3HT. Bottom-gate CNTM TFTs exhibited p-type behavior, mobilities of 13.7 cm²/Vs, on/off ratio of 10³ and minimal hysteresis. Top-gate graphene TFTs exhibited mobilities of 1.0x10⁴ cm²/Vs for holes and 4x10⁵ cm²/Vs for electrons. The organic TFT devices were fabricated using a variety of polymer dielectric layers including poly(hydroxystyrene) (PHS), polystyrene (PS), polycarbonate (PC) and poly(methylmethacrylate) (PMMA). The resulting TFTs showed little variation in mobility, but strong variation in threshold voltage for different dielectric layers. The transfer printing process relies primarily on differential adhesion for the assembly of both patterned and unpatterned films onto a common flexible, plastic substrate. It is a simple and robust process that is compatible with a wide range of materials. Plasma processing techniques are being adapted to control the surface energy of polymer and plastic surfaces in order to increase adhesion forces at the interface between polymer dielectric layers and plastic substrates. The printability and surface characterization of plasma treated polymer/plastic surfaces will be discussed. One goal of this work is to enable the incorporation of many different dielectric materials (including 10 test polymer dielectric films) and substrate materials (including 11 test plastic substrate sheets) into the fabrication of flexible electronics. This work partially supported by the Office of Naval Research and the Laboratory for Physical Sciences. *E.H. Lock, NRC/NRL Postdoctoral Research Associate.

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

The fabrication of ordered microstructures of colloidal crystals is increasingly attracting interest due to their potential applications as sensing, optical and photonic band-gap materials. Depending on the application (i.e. chemical or biochemical sensors, photonic chips), specific microstructured configurations of the colloidal crystal are needed. Most of the methodologies reported so far for the production of colloidal crystals are based on the directed self-assembly of micro or nanospheres, in which patterning and formation take place simultaneously in a template created beforehand, normally by the modification of the surface chemical or topographic properties. However, methods for patterning the colloidal film after it has been formed are scarce. The interest in such methods lies in the fact that they allow fine control over the microstructure of the colloidal film by selective removal of a single layer of close-packed nanospheres. Recent top-down approaches to the micropatterning of nano-beads are based on soft lithography lift-off processes using PDMS stamps. Removal of nano-beads strongly adhering to the substrate is however hard to realize and limitations related to the PDMS structural properties, i.e. deformation, appear. Normally, the beads have to be loosely attached so that bead transfer or removal is not inhibited. In this work, a new soft-lithographic method for micro-patterning nano-bead arrays, based on structured poly(methyl methacrylate) (PMMA) and using a nanoimprinter apparatus, is

described. The properties of the PMMA, with respect to hardness and flexibility, are promising for resolving sub-micron patterns of nanoparticles. The use of the nanoimprinter allows careful control of the temperature and pressure during the contact-stripping operation; this ensures accurate removal of nanoparticles over large areas even when they are strongly attached to the substrate. Patterns of polystyrene nano-beads in several micro-scale configurations have been obtained using beads of different diameters (100 ~ 500 nm) and with different levels of adherence to the substrate. The micropatterning of nanobeads thus achieved has been then used to create surfaces with nanoscale chemical contrast inside the micro-patterns. Having structured regions separated by flat, unstructured regions is advantageous for many applications, such as sensing platforms for parallel detection or cell culture platforms for examining cell-surface interactions at the nanoscale.

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

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

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

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

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

Nano-Imprint Lithography (NIL) is one of the most promising candidates (ITRS road map 2007) to address the 32 nm node and below thanks to a

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

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

For the realization of sub-10 nm resolution, soft lithography alternatives to conventional photolithography are being considered. In soft lithography, the imprint material is used for pattern definition and also as a mask for pattern transfer into underlying layers. For successful nanoscale pattern transfer, a rational design of polymer resists and an atomistic understanding of plasma-polymer interactions are required. In this study, the effect of different species of the plasma (ions, UV, neutrals) on model polymers with distinct chemical structure (styrene-, acrylate-, methacrylate-, and vinylpyridine-based) was investigated. Model polymers were exposed to Ar and C₄F₈/Ar plasmas. Modification of the polymer surface was characterized using in situ ellipsometry, X-ray photoelectron spectroscopy, and atomic force microscopy (AFM). The effect of crosslinking and chain scission reactions, as well as oxygen containing functional groups, is considered. Mechanisms of plasma-polymer interactions for the different polymer structures are proposed. Finally, select polymers (poly(styrene), poly(α -methylstyrene), and poly(4-vinylpyridine)) were used as imprint materials, patterned, and plasma processed. The top and sidewall profiles and morphologies were examined by AFM and secondary electron microscopy before and after exposure. The importance of polymer structure and plasma species on pattern transfer in soft lithography is discussed.

Nanometer-scale Science and Technology

Room: 311 - Session NS+NC-ThM

Nanoscale Assembly

Moderator: L.E. Ocola, Argonne National Laboratory

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

The combination of supramolecular networks with thiol-based self-assembled monolayers (SAMs) offers interesting opportunities as the flexibility in surface functionalisation afforded by SAMs can be carried to an unprecedented level of precision. The scope for nanotechnological applications broadens even further by processing these hybrid systems in an electrochemical environment. Recently we have shown that an extended bimolecular network on Au(111) with a periodicity of 3.5 nm can be prepared from a solution of perylene-3,4,9,10-tetracarboxylic di-imide (PTCDI) and 1,3,5-triazine-2,4,6-triamine (melamine) and that this open

hexagonal structure is sufficiently robust to act as template for thiol adsorption.¹ Proper control of the preparation parameters allows filling of the network pores without altering the framework. This leads to patterned self-assembled monolayers that reflect the periodicity and symmetry of the network with islands of thiol molecules kept apart by the PTCDI-melamine backbone. This hybrid structure can then be used as nanoscaled template for the electrodeposition of metal. Using scanning tunneling microscopy the underpotential deposition (UPD) of Cu was investigated where a monolayer of Cu is intercalated at the molecule-substrate interface. In contrast to continuous thiol SAMs where Cu UPD originates at major defects in the SAM and spreads by interfacial diffusion,² the hybrid structure acts as a barrier against interfacial diffusion and, thus, confines metal electrodeposition to the thiol-filled cells.¹ As a result a regular pattern forms where metal UPD islands are separated by the PTCDI-melamine framework.

¹ Madueño, R.; Räsänen, M.; Silien, C.; Buck, M. *Nature* 2008 (in print).

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

8:20am **NS+NC-ThM2 FIB Induced Self-Assembly of InAs Quantum Dots.** *M.J. Noordhoek, J.Y. Lee, H. McKay, A. Dehne, P. Rudzinski, J.M. Millunchick, University of Michigan - Ann Arbor*

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

8:40am **NS+NC-ThM3 Fabrication and Characterization of Conjugated Organosilicon Nanostructures with UHV STM and X-Ray Spectroscopy.** *M.A. Walsh, J.-C. Lin, J.-H. Kim, Northwestern University, K.H. Bevan, Purdue University, G.Y. Stokes, F. Geiger, S.T. Nguyen, M.J. Bedzyk, M.C. Hersam, Northwestern University*

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

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

9:00am **NS+NC-ThM4 The Driving Forces Underlying the Formation of Chiral Domains of Fluorinated Diacids on HOPG**, *S.N. Patole, C.J. Baddeley, M. Schuler, D. O'Hagan, N.V. Richardson*, University of St Andrews, UK

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

9:20am **NS+NC-ThM5 Potential-Controlled Force Curve Measurements between Electroactive Self-Assembled Monolayers**, *Y. Yokota, T. Yamada*, RIKEN (The Institute of Physical and Chemical Research), Japan, *M. Kawai*, RIKEN and The University of Tokyo, Japan

It has been known that atomic force microscopy (AFM), in addition to providing topographic information, can be used to discriminate surface functional groups.¹ One of the most established methods is based on the surface sensitivity of the adhesion force between the tip and sample. Several groups have tried to electrochemically modify the interfacial properties by applying the appropriate potential.² We present the force curve measurements between electroactive ferrocene (Fc)-terminated Self-assembled monolayers (SAMs) under independent control of the tip and sample potentials. From the cyclic voltammetry of Fc SAM, the electronic states of Fc moieties in each force curve measurement were characterized.³ The adhesion force of Fc SAM was drastically changed with the oxidation state of the Fc moieties (Fc or Fc⁺). According to the previous wettability measurements, hydrophobicity of the Fc-terminated SAMs is decreased with the oxidation of Fc moieties.⁴ Because the adhesion force in aqueous solutions is largely determined by hydrophobicity, the oxidation-state dependence of the hydrophobicity is responsible for the adhesion force change. We performed two control experiments using methyl (CH₃) and amino (NH₃⁺)-terminated SAMs. Unlike in the case of Fc SAM, the force curves, both the approach and retraction curves, did not change with the applied potential. This indicates that the force curve measurements in this study are largely regulated by the effects of surface functional group rather than charging of double layer. Although Fc⁺ and NH₃⁺ SAMs contain almost the same amount of functional groups, their repulsive forces between the tip and sample considerably differed depending on the surrounding environment of counter anions. These results demonstrate that this AFM-based technique can be a powerful tool for investigating the ion pair formations.

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

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

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

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

9:40am **NS+NC-ThM6 Self-Assembly of Nanostructures and Nanocomposites using De Novo Designed Helix- Loop- Helix Polypeptides**, *D. Aili, K. Enander*, Linköping University, Sweden, *L. Baltzer*, Uppsala University, Sweden, *B. Liedberg*, Linköping University, Sweden

Self-assembly has emerged as a promising and powerful technique for fabrication of complex hybrid materials and nanocomposites. This contribution will discuss how folding of a set of de novo designed polypeptides can be utilized for the assembly of fibers, fibrous nanostructures and gold nanoparticles. The 42-mer polypeptides fold into four-helix bundles upon dimerization. The peptides are rich in either Glu or Lys which render them a high negative or positive net charge, respectively. Charge repulsion prevents homodimerization at neutral pH while promoting

heterodimerization through the formation of stabilizing salt bridges. For the Glu rich polypeptide, homodimerization can be induced at acidic (pH<6) or by addition of certain metal ions, such as Zn²⁺.¹ The polypeptides have a single Cys in the loop region to facilitate directed immobilization onto gold substrates. The Cys can also be utilized to connect two polypeptides via a disulphide bridge. The disulphide-linked polypeptides spontaneously and rapidly assemble into micrometer long fibers with a diameter < 5 nm as a result of a propagating association mediated by folding. In addition, the fibers have been observed to assemble into highly symmetric nano-rings. Furthermore, the polypeptides enable reversible, folding induced assembly of gold nanoparticles with defined interparticle distances.¹ Aggregation of polypeptide functionalized nanoparticles can be induced in a number of ways utilizing the highly specific interactions involved in both homodimerization and hetero-association. Furthermore, particle aggregation can be utilized to induce folding of the immobilized polypeptides. Helix-loop-helix polypeptides can also be utilized as a robust scaffold, or synthetic receptor, for biosensor applications.² The sensor scaffold was, as a proof of concept, site-selectively modified with a benzenesulfonamide moiety that provides a specific recognition site for Human Carbonic Anhydrase II (HCAII). Gold nanoparticles functionalized with the sensor polypeptide enabled simple colorimetric detection of HCAII.

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

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

10:40am **NS+NC-ThM9 Non-IPR C₆₀ Solids**, *D. Löffler*, Universität Karlsruhe, Germany, *N. Bajales*, Universidad Nacional del Litoral-CONICET, Argentina, *M. Cudaj, P. Weis, A. Böttcher, M.M. Kappes*, Universität Karlsruhe, Germany

Thin monodisperse films consisting of primarily non-IPR C₆₀ isomers (IPR = Isolated Pentagon Rule) have been generated by depositing vibrationally excited C₆₀ ions on HOPG and subsequently sublimating the undesired IPR C₆₀(I_h) isomer from the deposited mixture. The deposition procedure is based on UHV-compatible soft-landing of mass-selected carbon cluster ions on substrates (Low Energy Cluster Beam Deposition, LECBD). Beams of non-IPR C₆₀ cations were produced by electron-impact mediated heating and ionization of various buckminsterfullerenes. The associated excitation processes activate the Stone-Wales rearrangement of carbon atoms in the cage (S-W), which creates non-IPR sites on C₆₀ cages. The relative amount of these S-W isomers, C₆₀(S-W), deposited from the beam of hot C₆₀ ions scales with the kinetic energy of electrons used for excitation/ionization. Essentially pure C₆₀(S-W) films were obtained simply by heating as deposited (mixed isomer) films up to ~600 K. This results in the thermal desorption of most IPR cages, C₆₀(I_h). The topography of the resulting films, as studied by means of AFM, is governed by the aggregation of the C₆₀(S-W) cages and reflects intercage bonds constituted by non-IPR sites. These covalent intercage bonds are responsible for the higher stability of the C₆₀(S-W) films as mirrored by a sublimation offset at ~1100 K (compared to C₆₀(I_h) which sublimates at ~ 550 K). In contrast to the characteristic doublet structure of the HOMO-derived band in C₆₀(I_h) films, the valence band of the C₆₀(S-W) films exhibits a triplet with a well distinguishable additional peak at a binding energy of ~2.6 eV. This results from electronic modifications induced by intercage bonds. The C₆₀(S-W) films exhibit a narrower HOMO-LUMO gap than found for C₆₀(I_h) films.

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

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

effectiveness of such an assembling approach, thus envisioning promising application for the nanostructured materials in optoelectronic and sensing field.⁴ Acknowledgements: PRISMA-INSTM 05MADA1 and EC NaPa-NMP4-CT-2003-500120 projects are acknowledged for the financial support.

¹E. Fanizza et al., (2007) *Advanced Functional Materials*, 17, 201

²N. Depalo et al., *J. Phys. Chem B* (2006), 110, 17388

³E. Sardella et al, *Plasma Process. and Polym.* (2006) 3, 456

⁴R. Comparelli et al. in: *Nanomaterials for Biosensors Vol. 8 Nanotechnologies for the Life Sciences*; WILEY-VCH, 2006, 123

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

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

Surface Science

Room: 207 - Session SS1-ThM

Growth and Etching on Surfaces

Moderator: A.A. Baski, Virginia Commonwealth University

8:00am **SS1-ThM1 Step Etching and Restructuring on Cl₂-exposed, Cl-saturated Si(001)-(2x1)**, *R.E. Butera, J.H. Weaver*, University of Illinois at Urbana-Champaign

We use scanning tunneling microscopy and density functional theory to investigate the etching of rebonded step atoms and the concomitant restructuring of the B-type step for Cl₂-exposed, Cl-saturated Si(001)-(2x1) at 675 K ≤ T_S ≤ 725 K. Previous studies have shown that these exposure conditions allow uptake beyond "saturation," providing inserted Cl moieties, Cl_i, that lead to novel etching patterns without regrowth structures. Using surfaces with narrow terraces, we show that Cl_i diffuses to the rebonded S_B step and our calculations identify a stable adsorption configuration that bridges the rebonded and non-rebonded step atoms. Step etching removes the rebonded step atoms and results in the formation of an atom-wide vacancy line (AVL) along the step. Step restructuring begins with AVL diffusion into the terrace and ends with step retreat by one dimer unit to reestablish the rebonded S_B step structure. We use theory and experiment to show that restructuring is driven by the reduction of step energies and adsorbate-adsorbate repulsion. These results identify the rebonded step structure as the most energetically favored step structure on Cl-terminated Si(001)-(2x1).

8:20am **SS1-ThM2 Ion Scattering from Au Nanoclusters formed by Buffer Layer Assisted Growth**, *S. Balaz, J.A. Yarmoff*, University of California, Riverside

Ion scattering is used to probe the atomic and electronic structure of Au nanocrystals grown by Buffer Layer Assisted Growth (BLAG). Amorphous solid water (ASW) was adsorbed as a buffer layer onto SiO₂/Si(111) at liquid nitrogen temperature. Au was then evaporated onto the buffer layer to form nanoclusters. The samples were subsequently annealed to room temperature, causing the water to desorb and the clusters to deposit directly onto the substrate. Time-of-flight (TOF) spectroscopy was used to measure 2 keV 7Li⁺ and 39K⁺ scattered from Au atoms both at low temperature when the clusters reside atop the buffer layer, and after desorbing the water. Small Au depositions yielded a sharp single scattering peak that indicates single layer structures. Following larger depositions, multiple scattering features were present indicating the formation of

multilayer nanoclusters. The neutral fraction of scattered K⁺, which provides an indication of the filled quantum states, starts at ~50% for small Au coverages and decreases with further deposition, indicating changes in the quantum state occupancy with cluster size.

8:40am **SS1-ThM3 Competition Between Particle Formation and Burrowing: Gold on Bismuth**, *P. Swaminathan, J.S. Palmer, J.H. Weaver*, University of Illinois at Urbana-Champaign

We discuss Au nanoparticle formation on Bi films under conditions where burrowing of the formed Au particles into the film is competitive to growth. Burrowing occurs because the surface free energy of Bi is lower than that of Au, the Au-Bi interface energy is small, and the kinetics, in terms of high surface and grain boundary diffusion rates, are favorable. The negligible solid solubility of Au in Bi at low temperatures means that alloy formation effects can be neglected. By changing deposition temperatures and rate, we show the effect of burrowing on the final size distribution. These results are supported by kinetic Monte Carlo simulations that include atom impingement, surface diffusion, and burrowing rates as parameters. Burrowing broadens and splits the size distribution as small particles are removed from the surface continuously and those that remain grow to larger sizes by adatom capture. These results are important for systems where nanostructures are assembled on low surface energy substrates, and they specify the conditions where growth is affected by burrowing.

9:00am **SS1-ThM4 Optical Anisotropy Induced by Oblique Incidence Ion Bombardment of Ag(001)**, *H. Wormeester, F. Everts, B. Poelsema*, University of Twente, The Netherlands

Oblique incidence ion sputtering has become a widely used method for the creation of highly regular patterns of lines and dots. On a Ag(001) surface oblique incidence sputtering creates a ripple pattern that exhibits plasmonic features. The photon energy of this plasmonic feature depends on the ripple periodicity. The development of these anisotropic features is measured in-situ with the optical technique Reflection Anisotropy Spectroscopy (RAS). The ion induced nanopatterns are prepared using 2 keV Ar ions with a flux of a few Ma/cm² in a temperature range of 300 - 420K. With RAS, a periodicity of ripples above 200 nm is measured by a shift in photon energy of the plasmon resonance. Features with a smaller periodicity show a plasmon resonance around 3.65 eV. For very grazing incidence sputtering, 80° polar angle of incidence, only a resonance feature around 3.65 eV is observed. High resolution LEED measurements after sputtering confirm the formation of 1D nanoripples. For a polar angle of incidence of the ion beam of 70° a shift in the maximum of the plasmon resonance feature is observed. These spectra can be well described within the Rayleigh-Rice description for scattering from a slightly rough surface. The formation of nanoripples, i.e. a 1D roughening of the surface perpendicular to the direction of the ion beam, suffices to describe the measured optical data. The evolution of the rms, wavelength and wavelength distribution of the ion bombardment induced nanoripples is obtained from in-situ measurements. For a polar angle of the ion beam of 61° we find that also the roughening in the direction along the nanoripples has to be taken into account to describe the optical spectra.

9:20am **SS1-ThM5 Producing Ultraflat Si(100) Surfaces with Aqueous Etching: STM and FTIR Yield Mechanistic Insights**, *M.A. Hines*, Cornell University **INVITED**

The production of atomically flat Si(100) surfaces is a long-standing technological challenge, as Si(100) is the basis for today's microelectronic devices. From a chemist's standpoint, the study of etch morphologies yields fascinating insights into surface chemistry, as etching reactions literally write a record of their reactivity on the etched surface. We use a combination of STM and vibrational spectroscopy to show that a simple aqueous etchant can produce Si(100) surfaces of surprising and unprecedented smoothness. The etched surface is characterized by long rows of H-terminated silicon atoms. This structure is favored because it minimizes interadsorbate repulsion on the surface. A new technique for the analysis of surface infrared absorption spectra¹ is used to deconvolute the well-known vibrational spectrum of the etched H/Si(100) surface. This analysis yields a relatively simple picture of the structure of the etched surface -- a picture that is much simpler and much smoother than previous analyses. The significant effects of interadsorbate strain on the spectrum will also be discussed. Finally, the influence of gas evolution on the mesoscale roughness of etched surfaces will be discussed. Again, the fascinating patterns that form during etching yield new insights into the chemistry of etching.

¹I. T. Clark, B. S. Aldinger, A. Gupta, and M. A. Hines, *J. Chem. Phys.* 128, 144711 (2008).

10:40am **SS1-ThM9 Focused Ion Beam (FIB) Patterning and Selective Decomposition of III-V Semiconductors**, *K.A. Grossklau, J.M. Millunchick*, University of Michigan

The use of focused ion beams (FIB) has been identified as a method by which III-V substrates may be modified in a variety of ways for subsequent film growth. Presented here are the initial results of research exploring the use of FIB to modify III-V semiconductor surfaces and directly mill 3-D square array and hole patterns. Studies thus far have examined the FIB response of GaAs, InAs, and InP wafer substrates, along with AIAs layers grown on GaAs substrates. Each of these materials has been found to respond differently to the ion beam. Through use of the FIB to chemically decompose selected sample areas, group III nanostructures have been produced in patterned areas on InAs, GaAs, and InP, while AIAs has been shown to be resistant to metal nanostructure formation. The appearance and distribution of these nanostructures has been found to depend on the ion dose used for patterning. Nanostructure size and distribution on InP in particular has been shown to vary with ion dose and time from milling. It has been shown that ridge-like features act as preferential sites for the self-assembly, providing a method for the regular placement of metallic nanostructures. The causes for the different FIB response of each material will be discussed relative to their different material properties and predicted ion beam response. Proposed routes for controlling or eliminating the formation of group III nanostructures and the results of preliminary attempts to do so will be presented. The FIB patterning conditions and the patterns created thus far will be discussed in terms of their suitability for the creation of modified substrates upon which low defect density lattice mismatched films may be grown. As part of this additional patterning types and geometries for future examination and film growth experiments will also be discussed.

11:00am **SS1-ThM10 Electron Induced Deposition of Amorphous Carbon Nitride Films**, *H. Fairbrother, J.M. Gorham, J.D. Wnuk*, Johns Hopkins University

Nitrogen doped carbonaceous films have attracted intense experimental and theoretical interest due to the beneficial effects that nitrogen incorporation has on the wear resistance, adhesion characteristics and optical/electronic properties of amorphous carbonaceous films. Motivated by a desire (i) to understand the structure of amorphous carbon nitride films deposited by electron beam induced deposition (EBID) and (ii) to better understand the role that electrons play in moderating the microstructure and film growth of plasma deposited nitrogen doped carbonaceous films, we have studied the deposition of amorphous carbon nitride films from a 1,2-diaminopropane precursor molecule exposed to low energy (< 5keV) electrons. Our experimental approach involved initially depositing nanometer-scaled thin films of the precursor at low temperatures under ultra-high vacuum (UHV) conditions. The influence of electron irradiation on the chemical composition and bonding within the deposited film was then probed using reflection absorption infrared spectroscopy (RAIRS) in combination with x-ray photoelectron spectroscopy (XPS), while complementary data of the gas phase species evolved during electron irradiation were studied with mass spectrometry (MS). The electron stimulated decomposition of adsorbed 1,2-diaminopropane proceeded with the loss of both C-H and N-H bonds and the formation of an amorphous carbon nitride film. Upon more prolonged electron beam irradiation, nitrile (C≡N) species were formed. This observation suggests that electrons may play an important role in moderating the chemical structure of plasma deposited carbon nitride films. Hydrogen was the principal gas phase product evolved during film deposition. The loss of C-H and N-H bonds from the film, as well as the hydrogen evolution, were modeled by a first-order kinetic process with a rate constant that increases linearly with electron fluence. This information obtained under UHV conditions will also be compared with data obtained from the growth kinetics and structure of amorphous carbon nitride films grown using EBID of vapor phase 1,2-diaminopropane, studied using a combination of auger electron spectroscopy and atomic force microscopy. Results will also be presented on the role that the incident electron energy and the substrate exert in determining reaction rates and growth kinetics.

11:20am **SS1-ThM11 Low Energy Electron Induced Decomposition of Adsorbed Methylcyclopentadienylplatinum(IV)-trimethyl**, *J.D. Wnuk, J.M. Gorham*, Johns Hopkins University, *W.F. Van Dorp*, Rutgers, the State University of New Jersey, *C.W. Hagen*, Delft University of Technology, The Netherlands, *T.E. Madey*, Rutgers, the State University of New Jersey, *D.H. Fairbrother*, Johns Hopkins University

Electron beam induced deposition (EBID) of volatile organometallic precursors has emerged as an effective and versatile route to creating 2-D and 3-D metallic nanostructures. In an effort to better elucidate the process by which these structures are formed, we have studied the effect of low energy (500eV) electrons on sub-monolayer coverages of methylcyclopentadienylplatinum(IV)-trimethyl (MeCpPtMe₃) adsorbed onto gold substrates in situ under ultra-high vacuum conditions using a

combination of mass spectrometry, reflection absorption infrared spectroscopy (RAIRS) and x-ray photoelectron spectroscopy (XPS). Electron beam irradiation produces a carbonaceous film that contains Pt atoms in an oxidation state which is intermediate between metallic Pt and the parent Pt(IV) species. XPS analysis of the Pt(4f) region indicates that the conversion of Pt species follows first order kinetics, with a rate constant proportional to the target current. Electron stimulated decomposition of adsorbed MeCpPt(IV)Me₃ is also accompanied by the evolution of gas phase methane and hydrogen as well as the loss of the C-H bonds associated with the parent MeCpPt(IV)Me₃ compound. The kinetics of methane and hydrogen production and the loss of C-H groups from the adsorbate layer can all be described by first order kinetics, with calculated reaction cross-sections comparable to the XPS-measured value. In conjunction, XPS, RAIRS and MS data suggests that a single electron event is responsible for decomposition of the parent compound and the formation of the platinum containing carbonaceous film. Electron beam irradiation also results in a reproducible change in the film's Pt/C ratio, whose magnitude is consistent with the idea that electron beam decomposition is initiated by a single Pt-CH₃ bond cleavage event. The average cross-section for the electron stimulated decomposition of adsorbed MeCpPt(IV)Me₃ via the different pathways at a specific electron beam energy of 500 eV is measured to be $1.5 \times 10^{-16} \text{ cm}^2$. Results from this study, carried out under well-defined reaction conditions where changes in the gas phase composition and the film's surface composition can be monitored simultaneously, provide new insights into the EBID process.

11:40am **SS1-ThM12 A Study of the Surface Chemistry and Cross Sections for Electron Induced Dissociation using Temperature Programmed Desorption**, *W.F. Van Dorp*, Delft University of Technology, The Netherlands, *S. Zalkind, B. Yakshinskiy, T.E. Madey*, Rutgers, the State University of New Jersey, *J.D. Wnuk, J.M. Gorham, H. Fairbrother*, Johns Hopkins University, *C.W. Hagen*, Delft University of Technology, The Netherlands

Electron beam-induced deposition (EBID) is a technique where adsorbed precursor molecules are dissociated by a focused beam of electrons to define metallic or semi-conducting patterns. Control over the process has developed to the extent that the amount of deposited material can be controlled (nearly) to the level of single molecules.¹ However, the purity of the deposits is not yet well controlled due to lack of knowledge of the precise nature of the precursor dissociation. Therefore, we study the adsorption behaviour of (CH₃)₃-Pt-C₅H₄CH₃ (a typical EBID precursor) and the dissociation cross section as a function of incident electron energy using Temperature Programmed Desorption (TPD).^{2,3} TPD experiments using a Au(110) sample as substrate indicate that the first monolayer in contact with the substrate has a higher desorption temperature than condensed multilayers. The adsorption energy for the monolayer in contact with the Au is estimated to be 55 kJ/mol. The desorption behaviour in the first monolayer is first order and multilayers do not form until after the first monolayer has formed; the precursor desorbs molecularly. The precursor desorbs (nearly) completely below 0 °C. To study the adsorption behaviour in a condition more typical of an EBID experiment, we deposited a several nm thick carbon/Pt containing layer on the sample. TPD measurements using this "realistic" surface show that the desorption behaviour is similar to that on clean Au(110). The peaks have their maxima in the same range of temperatures, although the peaks are wider. Using this "realistic" C/Pt surface, we studied the effect of broad beam electron irradiation on the TPD spectrum of a single monolayer of precursor. As the total electron dose increases, the area under the TPD peak for m/z = 289 decreases. Cross sections for dissociation can be calculated from the reduction in the area under the TPD peak and are about 10^{-16} cm^2 for electron energies between 40 eV and 3 keV, comparable to those for electron induced dissociation in the gas phase.

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² N.S. Faradzhev, C.C. Perry, D.O. Kusmierek, D.H. Fairbrother, T.E. Madey, *J. Chem. Phys.* 121 (2004) 8547.

³ C. C. Perry, N. S. Faradzhev, D. H. Fairbrother, T. E. Madey, *Int. Rev. Phys. Chem.* 23 (2004) 289.

Thursday Afternoon, October 23, 2008

Biomaterial Interfaces

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

Plasmonics and Magneto/Plasmonics Aimed at Biosensing

Moderator: F. Höök, Chalmers University of Technology, Sweden

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

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

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

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

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

Transient protein-protein interactions are essential on almost every level of cellular function. In addition, protein aggregates play various roles in cell signaling pathways and have been implicated in the onset of many neurodegenerative conditions such as Alzheimer's disease. Although various structures of protein complexes have been widely studied, the mechanisms involved in protein binding events are not clearly understood, and the transient dynamics of this formation have proven difficult to study. Investigation of the mechanisms of protein agglomeration and binding, however, is essential to elucidating the role of these structures in diseases. Here we exploit the multi-array quantitative capabilities of angle-resolved surface plasmon resonance imaging (SPRi) to perform kinetic and thermodynamic measurements of protein-protein interactions. Specifically, the agglomeration and small molecule inhibition of Tumor Necrosis Factor (TNF) family members whose primary role is the regulation of immune cells is under investigation. Surface fabrication techniques coupled with

multi-channel microfluidic delivery will be employed in order to introduce protein binding partners and small molecules to the surface. Effects of density, orientation, and heterogeneity of surface immobilized protein molecules on protein binding efficiency and kinetics will be investigated and optimum surface fabrication conditions will be identified. In addition, a unique multi-wavelength SPRi approach will be implemented to simultaneously determine dielectric constants and thicknesses of protein layers on a surface. These studies will therefore allow aggregate and nonaggregate structures at the surface to be clearly differentiated. The results of these fundamental studies will allow a broader understanding of how proteins act cooperatively.

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

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

References

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- ²A. Valsesia, et al., Langmuir 2006, 22, 1763.
- ³P. Lisboa, et al., Applied Surface Science, 2006, 253, 4796.

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

In recent years Surface Plasmon Resonance (SPR) sensors have been extensively used in bio-sensing applications. SPR is a charge density oscillation at the boundary between a metal and a dielectric material that gives rise to highly confined fields at the interface. As a consequence the SPR excitation condition is very sensitive to changes in refractive index in the dielectric medium and hence to bio-molecules adsorbed at the metal surface. Nevertheless, the required detection sensitivity for low concentrations of small molecules exceeds current SPR sensors. A new kind of sensors combining plasmonic and magneto-optical (MO) properties, i.e. magneto-plasmonic devices, is being actively investigated. In particular, Au-Co-Au trilayers have been found to increase sensitivity in this type of biosensors.¹ This is due to MO activity enhancement in the Co film caused by the high electro-magnetic field created by SPR.² We will report on Au-Co-Au thin film tri-layers grown on glass using UHV magnetron sputtering. The optimization of growth conditions and accurate control of films thickness is critical to achieve a remarkable increase in MO activity and hence in overall sensitivity. A practical issue in these multilayer systems is the bad adhesion of Au to glass causing degradation of the sensor when exposed to a water flux. We will show how to circumvent this problem by inserting Cr or Ti thin buffer layers. A different approach to magneto-plasmonic materials, namely fabrication of Au-Co nano-composite

materials in thin film form, will also be presented. These materials are expected to exhibit enhanced MO response due to localized surface plasmon resonances (LSP) within the Co nano-particles and also considerable reduction of light absorption associated with ferromagnetic materials thus increasing the overall sensitivity of the bio-sensor. Parameters such as shape, size and inter-particle distance can be tuned to control the optical and magnetic properties of the material. Au-Co nanocomposite materials in thin film form were obtained by magnetron sputtering co-deposition of Au and Co where parameters such as Au and Co concentration, deposition temperature and film thickness were accurately controlled. Finally, different optical configurations for the excitation of the surface plasmon resonance will be discussed.

¹ B. Sepulveda et al. Opt. Lett. 31, 1085 (2006).

² V. I. Safarov et al. PRL 73, 3584 (1994).

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

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

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

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

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

Biological and Molecular Applications of Nanostructures

Moderator: P. Kingshott, The University of Aarhus, Denmark

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

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

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

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

particularly advantageous from the perspective of rinsing after each surface treatment protocol. It should be mentioned that because particles are covered only on one side, two types of surfaces, metal and exposed polystyrene, can be selectively used for surface modifications; if necessary two sides can be modified with two distinct species at the same time to give higher functionalities.

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

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

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

Fabrication and characterisation of nanopatterned surfaces are topics of many past and present research studies. Recently many techniques have been investigated for the fabrication of nanopatterned surfaces. Among them colloidal lithography combined with plasma polymer deposition and/or self-assembly has shown to be a flexible technology for producing large area nanostructured surfaces. At the same time investigations have increasingly focused on the behavior of biomolecules (i.e. protein, nucleic acid) when interacting with surfaces and/or particles with nanometre dimensions. Although many studies have been done on the surface/biomolecule interaction mechanisms and the conformation changes that molecules undergo after the interaction with macroscopic surfaces it is much less well understood how the biomolecules interact with surfaces that have been previously functionalised with nanofeatures. In particular little is known about the interactions which occur with features with dimensions comparable with those of the biomolecules themselves and how, after the interaction, the native molecule conformation changes. We have optimized a procedure for fabricating nanopatterned surfaces at the sub500 nm scale in which a hexagonal close packed array of bioadhesive gold nanoareas are embedded in an anti-fouling matrix (PEO-like polymer). The surfaces fabricated in this way were characterized by AFM analysis and their interaction with amino functionalised Au nanoparticles were investigated. The AFM images show the crystalline arrangement of nanopattern array and the localization of the H₂N-Au nanoparticles in the bioadhesive areas. A SPR Imaging system was used to perform kinetics studies on the adsorption and interaction behaviour of biomolecules on these surfaces. At the same time, the detection performance of these surfaces when employed as a transduction platform for studying biomolecule interactions has been investigated. To do this, a recognition biomolecule was immobilized on the surface and the affinity reaction with a specific target molecule was monitored in real time by means of the SPRi system. The investigated surfaces showed an enhancement of the affinity reaction efficiency with respect to the non structured surfaces. The results obtained show that nanostructuring the surfaces makes it possible to improve the binding site accessibility of the immobilized biological probes without significantly modifying the native biomolecule conformation.

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

We have fabricated Si multiple internal reflection infrared waveguides embedded with a parallel array of nanofluidic channels (100 nm W × 500 nm D) and studied field-effect-transistor (FET) flow control and separation of proteins, using scanning laser confocal fluorescence microscopy (SL-CFM) and multiple internal reflection Fourier transform infrared spectroscopy (MIR-FTIRS). For fluidic FET, a DC potential is applied to a highly doped gate area in the mid-section of nanochannels, in addition to a longitudinal electric field along the nanochannels. The gate potential controls the surface charge on SiO₂ channel walls and therefore their ζ-potential. Depending on the polarity and magnitude, the gate potential can accelerate, decelerate, or reverse the flow of proteins. In addition, our MIR-FTIR analysis demonstrates that fluorescein dye molecules, used here as a pH indicator, are hydrogenated and dehydrogenated in response to the gate bias and subsequent pH shift. Using fluorescein, we have thus measured a pH shift caused by the surface charge modulation and longitudinal electrical field. We observe that this pH shift is further influenced by water electrolysis occurring at the electrodes that drive the electroosmotic flow as well as at the gate where a leakage current unavoidably flows through a thermal SiO₂ layer. Using this pH manipulation and generating a pH gradient along the nanochannels, we have conducted isoelectric focusing and separation of proteins with different isoelectric points (Ip). In this presentation, we will further discuss protein separations, using transverse electromigration based on their different valence charges in relation to the surface charge on channel walls.

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

Surface coatings are often used to control the degree of the interaction between the material and the surrounding environment. Paints and lacquers are the most common and widespread coatings. Recent developments in the process of micro- and nanostructures lead to the demand of thinner coatings, which maintain the aspect ratio and preserve the fine structures. Such conditions can be fulfilled by the use of self-assembled monolayers.¹ Due to the large spectrum of applications are nowadays high-throughput approaches required to screen through a large number of parameters, ranging from the substrate up to the different assembly conditions (temperature, solvent, pH). We designed a surface modification screening platform (SuMo-device), which allows the parallel execution of different surface-modification experiments while allowing a single measure for the adlayers characterization, thus enhancing the efficiency of the experiment. The seventy wells (working area/well: 7mm²; Volume/well: 20µmL) provided by the SuMo-device, were verified with solutions having different concentrations of the grafted copolymer; poly (L-lysine)-grafted-poly ethylene glycol, which is known to adsorb electrostatic to different metal oxide substrates and to render the surface resistant against non-specific protein adsorption (non-fouling), and thus resulting in adlayers with different coverage and thickness.² A secondary adsorption of fluorescein isothiocyanate labeled fibrinogen (FITC-fbg) enables to test the non-fouling behavior and therefore the quality of the polymer layer, by the measurement of the fluorescence with a microarray scanner.³ A standard evaluation procedure was introduced to enable a quantification of the fluorescent response. The Limit of Detection (LOD) was calculated from the standard curve and requires a minimum FITC-fbg concentration of 0.002mg/mL (incubation: 1 h at 25°C). The fluorescence data were compared and found to correlate with layer thickness (ellipsometry) and with the in situ mass adsorption curve obtained by optical biosensor devices. Thus, we conclude that our approach offers a faster and more efficient way to screen between different possible coatings strategies, similarly to drug discovery processes.

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

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

show preferential adhesion on the active region indicating the ability of this method for the design of biosensing platforms.

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

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

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

In this work we fabricated and characterized microarrays of proteins of the extra cellular matrix (ECM) for stem cells adhesion studies. Plasma deposited poly(ethylene) oxide (PEO-like) film coated glass slides has been chosen for its dual properties, being protein and cell repellent in wet conditions and protein adhesive in dried conditions. The microarrays were created by direct microspotting of the proteins on the PEO films with optimized printing buffer by using a non-contact printing technology. The stability and the quality of the spots of fibronectin used as model protein were assessed by Time of Flight- Secondary Ion Mass Spectrometry (ToF-SIMS) and ellipsometry was used to determine the amount of protein immobilized on each spot after rinsing of the substrate with water. It was found that when fibronectin is spotted at a concentration higher than 84 µg/ml, the protein forms a monolayer with a density of 112 ± 4 ng/cm² with a low surface coverage but quite regular spatial distribution as confirmed by Atomic Force Microscopy (AFM) measurements. The active conformation of the spotted fibronectin as a function of the spotted concentration was verified by performing an immunoassay with antibodies specific for the fibronectin RGD sequence by Surface Plasmon Resonance (SPR) imaging. Human Umbilical Cord Blood Neural Stem Cells (HUCB-NSCs) were cultured on different ECM protein arrays (fibronectin, laminin, collagen I, collagen III and collagen V) showing a protein type and concentration dependent adhesion and growth on the micro-spots. No cells were found in-between the spots thanks to the anti adhesive properties of the PEO-like film. The cell nuclei were stained for cell counting and preliminary specific cell staining was performed to evaluate the differentiation stage of HUCB-NSCs on fibronectin spots. The array platform developed in this study provides a promising approach to investigate in a high throughput manner how insoluble factors patterned on the surface influence stem cell adhesion and development.

In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference

Room: 310 - Session IS+NC-ThA

In Situ Microscopy - Dynamic Nanoscale Processes

Moderator: D.J. Miller, Argonne National Laboratory

2:00pm **IS+NC-ThA1 In-situ Electromagnetic Field Experiments in the Analytical Electron Microscope**, *N.J. Zaluzec, D.J. Müller*, Argonne National Laboratory

INVITED

The term in-situ microscopy has been traditionally used to describe studies of liquid/solid or gas/solid interactions. While this is an important aspect of materials characterization it represents only one regime of the study of materials under real-world environments. Recent work at the ANL EMCenter has focused upon dynamic studies of materials in the analytical electron microscope (AEM) using electromagnetic excitation and the observation and characterization using both imaging and spectroscopy. In magnetic and anti-ferromagnetic materials we drive transitions between states by means of externally applied fields and/or temperature and observe both qualitatively and quantitatively the changes which occur as a function of the driving transition. In the area of nanoscale materials we are investigating the use of in-situ optical excitation of novel structures and then performing simultaneous electron spectroscopy to elucidate the changes in their plasmonic features. Some aspects of this work have reached the routine level, while others particularly those requiring time synchronized excitation and observation are more demanding requiring significant modifications of conventional instrumentation.

2:40pm **IS+NC-ThA3 In-Situ Electron Microscopy Enabled by a TEM-SPM Platform**, *J. Huang*, Sandia National Laboratories

INVITED

Transmission electron microscopy (TEM) is a powerful tool for structural characterization of materials. However in-situ studies of the mechanical, electrical and thermal properties of materials at a nanometer scale are still challenging. A scanning probe microscopy (SPM), including scanning tunneling microscopy (STM), atomic force microscopy (AFM), and nano-indenter, explores the physical and mechanical properties of materials down to a single atom level but without internal structural information. A combined TEM-SPM platform, which integrates a fully functional SPM into a TEM, takes advantage of both the SPM and the TEM capabilities and provides unprecedented opportunities to probe the structural, mechanical, electrical, and thermal properties of materials in-situ down to a nanometer scale. This allows for direct correlation of the physical and mechanical properties to the atomic-scale microstructure. In this talk, I will review our recent progress in using the TEM-SPM platform to probe the electrical and mechanical properties of carbon nanotubes.¹ First, individual multiwall carbon nanotubes are peeled off layer-by-layer by electric breakdown inside the TEM. This provided new insights into the transport property of nanotubes. Second, plastic deformation, such as superplasticity, kink motion, dislocation climb, and vacancy migration, was discovered in nanotubes for the first time. Emerging directions of using the TEM-SPM platform to enable in-situ thermal/thermoelectric property measurements will be discussed.

¹J.Y. Huang et al., Nature 439, 281 (2006); J.Y. Huang et al., Phys. Rev. Lett. 94, 236802 (2005); 97, 075501 (2006); 98, 185501 (2007); 99, 175593 (2007); 100, 035503 (2008).

3:20pm **IS+NC-ThA5 Investigating Sliding-induced Graphitization of Diamond-like Carbon Films by In Situ TEM**, *A. M'ndange-Pfupfu, L.D. Marks*, Northwestern University, *O.L. Eryilmaz, A. Erdemir*, Argonne National Laboratory

The field of tribology - the study of contacting surfaces in relative motion - has long suffered from the problem of buried interfaces, forcing researchers to conduct experiments completely blind to the underlying mechanical deformation and structural processes that dictate friction behavior. Using a unique in-situ TEM nanomanipulation technique, we can dynamically observe the sliding interface at the single asperity level.¹ With this method, we can deeply probe the effects of film composition on surface behavior and by extension, on the tribology and wear properties of such films. In particular, we are interested in the precise mechanisms of graphitization seen in diamond-like carbon films.² The bonding configuration at the surface has been shown to play a significant role in nanotribological properties, along with experimental and growth parameters such as the relative amount of hydrogen present at the surface.³ By using electron energy loss spectroscopy combined with high resolution imaging, we can observe the changes in bonding that occur during graphitization as they happen. We study the results over a range of films with differing levels of hydrogenation.

¹A P Merkle and L D Marks. "Friction in Full View." Applied Physics Letters 90, 064101 (2007).

² Y Liu, A Erdemir, and E I Meletis. "A study of the wear mechanism of diamond-like carbon films." *Surface and Coatings Technology* 82 (1996) 48-56.

³ A V Sumant, et al. "Surface chemistry and bonding configuration of ultrananocrystalline diamond surfaces and their effects on nanotribological properties." *Physical Review B* 76, 235429 (2007).

4:00pm IS+NC-ThA7 Kinetics of Individual Nucleation Events during Nanoscale Vapor-Liquid-Solid Growth, F.M. Ross, IBM T. J. Watson Research Center **INVITED**

The growth of self-assembled nanostructures, such as nanowires, must be carried out with a high degree of control if electronic and optoelectronic devices are to be fabricated reliably. In particular, nucleation must be well controlled if a single nanostructure is to form at each location over a wafer. Using ultra high vacuum TEM, we have therefore examined nucleation in the model vapor-liquid-solid systems Si-Au and Ge-Au. We will present a quantitative analysis of both the initial transformation from solid Au to liquid Au-Si or Au-Ge eutectic and the subsequent formation of the nanowire nucleus. Quantitative measurements of nucleation and growth kinetics agree well with a simple model that provides a unified picture of the growth process. Nucleation is heterogeneous, occurring consistently at the edge of the liquid droplet, yet it is intrinsic and highly reproducible. We estimate the critical supersaturation required for nucleation, and find that size effects are surprisingly small, even for systems down to 12 nm in diameter. Nucleation is also important when forming nanowire heterostructures, and we examine this process in situ by observing the epitaxial nucleation of Si and Ge on wires formed of dissimilar materials such as GaP and GaAs. The observation and analysis of individual nucleation events in nanoscale systems leads to results that may be relevant to the formation of nanostructures for real-world applications.

4:40pm IS+NC-ThA9 Atomic Resolution In-Situ Environmental Transmission Electron Microscopy on Nanostructures, X.F. Zhang, Hitachi High Technologies America, Inc., T. Kamino, Hitachi High Technologies Corp., Japan **INVITED**

In recent years, progresses in in-situ transmission electron microscopy (TEM) provided unique imaging and analytical capabilities for studying structural evolutions in versatile environments. Aiming at atomic resolution in-situ TEM capability, we have developed various sample holders including gas injection-heating holder, single- and double-tilt heating holders, and double-heater sample holder.^{1,2} Using these sample holders, in-situ heating TEM studies in vacuum or in a gas environment, and in-situ evaporation deposition can be done in a standard Hitachi 300 kV H-9500 high-resolution transmission electron microscope,³ true atomic resolution can be achieved at elevated temperatures for example at 1500°C, and digital recording of the dynamic structural evolutions is realized using a high speed CCD camera. Various nanomaterials have been studied at elevated temperatures with or without a gas environment. Effects of electron beam irradiation on nanomaterials were also evaluated. It has been found that 300 kV electron beam could alter some nanostructures at room temperature even though the nanomaterials were composed of 'robust' materials such as carbon and metals. However, when heating samples to elevated temperatures, electron beam irradiation helped in-situ TEM study in many ways that it might minimize knock-on damages, burn off amorphous surface layers, or trigger structural changes in nanostructures. In study of metallic nanoparticles, atomic layer-by-atomic layer structural changes at various temperatures have been observed directly, the changes in structure would be impossible to be explained without the in-situ atomic resolution TEM. Structural changes in oxide nanoparticles were observed at high temperatures and the atomic resolution TEM helped to understand the phase transformation process. These data provide insights into the structural processes in the middle stage before the environmental impacts became catastrophic to materials, therefore can help to elucidate puzzled phenomena often encountered in ex-situ experiments or in in-situ TEM experiments at low resolution or with too long time intervals for image recording.

¹ T. Kamino and H. Saka, *Microsc. Microanal. Microstruct.* 4 (1993) p. 127.

² T. Kamino, T. Yaguchi, M. Konno, A. Watabe, T. Marukawa, T. Mima, K. Kuroda, H. Saka, S. Arai, H. Makino, Y. Suzuki and K. Kishita, *J. of Electron Microscopy* 54 (2005) p. 497.

³ X.F. Zhang and T. Kamino, *Microscopy Today* 9 (2006) p. 16.

5:20pm IS+NC-ThA11 In-Situ Transmission Electron Microscopy Studies of Chemical and Thermal Stabilities of Carbon-Coated Titania Nanoparticles, M. Pozuelo, University of California, Los Angeles, X.F. Zhang, Hitachi High Technologies America, Inc., J.H. Park, University of California Los Angeles, R. Koc, Southern Illinois University at Carbondale, S. Kodambaka, University of California, Los Angeles

Transition-metal carbides such as titanium carbide (TiC) form a technologically-important class of materials with applications in a wide variety of areas including catalysis, energy storage, high-temperature corrosion- and oxidation-resistant coatings, and as structural composites. For all these applications, high surface area, small size, and phase-pure particles are desirable. One of the common methods for TiC production is carbothermal reduction of TiO₂ at elevated temperatures (>1200 °C). This

reduction reaction is suggested to occur via successive formation of lower oxides of titanium along with the emission of CO and CO₂ gases. However, the exact details of the reaction kinetics, which control the final particle size, shape, and crystal structure are largely unknown. As a first step toward the development of a fundamental understanding of the carbothermal reduction process we chose carbon-coated TiO₂ particles as a model system. Using in situ lattice-resolution transmission electron microscopy (TEM), we study the chemical and thermal stabilities of individual C-coated titania (TiO₂) nanoparticles during annealing in vacuum at temperatures up to 1000 °C. First, C-coated titania particles are prepared by pyrolysis of propylene (C₃H₆) gas in an oxygen-free environment at ~ 600 °C in a tube furnace filled with titania powders (average size ~ 20 nm). This process resulted in a uniform coating of pyrolytic carbon shell (thickness ~2-5 nm) around individual oxide particles. In situ TEM experiments are carried out at Hitachi EM Lab in Pleasanton, California using an atomic resolution Hitachi H-9500 300 kV TEM (base pressure ~ 10⁻⁶ Torr) which allows in-situ heating in vacuum or in a gas environment. The oxide-core/C-shell nanoparticles are deposited directly onto a heating filament of the gas injection-heating TEM sample holder. Lattice-resolution TEM images are acquired at video rate (15 frames/s) while heating the particles in vacuum for times up to 5 h. Energy dispersive X-ray spectra (EDX) are obtained at room temperature from the samples before and after the annealing experiments. We find several interesting phenomena: 1) crystallization of carbon to form graphene layers preferentially on the lowest-energy planes of TiO₂; 2) shrinking and eventual disappearance of the oxide cores while being encapsulated by carbon, resulting in the formation of hollow-core graphene shell structures; 3) reduction of TiO₂ to lower oxides. These studies provide atomic-scale insights into the early stage carbothermal reduction process leading to the synthesis of TiC particles.

Nanomanufacturing Focus Topic

Room: 309 - Session NM+MS+NS+NC-ThA

Nanomanufacturing II: Nanostructures

Moderator: J. Murday, University of Southern California

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

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

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

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

Semiconductor nanocrystals, aka quantum dots, have become the prototypical material for the emergence of new properties when dimensions are reduced to the nanometer range. The size dependent properties of excitons and multiexcitons in quantum dots, coupled with a material that can be engineered and processed from solution, has led to potential applications in fields that include emissive displays, solar energy conversion, and biological and biomedical fluorescence imaging. A fundamental understanding of exciton processes is critical for any of these applications to become realized. The design and synthesis of well characterized materials is obviously key, not only of the functional inorganic particle itself, but also the ligand shell that protects it and couples

it chemically to molecules and matrices of interest. This talk will review some of the chemistry and photophysics of quantum dots and then explore the fundamental properties and challenges behind broadly applying quantum dots as light emitters and light absorbers in devices and for biological imaging.

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

Self-assembled semiconductor quantum dots are a candidate for use in potential nanoelectronic device architectures such as quantum cellular automata and magnetic spin exchange switches. It is possible to grow quantum dots (QDs) with relatively uniform size-distributions using heteroepitaxial techniques, but in order to apply QDs in such nanoelectronic devices they must also be spatially ordered into patterns of varying complexity. In addition, the QDs must possess the magnetic or electronic properties required for device operation. We have previously demonstrated the use of Ga⁺ focused ion beam (FIB) templating of Si surfaces prior to growth in order to fabricate patterns of Ge(Si) QDs of any desired complexity. Our current work employs a mass-selecting FIB with liquid metal alloy ion sources, enabling the generation of a wide range of separated species in focused beams, to template QD structures and electrically or magnetically dope them at a dot-by-dot level for nanoelectronic device applications. Ions can be selected according to isotope mass and charge state by using a mass-selecting Wien filter. Suitable alloy sources then provide the ability to template a Si substrate with electrically non-invasive ions (i.e. Si or Ge) and implant dopant ions for electronic or magnetic activation (e.g. with B or Mn), with resolution of < 50nm and doses down to a few ions per dot. Key technical issues we are addressing include i) the attainable limits of spatial resolution and the dot-by-dot implantation dose, ii) comparisons between Ga and Si ion templated growth, iii) physical alignment between a templating ion beam and a dopant implantation ion beam and iv) procedures for eliminating unwanted exposure of adjacent areas of the sample to implantation ions.

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

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

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

Surface plasmon enhanced techniques provide promising methods to improve the light emission efficiency of semiconductor materials. In this talk, we present the growth of noble metal/CdS hybrid semiconductor nanowires, and the plasmon-enhanced photoluminescence from these nanowires. In our previous studies, we demonstrated the straightforward fabrication of ordered linear arrays of spherical silver nanoparticles with gaps between the individual nanoparticles of less than 10 nm on highly oriented pyrolytic graphite (HOPG) surfaces using physical vapor deposition (PVD) under controlled experimental conditions. These silver nanoparticle arrays were capable of supporting very strong surface plasmon resonances, which was demonstrated by our polarized surface enhanced Raman scattering experiments. In this presentation, we describe experiments where following the PVD growth of Ag or Au nanoparticle arrays on HOPG surfaces, we electrochemically deposit cadmium around these nanoparticle arrays to form hybrid nanowires as thin as 50-60 nm in width. Further annealing of these hybrid nanowires in H₂S at temperatures

of 300-320°C enables the formation of CdS nanowires around the Ag or Au nanoparticle cores. Using this combined PVD/electrochemistry/chemical modification approach we have been able to generate ordered 2-D arrays of hybrid semiconductor nanowires that are as small as 100 nm in diameter and 100s of microns in length. Under light illumination, the surface plasmon supported by the Ag or Au nanoparticle cores enhances the photoluminescence of the outer CdS nanowires.

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

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

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

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

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

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

Advanced luminescent materials have practical applications in nearly all devices involving the artificial production of light and considerable research has been carried out to synthesize new luminescent materials. Their luminescent properties have been shown to be dependent on the size and morphology of the crystallites, hence materials with dimensions in the nanometer regime emerges as promising materials. These attributes make them viably applicable in nanoscaled electronics, photonics, display and advanced bioanalysis. In this talk, we present our recent work on the fabrication of rare-earth doped metal oxide nanostructures, including Er:Y₂O₃ nanotubes (NTs) and nanoparticles (NPs) and Er:La₂(Zr_xHf_{1-x})₂O₇ NPs, by hydrothermal and molten-salt syntheses.^{1,2} The formation of nanostructures were probed in-situ by time-resolved synchrotron x-ray diffraction and absorption spectroscopy to delineate the process-structure-property relations. The as-synthesized nanostructures were further characterized by electron microscopy and various spectroscopy³ to be single crystalline, with well controlled size distributions around 100-400 nm in outer diameter and 2-5 μm in length for Er:Y₂O₃ NTs, around 80 nm in diameter for Er:Y₂O₃ NPs, and around 15 nm in diameter for Er: La₂(Zr_xHf_{1-x})₂O₇ NPs. The erbium coordination number and local bonding environment were shown to dictate the measured photoluminescent characteristics, including photoluminescence and cathodoluminescence. Specifically, these 0-100% erbium-doped oxide nanostructures have sharp and well-resolved photoluminescent behavior in the near-infrared region, outstanding green and red upconversion emissions, and excellent cathodoluminescent properties. These properties make these nanostructures promising for applications in display, bioanalysis and telecommunications.

¹ Mao, et al. Synthesis and luminescence properties of erbium-doped Y₂O₃ nanotubes, *J. Phys. Chem. C*, 112, 2278 (2008).

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

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

Nanolithography and Manipulation

Moderator: J.N. Randall, Zyvex Labs

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

Patterned media for storage applications at densities beyond 1Tb/in² requires fabrication of periodic patterns at 27nm full pitch and smaller. Templating patterns at these dimensions is particularly challenging when considering the stringent quality restrictions imposed by storage applications in terms of feature size distribution, line edge roughness, placement and long-range ordering. We present here a guided self-assembly approach that combines e-beam lithography with block copolymer self-assembly. E-beam lithography is used to pre-pattern a guiding substrate defining features with registration and long-range orientational and translational order. A block copolymer film is applied on top of the guiding pattern. The uniformity of the self-assembled features effectively corrects noise and non-uniformities introduced by the e-beam and the e-beam resist. We use image processing to quantify the pattern quality rectification achieved by the block copolymer. We also use this guided self-assembly approach as a pattern density multiplier. The self-assembled pattern can be used to multiply the density of e-beam features by at least a factor of four. This density multiplication approach enables the possibility to pattern features at resolutions not accessible by state-of-the-art e-beam lithography but still taking full advantage of its registration and long-range ordering properties.

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

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

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

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

reduced using shorter wavelengths. This technique establishes a new paradigm for high throughput nano-lithography, allowing rapid, economical and simple creation of large areas of uniform nanostructures.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Advanced Surface Engineering

Room: 204 - Session SE+TF+NC-ThA

Glancing Angle Deposition (GLAD) II

Moderator: D. Gall, Rensselaer Polytechnic Institute

2:00pm **SE+TF+NC-ThA1 Glancing Angle Deposition at the Nano-Bio Interface**, *Y. Zhao*, University of Georgia **INVITED**

Glancing angle deposition (GLAD) technique is a physical vapor deposition method to design three-dimensional nanostructures by programming the vapor incident angle and substrate azimuthal rotation. This method offers large area growth of aligned nanorod arrays with additional capability of self-alignment. There is almost no limitation on materials that can be fabricated into desired nanostructures. With recent advance in a multilayer deposition procedure, one can design complex and multifunctional heterogeneous nanostructures. In addition, with a co-deposition system of two or more sources, novel nanocomposites or doped nanostructure arrays can be produced, which results in nanostructures with different morphology. Here, I will highlight our recent progress in multi-component nanorod array fabrication and their potential biological applications. We find that aligned silver nanorod array substrates can be used as a high sensitive virus and bacteria sensor base on surface enhanced Raman spectroscopy (SERS) principle. This SERS based sensor can be used to detect the molecular

fingerprints of several important human respiratory viruses including respiratory syncytial virus, rhinovirus, adenovirus, human immunodeficiency virus, influenza virus, and bacteria, with high sensitivity and selectivity, and to discriminate between different virus/bacterium strains. Using a unique multilayer deposition configuration, catalytically driven nanomotors have been fabricated and demonstrated, which can directly convert chemical energy into mechanical energy. This device holds a great potential to mimic smart biological systems via hybrid organic-inorganic nanostructures.

This work was supported by NSF, NIH, and ARL.

2:40pm **SE+TF+NC-ThA3 Growth and Characterization of Magnesium, Magnesium Alloy, and Doped TiO_x Sculptured Thin Films (STFs)**, *S.M. Pursal, M.W. Horn, B.A. Shaw*, The Pennsylvania State University

Bioabsorbable materials such as magnesium, which is essential for cellular function, have recently been studied for use in heart stents, bone plates and screws, and dental and orthopedic implants. However, the use of vapor deposition to form non-equilibrium magnesium alloys has had little if any commercial interest even though certain properties of these alloys, namely corrosion resistance, can be improved. Engineering of surface morphology using dip coatings and etching has been used in biomedical materials to enhance certain application specific surface properties. Sculptured thin film (STF) technology potentially provides a path to merge the advantages of non-equilibrium alloy formation and engineering nanoscale surface morphology. We present here our results utilizing a vapor co-deposition scheme to improve nucleation and corrosion properties of magnesium alloys. By utilizing co-deposition with materials such as titanium, yttrium, zirconium, and others the growth mode of magnesium can be modified and the solid solution limit can be surpassed leading to an improvement in corrosion resistance. Characterization of the growth of magnesium alloy thin films has been done utilizing various alloying elements, substrate temperatures, post-deposition treatments, and substrate positions (to deposit STFs). The results point towards a growth mode controlled by crystallization effects that are not common in higher melting temperature materials. The results of the study are presented in terms of x-ray diffraction data, microscopy analysis of growth evolution, and corrosion testing. We will also present results that extend our work on TiO_x chiral STFs utilizing the circular Bragg phenomenon (CBP) for sensor applications. The CBP is observed in the circularly polarized transmission spectrums of chiral STFs as a stop band for co-handed light. The location and shape of this stop band is dependant on the material properties among other factors. Using an impurity material from a second source may allow added sensitivity for sensor applications while maintaining STF morphology and function.

3:00pm **SE+TF+NC-ThA4 Performance and Response Time of Nanostructured Relative Humidity Sensors**, *M.T. Tashchuk, J.J. Steele, M.J. Brett*, University of Alberta, Canada

Applications requiring relative humidity (RH) measurement will require differing sensitivity, range of humidity operation, and response times. These properties are determined by the properties of the sensing medium: material, porosity, surface area, pore size distribution and morphology. We have been investigating the use of glancing angle deposition (GLAD) for the fabrication of RH sensors with interdigitated electrode (IDE) substrates.^{1,2} While GLAD offers some significant advantages for RH sensors, there remain a number of open questions regarding the underlying physics of GLAD RH sensor performance and response time. The response of our devices depend on the extremely large low frequency dielectric constant of water adsorbed to metal oxides, which can result in a three order of magnitude change in capacitance as RH is increased from 0 to 100%. We have recently employed an electromagnetic model with simple dielectric mixing laws to compare our device performance with literature values for dielectric constants.² Further work is ongoing to include structural effects in the dielectric mixing laws to improve accuracy. Response time varies with the size and nature of pores in our sensors, which in turn relies on column properties such as diameter and surface roughness. Experimental values for response time of the GLAD RH sensors have been reported, but a neither a model nor thorough study of response time as a function of deposition angle and film thickness has been presented. Constructing a model for our devices requires an understanding of the diffusivity of GLAD films, the interaction between water vapour and TiO₂, and the electromagnetic behaviour of IDE devices. In this paper we characterize the performance and response time of GLAD RH sensors as a function of film thickness and deposition angle. The microstructure column radius as a function of film thickness and deposition angle is investigated. A 1D numerical model describing response time of our devices is developed, which includes diffusion, adsorption and IDE physics. The modeling results are compared with our experimental data, and demonstrates that response time of our sensors is dominated by adsorption.

¹ J.J. Steele, G.A. Fitzpatrick, and M.J. Brett. IEEE Sensors Journal, Vol. 7:955 – 956, 2007.

² J.J. Steele, M.T. Tashchuk, and M.J. Brett. IEEE Sensors Journal, (In Press), 2008.

3:20pm **SE+TF+NC-ThA5 Patterned Ag Nanorod Arrays as SERS Substrates by Template Mediated Oblique Angle Deposition.** *Y. Liu, Z. Zhang, Y. Zhao*, University of Georgia

Surface enhanced Raman scattering (SERS) is widely used in the analytical, biomedical, clinical, environmental, and security applications. The practical application of a SERS-based sensor requires an efficiency SERS substrate which can not only provide a high enhancement factor, but also be uniform, stable and reproducible. In this work, a highly ordered, uniform and periodic patterned Ag nanorod arrays as SERS substrates are fabricated by combining electron beam lithography (EBL) and oblique angle deposition (OAD) techniques. Two dimensional nano Au post arrays with different separations are fabricated by EBL. There are only very weak SERS signal can be detected after the Au post arrays are treated by a $1 \mu\text{L } 10^{-4} \text{ M BPE}$ (trans-1,2-bis (4-pyridyl) ethene) droplet. However, after a layer of $\sim 400 \text{ nm}$ Ag nanorods are deposited on those BPE treated Au post array, strong SERS signals have been obtained. Furthermore, the SERS intensities become more than 8 times stronger, after the Ag arrays are further treated by a droplet of $1 \mu\text{L } 10^{-5} \text{ M BPE}$. These results demonstrate that most SERS signals could come from the molecules adsorbed on the side surfaces of the Ag nanorods, rather than the ends. The SERS signal is also strongly dependent on the separation of the Au posts. A numerical calculation on the electric field enhancement has been carried out to confirm this result.

4:00pm **SE+TF+NC-ThA7 Quantification of Porosity and Deposition Rate of Nano-Porous Films Grown by Oblique Angle Deposition.** *D.J. Poxson, F.W. Mont, M.F. Schubert, J.K. Kim, E.F. Schubert*, Rensselaer Polytechnic Institute

We propose analytic formulas accurately predicting the refractive index and film thickness of obliquely deposited thin films for a given incident angle. Recently, it was shown that accurate control of the refractive index of physical-vapor deposited thin film materials can be achieved through the use of oblique-angle deposition. Refractive index tunability and low refractive index (low-n) films are highly desirable for a variety of optical applications. For example, broadband antireflection coatings, omnidirectional reflectors, distributed Bragg reflectors, optical micro-resonators, light-emitting diodes, photovoltaic solar cells, and optical interconnects. While the qualitative tenets of oblique-angle deposition were demonstrated over a century ago, no quantitative formulas for the porosity and deposition rate have been described in the literature. In this work, we propose a model relating the porosity and deposition rate of a material to its vapor flux incidence angle for oblique-angle deposition. Our model is based upon geometrical arguments, employs a single fitting parameter, and takes into account surface diffusion. We have measured the refractive index and thickness for SiO_2 and indium tin oxide (ITO) nano-porous films deposited over a wide range of deposition angles ($0^\circ < \theta < 90^\circ$). The porosity of a material is determined from the measured refractive index. Comparison of experimental SiO_2 and ITO porosity values and deposition rates with theory reveals excellent agreement. The theoretical model allows for the predictive control of refractive index, porosity, and deposition rate for all deposition angles, potentially a very useful tool in the development of high quality low-n optical coatings. Furthermore, given the set of basic assumptions used, we expect these formulas to be valid for a wide range of materials.

4:20pm **SE+TF+NC-ThA8 Sculptured Thin Films from Aluminum.** *E.B. Schubert, T. Hofmann, D. Schmidt, M.M. Schubert*, University of Nebraska-Lincoln

Three-dimensional (3D) structure design of chiral materials on the nanoscale is a current demand in modern material science and engineering and various intriguing applications are foreseen for example in the fields of optics, electromechanics or electromagnetic. Glancing angle deposition is a method which allows for "bottom-up" fabrication of 3D shaped and tailored chiral nanostructures arranged in sculptured thin films (STF). We will present an investigation of the growth of STF's from aluminum on highly p-type doped silicon substrates by using either ion beam sputtering or electron beam evaporation. Various growth schemes have been used to obtain films with different nanostructure shapes such as posts, plates, screws or spirals. The films have been characterized regarding their optical and electrical properties by means of 4×4 Mueller-Matrix ellipsometry, IR spectroscopic ellipsometry and electrical measurements. Whereas Mueller-Matrix Ellipsometry reveals an optical response which can be related to the symmetry of the three-dimensional nanostructures,¹ the IR data give hint to electron or lattice absorptions. We found that the IR optical response depends on the shape of the nanostructures. STF's from aluminum plates for example show a strongly metallic behavior, whereas films containing Al spirals show multiple resonances, with a periodic spectral distance of 7.2 THz between neighboring absorption features. The IR optical data for the Al nanocoils are discussed in terms of coupled inductance and capacitance pairs, where the inductance is formed from the coil itself and the depletion layer capacitance is created on the footprint of the metallic Al coil with the highly p-type doped Si substrate. A Drude-like background term, which

accounts for free carriers in the aluminum nanospirals was also used during sample regression. It is found, that resistivity and free mean path of the electron depends of the shape of the Aluminum nanostructures as well. This behavior is verified by electrical measurements under dc conditions.

¹ D. Schmidt, E. Schubert, and M. Schubert, phys. stat. sol. (a) 205, 748 (2008).

4:40pm **SE+TF+NC-ThA9 Mueller Matrix Ellipsometry Studies of the Optical Properties and Structure of Serial Bi-Deposited Titanium Oxide Sculptured Thin Films.** *N.J. Podraza, S.M. Pursel*, The Pennsylvania State University, *R.W. Collins*, University of Toledo, *M.W. Horn*, The Pennsylvania State University

In this work, titanium oxide (TiO_2) chiral sculptured thin films (STFs) are fabricated using serial bi-deposition (SBD) electron beam evaporation and studied using Mueller matrix ellipsometry (MME). Chiral STFs are of interest for a wide range of applications in optoelectronic devices such as photovoltaics, microelectronic devices, microcavities, biological sensors, and bioabsorption devices. These films can be described as assemblies of upright, parallel, helical columns. Their helicoidal morphology, being periodic, engenders the circular Bragg phenomenon: circularly polarized light couples to the helices present in the film, if the handedness of the light and the STF coincide, resulting in enhanced reflectance in the Bragg regime spectral range. TiO_2 STFs fabricated using SBD are of particular interest for fundamental studies due to its high bulk index of refraction and films prepared using this technique can be fabricated to exhibit Bragg resonances in the visible spectral range at wavelengths $\sim 450\text{-}650 \text{ nm}$. Although normal incidence transmission and reflection measurements can demonstrate this behavior, it is often impossible to discern the various optical and structural properties of optically anisotropic materials like STFs. MME, however, allows us to extract each of the principal indices of refraction (n_x, n_y, n_z) as well as the microstructural parameters such as film thickness and the initial polar and in-plane orientation of the helices. The complete Mueller matrices for SBD TiO_2 STFs are measured using a dual-rotating compensator spectroscopic ellipsometer over a spectral range from 250-825 nm in transmission mode at normal incidence ($\Theta_i = 0^\circ$) and non-normal incidence ($5^\circ \leq \Theta_i \leq 55^\circ$). The normal incidence measurements provide the principal indices of refraction and the microstructure, while the non-normal incidence measurements allow us to monitor the blue-shift in the Bragg resonance with increasing angle of incidence. The fundamental understanding gained from MME is expected to provide assistance in further engineering and optimizing these types of materials for specific applications requiring control of the Bragg resonance feature.

5:00pm **SE+TF+NC-ThA10 Low Hydrogen Desorption Temperature of Hydrided Pd Coated Novel Mg Nanoblades.** *F. Tang, T. Parker, H.-F. Li, G.-C. Wang, T.-M. Lu*, Rensselaer Polytechnic Institute

We grew Mg nanoblades standing nearly vertically on the substrates by oblique angle vapor deposition. The thickness of the nanoblades along the vapor incident direction ranges from $\sim 15 \text{ nm}$ to $\sim 30 \text{ nm}$ at a vapor incident angle $\sim 75^\circ$, while the width perpendicular to the incident vapor direction is as wide as a few hundred nm.¹ These novel nanoblade structures have several advantages over the bulk materials for hydrogen storage: such as a large surface-area-to-mass ratio of $\sim 60 \text{ m}^2/\text{g}$ and ultrathin thickness ($\sim 22 \text{ nm}$), which will significantly enhance the kinetics of hydrogen absorption/desorption. The spacing between the nanoblades can also accommodate the large volume change ($\text{Mg} \leftrightarrow \text{MgH}_2$) during hydrogenation/de-hydrogenation processes. We have studied hydrogenation/de-hydrogenation properties of ultrathin Mg nanoblades coated with Pd as a catalyst, using in situ temperature desorption spectrum (TDS), ex situ scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The Pd coated Mg nanoblades were hydrogenated at a pressure of 1 bar with substrate held at $\sim 333 \text{ K}$ for ~ 15 hours. The de-hydrogenation property of the hydrided Pd/Mg/Pd nanostructure was characterized in situ by TDS, which showed that the hydrided nanostructure has a low hydrogen desorption temperature at $\sim 365 \text{ K}$. Through a combinational microstructure by TEM and TDS analyses of hydrided nanoblades as well as hydrided nanoblades covered with additional Mg layers, we found that the effect of Pd catalyst on reducing the hydrogen desorption temperature is significantly stronger than the conventionally proposed grain size and strain effects. The ex situ SEM images showed that the hydrided Pd/Mg/Pd and hydrided Pd/Mg (one sided Pd coating) nanoblades became highly curved. Various shapes such as circular, helical or spiral have been formed in the hydrided Pd/Mg nanoblade films. The formation of these curly structures could be related to the strain induced by the partial decomposition of MgH_2 after the sample was exposed to air. The understanding of hydrogenation/de-hydrogenation properties of Pd coated Mg nanoblades could help us in designing promising nanoscale metal hydrides for hydrogen storage with low desorption temperatures. FT was supported by the NSF award 0506738 and TP was supported by the DOE (education) GAANN P200A030054.

5:20pm **SE+TF+NC-ThA11 Improving Stiffness of Silicon Chevrons by 1.2 MeV Ar⁸⁺ Ion Irradiation.** *R. Nagar*, Indian Institute of Technology Delhi, *C. Patzig, B. Rauschenbach*, Leibniz-Institute of Surface Modification Leipzig, Germany, *P. Kumar, D. Kanjilal*, Inter-University Accelerator Centre, India, *B.R. Mehta, J.P. Singh*, Indian Institute of Technology Delhi

Five-armed silicon chevrons were grown by oblique angle ion beam sputter deposition on Si(111) substrates pre-patterned with 260 nm diameter silica spheres and 500 nm diameter polystyrene spheres. The patterning spheres self-assemble in hexagonal network, act as nucleation sites, and control the dimensions as well as the distance between the growing chevrons. The chevron arms are about 500 nm long, 350 nm wide and 200 nm thick with odd numbered arms making an angle of about 45° and even numbered arms an angle of about 55° from the vertical. In order to tailor the mechanical strength of the chevron coatings, the samples were irradiated with 1.2 MeV Ar⁸⁺ ions at liquid nitrogen temperature at different fluences of 10¹⁵, 10¹⁶ and 10¹⁷ ions/cm². The range of Ar ions in the amorphous Si matrix as determined by the simulation code SRIM is about 1.1 μm. Therefore, the Ar ions traverse the complete length of the chevrons before getting implanted in the Si(111) substrate. The spring constant of the chevrons was determined by force-distance spectroscopy using an atomic force microscope. Results show that the spring constant of the irradiated Si chevrons grown on 260 nm diameter silica spheres increases from 480 N/m for pristine to 1320 N/m for a fluence of 10¹⁶ ions/cm². For chevrons grown on 500 nm diameter polystyrene spheres, an increase from 370 N/m for pristine to 1325 N/m for fluence of 10¹⁷ ions/cm² is observed. Thus, irradiated chevrons are stiffer as compared to pristine ones. Finite element analysis of chevrons provides an insight into the dynamics of the resulting deformations when the chevrons are loaded. The modeling establishes that for these odd-armed chevrons a vertically downward load results in a torque about the base of the chevrons. The load produces a significantly larger lateral stress/displacement relative to the vertical, thus making them more robust to the loading force. Investigations by micro-Raman and glancing angle X-ray diffraction suggest that the Ar irradiation fosters a transformation from amorphous to poly-crystalline Si. The improved mechanical strength of the chevrons indicates that ion irradiated chevron coatings are capable of withstanding higher loads as compared to pristine coatings without getting delaminated.

Surface Science

Room: 207 - Session SS1+NC-ThA

Water-Surface Interactions

Moderator: M. Salmeron, Lawrence Berkeley National Laboratory

2:00pm **SS1+NC-ThA1 Structure and Kinetics of Nanoscale Amorphous and Crystalline Ice Films on Various Substrates.** *B.D. Kay, J.L. Daschbach, Z. Dohnálek, G.A. Kimmel, J. Matthiesen, N.G. Petrik, R.S. Smith, T. Zubkov*, Pacific Northwest National Laboratory **INVITED**

Molecular beam scattering, programmed desorption (both TPD and isothermal), and vibrational spectroscopy are used to study the chemical kinetics and reaction dynamics of molecular processes occurring both on the surface and within the bulk of amorphous and crystalline ice films. Molecular beams are used to synthesize chemically and structurally tailored thin films on various substrates including Pt(111), Pd(111), C(111) and FeO(111). These films can have morphologies ranging from dense and smooth, to highly porous depending on growth conditions. The precise control of the film structure allows physicochemical processes such as densification, crystallization, diffusion, isotope exchange, solvation, and dewetting to be studied in detail. The experimental methods, results, and their relevance to supercooled water, astrophysical icy bodies, wetting phenomena and nanoporous materials will be presented. Pacific Northwest National Laboratory is a multiprogram national laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

2:40pm **SS1+NC-ThA3 Iron Phthalocyanines on Au(111) and their Interaction with Water.** *C. Isvoranu, E. Ataman, K. Schulte*, Lund University, Sweden, *A. Rienzo, G. Magnano, J.N. O'Shea*, University of Nottingham, UK, *J.N. Andersen, J. Schnadt*, Lund University, Sweden

Phthalocyanines are an extensively studied class of molecules due to their chemical and thermal stability and high polarizability. These characteristics make the phthalocyanines and related molecules interesting for a wide range

of applications such as in molecular electronics, gas sensing devices, or as cathode and/or anode materials in fuel cells. Often, in such applications the molecules will be in contact with either liquid water as an important component of the application or with water from the ambient atmosphere. In spite of the ubiquity of the water – molecule interaction, investigations of the atomic-scale properties of the interaction of organic and organometallic molecules with water in general and of phthalocyanines with water in particular are scarce. Here, we have studied the adsorption of iron phthalocyanines on Au(111) by x-ray photoelectron and x-ray absorption spectroscopies at both sub- and full monolayer coverages and we have characterized the interaction of the different preparations with small amounts of water. For the water-free preparations, the results indicate that the full monolayer is dominated by a single molecular species, while several distinct species are observed for the submonolayer coverages. Tentatively, these different species are assigned to structures previously observed by scanning tunnelling microscopy (STM).¹ The present results show clearly that the interaction between the substrate and adsorbate differ strongly between the submonolayer and full monolayer structures, with the interaction appearing considerably stronger for the submonolayer structures. Iron phthalocyanine monolayers on Au(111) are inert to water with no change observed in the spectral characteristics of the molecular layer when exposed to water. Quite in contrast, the submonolayers exhibit strong modifications of the spectral appearances, which can be assigned to an interaction between the molecular adsorbates and water. Surprisingly, the observed chemical shifts point to a more subtle interaction of water with the iron phthalocyanines than a mere hydrogen bond formation between the water and the phthalocyanines.

¹ Z.H. Cheng, L. Gao, Z.T. Deng, N. Jiang, Q. Liu, D.X. Shi, S.X. Du, H.M. Guo, and H.-J. Gao, *J. Phys. Chem. C* 111 (2007) 9240.

3:00pm **SS1+NC-ThA4 Water Diffusion on Pt(111) Terrace, Kink and Steps: Density Functional Theory Study of Water Interaction and Diffusion.** *L. Arnadottir, E.M. Stuve*, University of Washington, *H. Jónsson*, University of Iceland

Density functional theory (DFT PW91) calculations were used to study diffusion of water molecule on a flat Pt(111) terrace as well as on kinks and step edges. Diffusion on the (111) terrace is predicted to become active on the time scale of seconds at 74 K in reasonable agreement with experimental results (Daschbach et al. *J. Chem. Phys.* 120 (2004) 1516). The binding of water at steps and kinks on Pt(111) surface is substantially stronger than at the flat terrace, by 0.16 eV and 0.25 eV, respectively. The diffusion barriers of a single water molecule moving along the flat terrace up to a kink site or moving along the step edge are all comparable, while the barrier of diffusion up to a step edge is significantly lower than all of the other barriers calculated. Consequently, the barrier for diffusion from the step edge down to the terrace is substantially larger than for diffusion along the flat terrace. At low coverage, clusters of water molecules would, therefore, be expected to align along the upper side of step edges. This is consistent with experimental STM images taken by Morgenstern et al. (Morgenstern et al. *Phys. Rev. Lett.* 77 (1996) 703).

3:20pm **SS1+NC-ThA5 Growth of Ice Multilayers Studied with STM.** *K. Thürmer, N.C. Bartelt*, Sandia National Laboratories

Much progress has been made in the past few years in determining the structure and morphology of ice films on Pt(111). In our work we use STM to explore how metal-water interactions determine the ice-film morphology by tracking the film evolution during growth and annealing. We find that ice films as many as 30 molecular layers thick can be imaged with STM when negative sample biases of <-6(±1)V and sub-picoamp tunneling currents are used. As reported before by others, we observe that water deposited onto Pt(111) below 120K forms amorphous films, whereas metastable cubic ice appears between 120 and 150K. At 140K the first layer of water wets the Pt(111) substrate. At a mean film thickness of ~1nm the film consists of individual regularly-shaped 2-3 nm high crystallites, embedded in a one bilayer high wetting layer. We analyze the annealing behavior of these crystallites and report¹ that their dewetting is limited by the nucleation of new molecular layers on their top facets. By measuring nucleation rates as a function of crystallite height we estimate the strength of the driving force for dewetting. Upon deposition of additional water the crystallites coalesce and eventually, at ~5-10 nm mean thickness, the film becomes continuous, with the exception of a few remaining pinholes. A common, but not well understood observation is that ice grows between 120 and 150K in its metastable cubic 1c variant rather than in its equilibrium hexagonal form ice 1h. We find evidence for ice 1c in thicker films and suggest that it is a consequence of the mismatch in the atomic Pt-step height and the ice-bilayer separation. We propose a mechanism of cubic-ice formation via growth spirals around screw dislocations.

¹ K. Thürmer and N. Bartelt, *Phys. Rev. Lett.* 100, 186101 (2008).

4:00pm **SS1+NC-ThA7 Ice Nanoclusters on Au(111): Formation of a Unique Double Bilayer**, *D.J. Stacchiola, J.B. Park, S. Ma, P. Liu, J.A. Rodriguez, J. Hrbek*, Brookhaven National Laboratory

The nucleation of water into ice on solid surfaces has far reaching consequences in physical and biological systems. We have used ice multilayers grown on gold surfaces to prepare oxide nanoparticles. Profound differences on the nanoparticle nucleation pattern were observed when a different oxidant, such as NO₂ multilayers, was employed. To gain insight into the origin of this nucleation behavior we have studied the formation of ice nanoclusters on Au(111) combining STM, TPD and IRAS results with DFT calculations. The nucleation of single water molecules in the elbows of the herringbone reconstruction of Au(111) has been previously reported, as well as the study of the initial formation of small clusters, with 6 or more water molecules, on other hydrophobic surfaces such as Ag and Cu. However, not detail studies on the initial formation of water multilayers on Au(111) surfaces have been reported. In the case of a hydrophilic surface such as Pt(111), where a wetting bilayer is formed in the interface, it has been very recently shown that the growth of thicker layers leads to the formation of isolated ice islands on top of the interfacial bilayer, with 5 or more bilayers of water per island. We will show in this presentation that in the case of Au(111) no wetting interfacial bilayer is formed, due to the gold hydrophobic character and large lattice mismatch with ice Ih, and the initial growth of multilayers proceeds through the formation of isolated ice clusters with a unique double bilayer structure. An absence of dangling hydroxyl groups on the ice clusters points to participation of all hydrogens in hydrogen bonding within and between the two bilayers, and renders the surface of the double bilayer hydrophobic.

This research was carried out at Brookhaven National Laboratory and supported by the US Department of Energy (Chemical Sciences Division, DE-AC02-98CH10886).

4:20pm **SS1+NC-ThA8 Isotopic Effects in the Mixing Between Surface and Bulk Molecules at the Surface of Amorphous Solid Ice Studied by FTIR and DFT Calculations**, *P. Uvdal, J. Blomquist*, Lund University, Sweden

We have studied the exchange between surface and bulk molecules on amorphous solid ice using infrared vibrational spectroscopy. Intact molecules are grown in a layer by layer fashion, on Cu(100), allowing the formation of isotopically uniform layers at 84 K. A bulk layer consisting of 3-5 bilayers of ice of isotope A was exposed to 0.15 monolayers of isotope B. Three different water isotopes were used in this study, H₂¹⁶O, D₂¹⁶O and H₂¹⁸O. By studying the free O-H(D) stretch, present only at the ice surface, all isotopes could be spectroscopically identified. In particular, the decrease of isotope B could be monitored, along with the concomitant increase of isotope A, as a function of temperature. It is observed that mixing between surface and bulk water starts already at 100K. There are also a clear difference between the different isotopes. H/D exchange is observed and will be discussed. The vibrational data is interpreted with the aid of DFT cluster calculations.

4:40pm **SS1+NC-ThA9 The Adsorption of Water on Cu₂O and Al₂O₃ Thin Films**, *X. Deng, T. Herranz, C. Weis, H. Bluhm, M. Salmeron*, Lawrence Berkeley National Laboratory

The initial stages of water condensation, approximately 6 molecular layers, on two oxide surfaces, Cu₂O and Al₂O₃, have been investigated using ambient pressure x-ray photoelectron spectroscopy at relative humidity values (RH) from 0 to > 90%. Water adsorbs first dissociatively on oxygen vacancies producing adsorbed hydroxyl groups in a stoichiometric reaction: $O_{lattice} + Vacancies + H_2O = 2OH$. The reaction is completed at ~1% RH and is followed by adsorption of molecular water. The thickness of the water film grows with increasing RH. The first monolayer is completed at ~15% RH on both oxides and is followed by a second layer at 35-40% RH. At 90% RH, about 6 layers of H₂O film have been formed on Al₂O₃. The wetting process and the essential role of OH on oxide surfaces will also be discussed.

5:00pm **SS1+NC-ThA10 The Reactive Uptake of Water and CO₂ on MgO(100) Monitored by Ambient Pressure XPS**, *J.T. Newberg, D.E. Starr*, Lawrence Berkeley National Lab., *S. Yamamoto, S. Kaya, H. Ogasawara*, Stanford Synchrotron Radiation Lab., *T. Kendelewicz*, Stanford University, *M. Salmeron*, Lawrence Berkeley National Lab., *G.E. Brown*, Stanford University, *A.R. Nilsson*, Stanford Synchrotron Radiation Lab., *H. Bluhm*, Lawrence Berkeley National Lab.

The MgO(100) substrate is one of the most widely studied surfaces for water adsorption.¹ However, fundamental questions about whether water adsorbs molecularly or dissociatively under ambient conditions remains unanswered. This has been due in part to the lack of an in situ, chemically specific, surface sensitive technique. CO₂ is an important greenhouse gas, and the carbonation of MgO in mineral deposits has been suggested as a potential medium for CO₂ sequestration.² Here we present results from the investigation of the interaction of water with MgO(100)/Ag(100) films

using ambient pressure XPS (AP XPS). With AP XPS we can quantitatively probe the water film thickness along with the chemical speciation of the solid substrate, while in equilibrium with water vapor. We have characterized the uptake of water on MgO at water pressures from 10⁻⁹ to 1 Torr, up to a maximum of 25% relative humidity (RH). In addition, we monitored the interaction of CO₂ with the metal-oxide surface. At room temperature, both MgO hydroxylation and molecular water adsorption were observed at < 10⁻⁶ Torr. At ~0.1% RH about 0.3 ML of molecular water was observed (1 ML = 0.31 nm). However, at this RH the surface of MgO was completely passivated with an overlayer of hydroxide that has a thickness similar to that of brucite (Mg(OH)₂, 1 ML = 0.48nm). As the RH was increased to 25% RH, the Mg-hydroxide overlayer thickness remained at ~1 ML, while the molecular water film increased to ~1.5 ML. Preliminary results for CO₂ showed some dependency of RH on the reactivity towards the metal-oxide surface. The formation of a brucite-like overlayer is consistent with a favorable Gibbs free energy for the bulk reaction of liquid and gas phase water with MgO (-27 and -36 kJ/mol, respectively). A similar phenomenon was observed with AP XPS for water on hematite (Fe₂O₃).³ These results indicate that even under the lowest ambient RH values in the environment, metal-oxides that have thermodynamically stable hydroxides are chemically transformed at the surface due to thin film water. Thus, the presence of thin film water can have implications for how mineral surfaces interact with organic, biological and inorganic species in the environment.

¹ M.A. Henderson 2002 Surf. Sci Rep. 46 1.

² T. Koljonen et al. 2004 Energy 29 1521.

³ S. Yamamoto et al. publication in preparation.

5:20pm **SS1+NC-ThA11 Water-Stabilized Reconstructions on Polar Surfaces of Rocksalt Oxides**, *J. Ciston, L.D. Marks*, Northwestern University

We have investigated the stabilizing effect of water on the $\sqrt{3}\times\sqrt{3}$ -R30° and 2x2 reconstructions of the MgO(111) and NiO(111) surfaces using a combination of x-ray photoelectron spectroscopy (XPS) and transmission electron diffraction (TED). Combined experimental analysis has confirmed that the MgO(111)- $\sqrt{3}\times\sqrt{3}$ -R30° is stable only in the presence of hydroxyl groups on the surface, which is contrary to previously published structures. Experimental refinements of the valence charge density at these surfaces will also be discussed. Our experimental studies have been coupled with full-potential, all-electron density functional theory calculations to estimate surface energies and perform structural relaxations. The NiO system is particularly difficult to calculate due to highly localized and correlated 3d electrons. This has necessitated the use of a hybrid exchange-correlation functional in which the generalized gradient approximation is augmented with a 25% mixing of Hartree-Fock exact exchange for the 3d shell. This methodology substantially improves the accuracy of DFT-calculated surface energies, sometimes by several eV.

Nanometer-scale Science and Technology

Room: 311 - Session NS+NC-FrM

Nanoscale Processes

Moderator: N.A. Burnham, Worcester Polytechnic Institute

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

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

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

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

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

Nitrogen (N)-adsorbed Cu(001)-c(2x2) nanopatterned surfaces are used as templates to guide the growth of low-dimensional C₆₀ molecular nanostructures. The detailed nucleation and growth behaviors are studied by in situ scanning tunneling microscopy (STM). At room temperature, on the 0.3 ML-N-covered surface, where 5x5 nm² patches of the c(2x2)-N surface are squarely arranged and bare Cu(001) surface. In other word, the bare Cu surface forms a nanogrid. Here ML is defined as the Cu atom density of the clean Cu(001) surface. During the initial stages of growth, C₆₀ molecules preferentially adsorb on the bare Cu regions on a partially N-covered grid surface. Subsequently a two-dimensional molecular nanomesh is formed after C₆₀ covers all the bare Cu regions. Further deposition leads to C₆₀ growth on the c(2x2)-N areas until the first molecular layer is completed. For N-saturated surface with trench structures, the <010> steps of these structures serve as initial anchoring sites for C₆₀ growth. From there, the growth proceeds two-dimensionally until a single C₆₀ layer is achieved due to island coalescence. In contrast, no nucleation site was observed when the <110> steps were predominant on the surface. At least up to 6 mono-molecule layer, the growth proceeds layer-by-layer i.e., the overlayer morphologies are directed by the underlying substrate pattern in both (partially and fully N-covered) surfaces. Four rotational domains are observed for the quasi-hexagonally close-packed C₆₀ overlayer with a nearest-neighbor C₆₀-C₆₀ distance of 1.02 nm. It is found that the interaction between C₆₀ and the c(2x2)-N surface is fairly weak, likely to be dominated by van der Waals forces, whereas the C₆₀-Cu interface is chemisorbed. Site-specific electronic effects between these two regions can be resolved by STM even for thick films.

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

This study explores theoretically features unique to the chemical equilibrium in a nano-confined reaction mixture, which is closely related to newly developed routes for the synthesis of organic molecules and inorganic nanoclusters. Remarkable modifications in the equilibrium state of a closed small system compared to its (macroscopic) thermodynamic limit (TL) are predicted for several model reactions. Thus, canonical ensemble based statistical-mechanical formulation and computations show that a decrease in the overall number of molecules can lead to significant enhancement of the equilibrium extent of exothermic reactions. In particular, plots of lnK vs. 1/T exhibit below a certain temperature an increase in the slope, relative to the TL case, by a factor equal to the sum of the ingredient stoichiometric coefficients. In order to exemplify the smallness effect on K, the reaction 2AB(ad)=A₂(ad)+B₂(ad) on a surface is modeled for different overall number of molecules with emphasis on the roles of fluctuations and off-stoichiometric effects. The modeling is extended to the gaseous phase using the "harmonic oscillator-rigid rotor" approximation for the exothermic reaction 2NO(g)=N₂(g)+O₂(g), demonstrating the generality of the confinement-smallness effect. The enhancement is significant also in case of the addition reaction A+B=C, taking place in a closed tetrahedral "cage" as a model for a molecular capsule. The computations show that the temperature range of variations in the lnK vs. 1/T slope (from ΔH° to 2ΔH°) strongly depends on the reaction exothermicity. These phenomena are relevant to reactions taking place under certain conditions in a confined nano-space, such as catalytic nanoreactors ranging from molecular capsules and micelles¹ to zeolite cavities² and carbon nanotubes.³ While in catalysis the system is typically open, in nanoreactors there can be situations, such as the occurrence of rapid pre-equilibrium or "product inhibition", in which the reaction mixture is confined effectively. Then, conclusions of the closed system present modeling should be valid and taken into account as an appreciable contribution to the reaction equilibrium yield.

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

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

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

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

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

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

Hexa-peri-hexabenzocoronene (HBC) and HBC-derivatives can self-assemble in form of columnar film structures, which have recently attracted a significant amount of attention with regard to one-dimensional charge transport. The HBC molecules are known to form the large ordered columnar rows studied by various methods. In previous work the preparation of vertically oriented columnar rows has been achieved by employing a zone casting technique.¹ Here, we demonstrate another approach to fabricate such columnar system by an immersion process, where one-dimensional columns are formed by the self organization of discotic HBC molecules modified by thiol (-SH) anchors adsorbed on Au(111) substrates. The molecular arrangements and charge transport of such columnar films is investigated by scanning tunneling microscopy (STM) and current imaging tunneling spectroscopy (CITS). The HBC self-assembled monolayer (SAMs) are found to consist of long range ordered

domains consisting of equidistant paired rows. Each row consists of a one-dimensional column of closely packed stacked HBC units. The periodicity between these rows amounts to be twice than the diameter of the HBC-molecules. From the STM data and the molecular orientation obtained from near-edge x-ray absorption spectroscopy (NEXAFS) a structural model is derived. The current-voltage (I-V) characteristics measured by locally positioned STM tip above the HBC-SAM at 298 K and at 80 K exhibit a pronounced temperature dependence, indicates the presence of an additional charge transport mechanism including a hopping between the adjacent HBC disks aside from direct tunneling

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

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

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

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

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

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

Indium filled indium oxide tubular nanoarrows have been synthesized on silicon substrates by using simple horizontal tube furnace kept at 960°C and atmospheric pressure. Indium oxide powder mixed with carbon (1:1) in the presence of reducing ambient has been used for the growth of indium oxide nanotubular structures. A constant flow of Ar gas at the rate of 200 ml/min.

was maintained during the growth. The transmission electron microscopy (TEM) studies show the presence of indium inside the indium oxide tubular base extended with octahedron tip. The octahedron tip is sharp and has the diameter as low as 10 nm. High resolution TEM studies reveal that the structures are crystalline in nature and growth direction to be $\langle 100 \rangle$. The bottom-vapor-solid growth mechanism has been used to explain the role of reducing ambient in self catalytic growth of indium filled indium oxide tubular nanoarrows. The electron-beam induced mass transport of indium filled in indium oxide nano structures has been studied using TEM with the background pressure of specimen chamber at 10^{-7} mbar and room temperature. The electron beam current has been varied from 0.8 μ A to 24.7 μ A to study the onset of phase transformation of indium from solid to liquid in different nanotube structures having diameter ranging from 30 nm to 150 nm. The electron-beam irradiation results in the melting and transport of indium inside the tubular structures. The real time imaging in TEM measurements have been used to study the mass transport properties. The synthesis of indium filled indium oxide tubular nanoarrows and the observed indium transport may have the potential nanotechnological applications.

11:20am **NS+NC-FrM10 Etch Stop Control and Low-Damage Atomic-Layer Etching of HfO₂ using BCl₃ and Ar Neutral Beam**, *J.B. Park, S.D. Park, W.S. Lim, G.Y. Yeom*, Sungkyunkwan University, Korea

The downscaling of metal-oxide-semiconductor field-effect transistors (MOSFETs) has created the need for high-dielectric-constant k materials to replace SiO₂ for reducing the gate-leakage current while maintaining the gate-dielectric capacitance. Therefore, there have been many studies on the dry etching of HfO₂ using halogen-based plasma etching for applications to MOSFET devices. A precise etch rate is required in the plasma etching for HfO₂ instead of a high etch rate due to the low thickness of the material. Moreover, an extremely high etch selectivity over the under layer material is required. In addition, the damage on the etched surface is intolerable. However, the conventional plasma-etching processes tend to physically damage the surface of the devices by creating surface defects, including structural disruption, an intermixing layer, or stoichiometry modification, and increasing surface roughness, due to use of energetic reactive ions to achieve vertical etch profiles. In addition, these halogen-based plasma etchings showed finite etch selectivity between HfO₂ and the under lying materials. These problems decrease the device performance. Atomic-layer etching (ALET) may be the most suitable method for etching HfO₂ in next-generation MOSFET devices because it may etch HfO₂ with no physical damage and with atomic-scale etch controllability. The etch characteristics of HfO₂ by ALET were investigated using a BCl₃/Ar neutral beam. The effect of ALET on surface modification and etch-depth control was also examined. Self-limited etching of HfO₂ could be obtained using BCl₃ ALET. This was attributed to the absorption of BCl₃ by the Langmuir isotherm during the absorption stage and the vaporization of hafnium-chlorides/boron oxychlorides formed on the surface during the desorption stage. In addition, the surface composition of HfO₂ was not altered by etching during ALET.

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

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

large as above a few micrometers. Exposure levels to airborne nanoparticles were affected by the properties of nanoparticles (size, shape, density), humidity and the airflow pattern of the environment. Our study is committed to ensuring that nanoparticle research is carried out in a healthful and environmentally beneficial manner. Complete results will be fully discussed in the presentation.

Surface Science

Room: 207 - Session SS+AS+NC-FrM

Environmental Surfaces and Water Interaction with Oxide Surfaces

Moderator: B.D. Kay, Pacific Northwest National Laboratory

8:20am SS+AS+NC-FrM1 **Heterogeneous Reactivity of O₃ and OH Radical with Potassium Iodide**, M.A. Brown, T.M. McIntire, M.J. Krisch, University of California, Irvine, V. Johánek, University of Virginia, P.D. Ashby, Z. Liu, Lawrence Berkeley National Laboratory, A. Mehta, Stanford Linear Accelerator Center, D.F. Ogeltree, M. Salmeron, Lawrence Berkeley National Laboratory, J.C. Hemminger, University of California, Irvine

Sea salt aerosols are known to undergo heterogeneous reactions with atmospheric oxidants, resulting in halide depletion as they travel through polluted regions of the environment. The subsequent photochemistry of halide compounds (including halogenated oxides) strongly influences the chemical composition of the atmosphere. The results from uptake measurements of O₃ and OH radical on potassium iodide will be discussed. The reactivity of KI with O₃ and OH radical are remarkably different and result in reaction products of KIO₃ and KOH, respectively. We describe results from X-ray photoemission spectroscopy, X-ray diffraction, Atomic Force Microscopy and IR spectroscopy. In the case of O₃, under conditions in which the KI surface is devoid of adsorbed water molecules the reaction is self-passivating, and results in a thin layer of KIO₃ with an rms roughness of 3.6 nm. Subsequent exposure to water vapor mobilizes the KIO₃ oxide layer, revealing additional KI substrate that is readily available for further oxidation. As such, under conditions of low relative humidity the uptake of O₃ onto KI is not expected to be self-passivating. Under similar conditions, the reaction of OH radical with KI results in halide vacancies (iodide is released into the gas phase) created in the outermost surface lattice sites. The iodide vacancies are filled with OH- to generate a layer of KOH that is self-passivating following prolonged exposures. There is no spectroscopic evidence of stable oxidized iodide reaction products. AFM and IR results will also be discussed.

8:40am SS+AS+NC-FrM2 **Reactivity of Fe⁰ Atoms, Clusters and Nanoparticles with CCl₄ Multilayers on FeO(111)**, G.S. Parkinson, Z. Dohnálek, R.S. Smith, B.D. Kay, Pacific Northwest National Laboratory

There is currently much interest in the development of Fe⁰ nanoparticles as an agent for the destruction of chlorinated hydrocarbons in environmental remediation applications. However, the fundamental reaction pathways for the interaction of nano-Fe⁰ with such target molecules is unknown, and this presents a major obstacle to the design of improved particles. Our work utilizes a novel "atom dropping" technique where Fe⁰ atoms, clusters and nanoparticles are deposited into CCl₄ multilayers on FeO(111) at 30 K in ultra-high vacuum. A series of temperature programmed desorption and X-ray photoelectron spectroscopy experiments will be described which demonstrate an interesting size effect whereby isolated atoms and small clusters exhibit markedly different reactivity and product branching ratio to nanoparticles. The results will be discussed in the context of relevant theoretical calculations and the reaction pathways identified. The research described here was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

9:00am SS+AS+NC-FrM3 **New Paradigms for Environmental Surfaces: Structure and Reductive Transformation at α -Fe₂O₃/Water Interfaces**, K.M. Rosso, S.V. Yanina, S. Kerisit, Pacific Northwest National Laboratory

INVITED

The semiconducting properties of a wide range of minerals are often overlooked in the study of their interfacial chemical behavior. As a case study, reductive transformation of α -Fe₂O₃ (hematite) in aqueous solutions is a central part of the natural iron cycle in the environment. The transformation involves reduction of surface Fe(III) to Fe(II) by electron transfer, followed by Fe(II) solubilization and precipitation of new phases. It is a long-held perception that locations of Fe(III) reduction at the interface

with aqueous solution correspond directly to sites of Fe(II) release. However, hematite is a semiconductor with a propensity for moderate electron diffusivity in the surface and bulk. Hematite surfaces are also reactive with water and ions leading to surface charging behavior that is closely dependent on the crystallographic termination. Our recent focus has been on understanding how these qualities create unique conditions for the interfacial electron transfer involved in reductive transformation. We show using atomic force microscopy and surface-specific potentiometry evidence that these qualities couple interfacial electron transfer reactions at hematite (001) surfaces with those occurring at crystallographic edge terminations such as (012) via current flow through the crystal bulk. At low pH, divergent charging behavior between (001) and (012) surfaces yield a surface potential bias across the crystal of several hundred millivolts capable of biasing diffusion of charge carriers. We examined this aspect in detail with atomistic simulations of electron diffusion in bulk hematite and at (001) and (012) surfaces using a small polaron hopping model. The model supports the experimentally evident reductive transformation process of net oxidative adsorption of Fe(II) at (001) surfaces coupled by bulk charge transport to net internal reductive dissolution of Fe(III) at edge surfaces. This new paradigm for hematite reductive transformation has important implications for our understanding of the natural iron cycle in the environment. More generally, the apparent importance of chemically induced bulk crystal conduction is likely to be generalizable to a host of naturally abundant semiconducting minerals playing varied key roles in soils, sediments, and the atmosphere.

9:40am SS+AS+NC-FrM5 **Molecular Beam Studies of Supercooled Mixtures of Methanol and Water**, J. Matthiesen, R.S. Smith, B.D. Kay, Pacific Northwest National Laboratory

Molecular beams, temperature programmed desorption, and infrared spectroscopy were used to study the diffusive intermixing of amorphous water and methanol nanoscale films. Composite films with initially separated layers were created by sequential dosing at 25 K in UHV. The films were then heated and the extent of intermixing was determined by the onset of desorption of the underlayer species and changes in the infrared spectra. Both linear ramp and isothermal experiments were conducted. In a series of experiments the layer thickness, film composition, and heating rate were varied to extract quantitative temperature dependent diffusivities. Isotopically labeled methanol was used to mimic tracer-type experiments. These results compare favorably to the results obtained from separated layer experiments. Numerical simulations of the diffusive intermixing were used to quantitatively model the experimental results. The details of the experiment and the interpretation of the results will be discussed in detail. The research described here was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

10:00am SS+AS+NC-FrM6 **DFT Study of Water Adsorption on SrTiO₃ (001) Bulk Termination and 2x1 Reconstruction**, A.E. Becerra-Toledo, L.D. Marks, Northwestern University

Strontium titanate, SrTiO₃, has been studied extensively as a model perovskite system. Among other advances, its variety of cation oxidation states has provided critical insights into oxide surface reaction mechanisms. Understanding the reaction of ubiquitous water molecules with SrTiO₃ surfaces is of great importance to environmental science and catalysis. Density functional theory (DFT) calculations were performed to study the adsorption of water molecules on two different SrTiO₃ (001) surfaces. A repeated slab model was employed to study both a bulk-like TiO₂ surface termination and a 2x1 surface reconstruction. While similar studies have been carried out in the past, our treatment using a full-electron potential and a linear augmented plane wave plus local orbital (LAPW+lo) basis more accurately models the spatial character of single-particle wavefunctions. Two different exchange-correlation functionals were employed: the PBE¹ generalized gradient approximation (GGA) and the TPSS² meta-GGA. On the TiO₂-terminated surface, both molecular and dissociative adsorption of water were modeled. The results did not show a significant dependence on the choice of exchange-correlation functional. Most importantly, the adsorption energies for molecular and dissociative adsorption were more similar than has been previously reported,³ and therefore favor the coexistence of hydroxyl groups and molecular water on the surface. On the 2x1 surface reconstruction, which was solved by Erdman et al.⁴ and is typically formed under oxidizing conditions, dissociative adsorption was studied with several distinct stable structures considered. The most stable of these showed an adsorption energy (per H₂O molecule) much larger than that observed for the bulk TiO₂ termination. In all cases we observe the effect of hydrogen bonding between adsorbate and surface anions on the stabilization of the structures.

¹ Perdew, J.P. et al. Phys.Rev.Lett. 77, 3865 (1996).

² Tao, J. et al. Phys.Rev.Lett. 91, 146401 (2003).

10:20am **SS+AS+NC-FrM7 Unraveling a Reaction on an Oxide Surface Step by Step: Formation of Water from Oxygen through Successive H Transfer Reactions on TiO₂(110).** *F. Besenbacher, J. Matthiesen, S. Wendt, J.Ø. Hansen, E. Laegsgaard, B. Hammer*, University of Aarhus, Denmark

By means of high-resolution scanning tunneling microscopy (STM) measurements and density functional theory (DFT) calculations we studied the reaction between O₂ and H atoms on reduced rutile TiO₂(110). We identified chemisorbed OH₂ species as the initial intermediate that is produced by H transfer reactions to O₂ molecules, which concomitantly dissociate. Through further successive H transfer reactions, mediated by co-adsorbed water, the OH₂ species are finally transformed into water dimers. Our data exemplify how time-lapsed STM imaging, in combination with DFT calculations, can be successfully used to unravel reactions on surfaces with a high number of intermediates.

10:40am **SS+AS+NC-FrM8 Water Dissociation on Single Crystalline Anatase TiO₂(001) Studied by Core Level Photoelectron Spectroscopy.** *A. Sandell*, Uppsala University, Sweden, *J. Blomquist*, Lund University, Sweden, *L.E. Walle*, NTNU, Norway, *P. Uvdal*, Lund University, Sweden, *A. Borg*, NTNU, Norway

The interaction of water and TiO₂ surfaces has been intensely studied since the discovery of photoinduced splitting of water into hydrogen and oxygen on a rutile TiO₂ single crystal in 1972.¹ However, even though the anatase TiO₂ polymorph is more widely used as photocatalyst than rutile studies of the adsorption of water on well-defined anatase TiO₂ surfaces are scarce. So far, the efforts have mainly been theoretical. Based on calculations it has been proposed that molecular water adsorption is favored on the (101) surface, whereas water dissociation is favored on the (001) surface.^{2,3} This implies that the (001) surface may be very important in spite of it being the minority surface termination of anatase crystallites. In this contribution, we present the first study on the coverage dependent adsorption of water on the anatase TiO₂(001)-(4x1) surface using core level photoemission spectroscopy. Data with high surface sensitivity were recorded at the MAX-lab synchrotron radiation source. Two types of anatase TiO₂(001)-(4x1) surfaces were prepared: One by MOCVD growth on a lattice matched substrate [SrTiO₃(001)] and one by cleaning of a natural single crystal. Our results confirm that water dissociate on the anatase TiO₂(001)-(4x1) surface. We can define two adsorption phases: Phase 1 consists only of dissociated water, observed as OH-groups. This phase is found at low coverage at low temperature (190 K) and is the only state of adsorbed water above ~230 K. The saturation coverage of phase 1 agrees with the number of four-fold coordinated Ti ridge atoms of the (4x1) surface reconstruction. Phase 2 is found at higher coverage, reached at low temperature. It consists of a mixture of dissociated and molecular water with a ratio of 1:1 at 170 K. The hydroxyl coverage of phase 2 is approximately two times that of phase 1.

¹ A. Fujishima and K. Honda, Nature (London) 238, 37 (1972).

² A. Vittadini, A. Selloni, F. P. Roitzinger, and M. Grätzel, Phys. Rev. Lett. 81, 2954 (1998).

³ X.-Q. Gong and A. Selloni, J. Phys. Chem. B 109, 19560 (2005).

11:00am **SS+AS+NC-FrM9 Study of the Oxidation of Titanium and the Adsorption of Biomolecules on Titanium by Means of Electrochemical Quartz Crystal Microbalance with Dissipation Supported by X-ray Photoelectron Spectroscopy.** *I. Van De Keere*, Vrije Univ. Brussel, Belgium, *S. Svedhem*, *A. Kunze*, Chalmers Univ. of Tech., Sweden, *J. Vereecken*, Vrije Univ. Brussel, Belgium, *B. Kasemo*, Chalmers Univ. of Tech., Sweden, *A. Hubin*, Vrije Univ. Brussel, Belgium

Titanium is frequently used as a biomaterial in orthopaedics and cardiovascular devices. The metal is covered with a native oxide layer of a few nm, which contributes to the high biocompatibility of Ti implants. One of the surface properties of a biomaterial, which plays an important role in the interaction with biomolecules is electrostatic interaction at the surface. By varying the potential of Ti, the surface charge of Ti changes, and electrostatic interactions are likely to be influenced. The goal of the present study is to investigate the influence of an electric field on the adsorption of biomolecules, such as proteins and lipids, onto Ti surfaces and their conformational changes with electrochemical quartz crystal microbalance with dissipation (ECQCMD). QCMD is a well-established technique for monitoring mass and film thickness (through the frequency shift) and to obtain information about the viscoelastic properties of the adsorbed layers (through the dissipation shift). It has recently become possible to carry out combined QCMD and electrochemical measurements using a specially designed flow cell. This combination is valuable for adsorption studies under the influence of external fields and/or where one wants to in situ change the oxide layer thickness. A difficulty arises upon using Ti compared to other model substrates as gold since the surface of Ti is always covered with a native oxide layer, which may grow upon application of an

external potential to the Ti surface. Firstly, the oxidation of Ti in buffer under the influence of an electric field was investigated, because a stable oxide layer was desired before investigating the interaction of biomolecules with Ti under applied external potential. With ECQCMD, quantitative information on the growth behaviour and the thickness of the Ti oxide layer was obtained. The calculated thickness from ECQCMD was correlated with the depth profiles obtained from X-ray Photoelectron Spectroscopy (XPS). Secondly, the adsorption of biomolecules on Ti was studied. The influence of an external potential applied to the Ti-surface on the formation of supported lipid bilayers of DOEPC (positively charged phospholipid) is pronounced. The moment of vesicle rupture, which precedes the formation of bilayers, is delayed significantly upon application of a potential of 0 V vs SHE, compared to open circuit potential and 0.6 V vs SHE. For these two potentials, the rupture of vesicles occurs faster and at the same moment.

11:20am **SS+AS+NC-FrM10 Acidic Dissolution Mechanism, pH-dependent Stabilization and Adhesion of Single Molecules on Single Crystalline ZnO(0001)-Zn Model Surfaces Studied by in-situ AFM and DFT Simulations.** *M. Valtiner*, Max-Planck-Institut für Eisenforschung, Germany, *G. Grundmeier*, University of Paderborn, Germany

The surface chemistry at oxide/water interfaces is a key issue in adhesion science and related areas such as corrosion science. De-adhesion processes as well as corrosion processes are often accompanied by a change of the pH at the interface. Hence an atomistic understanding of oxide dissolution promoting effects of H⁺, OH⁻ and anions, as chlorides or sulfates, are an important aspect of de-/adhesion, metal corrosion and its inhibition. In this context, experimental results on single crystalline ZnO(0001)-Zn model surfaces and DFT-based ab-initio studies will be discussed. First, it will be shown that single crystalline ZnO(0001)-Zn model surfaces can be prepared easily and surprisingly clean under ambient conditions by introducing hydroxide stabilization via a wet chemical etching step. The prepared model surfaces will be discussed by AFM, LEED, angle resolved XPS, ToF-SIMS and Auger spectroscopy data.¹ Secondly, the stability of these ZnO(0001)-Zn surfaces in electrolyte solutions will be demonstrated by a combined approach of in-situ AFM imaging and ex-situ LEED investigations. It will be shown that ZnO(0001)-Zn surfaces are stable and single crystalline in aqueous solutions within a wide pH range due to hydroxide stabilization. An in-situ AFM study of the acidic dissolution allowed an imaging of the dissolution process and hence a mechanistic understanding of the dissolution process of ZnO can be supported.² Moreover, Single Molecule Adhesion studies - by means of single molecule desorption of polyelectrolyte molecules - on these surfaces at variation of the pH level will be presented. Finally, the potential of a synergistic combination of these approaches with ab-initio based simulation methods will be highlighted.

¹ M. Valtiner, S. Borodin, G. Grundmeier; Physical Chemistry Chemical Physics, 9(19), (2007) 2406-2412.

² M. Valtiner, S. Borodin, G. Grundmeier; Langmuir (2008), ASAP Article: 10.1021/la7037697.

11:40am **SS+AS+NC-FrM11 The Adsorption of Water on a PdO(101) Thin Film on Pd(111).** *H.H. Kan*, *R.J. Colmyer*, *J.F. Weaver*, University of Florida

Palladium oxide (PdO) is an excellent catalyst for the oxidation of hydrocarbons and CO under oxygen-rich conditions. Unfortunately, however, many fundamental questions about the surface chemistry of PdO have remained unanswered since it has been challenging to prepare well-defined PdO surfaces for detailed experimental investigations. In this talk, I will discuss our recent experimental study of the adsorption of water on a PdO(101) thin film that was grown in ultrahigh vacuum by oxidizing Pd(111) using an oxygen atom beam. From temperature programmed desorption (TPD) measurements, we find that water can populate several adsorbed states on PdO(101). Physisorbed water molecules populate both monolayer and multilayer states on PdO(101), with desorption from these states yielding TPD peaks at 150 and 197 K, respectively. The desorption temperature from the physisorbed monolayer is about 35 K higher for PdO(101) compared with Pd(111), which suggests that hydrogen-bonding enhances the physisorption bond strength on the oxide. We also observe a relatively broad desorption feature of water from PdO(101) that appears to consist of two components centered at 320 K and 350 K. We present evidence that these components arise from distinct states of molecularly and dissociatively chemisorbed water, respectively, and that both forms of chemisorbed water bind to coordinatively unsaturated Pd cations that are prevalent on the PdO(101) surface. Finally, although the dissociative chemisorption of water presumably involves hydrogen transfer to an oxygen anion of the oxide, we observe only small amounts of oxygen exchange between water and the oxide in experiments with oxygen-labeled water. This finding suggests that water dissociation produces inequivalent hydroxyl groups on PdO(101).

Surface Science

Room: 208 - Session SS+EM+NC-FrM

Semiconductor Surfaces

Moderator: V.M. Bermudez, Naval Research Laboratory

8:20am **SS+EM+NC-FrM1 From Nanochemistry to Active Nano-Objects at Semiconductor Surfaces, P.G. Soukiasian**, Commissariat à l'Energie Atomique and Université de Paris-Sud/Orsay, France **INVITED** Silicon carbide (SiC) surfaces/interfaces are studied by atom-resolved scanning tunneling microscopy and spectroscopy (STM/STS) using electrons and/or photons, synchrotron radiation-based photoelectron spectroscopies (XPS, UPS, μ -spot XPS) and/or diffraction, low energy electron microscopy (LEEM) experimental techniques and density functional theory. Such important issues as self-organized active metal nano-objects, defects and an amazing nanochemistry will be presented and discussed. It includes: The 1st example of H/D-induced clean/pre-oxidized semiconductor surface metallization, with an isotopic effect occurring using D; Selective formation of ultra-thin nitride layer at Si-SiC interface; Atomic crack defects developing at SiC surfaces; Anisotropic metal diffusion, metal atom pairs, chains and wires formation; Massively parallel active architecture based on metal/Si nanowires exhibiting a negative differential resistance behavior. These findings impact some important issues such as i) metallization of wide band-gap chemically passive semiconductor surfaces which is of particular interest in interfacing with biology, ii) selective SiC interface passivation especially useful in limiting dopant diffusion, iii) identifying and understanding some unusual defects most likely involved in the high density of interface states recurrent at SiC interfaces, and iv) achieving a massively parallel active architecture in the solid state.

9:00am **SS+EM+NC-FrM3 Chemistry of the Si-rich β -SiC(100) Surface Compared to the Si(100) Surface, S.M. Casey, L.N. Adhikari**, University of Nevada, Reno

The chemistry of the Si-rich β -SiC(100) surface has been studied using density functional theory (DFT) computational methods and small clusters to model the surface reactivity. Results for the reactions of the cluster models of the silicon carbide surface with ammonia and small alcohols and amines will be presented and the energetics compared to the corresponding pathways on the Si(100) surface. The computational results generally show that the silicon-rich silicon carbide surface exhibits stronger interactions with these types of adsorbates by 5-10 kJ/mol relative to the clean silicon surface. The major difference is that the silicon carbide surface has no closely bordering reactive silicon surface dimers, and, thus, the "intrinsic" reactivity of the silicon surface dimer can be examined without complicating multi-dimer reactions. The computational results will also be compared to experimental thermal desorption studies on these surfaces. The thermal desorption results are in general agreement with the DFT results.

9:20am **SS+EM+NC-FrM4 Surface Band Bending in GaN, M. Ruchala, M. Foussekis, H. Morkoc, M.A. Reshchikov, A.A. Baski**, Virginia Commonwealth University

In spite of tremendous progress in the development of nitride semiconductors, the detrimental effects of surfaces and interfaces on the electrical and optical properties of devices based on these semiconductors is often underestimated. We have investigated band bending at the surface of undoped GaN and its change caused by illumination (photovoltage) with scanning Kelvin probe microscopy (SKPM) in ambient and with a Kelvin probe attached to an optical cryostat in high vacuum. In the microscopy set-up, we charged the surface and increased band bending by several eV using conductive atomic force microscopy (CAFM), and then used SKPM to observe discharge transients of the surface band bending in dark from room temperature (RT) to 35 °C, as well as under sub-bandgap illumination. In the Kelvin probe set-up, we measured the photovoltage spectrum and its transients after UV illumination at temperatures from RT to 125 °C in vacuum and air ambient. These two complementary techniques provide independent information about surface band bending and its transient behavior after charge injection or illumination. The rate of restoration of the initial band bending in dark for both experiments (after CAFM charging or after flattening of band bending due to illumination) increased at higher temperatures and typically exhibited a quasi-logarithmic time dependence. The results indicate that the restoration of band bending disturbed from equilibrium occurs primarily by means of adsorption of some species from air, and not by thermionic emission of electrons over the surface potential barrier. Indeed, transients of the photovoltage (PV) caused by UV illumination in the Kelvin probe strongly depended on the ambient. In air ambient under illumination, the PV signal increased to its maximum of 0.65 V in a few seconds and then gradually decayed by 0.3 V over 3 h, whereas in vacuum the signal quickly increased to 0.55 V and then slowly increased

by 0.1 V over 3 h. This behavior indicates the photo-induced adsorption of negatively charged species in ambient or the photo-induced desorption of such species in vacuum. With regard to temperature, the initial band bending increased by 0.2 V from RT to 125 °C due to more bulk electrons overcoming the surface barrier and becoming trapped at surface states. Experiments are now in progress in the Kelvin probe to investigate the band bending behavior as a function of introduced gas species such as oxygen or water vapor.

9:40am **SS+EM+NC-FrM5 An Accelerated Molecular Dynamics Study of Diffusion on the GaAs (001) β 2(2x4) Reconstruction, M.H. Mignogna, K.A. Fichthorn**, The Pennsylvania State University

The GaAs (001) β 2(2x4) reconstruction is the most commonly used substrate for growth in GaAs homoepitaxy by molecular beam epitaxy. Kinetic Monte Carlo (KMC) simulations based on first-principles calculations¹ have illuminated the mechanisms for recovering this reconstruction during growth. However, the KMC simulations are based on rates of processes that occur on perfect β 2(2x4) unit cells. In experimental studies with reflection high-energy electron diffraction and scanning-tunneling microscopy, the surface is observed to exhibit domains of perfect β 2(2x4) unit cells, but long-range disorder persists and a possible origin is out-of-phase β 2(2x4) domains.² To examine the atomic-scale processes that lead to long-range disorder, as well as to characterize diffusion and the early stages of homoepitaxy on this surface, we employ accelerated molecular dynamics (MD). Our simulations are based on a semi-empirical, Tersoff-type potential that exhibits good agreement with a variety of bulk and surface properties of GaAs. Using accelerated MD we can probe long time scales, extending into the microsecond range and beyond. On the bare surface, we observe breaking, re-forming, and shifting of As row and trench dimers, that promotes the formation of out-of-phase domains of β 2(2x4) unit cells and leads to long-range disorder of the surface. The kinetic processes of the As dimers affect the surface diffusion of Ga adatoms, as well as the initial morphologies that occur during growth.

¹ P. Kratzer, E. Penev, M. Scheffler, Appl. Phys. A 75, 79 (2002)

² D.W. Pashley, J.H. Neave, B.A. Joyce, Surf. Sci., 582, 189 (2005).

10:00am **SS+EM+NC-FrM6 First Principles Investigation of Dimer Ordering on III-V Semiconductor Surfaces, J.C. Thomas, J.E. Bickel, J.M. Millunchick, A. Van der Ven**, University of Michigan

Surface disorder can contribute significantly to optoelectronic, thermodynamic, kinetic and interfacial properties of epitaxial thin films, especially at the nano-scale. Surface reconstructions, which decrease surface free energy relative to bulk configurations via a reduction in unfavorable bonding and increase in configurational entropy, play a vital role in the determination of these properties. In this work, the effect of finite temperature on the free energy of surface reconstructions is investigated in order to determine the role of entropy in surface dimer concentration and ordering. As a model system, we consider the α 2(2x4) and β 2(2x4) reconstructions on the (001) surface of homoepitaxial InAs, as these reconstructions are not only well studied, but are also stable within a continuous interval of chemical potential. A first principles model Hamiltonian is developed within the cluster expansion formalism and applied to equilibrium Monte Carlo simulations to obtain accurate thermodynamic quantities, as well as configurational trends. For example, fitting to energies for seven different dimer configurations of these 2x4 reconstructions, calculated via density functional theory show that there is an energetic preference for third nearest neighbor pairing (along the diagonal), giving rise to a "zig-zag" ordering of dimers, referred to as the z(4x4). Evidence of this structure has been previously reported. Monte Carlo simulations show the α 2(2x4) to be stable within an intermediate range of chemical potentials, giving way to the β 2(2x4) at higher chemical potential. The transition between configurations shows a step-like behavior at low temperatures, smoothing out at higher temperatures. The fraction of the α 2(2x4) that possesses the z(4x4) ordering was determined from averaged correlations. The coverage is about 60% at room temperature, and decreases to approximately 50% at typical growth temperatures, in reasonable agreement with published results. We show that size mismatch strain in ternary III-V alloys drives In surface segregation in GaAs and locks in a zig-zag ordering of As surface dimers.

10:20am **SS+EM+NC-FrM7 Hydroxyl Termination and Passivation of the Group III-rich (4x2)/c(8x2) Surfaces of InAs(001) and InGaAs(001) Surface Studied by STM, STS, and DFT, J.B. Clemens, T. Song, A.C. Kummel**, University of California, San Diego

Atomic Layer Deposition requires the substrate to have a chemical passivation/termination layer consisting of reactive groups that initiate the ALD reaction. A suitable passivation/termination layer would have ligands that mimic the surface during growth, such as hydroxyl (OH⁻).^{1,2} Scanning tunneling microscopy was used to study the initial bonding configuration of hydroxyl onto the group III-rich InAs(001)-(4x2)/c(8x2) surface, which is

almost identical to the InGaAs(001)-(4x2)/c(8x2) surface. These surfaces are more resistant to oxidation than group V-rich surfaces, which is true of many III-arsenide semiconductors, and therefore is a better starting template for ALD.³ Aqueous (30%) hydrogen peroxide vapour is used as the OH source. After annealing, the surface reaction forms well-ordered interfaces that terminate at about one ML indicating that this process is self-limiting. Substrate lattice disruption is minimal following OH desorption after annealing at 350° C. If pure water vapour is used as a control dose, less surface reaction occurs and it centers at surface defect sites. Density functional theory was used to model the interaction of InGaAs(001)-(4x2) with OH, H, and H₂O. Energies and kinetics of adsorption and desorption of OH, H, and H₂O are presented, which compares the stability of the HOOH/H₂O vs the H₂O only termination/passivation methods. DFT results show that the OH passivation method using HOOH is stable at high temperatures that are typically found under ALD growth conditions, while the passivation method using only water is not. The electronic structure was probed using scanning tunneling spectroscopy. On the clean as-prepared substrates, both n- and p-type InAs(001)-(4x2)/c(8x2) show n-type behavior, consistent with literature.^{4,5} Upon OH termination, both surfaces exhibit n-type behavior, with the Fermi level about 0.1 eV below the CB minimum. This shows no evidence for midgap Fermi level pinning, suggesting that this method has potential for high-κ gate oxide ALD on III-V semiconductor surfaces.

¹ K. Kukli, et al., J. Appl. Phys., 92, 1833 (2002).

² J. Aarik, et al., Appl. Surf. Sci., 161, 385 (2000).

³ D. Winn, et al., J. Chem. Phys., 127, 134705 (2007).

⁴ L. Olsson, et al., Phys. Rev. Lett., 76, 3626 (1996).

⁵ P. De Padova, et al., Surf. Sci., 482-485, 587 (2001).

10:40am **SS+EM+NC-FrM8 Pit Nucleation in the Presence of (nx3) and β2(2x4) Surface Reconstructions on In_{0.81}Ga_{0.19}As/InP Films, L.E. Sears, A. Riposan, J.M. Millunchick, University of Michigan - Ann Arbor**

The growth of heteroepitaxial films with high misfit strains on the crystallographic surface such as InGaAs/GaAs usually occurs in the Stranski-Krastanov mode, whereby coherent islands form on a planar wetting layer as a way to relieve strain due to a lattice mismatch. Theory has shown that both islands and pits can relieve strain on high misfit, low temperature films,¹ but experimentally only islands are typically observed as the initial mechanism of strain relief. We have discovered a growth regime in which pits relieve strain rather than islands due to a decrease in surface energy with increasing indium content. Models have predicted that altering the growth conditions, such as growth rate and temperature, or materials properties, such as surface energy or lattice mismatch, can lead to the nucleation of pits initially on the surface instead of islands,^{1,2} but little experimental data exists to support those claims. We examine the growth of In_{0.27}Ga_{0.73}As/GaAs(001) and In_{0.81}Ga_{0.19}As/InP(001), which both have the same lattice mismatch strain, and show that In composition is important in determining the type of 3D features that nucleate on the surface. As the critical thickness is exceeded, low indium composition films have a tendency to form 3D islands as the primary strain relief mechanism. On the other hand, pits are the preferred strain relief mechanism in high In composition films grown with the same growth conditions and lattice mismatch. Increasing the indium content results in a more metallic surface that has a lower surface energy (γ) and models have predicted that at sufficiently low γ pit nucleation is favored over islands as the initial strain relief mechanism.² Models have suggested that the presence of β2(2x4) reconstructions may also act as strain relief mechanism in In_{0.81}Ga_{0.19}As/InP(001) films.³ Analysis of the atomic surface structure of these films using scanning tunneling microscopy show that the reconstructions are also affected by the presence of pits, lending more evidence to surface reconstructions as a mechanism for strain relief.

¹ Lung MT, Lam CH, and Sander LM, Phys. Rev. Lett. 95 (086102) AUG 18 2005

² Bouville M, Millunchick JM, Falk ML, Phys. Rev. B 70 (235312) DEC 10 2004

³ Riposan A, C. Pearson, and JM Millunchick, J. Vac. Sci. Technol. A 24 (2041) OCT 10 2006.

11:00am **SS+EM+NC-FrM9 In-situ ALD Studies of Al- and La-oxide on In_{0.53}Ga_{0.47}As, M. Milojevic, University of Texas at Dallas, B. Brennan, Dublin City University, Ireland, H.C. Kim, University of Texas at Dallas, F.S. Aguirre-Tostado, The University of Texas at Dallas, J. Kim, R.M. Wallace, University of Texas at Dallas, G. Hughes, Dublin City University, Ireland**

The combination of high k dielectric materials on high mobility III-V semiconductors offers the potential for MOSFETs with larger transconductance at lower operating voltages than are currently achievable with silicon based devices. Arsenic and gallium oxidation states are suspected to be the cause of Fermi level pinning, and therefore the removal or minimization of such states is required in order to develop practical devices. This study investigates the atomic layer deposition (ALD) of aluminium and lanthanum oxide based high-k dielectrics on the ammonium sulphide (NH₄)₂S and ammonium hydroxide NH₄OH treated In_{0.53}Ga_{0.47}As surface grown by metal organic vapour phase epitaxy (MOVPE) on lattice

matched InP substrates using in-situ surface chemical analysis. Monochromatic, in-situ X-ray photoelectron spectroscopy (XPS) and ex-situ atomic force microscopy (AFM) were used to determine optimal (NH₄)₂S conditions based on varying the sulphur concentration, temperature and treatment time. The ALD of the high-k films carried out at 300°C consists of a metal precursor pulse followed by a water pulse with an high purity N₂ carrier gas and was sequentially examined with in-situ XPS after every half cycle of the deposition process to determine the initial interfacial oxide and substrate reactions taking place during the growth. A 'clean up' effect, whereby the ALD process reduces native oxides at the surface during high-k deposition, is well known for thin dielectric films. In the case of TMA/water based deposition of Al₂O₃, we have found that the first TMA pulse is responsible for the removal of virtually all of the arsenic oxide left on the surface after the pre-treatments, especially with (NH₄)₂S, to within the detection limits of XPS. Gallium oxide bonding is reduced to approximately a monolayer consistent with a Ga-O-Al bond at the interface. Similar results for La-based precursor reactions will also be presented. Capacitance-voltage measurements were also carried out on metal oxide semiconductor MOS devices formed after the high-k dielectric growth. Supported by MARCO MSD Focus Center, Science Foundation Ireland, and FUSION.

11:20am **SS+EM+NC-FrM10 Atomic Scale Investigation of Mn Impurities on the InAs(110) Surface, Y.J. Song, University of Maryland, College Park and NIST, G.M. Rutter, P.N. First, Georgia Institute of Technology, N. Zhitenev, J.A. Stroscio, National Institute of Standards and Technology**

Increased interest in spin-based electronics as a replacement for charge-based electronics has led to significant scientific attention to dilute magnetic semiconductors (DMS). One of the main dilute magnetic semiconductors involves doping III-V semiconductors with Mn acceptors with the aim of achieving high Curie temperatures. In the present work, we studied Mn deposited on the InAs(110) surface with low temperature scanning tunneling microscopy and spectroscopy (STM/STS). Single Mn atoms were deposited onto a cleaved n-InAs(110) surface at cryogenic temperatures. The as-deposited Mn adatoms were found to be in two distinct configurations. About 10% of the Mn adatoms appear in the topographic images to be positively charged. The other 90% appear to be in a neutral configuration. Both types of adatoms can undergo an exchange process whereby the surface Mn atom substitutes for an In atom in the top surface layer. This process involves raising the sample tunneling voltage beyond a certain threshold voltage of approximately -0.6 eV for both types of Mn adatoms. This process is similar to that seen in the Mn/GaAs system.¹ And we also studied that in-situ deposition of Mn onto a cleaved n-doped InAs(110) substrate at low temperature produces an adsorbate-induced 2DEG at the InAs surface. Spatial properties of Landau level quantization² in high magnetic fields of both the 2D sub-bands and 3D conduction bands were studied in relation to the configuration of Mn atoms on the surface.

¹ D. Kitchen et al, Nature 442, 436 (2006)

² M. Morgestern et al, Phys. Rev. Lett. 90, 56804 (2003).

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Ada, E.: NS+NC-FrM11, 89
Adhikari, L.N.: SS+EM+NC-FrM3, 92
Adler, S.B.: EN+AS+EM+TF-WeM4, 42
Agarwal, A.: PS-TuM11, 22
Agarwal, S.: TF-MoA4, 16
Agarwal, V.: NS+NC-WeA5, 58
Agheli, H.: BI+NC-ThM5, 65
Agostiano, A.: NS+NC-ThM10, 74
Aguirre-Tostado, F.S.: SS+EM+NC-FrM9, 33
Ahren, M.: MI+NC-WeM11, 44
Aili, D.: NS+NC-ThM6, 74
Akbari, A.: SE+NC-WeA1, 61
Akhmetov, A.: BO+AS+BI-WeA5, 53
Akhtar, S.: GR+EM+NC-TuM6, 20
Akin, D.: BM+BI+BO+NC-TuA1, 27
Albrecht, T.R.: NS+NC-ThA1, 83
Alexander, M.R.: BO+PS+AS+BI+SS-TuA1, 28
Alizadeh, A.: NM+EM+PS+NS+NC-ThM12, 73
Allara, D.L.: NS+NC-TuM3, 20
Allred, D.: NS+NC-WeM9, 46
Altfeder, I.B.: NS+NC-TuA11, 34
Altman, E.I.: SS+NC-MoA8, 14; SS2+NC-WeM1, 48
Amama, P.: IS+NS+TR+NC-ThM5, 70
Ambaye, H.: MI+NC-WeM12, 44
Amonette, J.E.: IS+NS+TR-WeA5, 56
Andersen, J.N.: SS1+NC-ThA3, 86
Anderson, D.G.: BO+PS+AS+BI+SS-TuA1, 28
Andersson, K.: SS+NC-MoM10, 5
Arlinghaus, H.F.: BO+AS+BI-WeA8, 53
Armani, A.M.: BI+NC-WeM9, 40
Arnadottir, L.: SS1+NC-ThA4, 86
Arpanaei, A.: BI+NC-TuA3, 25
Arraud, N.: BI+SS+NC-MoA8, 10
Artyushkova, K.: BO+PS+AS+BI+SS-TuA12, 29
Ashby, P.D.: SS+AS+NC-FrM1, 90
Ashegi, M.: NS+NC-FrM7, 89
Asscher, M.: SS1+NC-TuA12, 36
Asunskis, D.J.: EN+EM+NS+P+A+T+V-ThM6, 69
Ataman, E.: SS1+NC-ThA3, 86
Au, Y.: MS+NC-MoM8, 3
Au, Y.Y.: NS+NC-WeA8, 58
Awo-Affouda, C.: MI-WeA8, 57;
NM+MS+NS+NC-WeM3, 44

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Babaud, L.: PS1-WeA3, 60
Baber, A.E.: EN+BI+SS+SE-TuM11, 18; NS+NC-TuA9, 34; NS+NC-WeA10, 59; SS1+NC-TuA9, 36
Bachmann, J.: TF+NC-MoM7, 6
Baddeley, C.J.: NS+NC-ThM4, 74
Baddorf, A.P.: SS2+NC-WeM2, 49
Badi, N.: EN+AS+EM+TF-WeM3, 42
Baer, D.R.: IS+NS+TR+NC-ThM10, 71;
IS+NS+TR-WeA5, 56
Bagge-Hansen, M.: GR+TF+NC-MoM7, 1
Bain, J.A.: MI+NC-WeM9, 43
Bajales, N.: NS+NC-ThM9, 74
Baker, T.A.: SS2+NC-WeM5, 49
Baklanov, M.R.: PS-TuM2, 21
Balaz, S.: SS1-ThM2, 75
Ballarotto, V.W.: NM+EM+PS+NS+NC-ThM4, 72
Ballav, N.: BO+AS+BI+NC-WeM1, 40
Baltzer, L.: NS+NC-ThM6, 74
Bañares, M.A.: IS+NS+TR-WeA3, 56

Banerjee, S.K.: NM+MS+NS+NC-WeM5, 44
Banna, S.: PS-TuM11, 22
Bargar, J.: AS-MoA10, 9
Baricuatro, J.H.: EN+EM+NS+P+A+T+V-ThM12, 69
Barlow, D.E.: BO+AS+BI-WeA2, 53;
GR+TF+NC-TuA5, 31
Barnes, T.M.: NS+NC-FrM8, 89; NS+NC-WeA4, 58
Barnett, S.A.: EN+AS+EM+TF-WeM4, 42
Barnola, S.: NM+EM+PS+NS+NC-ThM11, 72
Barricklow, K.: EN+AS+TF+VT+NC-WeA1, 55
Barry, P.: TR+NS+EM+NC-WeA4, 63
Bartels, L.: SS2+NC-WeM11, 50
Bartelt, N.C.: GR+EM+NC-TuM11, 20;
IS+NS+TR+NC-ThM1, 70; SS+NC-MoM5, 4;
SS1+NC-ThA5, 86
Barth, K.L.: EN+AS+TF+VT+NC-WeA1, 55
Barton, R.: MN+NC-MoA7, 13
Bartynski, R.A.: EN+EM+NS+P+A+T+V-ThM10, 69; SS2+NC-WeM10, 50
Bashir, A.: NS+NC-FrM6, 88
Bashir, R.: BM+BI+BO+NC-TuA1, 27
Baski, A.A.: SS+EM+NC-FrM4, 92
Baudemprez, B.: MS+NC-MoM1, 2
Bawendi, M.: NM+MS+NS+NC-ThA3, 81
Bazin, A.: PS1-WeA10, 61
Becerra-Toledo, A.E.: SS+AS+NC-FrM6, 90
Bedzyk, M.J.: NS+NC-ThM3, 73; TF-MoA1, 15
Beebe, Jr., T.P.: BI+NC-TuA12, 26; BI+NC-TuA4, 25
Behm, R.J.: BO+AS+BI+NC-WeM5, 40
Bellisario, D.O.: NS+NC-TuA9, 34; NS+NC-WeM4, 45
Belov, M.: NS+NC-TuA4, 34
Bensaoula, A.: EN+AS+EM+TF-WeM3, 42
Benz, L.: SS+NC-MoA9, 14; SS2+NC-WeM5, 49
Bérat, R.: BI+SS+NC-MoA8, 10
Berber, S.: BO+EM+BI+NC-ThM12, 68
Berger, C.: GR+EM+NC-TuM2, 19; GR+SS+NC-MoA5, 11
Bermudez, V.M.: SS+NC-MoA1, 14
Bersch, E.: EN+EM+NS+P+A+T+V-ThM10, 69
Besenbacher, F.: BI+NC-TuA8, 26; BI+SS+NC-MoA1, 9; SS+AS+NC-FrM7, 91
Bevan, K.H.: NS+NC-ThM3, 73
Beyer, A.: GR+TF+NC-MoM5, 1
BHadj Hamouda, A.: SS1+NC-WeM1, 47
Bhandari, H.: MS+NC-MoM8, 3
Bickel, J.E.: SS+EM+NC-FrM6, 92
Biris, A.S.: NS+NC-WeM11, 46
Bischoff, L.: NM+MS+NS+NC-ThA5, 82
Bistrizter, R.: NM+MS+NS+NC-WeM5, 44
Biswas, S.: EN+AS+TF+VT+NC-WeA5, 55;
EN+EM+NS+P+A+T+V-ThM11, 69
Blackburn, J.L.: NS+NC-FrM8, 89; NS+NC-WeA4, 58
Blau, H.M.: BI+NC-TuA1, 25
Blaze, M.: BO+AS+BI-WeA5, 53
Blom, T.: GR+TF+NC-TuA3, 31
Blomfield, C.J.: AS-MoA9, 8
Blomquist, J.: SS+AS+NC-FrM8, 91; SS1+NC-ThA8, 87
Bluhm, H.: SS+NC-MoM11, 5; SS1+NC-ThA10, 87; SS1+NC-ThA9, 87
Bockenbauer, S.: SS1+NC-WeM10, 48
Bode, M.: NS+NC-TuM9, 21
Boggs, M.E.: BI+NC-TuA12, 26; BI+NC-TuA4, 25
Boland, T.: BI+NC-ThM6, 65
Bolduc, M.: NM+MS+NS+NC-WeM3, 44
Bolotin, I.L.: EN+EM+NS+P+A+T+V-ThM6, 69
Bolotin, K.: GR+EM+NC-TuM3, 19
Bonnell, D.A.: NS+NC-TuM5, 20

Borg, A.: SS+AS+NC-FrM8, 91
Borghesi, A.: BO+AS+BI+NC-WeM9, 41
Bot, C.: BO+AS+BI+NC-WeM6, 41
Botiz, I.: EN+EM+NS+P+A+T+V-ThM9, 69
Böttcher, A.: NS+NC-ThM9, 74
Bottenus, D.R.: BO+NS+BI+NC-ThA7, 79
Bouchu, D.: MS+NC-MoM7, 3
Boukhalvalov, D.W.: GR+EM+NC-TuM6, 20
Boullart, W.: PS-TuM2, 21
Bouter, A.: BI+SS+NC-MoA8, 10
Bowman, C.: SE+NC-WeA12, 63
Bozzolo, G.: SS+NC-MoM2, 4
Brand, H.R.: IS+NS+TR-WeA2, 56
Breese, M.B.H.: GR+TF+NC-TuA12, 32
Bremer, S.: BO+NS+BI+NC-ThA11, 80
Brennan, B.: SS+EM+NC-FrM9, 93
Brenner, D.W.: TR+MN+NC-WeM3, 50
Bretagnol, F.: BO+NS+BI+NC-ThA11, 80;
BO+NS+BI+NC-ThA9, 79
Brett, M.J.: SE+TF+NC-ThA4, 84
Brianceau, P.: NM+EM+PS+NS+NC-ThM11, 72
Brihuega, I.: GR+SS+NC-MoA7, 11
Brisson, A.R.: BI+SS+NC-MoA8, 10
Broitman, E.: SE+NC-WeA10, 62
Bronikowski, M.: NS+NC-WeA1, 58
Brovko, L.: NS+NC-WeA11, 59
Brown, G.E.: SS1+NC-ThA10, 87
Brown, M.A.: SS+AS+NC-FrM1, 90
Brown, N.: BI+NC-ThM6, 65
Brozell, A.M.A.M.: BI+NC-ThM1, 65
Bruce, R.L.: NM+EM+PS+NS+NC-ThM12, 73
Brus, S.: MS+NC-MoM1, 2
Buck, M.: NS+NC-ThA3, 83; NS+NC-ThM1, 73
Budzioch, J.: BO+EM+BI+NC-ThM11, 67
Bui, H.P.: BI+NC-TuA4, 25
Bukasov, R.: BI+TF+MI+NS+NC-ThA3, 77
Bulleit, B.: BI+NC-TuA9, 26
Bulter, W.H.: MI+NC-WeM6, 43
Bunning, T.J.: SE+NC-WeA3, 62
Burgess, D.R.: TF-TuA11, 38
Buriak, J.M.: NS+NC-TuA4, 34
Burkov, Y.: IS+NS+TR-WeA2, 56
Burnham, N.A.: TR+MN+NC-WeM11, 51;
TR+NS+EM+NC-WeA9, 64
Burns, S.A.: BO+AS+BI-WeA11, 54
Burton, B.B.: TF-MoA3, 15
Burzynski, R.: NS+NC-ThA5, 83
Bussetti, G.: BO+AS+BI+NC-WeM9, 41
Bussmann, E.: SS1+NC-WeM10, 48; SS1+NC-WeM4, 47
Butcher, D.: SS+NC-MoM9, 5
Butera, R.E.: SS1-ThM1, 75
Buzanska, L.: BO+NS+BI+NC-ThA11, 80

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Cai, Z.: MI+NC-WeM4, 43
Calle, F.: SS+NC-MoM10, 5
Campbell, A.: TR+MN+NC-WeM2, 50
Campbell, C.T.: EN+EM+NS+P+A+T+V-ThM12, 69
Campbell, P.M.: GR+SS+NC-MoA3, 10
Campioni, M.: BO+AS+BI+NC-WeM9, 41
Canavan, H.E.: BO+PS+AS+BI+SS-TuA12, 29
Canfield, P.C.: SS+NC-MoM3, 4
Cao, S.: BO+AS+BI-WeA11, 54
Capadona, J.R.: BM+BI+BO+NC-TuA12, 28
Capaz, R.B.: SS1+NC-WeM12, 48
Carazzolle, M.F.: SS+NC-MoM1, 4
Cardona, C.: EN+EM+NS+P+A+T+V-ThM3, 68
Carlson, R.: BO+AS+BI-WeA5, 53
Carroll, M.S.: EN+EM+NS+PS-TuA4, 30
Carva, K.: GR+TF+NC-TuA3, 31
Casey, S.M.: SS+EM+NC-FrM3, 92

- Castner, D.G.: BM+BI+BO+NC-TuA3, 27;
BO+EM+BI+NC-ThM10, 67
- Castro, G.R.: SY+SS+BI-TuM11, 23
- Cavanagh, A.S.: TF+NC-MoM3, 5; TF+NC-MoM4, 6
- Ceccone, G.: BO+EM+BI+NC-ThM6, 67;
BO+NS+BI+NC-ThA9, 79;
BO+PS+AS+BI+SS-TuA11, 29
- Cederberg, J.G.: EN+EM+NS+PS-TuA4, 30
- Cerriotti, L.: BO+NS+BI+NC-ThA11, 80
- Chabal, Y.J.: GR+TF+NC-TuA8, 31; MN+NC-MoA10, 13
- Chagarov, E.: SS1+NC-WeM2, 47
- Chakraborty, S.: BI+TF+MI+NS+NC-ThA9, 78;
TR+NS+EM+NC-WeA9, 64
- Chan, Y.L.: MI+NC-WeM2, 43
- Chang, E.H.: BI+NC-WeM6, 39
- Chang, J.P.: AS-MoA10, 9; NM+MS+NS+NC-ThA11, 82; PS-TuM4, 22
- Chao, J.-J.: EN+EM+NS+P+A+T+V-ThM1, 68
- Chapon, P.: EN+AS+EM+TF-WeM3, 42
- Charpin, C.: NM+EM+PS+NS+NC-ThM11, 72
- Checka, N.: PS-TuM1, 21
- Chen, C.-H.: GR+TF+NC-TuA12, 32
- Chen, C.-L.: NS+NC-WeA5, 58
- Chen, C.-P.: BO+EM+BI+NC-ThM2, 66
- Chen, D.A.: SS+NC-MoA11, 15
- Chen, H.: GR+TF+NC-MoM7, 1
- Chen, H.Y.: EN+AS+EM+TF-WeM4, 42
- Chen, K.C.: BO+EM+BI+NC-ThM1, 66
- Chen, K.H.: BO+EM+BI+NC-ThM2, 66
- Chen, L.: EN+BI+SS+SE-TuM5, 18; PS1-WeA9, 60
- Chen, L.C.: BO+EM+BI+NC-ThM2, 66;
GR+TF+NC-MoM9, 2
- Chen, L.-Q.: SS2+NC-WeM2, 49
- Chen, S.: GR+TF+NC-TuA12, 32
- Chen, W.: MI+NC-WeM1, 42
- Chen, Z.: MI+NC-WeM4, 43
- Cheng, F.: BM+BI+BO+NC-TuA3, 27
- Cheng, Z.: SS2+NC-WeM11, 50
- Cheong, K.H.: BI+SS+NC-MoA3, 9
- Chevallier, J.: BI+NC-TuA8, 26
- Chhowalla, M.: GR+TF+NC-TuA10, 32
- Chiang, S.: SS1+NC-WeM9, 48
- Chiaradia, P.: BO+AS+BI+NC-WeM9, 41
- Chiari, M.: BM+BI+BO+NC-TuA5, 27
- Chiaroni, J.: NM+EM+PS+NS+NC-ThM11, 72
- Chiu, P.: TR+NS+EM+NC-WeA4, 63
- Cho, K.J.: GR+EM+NC-TuM12, 20; GR+TF+NC-TuA1, 31
- Cho, N.J.: BI+SS+NC-MoA3, 9
- Choi, J.W.: GR+TF+NC-TuA4, 31
- Chorkendorff, I.: SS+NC-MoM10, 5; SS1+NC-TuA8, 35
- Choudhury, S.: SS2+NC-WeM2, 49
- Christensen, S.T.: TF-MoA1, 15
- Chu, W.: MS+NC-MoM11, 3
- Chuang, C.-H.: GR+TF+NC-TuA12, 32; MI+NC-WeM2, 43
- Chung, C.Y.: SS+NC-MoM9, 5
- Chung, J.-Y.: NM+EM+PS+NS+NC-ThM4, 72
- Chung, Y.W.: SE+NC-WeA4, 62
- Cipriany, B.R.: MN+NC-MoA11, 13
- Ciston, J.: SS1+NC-ThA11, 87
- Clausen, B.S.: IS+NS+TR-WeA8, 56
- Clavero, C.: BI+TF+MI+NS+NC-ThA7, 77
- Clemens, J.B.: SS+EM+NC-FrM7, 92
- Clement, M.P.: NM+EM+PS+NS+NC-ThM11, 72
- Coecke, S.: BO+NS+BI+NC-ThA11, 80
- Coleman, V.: GR+TF+NC-MoM3, 1
- Colling, M.E.: SS2+NC-WeM5, 49
- Collins, K.: PS-TuM11, 22
- Collins, R.W.: SE+TF+NC-ThA9, 85
- Colmyer, R.J.: SS+AS+NC-FrM11, 91
- Colpo, P.: BI+TF+MI+NS+NC-ThA5, 77;
BO+NS+BI+NC-ThA11, 80; BO+NS+BI+NC-ThA5, 79; BO+NS+BI+NC-ThA9, 79;
BO+PS+AS+BI+SS-TuA11, 29;
NM+EM+PS+NS+NC-ThM5, 72
- Comparelli, R.: NS+NC-ThM10, 74
- Conny, J.M.: AS-MoA4, 8
- Conrad, E.H.: GR+EM+NC-TuM2, 19;
GR+SS+NC-MoA2, 10
- Coutts, T.J.: NS+NC-WeA4, 58
- Craighead, H.G.: MN+NC-MoA11, 13; MN+NC-MoA7, 13
- Cudaj, M.: NS+NC-ThM9, 74
- Culbertson, J.C.: GR+SS+NC-MoA3, 10
- Curri, M.L.: NS+NC-ThM10, 74
- Custance, Ó.: NS+NC-TuM11, 21
- Cvetko, D.: GR+EM+NC-TuM5, 19
- Czigány, Zs.: SE+NC-WeA10, 62
- D —
- da Silva, F.C.S.: MI+NC-TuA5, 32
- Dagata, J.A.: BI+NC-WeM6, 39
- d'Agostino, R.: NS+NC-ThM10, 74
- Dagotto, E.: MI+NC-WeM5, 43
- Damin, F.: BM+BI+BO+NC-TuA5, 27
- Dang, L.X.: EN+AS+TF+VT+NC-WeA3, 55
- Danila, A.: PS-TuM2, 21
- Darling, S.B.: EN+EM+NS+P+A+T+V-ThM9, 69
- Daschbach, J.L.: EN+AS+TF+VT+NC-WeA3, 55;
SS1+NC-ThA1, 86
- Datar, R.H.: TR+MN+NC-WeM10, 51
- Datye, A.: IS+NS+TR-WeA8, 56
- Davidson, S.D.: TF+NC-MoM4, 6
- Davies, M.C.: BO+PS+AS+BI+SS-TuA1, 28
- Davydov, A.: MI+NC-TuA5, 32
- de Araújo, M.M.: SS1+NC-WeM12, 48
- de Heer, W.A.: GR+EM+NC-TuM2, 19;
GR+SS+NC-MoA2, 10
- de Marneffe, J.-F.: MS+NC-MoM1, 2
- de Pablo, J.J.: NS+NC-ThA1, 83; NS+NC-ThM11, 75
- de Siero, A.: SS+NC-MoM1, 4
- DeGraf, C.: TR+NS+EM+NC-WeA9, 64
- deHeer, W.A.: GR+SS+NC-MoA5, 11
- Dehne, A.: NS+NC-ThM2, 73
- Delariva, A.: IS+NS+TR-WeA8, 56
- Delgado, G.: PS1-WeA2, 60
- Demaree, J.D.: TF-MoA5, 16
- Demers-Carpentier, V.: NS+NC-TuA10, 34
- Demirel, M.C.: TR+NS+EM+NC-WeA11, 64
- Demuyneck, S.: MS+NC-MoM1, 2
- Deng, X.: SS1+NC-ThA9, 87
- Denis, H.: NM+EM+PS+NS+NC-ThM11, 72
- Depalo, N.: NS+NC-ThM10, 74
- DeSario, P.A.: EN+BI+SS+SE-TuM5, 18
- Deshpande, R.: EN+AS+EM+TF-WeM1, 41
- Desikan, R.: TR+MN+NC-WeM10, 51
- Detcheverry, F.A.: NS+NC-ThA1, 83
- Dey, D.: NS+NC-ThA4, 83
- di Carlo, G.: BM+BI+BO+NC-TuA5, 27
- Diaconescu, B.: BO+EM+BI+NC-ThM12, 68
- Dickinson, G.: BO+AS+BI-WeA2, 53
- Dieing, T.: NS+NC-WeM12, 46
- Dielissen, S.A.F.: TF-MoA2, 15
- Dietzel, D.: TR+NS+EM+NC-WeA3, 63
- Dillon, A.C.: EN+AS+EM+TF-WeM1, 41
- Dimitrijevic, N.: EN+EM+NS+P+A+T+V-ThM9, 69
- Dobisz, E.A.: NS+NC-ThA1, 83
- Dohnalek, Z.: SS+NC-MoA5, 14; SS+NC-MoA7, 14
- Dohnálek, Z.: SS+AS+NC-FrM2, 90; SS1+NC-ThA1, 86
- Dokmeci, M.R.: NS+NC-WeA5, 58
- Dolatshahi-Pirouz, A.: BI+NC-TuA8, 26
- Donnelly, V.M.: PS1-WeA1, 59; PS1-WeA2, 60
- Doris, B.: MS+NC-MoM3, 3
- Dorman, J.: NM+MS+NS+NC-ThA11, 82
- Dou, X.: NS+NC-FrM6, 88
- Doyonnas, R.: BI+NC-TuA1, 25
- Drees, M.: EN+EM+NS+P+A+T+V-ThM3, 68
- Du, Y.: SS+NC-MoA5, 14; SS+NC-MoA7, 14
- Dubey, M.: BM+BI+BO+NC-TuA3, 27
- Ducker, R.E.: BI+NC-TuA11, 26
- Duden, T.: SS+NC-MoM5, 4
- Dugger, M.T.: TR+MN+NC-WeM5, 51
- Duguet, T.: SS+NC-MoM3, 4
- Dunning, J.: BM+BI+BO+NC-TuA12, 28
- Durand, A.M.: SS1+NC-WeM9, 48
- Durrani, F.: BO+AS+BI-WeA11, 54
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- Edvardsson, M.: BI+NC-ThM4, 65
- Egelhoff, W.: MI+NC-WeM1, 42
- Eggiman, D.: TR+NS+EM+NC-WeA9, 64
- Eichfeld, S.M.: NS+NC-WeA9, 58
- Einstein, T.L.: SS1+NC-WeM1, 47
- Eisman, G.: EN+AS+EM+TF-WeM11, 42
- Ekstrand, H.: BI+NC-ThM4, 65
- Elam, J.W.: EN+BI+SS+SE-TuM1, 18; TF+NC-MoM10, 6; TF-MoA1, 15
- Elibol, O.: BM+BI+BO+NC-TuA1, 27
- El-Kholy, I.A.: SS1+NC-WeM11, 48
- El-Kouedi, M.: NS+NC-WeM4, 45
- Ellenbecker, M.: NS+NC-FrM11, 89
- Elsayed-Ali, H.: SS1+NC-WeM11, 48
- Emoto, K.: BM+BI+BO+NC-TuA3, 27
- Emtsev, K.V.: GR+EM+NC-TuM1, 19
- Emziane, M.: EN+EM+NS+PS-TuA5, 30
- Enander, K.: NS+NC-ThM6, 74
- Engelhard, M.H.: IS+NS+TR-WeA5, 56
- Engelmann, S.: NM+EM+PS+NS+NC-ThM12, 73
- Engstrom, J.R.: TF+NC-MoM1, 5
- Engstrom, M.: MI+NC-WeM11, 44
- Enlow, J.O.: SE+NC-WeA3, 62
- Enzenroth, R.A.: EN+AS+TF+VT+NC-WeA1, 55
- Erdemir, A.: IS+NC-ThA5, 80; SE+NC-WeA8, 62
- Eriksson, O.: GR+EM+NC-TuM6, 20;
GR+TF+NC-MoM3, 1; GR+TF+NC-TuA3, 31
- Ermanoski, I.: SS1+NC-WeM4, 47
- Erwin, S.C.: NS+NC-TuA3, 33
- Eryilmaz, O.L.: IS+NC-ThA5, 80; SE+NC-WeA8, 62
- Escher, M.: SY+SS+BI-TuM11, 23
- Eu, I.: NM+EM+PS+NS+NC-ThM6, 72
- Evans, J.: SS1+NC-WeM5, 47
- Everts, F.: SS1-ThM4, 75
- Evoy, S.: NS+NC-TuA4, 34; NS+NC-WeA11, 59
- Ezirmik, V.: SE+NC-WeA8, 62
- F —
- Fadley, C.S.: AS-MoA7, 8
- Fairbrother, D.H.: SS1-ThM11, 76
- Fairbrother, H.: SS1-ThM10, 76; SS1-ThM12, 76
- Fairley, N.: AS-MoA9, 8
- Fang, N.X.: NM+MS+NS+NC-ThA1, 81
- Fanton, A.: NM+EM+PS+NS+NC-ThM11, 72
- Farkas, N.: BI+NC-WeM6, 39
- Farmer, J.A.: EN+EM+NS+P+A+T+V-ThM12, 69
- Favia, P.: NS+NC-ThM10, 74
- Feenstra, R.: GR+SS+NC-MoA11, 11
- Feibelman, P.J.: GR+EM+NC-TuM11, 20;
IS+NS+TR+NC-ThM1, 70
- Feng, X.F.: SY+SS+BI-TuM12, 24
- Feng, Z.: TF-MoA1, 15
- Ferreira, P.M.: NM+MS+NS+NC-ThA1, 81
- Fert, A.: MI-WeA11, 57
- Fichthorn, K.A.: SS+EM+NC-FrM5, 92
- Filikhin, I.: NS+NC-WeM10, 46
- Findenegg, G.H.: BO+AS+BI+NC-WeM2, 40
- Fiordaliso, E.: SS1+NC-TuA8, 35
- First, P.N.: GR+SS+NC-MoA2, 10; GR+SS+NC-MoA5, 11; GR+SS+NC-MoA8, 11;
GR+SS+NC-MoA9, 11; SS+EM+NC-FrM10, 93
- Floro, J.A.: NM+MS+NS+NC-ThA5, 82
- Fompeyrine, J.: AS-MoA10, 9
- Ford, J.J.: IS+NS+TR-WeA1, 55

- Forster, S.: BO+PS+AS+BI+SS-TuA5, **28**
 Förster, S.: BO+AS+BI+NC-WeM2, 40
 Foss, M.: BI+NC-TuA8, **26**
 Foucher, J.: PS1-WeA10, 61
 Fournée, V.: SS+NC-MoM3, 4
 Foussekis, M.: SS+EM+NC-FrM4, 92
 Frank, C.W.: BI+SS+NC-MoA3, **9**
 Franz, G.: BO+PS+AS+BI+SS-TuA10, **29**
 Freitag, B.: EN+AS+TF+VT+NC-WeA4, 55
 Freund, H.-J.: SS+NC-MoA3, **14**
 Fridman, A.: BO+PS+AS+BI+SS-TuA3, **28**
 Friend, C.M.: SS+NC-MoA9, 14; SS1+NC-TuA1, 35; SS2+NC-WeM5, 49
 Frisbie, C.D.: TR+NS+EM+NC-WeA1, 63
 Froemming, N.S.: SS1+NC-TuA2, 35
 Frost, R.: BI+NC-ThM4, 65
 Fu, J.: MS+NC-MoM11, **3**
 Fuchigami, K.: MI+NC-WeM5, 43
 Fuhrer, M.S.: NM+MS+NS+NC-WeM9, **44**
 Fujikawa, K.: TF-TuA12, 38
 Fulghum, J.E.: BO+PS+AS+BI+SS-TuA12, **29**
 Furlan, A.: SE+NC-WeA10, 62
- **G** —
- Gabalton, J.: IS+NS+TR-WeA8, 56
 Gadegaard, N.: BO+AS+BI-WeA12, 54
 Gademann, K.: BO+NS+BI+NC-ThA8, 79
 Gaillard, F.: MS+NC-MoM7, **3**
 Gall, D.: EN+AS+EM+TF-WeM11, 42
 Gallimore, A.D.: NM+EM+PS+NS+NC-ThM6, 72
 Gamble, L.J.: BM+BI+BO+NC-TuA3, 27; BO+EM+BI+NC-ThM10, **67**
 Ganguly, A.: BO+EM+BI+NC-ThM2, **66**
 Gao, G.: TR+NS+EM+NC-WeA8, 64
 Gao, L.: NS+NC-FrM5, **88**
 Gao, X.: GR+TF+NC-TuA12, 32
 Garcia, A.: BI+NC-TuA11, 26
 Gardella, J.A.: BO+AS+BI-WeA11, 54
 Gardella, Jr., J.A.: MI+NC-WeM3, 43
 Garner, S.R.: MN+NC-MoA5, 12
 Garnier, B.: BI+SS+NC-MoA8, 10
 Gasda, M.: EN+AS+EM+TF-WeM11, **42**
 Gaskill, D.K.: GR+SS+NC-MoA3, 10
 Gasper, G.L.: BO+AS+BI-WeA5, 53
 Geiger, F.: NS+NC-ThM3, 73
 Geim, A.K.: GR+EM+NC-TuM9, **20**
 Gel, M.: NS+NC-WeA11, 59
 Gellman, A.J.: SE+NC-WeA10, 62
 George, J.-M.: MI-WeA11, 57
 George, S.M.: TF+NC-MoM3, 5; TF+NC-MoM4, 6; TF-MoA3, **15**
 GeorgeJaffres, H.: MI-WeA11, 57
 Georgiadis, R.M.: BI+TF+MI+NS+NC-ThA4, 77
 Gerber, C.: BM+BI+BO+NC-TuA8, **27**
 Germinario, L.: TR+NS+EM+NC-WeA5, 64
 Gervais, L.: NS+NC-WeA11, 59
 Ghosh, A.W.: BI+NC-WeM3, 39
 Giacomo, J.: SS1+NC-WeM9, 48
 Giannaras, D.: BO+AS+BI-WeA12, 54
 Gielis, J.J.H.: TF-MoA11, **17**
 Gilbert, M.: NM+MS+NS+NC-WeM5, 44
 Gilchrist, B.: NM+EM+PS+NS+NC-ThM6, 72
 Gillaspie, D.T.: EN+AS+EM+TF-WeM1, 41
 Gilliland, D.: BO+EM+BI+NC-ThM6, 67; BO+NS+BI+NC-ThA11, 80; BO+NS+BI+NC-ThA9, 79
 Giorgi, J.B.: SS2+NC-WeM3, 49
 Glass, N.: NS+NC-WeA11, 59
 Glenn, J.S.: BI+SS+NC-MoA3, 9
 Goacher, R.E.: MI+NC-WeM3, **43**
 Godlewski, S.: BO+EM+BI+NC-ThM11, 67
 Goeke, R.: IS+NS+TR-WeA8, 56
 Goethals, A.M.: MS+NC-MoM1, 2
 Goldberg, B.B.: BM+BI+BO+NC-TuA5, 27
 Golden, M.S.: BI+TF+MI+NS+NC-ThA4, **77**
 Goletti, C.: BO+AS+BI+NC-WeM9, 41
 Gölzhäuser, A.: GR+TF+NC-MoM5, **1**
 Gong, B.: TF+NC-MoM5, 6
- Gong, J.L.: SS1+NC-TuA2, **35**
 Gonzales, J.M.: SE+NC-WeA9, 62
 Goodman, D.W.: SS+NC-MoM7, **4**
 Goodrich, T.L.: MI+NC-WeM4, 43
 Goossens, D.: MS+NC-MoM1, 2
 Gordon, R.G.: MS+NC-MoM8, 3; TF-MoA7, 16; TF-TuA3, 37; TF-TuA5, 37
 Gorham, J.M.: SS1-ThM10, 76; SS1-ThM11, 76; SS1-ThM12, 76
 Gorokhovskiy, V.: SE+NC-WeA12, **63**
 Gorriss, H.H.: BI+NC-WeM12, **40**
 Goryl, G.: BO+EM+BI+NC-ThM11, 67
 Goswami, R.: MI-WeA8, 57
 Gougousi, T.: TF-MoA5, **16**
 Gounou, C.: BI+SS+NC-MoA8, 10
 Gouraud, P.: PS1-WeA3, 60
 Gousev, E.: MN+NC-MoA10, 13
 Goux, L.: GR+TF+NC-TuA8, **31**
 Gouy, J.P.: NM+EM+PS+NS+NC-ThM11, 72
 Grahm, J.F.: NM+MS+NS+NC-ThA5, **82**
 Graham, M.E.: EN+BI+SS+SE-TuM5, 18
 Grainger, D.W.: BM+BI+BO+NC-TuA3, **27**; BO+EM+BI+NC-ThM10, 67
 Gras, R.: MS+NC-MoM7, 3
 Grass, M.: SS+NC-MoM9, 5
 Graves, D.B.: NM+EM+PS+NS+NC-ThM12, 73; PS1-WeA4, **60**
 Gray, J.L.: NM+MS+NS+NC-ThA5, 82
 Gray, K.A.: EN+BI+SS+SE-TuM5, 18
 Green, R.G.: SS2+NC-WeM3, **49**
 Grennberg, H.: GR+EM+NC-TuM6, 20; GR+TF+NC-MoM3, 1; GR+TF+NC-TuA3, 31
 Griffiths, M.: NS+NC-WeA11, 59
 Groff, J.: GR+TF+NC-MoM3, 1
 Gross, E.: SS1+NC-TuA12, **36**
 Grossklaus, K.A.: SS1-ThM9, **76**
 Grundmeier, G.: SS+AS+NC-FrM10, 91
 Grunze, M.: BO+AS+BI-WeA1, 53
 Gubbini, P.: NM+EM+PS+NS+NC-ThM11, 72
 Günther, J.U.: BO+AS+BI+NC-WeM2, 40
 Gueorguiev, G.K.: SE+NC-WeA10, 62
 Guerrero-Pérez, O.: IS+NS+TR-WeA3, 56
 Guha, J.: PS1-WeA1, 59; PS1-WeA2, **60**
 Guldi, D.: EN+EM+NS+P+A+T+V-ThM3, 68
 Gunnarsson, M.: BI+NC-WeM11, **40**
 Guo, Y.X.: SY+SS+BI-TuM12, 24
 Gupta, S.: MI+NC-TuA12, 33
 Guzman, R.: GR+TF+NC-TuA8, 31
- **H** —
- Hackley, J.C.: TF-MoA5, 16
 Hackley, V.A.: BI+NC-WeM6, 39
 Hadjar, O.: BO+AS+BI+NC-WeM11, 41
 Häge, M.: BO+PS+AS+BI+SS-TuA10, 29
 Hagen, C.W.: SS1-ThM11, 76; SS1-ThM12, 76
 Hall, A.J.: EN+EM+NS+PS-TuA10, **31**
 Hämäläinen, J.: TF-TuA9, 37
 Hamann, H.F.: NS+NC-FrM7, **89**; NS+NC-WeA8, 58
 Hammer, B.: SS+AS+NC-FrM7, 91
 Hammond, P.T.: EN+AS+EM+TF-WeM5, **42**
 Han, S.M.: BO+NS+BI+NC-ThA7, 79; EN+EM+NS+PS-TuA4, 30
 Hanbicki, A.T.: MI-WeA8, 57
 Hande, A.: TF-TuA1, 36
 Hanley, L.: BO+AS+BI-WeA5, **53**; EN+EM+NS+P+A+T+V-ThM6, 69
 Hansen, J.Ø.: SS+AS+NC-FrM7, 91
 Hansen, P.: IS+NS+TR-WeA8, 56
 Hansen, T.: IS+NS+TR-WeA8, 56
 Harrell, J.W.: MI+NC-TuA12, 33
 Harrell, L.E.: MN+NC-MoA5, 12
 Harrer, S.: NM+EM+PS+NS+NC-ThM3, 71
 Harris, J.: BM+BI+BO+NC-TuA12, 28
 Harris, V.G.: MI+NC-WeM4, 43
 Harrison, J.A.: TR+NS+EM+NC-WeA8, **64**
 Hasiwa, M.: BO+NS+BI+NC-ThA11, 80
 Hass, J.: GR+SS+NC-MoA2, **10**
- Haubrich, J.: SS+NC-MoA9, 14
 Hauge, R.H.: IS+NS+TR+NC-ThM5, 70
 Haugstad, G.: TR+NS+EM+NC-WeA1, **63**
 Haycock, J.W.: BI+NC-TuA10, **26**
 Heben, M.J.: NS+NC-FrM8, 89; NS+NC-WeA4, 58
 Hebert, D.: EN+EM+NS+PS-TuA10, 31
 Heikkilä, M.: TF-TuA9, 37
 Heinrich, A.: MI+NC-TuA1, **32**
 Helm, C.A.: BO+AS+BI+NC-WeM2, 40
 Helveg, S.: IS+NS+TR-WeA8, 56
 Hemminger, J.C.: NM+MS+NS+NC-ThA9, 82; SS+AS+NC-FrM1, 90
 Henkelman, G.: SS1+NC-TuA2, 35
 Hermans, J.: MS+NC-MoM1, 2
 Herranz, T.: SS1+NC-ThA9, 87
 Hersam, M.C.: NS+NC-ThM3, 73; NS+NC-WeM5, 45; TF-MoA1, 15
 Heske, C.: SY+SS+BI-TuM3, **23**
 Hess, A.: BM+BI+BO+NC-TuA12, **28**
 Hickman, S.A.: MN+NC-MoA5, **12**
 Hicks, R.F.: NS+NC-FrM5, 88
 Highsmith, A.L.: MI+NC-TuA12, 33
 Highstrete, C.: NS+NC-WeA9, 58
 Hill, E.W.: GR+EM+NC-TuM9, 20
 Himpel, F.J.: BO+PS+AS+BI+SS-TuA8, 29; PS1-WeA12, 61; SS1+NC-WeM10, 48
 Hines, D.R.: NM+EM+PS+NS+NC-ThM4, 72
 Hines, M.A.: SS1-ThM5, **75**
 Hiramatsu, M.: GR+TF+NC-MoM8, 2
 Hirschfeld-Warneken, V.: BO+NS+BI+NC-ThA3, **79**
 Hla, S.-W.: NS+NC-ThA7, **83**
 Hodges, J.T.: TF-TuA11, 38
 Hoex, B.: TF-MoA11, 17
 Hoffmann, P.: IS+NS+TR-WeA2, 56
 Hofmann, T.: SE+TF+NC-ThA8, 85
 Hogg, C.: MI+NC-WeM9, 43
 Holloway, B.C.: EN+EM+NS+P+A+T+V-ThM3, **68**; GR+TF+NC-MoM3, 1; GR+TF+NC-TuA3, 31
 Holub, M.: MI-WeA8, 57
 Honda, M.: PS1-WeA9, **60**
 Hone, J.: BO+NS+BI+NC-ThA1, 78
 Hong, B.: NS+NC-ThA10, 84
 Hook, B.: BI+NC-TuA9, 26
 Hook, D.A.: TR+MN+NC-WeM5, **51**
 Höök, F.: BI+NC-WeM11, 40
 Hori, M.: GR+TF+NC-MoM8, 2
 Horn, M.W.: SE+TF+NC-ThA3, 84; SE+TF+NC-ThA9, **85**
 Hossain, M.F.: EN+AS+TF+VT+NC-WeA5, 55; EN+EM+NS+P+A+T+V-ThM11, **69**
 Hoster, H.E.: BO+AS+BI+NC-WeM5, 40
 Howe, R.T.: MN+NC-MoA3, 12
 Howell, C.L.: BO+AS+BI-WeA1, 53
 Howland, M.: BI+NC-ThM1, 65
 Hoyt, D.W.: IS+NS+TR-WeA1, 55
 Hrbek, J.: EN+BI+SS+SE-TuM12, 19; SS1+NC-ThA7, 87; SS1+NC-TuA3, **35**
 Hsiao, C.-Y.: EN+EM+NS+P+A+T+V-ThM1, 68
 Hsu, K.: NM+MS+NS+NC-ThA1, 81
 Hu, J.: NS+NC-TuA11, 34
 Hu, J.Z.: IS+NS+TR-WeA1, 55
 Hu, X.: SS+NC-MoA11, 15
 Huang, J.: IS+NC-ThA3, **80**
 Huang, J.-S.: EN+EM+NS+P+A+T+V-ThM1, 68
 Hubert, D.H.W.: EN+AS+TF+VT+NC-WeA4, 55
 Hubin, A.: SS+AS+NC-FrM9, 91
 Hudson, E.A.: PS1-WeA2, 60
 Hueso, L.E.: MI-WeA11, 57
 Hughes, G.: SS+EM+NC-FrM9, 93
 Huijben, M.: SS2+NC-WeM2, 49
 Hull, C.: NM+EM+PS+NS+NC-ThM4, 72
 Hull, R.: NM+MS+NS+NC-ThA5, 82
 Hultman, L.: SE+NC-WeA10, 62; SE+NC-WeA5, 62

- Hunt, B.: NS+NC-WeA1, 58
Hupp, J.T.: TF+NC-MoM10, 6
Hurst, R.: BI+NC-TuA9, 26
Hutton, S.J.: AS-MoA9, 8
Hwang, C.: SS2+NC-WeM9, 49
Hyde, G.K.: TF+NC-MoM5, 6
- I —
Ichihara, C.: TF-TuA12, 38
Idriss, H.: SS+NC-MoA2, 14
Iimori, T.: NS+NC-FrM3, 88
Ikeda, T.: NS+NC-ThA11, 84
Ilic, B.R.: MN+NC-MoA11, 13; MN+NC-MoA7, 13
Imre, A.: MN+NC-MoA1, 12
Inaba, Y.: MI+NC-TuA12, 33
Ingvarsson, S.: NS+NC-WeA8, 58
Isaacs, J.: NS+NC-FrM11, 89
Iski, E.V.: NS+NC-TuA9, 34; NS+NC-WeM4, 45
Isvoranu, C.: SS1+NC-ThA3, 86
Ivanov, Tzv.: NS+NC-WeA12, 59
Ivory, C.F.: BO+NS+BI+NC-ThA7, 79
- J —
Jacob, K.: NM+MS+NS+NC-ThA1, 81
Jafri, S.H.M.: GR+TF+NC-TuA3, 31
Janshoff, A.: BI+NC-WeM5, 39
Jansson, U.: GR+EM+NC-TuM6, 20; GR+TF+NC-MoM3, 1; GR+TF+NC-TuA3, 31
Jazdzzyk, M.: BO+EM+BI+NC-ThM12, 68
Jee, H.S.: NS+NC-ThA5, 83
Jelinek, P.: NS+NC-TuM11, 21
Jenks, C.J.: SS+NC-MoM3, 4; SS+NC-MoM5, 4; SS1+NC-WeM5, 47
Jeon, H.T.: TF-MoA10, 17
Jernigan, G.G.: GR+SS+NC-MoA3, 10
Jespersen, M.L.: TR+MN+NC-WeM2, 50
Jesse, S.: SS2+NC-WeM2, 49; TR+NS+EM+NC-WeA5, 64
Jiang, H.: SE+NC-WeA3, 62
Jiang, H.Q.: BO+PS+AS+BI+SS-TuA8, 29; PS1-WeA12, 61
Jih, N.Y.: MI+NC-WeM2, 43
Jing, D.: SS+NC-MoM3, 4
Jinnai, B.: PS1-WeA11, 61
Johánek, V.: SS+AS+NC-FrM1, 90
Johansson, M.: SS1+NC-TuA8, 35
Johnson, P.D.: SS1+NC-WeM3, 47
Jones, J.G.: SE+NC-WeA3, 62
Jonker, B.T.: MI-WeA8, 57
Jönsson, H.: SS1+NC-ThA4, 86
Jönsson, P.: BI+NC-WeM11, 40
Joubert, O.: PS1-WeA10, 61; PS1-WeA3, 60; PS-TuM9, 22
Jung, S.: NS+NC-WeA1, 58
- K —
Käfer, D.: NS+NC-FrM6, 88
Kaiser, U.: MI+NC-TuA3, 32
Kalahari, V.: TR+NS+EM+NC-WeA1, 63
Kalinin, S.V.: NS+NC-WeM1, 45; SS2+NC-WeM2, 49; TR+NS+EM+NC-WeA5, 64
Käll, P.-O.: BO+EM+BI+NC-ThM5, 67; MI+NC-WeM11, 44
Kamino, T.: IS+NC-ThA9, 81
Kamins, T.: NS+NC-TuA4, 34
Kan, H.H.: SS+AS+NC-FrM11, 91
Kang, B.S.: BO+EM+BI+NC-ThM1, 66
Kang, H.: NS+NC-ThA1, 83
Kanjilal, D.: SE+TF+NC-ThA11, 86
Kano, H.: GR+TF+NC-MoM8, 2
Kappes, M.M.: NS+NC-ThM9, 74
Karis, O.: GR+TF+NC-MoM3, 1
Karpitschka, S.: IS+NS+TR-WeA2, 56
Kasemo, B.: BI+NC-ThM4, 65; BI+SS+NC-MoA10, 10; BO+AS+BI-WeA10, 54; SS+AS+NC-FrM9, 91
Katsnelson, A.: NS+NC-ThA4, 83
Katsnelson, M.I.: GR+EM+NC-TuM6, 20
- Kaufmann, S.: BI+NC-ThM11, 66; BI+NC-TuA5, 25
Kawai, M.: NS+NC-ThM5, 74
Kawai, T.: NS+NC-ThA11, 84
Kay, B.D.: SS+AS+NC-FrM2, 90; SS+AS+NC-FrM5, 90; SS1+NC-ThA1, 86
Kaya, S.: SS1+NC-ThA10, 87
Kazim, L.: BO+AS+BI-WeA11, 54
Kazmanli, K.: SE+NC-WeA8, 62
Keast, C.L.: PS-TuM1, 21
Kedzierski, J.: PS-TuM1, 21
Kell, C.D.: NM+MS+NS+NC-ThA5, 82
Kellogg, G.L.: SS1+NC-WeM4, 47
Kelly, M.: GR+TF+NC-MoM3, 1
Kemell, M.: TF-TuA9, 37
Kemps, R.: GR+TF+NC-TuA9, 31
Kendelewicz, T.: SS1+NC-ThA10, 87
Kercher, D.S.: NS+NC-ThA1, 83
Kerisit, S.: SS+AS+NC-FrM3, 90
Kern, K.: GR+SS+NC-MoA7, 11
Kessels, W.M.M.: TF-MoA11, 17; TF-MoA2, 15
Khajetoorians, A.A.: SS2+NC-WeM6, 49
Khan, S.A.: TF+NC-MoM9, 6
Khare, R.: PS1-WeA1, 59; PS1-WeA2, 60
Khatib, S.J.: IS+NS+TR-WeA3, 56
Khin, M.: BO+AS+BI-WeA11, 54
Khranovskii, V.: BO+EM+BI+NC-ThM5, 67
Khusnatdinov, N.: NM+EM+PS+NS+NC-ThM11, 72
Kim, B.I.: MI+NC-TuA4, 32
Kim, D.: SS2+NC-WeM11, 50
Kim, D.-H.: EN+EM+NS+PS-TuA3, 30
Kim, D.O.: TF-MoA10, 17
Kim, H.: BO+NS+BI+NC-ThA2, 78; MS+NC-MoM8, 3; TF-TuA4, 37; TF-TuA5, 37
Kim, H.C.: SS+EM+NC-FrM9, 93; TF-TuA1, 36
Kim, H.-D.: SS2+NC-WeM9, 49
Kim, H.J.: NS+NC-ThA10, 84
Kim, H.S.: EN+BI+SS+SE-TuM1, 18
Kim, H.Y.: GR+EM+NC-TuM12, 20
Kim, I.: SS2+NC-WeM9, 49
Kim, J.: GR+EM+NC-TuM12, 20; SS+EM+NC-FrM9, 93; TF-TuA1, 36
Kim, J.D.: SS2+NC-WeM6, 49
Kim, J.-H.: NS+NC-ThM3, 73
Kim, J.K.: MN+NC-MoA8, 13; SE+TF+NC-ThA7, 85
Kim, K.: SS1+NC-WeM1, 47
Kim, K.B.: MN+NC-MoA4, 12
Kim, K.T.: NS+NC-ThA5, 83
Kim, M.J.: GR+EM+NC-TuM12, 20; TF-TuA1, 36
Kim, P.: GR+EM+NC-TuM5, 19
Kim, S.H.: TR+MN+NC-WeM6, 51
Kim, S.M.: IS+NS+TR+NC-ThM5, 70
Kim, T.: EN+EM+NS+PS-TuA3, 30
Kim, W.: SS2+NC-WeM9, 49
Kim, Y.-H.: EN+AS+EM+TF-WeM1, 41
Kimes, W.A.: TF-TuA11, 38
Kimmel, G.A.: SS+NC-MoA10, 15; SS1+NC-ThA1, 86
King, W.P.: NS+NC-ThA9, 83
Kingshott, P.: BI+NC-ThM5, 65; BI+NC-TuA3, 25; BI+NC-TuA8, 26
Kioseoglou, G.: MI-WeA8, 57
Kiskinova, M.: SY+SS+BI-TuM9, 23
Kitada, N.: GR+TF+NC-MoM11, 2; GR+TF+NC-MoM4, 1
Kitchin, J.R.: SS1+NC-TuA9, 36
Kizilkaya, O.: SS2+NC-WeM4, 49
Klasson, A.: MI+NC-WeM11, 44
Kleiman, G.G.: SS+NC-MoM1, 4
Klein, L.J.: NS+NC-FrM7, 89; NS+NC-WeA8, 58
Klein, M.: IS+NS+TR+NC-ThM9, 71
Klein, T.M.: TF-MoA8, 16
Klerner, D.: BI+NC-WeM1, 39
Knippenberg, M.T.: TR+NS+EM+NC-WeA10, 64; TR+NS+EM+NC-WeA8, 64
- Knoll, W.: BI+SS+NC-MoA5, 9
Knoops, H.C.M.: TF-MoA2, 15
Knox, K.R.: GR+EM+NC-TuM5, 19
Kobayashi, A.: TF-TuA12, 38
Koc, R.: IS+NC-ThA11, 81
Kodambaka, S.: IS+NC-ThA11, 81
Koelsch, P.: BO+AS+BI-WeA1, 53
Kojima, K.: GR+TF+NC-MoM11, 2; GR+TF+NC-MoM4, 1
Komori, F.: NS+NC-FrM3, 88
Kondratenko, Y.V.: MS+NC-MoM2, 3
Kopczyk, M.: SS+NC-MoM2, 4
Köper, I.: BI+SS+NC-MoA5, 9
Koratkhar, N.: EN+AS+EM+TF-WeM11, 42
Kordes, M.E.: IS+NS+TR+NC-ThM2, 70
Koyama, K.: PS1-WeA11, 61
Kress, M.: NS+NC-WeM12, 46
Kriegeskotte, C.: BO+AS+BI-WeA8, 53
Krim, J.: NS+NC-TuA11, 34; TR+MN+NC-WeM1, 50; TR+MN+NC-WeM5, 51; TR+MN+NC-WeM9, 51
Krisch, M.J.: SS+AS+NC-FrM1, 90
Krishna, L.R.: SE+NC-WeA4, 62
Krishna, S.B.: NS+NC-TuA12, 34
Kuenh, S.: MN+NC-MoA5, 12
Küppers, J.: IS+NS+TR-WeA2, 56
Kukli, K.: TF-TuA9, 37
Kulisch, W.: BO+EM+BI+NC-ThM6, 67
Kumar, A.: NM+MS+NS+NC-ThA1, 81; NS+NC-TuA12, 34
Kumar, K.: BI+NC-ThM11, 66; BI+NC-TuA5, 25; NM+EM+PS+NS+NC-ThM9, 72
Kumar, M.: NS+NC-FrM9, 89
Kumar, P.: SE+TF+NC-ThA11, 86
Kummel, A.C.: SS+EM+NC-FrM7, 92; SS1+NC-WeM2, 47
Kung, S.C.: NM+MS+NS+NC-ThA9, 82
Kunze, A.: BI+NC-ThM4, 65; BO+AS+BI-WeA10, 54; SS+AS+NC-FrM9, 91
Kurtz, R.L.: SS2+NC-WeM4, 49
Kurz, V.: BO+AS+BI-WeA1, 53
Kushvaha, S.S.: GR+TF+NC-MoM1, 1
Kwak, J.H.: IS+NS+TR-WeA1, 55
Kwok, C.T.M.: MS+NC-MoM2, 3
- L —
LaBean, T.H.: BI+TF+MI+NS+NC-ThA10, 78
LaBella, V.P.: NM+MS+NS+NC-WeM3, 44
Labrake, D.: NM+EM+PS+NS+NC-ThM11, 72
Lachal, L.: NM+EM+PS+NS+NC-ThM11, 72
Laegsgaard, E.: SS+AS+NC-FrM7, 91
Lai-Kee-Him, J.: BI+SS+NC-MoA8, 10
Landers, R.: SS+NC-MoM1, 4
Langer, R.: BO+PS+AS+BI+SS-TuA1, 28
Laskin, J.: BO+AS+BI+NC-WeM11, 41
Lavios, P.: NM+EM+PS+NS+NC-ThM11, 72
Lazarides, A.A.: BI+TF+MI+NS+NC-ThA10, 78
Le Cunff, Y.: NM+EM+PS+NS+NC-ThM11, 72
LeClair, P.: MI+NC-WeM6, 43
Lee, B.: GR+EM+NC-TuM12, 20; TF-MoA1, 15; TF-TuA1, 36
Lee, D.K.: MS+NC-MoM8, 3
Lee, D.S.: GR+SS+NC-MoA7, 11
Lee, D.Y.: NM+EM+PS+NS+NC-ThM4, 72
Lee, G.: BI+NC-WeM4, 39; GR+TF+NC-TuA1, 31
Lee, J.S.: SS1+NC-WeM2, 47; TF-MoA10, 17
Lee, J.-U.: NM+MS+NS+NC-WeM1, 44
Lee, J.Y.: NS+NC-ThM2, 73
Lee, K.W.: TF-MoA10, 17
Lee, M.: NS+NC-WeA9, 58
Lee, S.-H.: EN+AS+EM+TF-WeM1, 41
Lee, W.K.: NS+NC-ThA9, 83
Leifer, K.: GR+EM+NC-TuM6, 20; GR+TF+NC-TuA3, 31
Leitão, A.A.: SS1+NC-WeM12, 48
Lele, T.: BO+EM+BI+NC-ThM1, 66
Leonhardt, D.: EN+EM+NS+PS-TuA4, 30

- Lerch, M.: SS+NC-MoM2, 4
 Leskelä, M.: TF-TuA9, 37
 Lewandowska, A.E.: IS+NS+TR-WeA3, 56
 Li, C.H.: MI-WeA8, 57
 Li, H.: TF-TuA3, 37; TF-TuA5, 27
 Li, H.-F.: SE+TF+NC-ThA10, 85
 Li, K.: TF-MoA8, 16
 Li, M.: SS+NC-MoA8, 14
 Li, N.: TF-MoA8, 16
 Li, X.: MI+NC-TuA12, 33
 Li, Z.: NS+NC-WeM11, 46
 Liang, S.: MI+NC-WeM5, 43
 Liang, T.: TR+NS+EM+NC-WeA4, 63
 Libera, J.A.: EN+BI+SS+SE-TuM1, 18
 Licciardello, A.: EN+AS+EM+TF-WeM3, 42
 Liedberg, B.: NS+NC-ThM6, 74
 Lim, B.: NS+NC-WeA1, 58
 Lim, W.S.: NS+NC-FrM10, 89
 Lin, C.-F.: EN+EM+NS+P+A+T+V-ThM1, 68
 Lin, E.K.: NM+EM+PS+NS+NC-ThM4, 72
 Lin, J.: BO+EM+BI+NC-ThM1, 66
 Lin, J.-C.: NS+NC-ThM3, 73
 Lin, M.-T.: GR+TF+NC-TuA12, 32; MI+NC-WeM2, 43
 Lin, T.C.: NM+EM+PS+NS+NC-ThM12, 73
 Lin, W.C.: MI+NC-WeM2, 43
 Lin, Y.: MS+NC-MoM8, 3
 Lipinsky, D.: BO+AS+BI-WeA8, 53
 Lisboa, P.: BI+TF+MI+NS+NC-ThA5, 77; BO+NS+BI+NC-ThA5, 79
 Liu, C.C.: BO+PS+AS+BI+SS-TuA8, 29; PS1-WeA12, 61
 Liu, D.-J.: SS1+NC-WeM5, 47
 Liu, D.-L.: TR+MN+NC-WeM11, 51; TR+NS+EM+NC-WeA9, 64
 Liu, G.: MS+NC-MoM9, 3
 Liu, J.: IS+NS+TR+NC-ThM10, 71; NM+EM+PS+NS+NC-ThM4, 72
 Liu, P.: EN+BI+SS+SE-TuM12, 19; SS1+NC-ThA7, 87
 Liu, T.: NM+EM+PS+NS+NC-ThM6, 72
 Liu, W.: AS-MoA11, 9
 Liu, X.: BO+PS+AS+BI+SS-TuA8, 29; PS1-WeA12, 61; SS1+NC-TuA1, 35
 Liu, Y.: GR+EM+NC-TuM1, 19; MS+NC-MoM8, 3; SE+TF+NC-ThA5, 85; TF-TuA5, 37
 Liu, Y.-S.: BM+BI+BO+NC-TuA1, 27
 Liu, Z.: SS+AS+NC-FrM1, 90; SS+NC-MoM9, 5
 Llyod, F.D.: NS+NC-ThM10, 74
 Luzzi Spetz, A.: BO+EM+BI+NC-ThM5, 67
 Locatelli, A.: GR+EM+NC-TuM5, 19
 Lock, E.H.: NM+EM+PS+NS+NC-ThM4, 72
 Löffler, D.: NS+NC-ThM9, 74
 Loginova, E.: GR+EM+NC-TuM11, 20; IS+NS+TR+NC-ThM1, 70
 Lograsso, T.A.: SS+NC-MoM5, 4
 Londergan, A.: MN+NC-MoA10, 13
 Long, B.: NM+EM+PS+NS+NC-ThM12, 73
 Long, J.P.: NS+NC-TuA2, 33
 Lozzi, L.: NM+MS+NS+NC-ThA10, 82
 Lu, B.: NS+NC-FrM3, 88
 Lu, J.: MI+NC-WeM1, 42
 Lu, P.: BO+AS+BI-WeA9, 54
 Lu, T.-M.: EN+AS+EM+TF-WeM11, 42; SE+TF+NC-ThA10, 85
 Lu, W.: BO+EM+BI+NC-ThM3, 66
 Lu, Z.: MI+NC-WeM6, 43
 Lua, S.Y.H.: GR+TF+NC-MoM1, 1
 Lucero, A.: BO+PS+AS+BI+SS-TuA12, 29
 Luere, O.: PS-TuM9, 22
 Lugli, P.: NM+EM+PS+NS+NC-ThM3, 71
 Lukaszew, R.A.: BI+TF+MI+NS+NC-ThA7, 77
 Luo, H.: MI+NC-WeM3, 43
 Luo, M.: SS2+NC-WeM11, 50
 Luo, W.: NM+MS+NS+NC-ThA9, 82
 Lutolf, M.P.: BI+NC-TuA1, 25
 Lyubinetzky, I.: SS+NC-MoA5, 14; SS+NC-MoA7, 14
 — **M** —
 Ma, S.: EN+BI+SS+SE-TuM12, 19; SS1+NC-ThA7, 87
 Maboudian, R.: MN+NC-MoA3, 12
 MacDonald, A.: NM+MS+NS+NC-WeM5, 44
 Mackus, A.J.M.: TF-MoA2, 15
 Madey, T.E.: SS1-ThM11, 76; SS1-ThM12, 76
 Madueño, R.: NS+NC-ThM1, 73
 Maeng, W.J.: TF-TuA4, 37
 Magnano, G.: SS1+NC-ThA3, 86
 Mahan, A.H.: EN+AS+EM+TF-WeM1, 41
 Mahmood, M.: NS+NC-WeM11, 46
 Maier, M.: NS+NC-WeM6, 46
 Majetich, S.A.: MI+NC-WeM9, 43
 Majumder, A.: EN+AS+TF+VT+NC-WeA5, 55
 Makabe, T.: PS-TuM3, 22
 Makinen, A.J.: NS+NC-TuA2, 33
 Maksymovych, P.: SS2+NC-WeM2, 49
 Malesevic, A.: GR+TF+NC-TuA9, 31
 Malm, J.: BO+AS+BI-WeA12, 54
 Malmberg, P.: BO+AS+BI-WeA3, 53
 Malmström, J.: BI+NC-ThM5, 65
 Manivannan, V.: EN+AS+TF+VT+NC-WeA1, 55
 Mankey, G.J.: MI+NC-WeM12, 44; MI+NC-WeM6, 43
 Mannelli, I.: BI+TF+MI+NS+NC-ThA5, 77; BO+NS+BI+NC-ThA11, 80; BO+NS+BI+NC-ThA5, 79; BO+PS+AS+BI+SS-TuA11, 29
 Manos, D.M.: GR+TF+NC-MoM7, 1
 Mäntylä, T.: TF-TuA10, 37
 Mao, Y.: NM+MS+NS+NC-ThA11, 82
 Marchiori, C.: AS-MoA10, 9
 Margot, J.: PS1-WeA1, 59
 Marks, L.D.: IS+NC-ThA5, 80; SS+AS+NC-FrM6, 90; SS1+NC-ThA11, 87
 Marohn, J.A.: MN+NC-MoA5, 12
 Marshall, C.L.: EN+BI+SS+SE-TuM1, 18; TF-MoA1, 15
 Martin, J.: TR+MN+NC-WeM11, 51
 Martin, M.: PS1-WeA10, 61
 Martin, R.M.: PS-TuM4, 22
 Martinez, E.: NM+EM+PS+NS+NC-ThM5, 72
 Martinez-Huerta, M.V.: IS+NS+TR-WeA3, 56
 Martinotti, D.: GR+EM+NC-TuM2, 19
 Martinson, A.B.F.: TF+NC-MoM10, 6
 Maruyama, B.: IS+NS+TR+NC-ThM5, 70
 Maslar, J.E.: TF-TuA11, 38
 Mastro, M.A.: NS+NC-TuA2, 33
 Mathur, N.D.: MI-WeA11, 57
 Matsumoto, K.: NS+NC-WeA3, 58
 Matthiesen, J.: SS+AS+NC-FrM5, 90; SS+AS+NC-FrM7, 91; SS1+NC-ThA1, 86
 Mattana, R.: MI-WeA11, 57
 Mayer, J.: GR+TF+NC-MoM5, 1
 Mayer, T.S.: NS+NC-WeA9, 58
 Mayrhofer, P.H.: SE+NC-WeA5, 62
 McArthur, S.L.: BI+NC-ThM12, 66; BI+NC-TuA10, 26; BO+NS+BI+NC-ThA10, 80; BO+PS+AS+BI+SS-TuA5, 28
 McBreen, P.H.: NS+NC-TuA10, 34
 McCarty, K.F.: GR+EM+NC-TuM11, 20; IS+NS+TR+NC-ThM1, 70; SS+NC-MoM5, 4
 McGill, P.: SS+NC-MoA2, 14
 McGrail, B.P.: EN+AS+TF+VT+NC-WeA3, 55
 McGruer, N.: TR+MN+NC-WeM1, 50
 McGuire, G.E.: SE+NC-WeA11, 63
 McIntire, T.M.: SS+AS+NC-FrM1, 90
 Mckay, H.: NS+NC-ThM2, 73
 McKean, R.: BI+NC-TuA10, 26
 Medico, G.: NM+EM+PS+NS+NC-ThM11, 72
 Mehta, A.: SS+AS+NC-FrM1, 90
 Mehta, B.R.: NS+NC-FrM9, 89; SE+TF+NC-ThA11, 86
 Mei, Y.: BO+PS+AS+BI+SS-TuA1, 28
 Mellhaoui, X.: PS1-WeA10, 61
 Memis, O.: NS+NC-ThA4, 83
 Menguelti, K.: PS1-WeA10, 61
 Mentés, T.O.: GR+EM+NC-TuM5, 19
 Merkel, M.: SY+SS+BI-TuM11, 23
 Mertens, M.: GR+TF+NC-TuA9, 31
 Mewes, T.: MI+NC-TuA10, 33
 Mignogna, M.H.: SS+EM+NC-FrM5, 92
 Miiller, D.J.: IS+NC-ThA1, 80
 Mikulski, P.T.: TR+NS+EM+NC-WeA8, 64
 Millan-Otaya, J.E.: GR+SS+NC-MoA2, 10
 Miller, B.P.: TR+MN+NC-WeM5, 51; TR+MN+NC-WeM9, 51
 Miller, G.: BO+EM+BI+NC-ThM12, 68
 Mills, C.A.: NM+EM+PS+NS+NC-ThM5, 72
 Millunchick, J.M.: NM+EM+PS+NS+NC-ThM6, 72; NS+NC-ThM2, 73; SS+EM+NC-FrM6, 92; SS+EM+NC-FrM8, 93; SS1-ThM9, 76
 Milojevic, M.: SS+EM+NC-FrM9, 93
 Min, C.: SS2+NC-WeM9, 49
 Min, H.: NM+MS+NS+NC-WeM5, 44
 Ming, F.: GR+EM+NC-TuM2, 19; GR+SS+NC-MoA2, 10
 Mishra, G.: BI+NC-ThM12, 66
 Miwa, K.: PS1-WeA8, 60
 Mizutani, G.: NS+NC-TuA1, 33
 M'ndange-Pfupfu, A.: IS+NC-ThA5, 80
 Mock, J.J.: BI+TF+MI+NS+NC-ThA10, 78
 Mohseni, H.: NS+NC-ThA4, 83
 Möller, J.: BO+AS+BI-WeA8, 53
 Mont, F.W.: SE+TF+NC-ThA7, 85
 Moodera, J.: MI-WeA1, 57
 Moore, E.F.: TF-TuA11, 38
 Moore, J.F.: BO+AS+BI-WeA5, 53
 Moreau, S.: MS+NC-MoM7, 3
 Morgante, A.: GR+EM+NC-TuM5, 19
 Mori, T.: PS-TuM10, 22
 Morikawa, T.: MN+NC-MoA9, 13
 Morita, S.: NS+NC-TuM11, 21
 Morkoc, H.: SS+EM+NC-FrM4, 92
 Morozovska, A.: SS2+NC-WeM2, 49
 Morris, D.: NM+EM+PS+NS+NC-ThM6, 72
 Mucherie, S.: EN+BI+SS+SE-TuM1, 18
 Müllen, K.: NS+NC-FrM6, 88
 Mukerjee, S.: EN+BI+SS+SE-TuM6, 18
 Mullet, C.: SS1+NC-WeM9, 48
 Mullins, C.B.: SS1+NC-TuA2, 35
 Mullins, D.R.: SS+NC-MoA11, 15
 Muratore, C.: SE+NC-WeA3, 62
 Murayama, T.: MN+NC-MoA9, 13
 Mure, S.: TF-TuA12, 38
 Murphy, S.: SS1+NC-TuA8, 35
 Murray-Dunning, C.: BI+NC-TuA10, 26
 Musinski, L.: NM+EM+PS+NS+NC-ThM6, 72
 Myers, J.D.: EN+EM+NS+P+A+T+V-ThM4, 68
 — **N** —
 Na, J.-S.: TF+NC-MoM5, 6; TF-TuA8, 37
 Nachimuthu, P.: IS+NS+TR-WeA5, 56
 Nagar, R.: SE+TF+NC-ThA11, 86
 Naik, R.: TR+MN+NC-WeM2, 50
 Nakatsuji, K.: NS+NC-FrM3, 88
 Nam, S.W.: MN+NC-MoA4, 12
 Nascente, P.A.P.: SS+NC-MoM1, 4
 Nath, N.: BI+NC-TuA9, 26
 Naumann, R.: BI+SS+NC-MoA5, 9
 Nazar, L.F.: EN+AS+EM+TF-WeM9, 42
 Nealey, P.F.: BO+PS+AS+BI+SS-TuA8, 29; NS+NC-ThA1, 83; NS+NC-ThM11, 75; PS1-WeA12, 61
 Neira, A.: SE+NC-WeA9, 62
 Nemanich, R.J.: GR+SS+NC-MoA1, 10
 Nest, D.G.: NM+EM+PS+NS+NC-ThM12, 73
 Newberg, J.T.: SS1+NC-ThA10, 87
 Nguyen, P.-C.: BO+EM+BI+NC-ThM10, 67
 Nguyen, S.T.: NS+NC-ThM3, 73
 Nguyen, T.: NS+NC-TuA1, 33
 Nicholas, R.J.: EN+EM+NS+PS-TuA5, 30
 Nie, S.: GR+SS+NC-MoA11, 11

- Nie, X.: TR+NS+EM+NC-WeA12, 64
 Niehus, H.: SS1+NC-WeM12, 48
 Nielsch, K.: TF+NC-MoM7, 6
 Nielsen, R.: SS1+NC-TuA8, 35
 Niinistö, J.: TF-TuA9, 37
 Nikiforov, M.P.: TR+NS+EM+NC-WeA5, 64
 Nilsson, A.R.: SS1+NC-ThA10, 87; SY+SS+BI-TuM1, 23
 Nimmo, J.: NS+NC-WeM10, 46
 Niño, M.A.: GR+EM+NC-TuM5, 19
 Nishikawa, O.: NS+NC-WeM3, 45
 Nishizuka, T.: PS-TuM10, 22
 Noordhoek, M.J.: NS+NC-ThM2, 73
 Noronha, P.: EN+AS+TF+VT+NC-WeA1, 55
 Norkov, J.K.: EN+BI+SS+SE-TuM9, 18
 Nottbohm, C.T.: GR+TF+NC-MoM5, 1
 Nozawa, T.: PS-TuM10, 22
 Nunney, T.S.: NS+NC-WeM11, 46
 Nurmi, J.T.: IS+NS+TR-WeA5, 56
 Nygren, H.: BO+AS+BI-WeA3, 53
- O —
- Ocola, L.E.: MN+NC-MoA1, 12
 O'Donnell, S.: EN+EM+NS+P+A+T+V-ThM5, 69
 Oehrlin, G.S.: NM+EM+PS+NS+NC-ThM12, 73; NM+EM+PS+NS+NC-ThM4, 72
 Ogasawara, H.: SS1+NC-ThA10, 87
 Ogeltree, D.F.: SS+AS+NC-FrM1, 90
 Ogletree, D.F.: NS+NC-WeA12, 59
 Oh, D.: GR+SS+NC-MoA5, 11
 Oh, S.J.: TF-MoA9, 16
 Oh, Y.-J.: BO+NS+BI+NC-ThA7, 79
 O'Hagan, D.: NS+NC-ThM4, 74
 Ohmann, R.: GR+SS+NC-MoA7, 11
 Ojifinni, R.A.: SS1+NC-TuA2, 35
 Ong, J.C.: MN+NC-MoA5, 12
 O'Patchen, J.L.: TF+NC-MoM4, 6
 Opila, R.L.: MS+NC-MoM9, 3
 Orihuela, B.: BO+AS+BI-WeA2, 53
 Orlando, T.M.: GR+SS+NC-MoA5, 11
 Osgood, R.M.: GR+EM+NC-TuM5, 19; SS1+NC-WeM3, 47
 O'Shea, J.N.: SS1+NC-ThA3, 86
 O'Sullivan, B.: BO+NS+BI+NC-ThA10, 80
 Outlaw, R.A.: GR+TF+NC-MoM3, 1; GR+TF+NC-MoM7, 1
 Ouyang, J.: EN+EM+NS+P+A+T+V-ThM4, 68
 Ow, S.Y.: BO+NS+BI+NC-ThA10, 80
 Ozkumur, E.: BM+BI+BO+NC-TuA5, 27
- P —
- Palma, M.: BO+NS+BI+NC-ThA1, 78
 Palmer, J.S.: SS1-ThM3, 75
 Pancotti, A.: SS+NC-MoM1, 4
 Papaefthimiou, V.: BO+AS+BI+NC-WeM2, 40
 Papastavrou, G.: BI+NC-TuA5, 25
 Pappas, D.P.: MI+NC-TuA5, 32
 Paraschiv, V.: PS-TuM2, 21
 Pargon, E.: PS1-WeA10, 61; PS1-WeA3, 60; PS-TuM9, 22
 Parikh, A.N.: BI+NC-ThM1, 65
 Parilla, P.A.: EN+AS+EM+TF-WeM1, 41
 Park, J.B.: NS+NC-FrM10, 89; SS1+NC-ThA7, 87
 Park, J.H.: IS+NC-ThA11, 81
 Park, J.-W.: NS+NC-TuA8, 34
 Park, K.: BM+BI+BO+NC-TuA1, 27
 Park, S.D.: NS+NC-FrM10, 89
 Park, S.Y.: GR+EM+NC-TuM12, 20
 Park, T.Y.: TF-MoA10, 17
 Parker, T.: SE+TF+NC-ThA10, 85
 Parkinson, G.S.: SS+AS+NC-FrM2, 90
 Parpia, J.M.: MN+NC-MoA7, 13
 Parsons, G.N.: TF+NC-MoM5, 6; TF+NC-MoM9, 6; TF-MoA9, 16; TF-TuA8, 37
 Passemard, G.: MS+NC-MoM7, 3
 Passian, A.: TR+MN+NC-WeM10, 51
 Patole, S.N.: NS+NC-ThM4, 74
 Patterson, M.C.: SS2+NC-WeM4, 49
- Patton, S.T.: TR+MN+NC-WeM2, 50
 Patzig, C.: SE+TF+NC-ThA11, 86
 Pawin, G.: SS2+NC-WeM11, 50
 Pearton, S.J.: BO+EM+BI+NC-ThM1, 66
 Pehrsson, P.E.: NS+NC-TuA2, 33
 Pellin, M.J.: TF+NC-MoM10, 6
 Peng, C.W.: MI+NC-WeM2, 43
 Peng, Q.: TF+NC-MoM5, 6; TF+NC-MoM9, 6
 Penner, R.M.: NM+MS+NS+NC-ThA9, 82
 Pennisi, C.P.: BI+NC-TuA8, 26
 Penso-Blanco, G.: NM+EM+PS+NS+NC-ThM3, 71
 Pereira-Medrano, A.G.: BO+PS+AS+BI+SS-TuA5, 28
 Pérez, R.: NS+NC-TuM11, 21
 Perez-Luna, V.H.: BI+TF+MI+NS+NC-ThA9, 78
 Perrin, F.: NM+EM+PS+NS+NC-ThM11, 72
 Perry, S.S.: TR+NS+EM+NC-WeA4, 63
 Persoons, R.: GR+TF+NC-TuA9, 31
 Petrik, N.G.: SS+NC-MoA10, 15; SS1+NC-ThA1, 86
 Pfefferle, L.: NS+NC-FrM1, 88
 Phaneuf, R.: NM+EM+PS+NS+NC-ThM12, 73
 Phillpot, S.R.: TR+NS+EM+NC-WeA4, 63
 Pilet, N.: SS2+NC-WeM1, 48
 Pillai, S.: BI+NC-TuA3, 25
 Pimpinelli, A.: SS1+NC-WeM1, 47
 Pint, C.: IS+NS+TR+NC-ThM5, 70; SS+NC-MoM2, 4
 Pirolo, K.F.: BI+NC-WeM6, 39
 Plummer, E.W.: MI+NC-WeM5, 43
 Podraza, N.J.: SE+TF+NC-ThA9, 85
 Poelsema, B.: SS1-ThM4, 75
 Poeppelmeier, K.R.: TF-MoA1, 15
 Pohl, K.: BO+EM+BI+NC-ThM12, 68
 Poirier, J.S.: PS1-WeA1, 59
 Polak, M.: NS+NC-FrM4, 88; SS1+NC-TuA10, 36
 Potapenko, D.V.: SS1+NC-WeM3, 47
 Pou, P.: NS+NC-TuM11, 21
 Powell, C.J.: AS-MoA4, 8
 Poxson, D.J.: SE+TF+NC-ThA7, 85
 Pozuelo, M.: IS+NC-ThA11, 81
 Prasad, P.N.: NS+NC-ThA5, 83
 Pratt, Jr., W.P.: MI-WeA9, 57
 Prauzner-Bechcicki, J.: BO+EM+BI+NC-ThM11, 67
 Priyantha, W.: SS+NC-MoM2, 4
 Prodan, C.: BO+AS+BI+NC-WeM6, 41
 Prodan, E.: NM+MS+NS+NC-WeM11, 45
 Prokes, S.M.: SS+NC-MoA1, 14
 Pursel, S.M.: SE+TF+NC-ThA3, 84; SE+TF+NC-ThA9, 85
 Pussi, K.: SS+NC-MoM5, 4
 Putkonen, M.: TF-TuA10, 37
- Q —
- Qiang, Y.: IS+NS+TR-WeA5, 56
 Qin, S.Y.: SS2+NC-WeM6, 49
 Qiu, H.: SS+NC-MoA2, 14
 Quiller, R.G.: SS+NC-MoA9, 14; SS2+NC-WeM5, 49
 Quinlan, R.A.: GR+EM+NC-TuM6, 20; GR+TF+NC-MoM3, 1; GR+TF+NC-TuA3, 31
 Quitariano, N.: NS+NC-TuA4, 34
- R —
- Rabuffetti, F.A.: TF-MoA1, 15
 Rachbauer, R.: SE+NC-WeA5, 62
 Rahman, T.S.: SS1+NC-TuA5, 35
 Rai, V.R.: TF-MoA4, 16
 Raimondo, L.: BO+AS+BI+NC-WeM9, 41
 Räisänen, M.T.: NS+NC-ThM1, 73
 Rajala, M.: TF-TuA10, 37
 Rajh, T.: EN+EM+NS+P+A+T+V-ThM9, 69
 Ramaker, D.E.: EN+BI+SS+SE-TuM6, 18
 Ramesh, R.: SS2+NC-WeM2, 49
 Ramirez, H.: AS-MoA11, 9
 Ranade, A.N.: SE+NC-WeA4, 62
- Rangan, S.: EN+EM+NS+P+A+T+V-ThM10, 69
 RangaPrasad, D.: TR+MN+NC-WeM10, 51
 Rangelow, I.W.: NS+NC-WeA12, 59
 Ratliff, J.S.: SS+NC-MoA11, 15
 Rauf, S.: PS-TuM11, 22
 Rauschenbach, B.: SE+TF+NC-ThA11, 86
 Rauscher, H.: BO+EM+BI+NC-ThM6, 67; BO+NS+BI+NC-ThA11, 80
 Rauter, F.: BO+PS+AS+BI+SS-TuA10, 29
 Reddy, B.: BM+BI+BO+NC-TuA1, 27
 Redwing, J.M.: NS+NC-WeA9, 58
 Register, L.F.: NM+MS+NS+NC-WeM5, 44
 Reimhult, E.: BI+NC-ThM11, 66; BI+NC-TuA5, 25
 Reinke, P.: EN+EM+NS+P+A+T+V-ThM5, 69
 Ren, F.: BO+EM+BI+NC-ThM1, 66
 Reshchikov, M.A.: SS+EM+NC-FrM4, 92
 Richardson, N.V.: NS+NC-ThM4, 74
 Riedl, C.: GR+SS+NC-MoA7, 11
 Riehle, M.O.: BO+AS+BI-WeA12, 54
 Rienzo, A.: SS1+NC-ThA3, 86
 Rinaldi, M.: NM+MS+NS+NC-ThA10, 82
 Riposan, A.: SS+EM+NC-FrM8, 93
 Ritala, M.: TF-TuA9, 37
 Rittschof, D.: BO+AS+BI-WeA2, 53
 Riviere, J.P.: SE+NC-WeA1, 61
 Roberts, A.J.: AS-MoA9, 8
 Robinson, J.T.: GR+TF+NC-TuA5, 31
 Rochat, N.: NM+EM+PS+NS+NC-ThM11, 72
 Rockett, A.: EN+EM+NS+PS-TuA10, 31
 Rodriguez, J.A.: EN+BI+SS+SE-TuM12, 19; SS1+NC-ThA7, 87
 Rogers, J.: NM+EM+PS+NS+NC-ThM1, 71
 Roh, Y.: NS+NC-ThA10, 84
 Roldan Cuenya, B.: SS1+NC-TuA11, 36
 Rooks, M.J.: MN+NC-MoA4, 12
 Roos, M.: BO+AS+BI+NC-WeM5, 40
 Rooth, M.: GR+TF+NC-MoM3, 1
 Roper, C.S.: MN+NC-MoA3, 12
 Rosei, F.: NS+NC-FrM3, 88
 Ross, C.A.: MI-WeA3, 57
 Ross, F.M.: IS+NC-ThA7, 81
 Ross, R.: EN+EM+NS+P+A+T+V-ThM3, 68
 Rossi, F.: BI+TF+MI+NS+NC-ThA5, 77; BO+EM+BI+NC-ThM6, 67; BO+NS+BI+NC-ThA11, 80; BO+NS+BI+NC-ThA5, 79; BO+NS+BI+NC-ThA9, 79; BO+PS+AS+BI+SS-TuA11, 29; NM+EM+PS+NS+NC-ThM5, 72
 Rossmel, J.: SS+NC-MoM10, 5
 Rossnagel, S.M.: MN+NC-MoA4, 12
 Rosso, K.M.: SS+AS+NC-FrM3, 90
 Rowan, S.: BM+BI+BO+NC-TuA12, 28
 Rowe, J.E.: GR+SS+NC-MoA1, 10
 Roy, S.: BM+BI+BO+NC-TuA10, 28
 Rubino, S.: GR+EM+NC-TuM6, 20
 Rubinovich, L.: NS+NC-FrM4, 88; SS1+NC-TuA10, 36
 Rubio-Zuazo, J.: SY+SS+BI-TuM11, 23
 Ruchala, M.: SS+EM+NC-FrM4, 92
 Ruden, A.: SE+NC-WeA9, 62
 Rudzinski, P.: NS+NC-ThM2, 73
 Ruemmele, J.A.: BI+TF+MI+NS+NC-ThA4, 77
 Ruggieri, F.: NM+MS+NS+NC-ThA10, 82
 Ruiz, A.: BO+NS+BI+NC-ThA11, 80; NM+EM+PS+NS+NC-ThM5, 72
 Ruiz, R.: NS+NC-ThA1, 83
 Rustum, Y.: BO+AS+BI-WeA11, 54
 Rutledge, J.: TR+MN+NC-WeM5, 51
 Rutter, G.M.: GR+SS+NC-MoA8, 11; SS+EM+NC-FrM10, 93
 Ryan, A.J.: BI+NC-TuA10, 26
 Ryu, S.H.: EN+EM+NS+PS-TuA3, 30
- S —
- Sable, J.: BO+NS+BI+NC-ThA1, 78
 Sailer, R.A.: SE+NC-WeA11, 63
 Saka, H.: IS+NS+TR-WeA10, 56

- Sakamoto, K.: NS+NC-FrM3, 88
 Salim, M.: BO+NS+BI+NC-ThA10, **80**;
 BO+PS+AS+BI+SS-TuA5, 28
 Salmeron, M.: SS+AS+NC-FrM1, 90; SS+NC-
 MoM9, 5; SS1+NC-ThA10, 87; SS1+NC-
 ThA9, 87
 Salmon, N.: IS+NS+TR+NC-ThM10, 71
 Samitier, J.: NM+EM+PS+NS+NC-ThM5, 72
 Sampath, W.S.: EN+AS+TF+VT+NC-WeA1, **55**
 Samuelson, L.: NM+MS+NS+NC-ThA7, **82**
 Samukawa, S.: PS1-WeA11, 61
 Sandell, A.: SS+AS+NC-FrM8, **91**
 Sanders, L.M.: IS+NS+TR-WeA8, 56
 Sandin, A.: GR+SS+NC-MoA1, **10**
 Sani, B.: BI+NC-ThM1, 65
 Santucci, S.: NM+MS+NS+NC-ThA10, 82
 Sanyal, B.: GR+EM+NC-TuM6, 20; GR+TF+NC-
 MoM3, 1; GR+TF+NC-TuA3, 31
 Saquing, C.: TF+NC-MoM9, 6
 Sardar, R.: NS+NC-TuA8, 34
 Sardella, E.: NS+NC-ThM10, **74**
 Sarov, Y.: NS+NC-WeA12, 59
 Sasakawa, K.: TF-TuA12, 38
 Sasaki, K.: PS1-WeA8, 60
 Sasaki, M.: PS-TuM10, 22
 Sassella, A.: BO+AS+BI+NC-WeM9, 41
 Sathiyarayanan, R.: SS1+NC-WeM1, 47
 Sato, Y.: SS+NC-MoM5, 4
 Sawkar-Mathur, M.: AS-MoA10, **9**
 Sawyer, W.G.: TR+NS+EM+NC-WeA4, 63
 Saxer, S.: BO+NS+BI+NC-ThA8, **79**
 Scarel, G.: TF+NC-MoM5, **6**
 Scarpa, G.: NM+EM+PS+NS+NC-ThM3, 71
 Schall, J.D.: TR+NS+EM+NC-WeA8, 64
 Schauer, S.: AS-MoA11, 9
 Schilp, S.: BO+AS+BI+NC-WeM1, 40
 Schirmeisen, A.: TR+NS+EM+NC-WeA3, 63
 Schmeißer, D.: IS+NS+TR-WeA2, 56
 Schmid, A.K.: SS+NC-MoM5, 4
 Schmidt, D.: SE+TF+NC-ThA8, 85
 Schmidt, R.: BO+AS+BI-WeA1, 53
 Schmidt, U.: NS+NC-WeM12, 46
 Schnadt, J.: SS1+NC-ThA3, **86**
 Schubert, E.B.: SE+TF+NC-ThA8, **85**
 Schubert, E.F.: SE+TF+NC-ThA7, 85
 Schubert, M.F.: SE+TF+NC-ThA7, 85
 Schubert, M.M.: SE+TF+NC-ThA8, 85
 Schuler, M.: NS+NC-ThM4, 74
 Schulte, K.: SS1+NC-ThA3, 86
 Schultz, P.: NM+MS+NS+NC-ThA1, 81
 Schulz, D.L.: SE+NC-WeA11, 63
 Schwartzman, M.: BO+NS+BI+NC-ThA1, **78**
 Schwarz, A.: MI+NC-TuA3, 32
 Schwarz, U.D.: SS2+NC-WeM1, 48
 Scott, F.J.: EN+BI+SS+SE-TuM6, 18
 Seal, S.: NS+NC-TuA12, 34
 Sears, J.A.: IS+NS+TR-WeA1, 55
 Sears, L.E.: SS+EM+NC-FrM8, **93**
 Sebba, D.S.: BI+TF+MI+NS+NC-ThA10, 78
 Seebauer, E.G.: MS+NC-MoM2, 3
 Seghete, D.: TF+NC-MoM3, **5**; TF+NC-MoM4, 6
 Selegard, L.: BO+EM+BI+NC-ThM5, **67**;
 MI+NC-WeM11, 44
 Senanayake, S.D.: SS+NC-MoA11, 15
 Sequeda, F.: SE+NC-WeA9, 62
 Seththapun, W.: EN+BI+SS+SE-TuM1, 18; TF-
 MoA1, 15
 Severson, M.: EN+EM+NS+P+A+T+V-ThM6, 69
 Seyller, Th.: GR+EM+NC-TuM1, 19
 Shahjahan, M.: EN+AS+TF+VT+NC-WeA5, 55;
 EN+EM+NS+P+A+T+V-ThM11, 69
 Shamiryan, D.: PS-TuM2, **21**
 Shang, H.: BI+NC-WeM4, 39
 Shanmuganathan, K.: BM+BI+BO+NC-TuA12, 38
 Sharma, A.: IS+NS+TR-WeA5, 56
 Sharma, N.: GR+SS+NC-MoA2, 10; GR+SS+NC-
 MoA5, **11**
 Sharma, R.: IS+NS+TR+NC-ThM3, **70**
 Shaw, B.A.: SE+TF+NC-ThA3, 84
 Sheehan, P.E.: GR+TF+NC-TuA5, **31**; NS+NC-
 ThA9, 83
 Sheetz, M.P.: BO+NS+BI+NC-ThA1, 78
 Shen, C.: NS+NC-ThA3, **83**
 Shen, J.: MI+NC-WeM5, 43
 Shen, M.: SS1+NC-WeM5, 47
 Shenai, D.V.: TF-MoA7, 16; TF-TuA3, 37; TF-
 TuA5, 37
 Shenderova, O.: SE+NC-WeA11, 63
 Sheng, J.: EN+EM+NS+PS-TuA4, 30
 Sherwood, P.M.A.: AS-MoA5, **8**
 Shih, C.K.: SS2+NC-WeM6, 49
 Shinkai, S.: NS+NC-ThA11, 84
 Shir, D.: NM+EM+PS+NS+NC-ThM1, **71**
 Shiu, H.-W.: GR+TF+NC-TuA12, 32
 Shiu, S.-C.: EN+EM+NS+P+A+T+V-ThM1, 68
 Shivaparan, N.R.: SS+NC-MoM2, 4
 Shumaker-Parry, J.S.: BI+TF+MI+NS+NC-ThA3,
77; NS+NC-TuA8, 34
 Sibener, S.J.: EN+EM+NS+P+A+T+V-ThM9, 69
 Siebentritt, S.: EN+EM+NS+PS-TuA8, **30**
 Signor, A.W.: SS+NC-MoM4, **4**
 Silien, C.: NS+NC-ThM1, **73**
 Simpkins, B.S.: NS+NC-TuA2, 33
 Singh, A.: NS+NC-WeA11, **59**
 Singh, G.: BI+NC-TuA3, **25**
 Singh, J.P.: NS+NC-FrM9, 89; SE+TF+NC-
 ThA11, 86
 Singh, V.: NS+NC-FrM9, 89
 Sinner, E.-K.: BI+SS+NC-MoA5, 9; BI+SS+NC-
 MoA7, **10**
 Sinnott, S.B.: TR+NS+EM+NC-WeA4, **63**
 Sirard, S.: PS1-WeA2, 60
 Sirdeshmukh, R.: MN+NC-MoA4, 12
 Sirghi, L.: BO+EM+BI+NC-ThM6, 67;
 BO+NS+BI+NC-ThA11, **80**
 Sjøvall, P.: BO+AS+BI-WeA10, **54**
 Sjøvall, P.: BI+NC-ThM4, 65; BO+AS+BI-
 WeA12, 54
 Skeldal, S.: BI+NC-TuA8, 26
 Skuza, J.R.: BI+TF+MI+NS+NC-ThA7, 77
 Slocik, J.: TR+MN+NC-WeM2, 50
 Smet, J.: GR+SS+NC-MoA7, 11
 Smith, A.M.: BI+NC-ThM1, 65
 Smith, D.R.: BI+TF+MI+NS+NC-ThA10, 78
 Smith, R.J.: SS+NC-MoM2, 4
 Smith, R.S.: SS+AS+NC-FrM2, 90; SS+AS+NC-
 FrM5, 90; SS1+NC-ThA1, 86
 Snow, E.S.: GR+TF+NC-TuA5, 31
 So, E.: TR+NS+EM+NC-WeA11, 64
 Soderlind, F.: MI+NC-WeM11, 44
 Söderlind, F.: BO+EM+BI+NC-ThM5, 67
 Soinen, P.: TF-TuA10, 37
 Soles, C.L.: NM+EM+PS+NS+NC-ThM4, 72
 Sologubenko, A.: GR+TF+NC-MoM5, 1
 Somorjai, G.A.: SS+NC-MoM9, 5
 Song, T.: SS+EM+NC-FrM7, 92
 Song, Y.J.: SS+EM+NC-FrM10, **93**
 Sonkusale, S.: NS+NC-WeA5, 58
 Soukiassian, P.G.: GR+EM+NC-TuM2, 19;
 SS+EM+NC-FrM1, **92**
 Spagnola, J.C.: TF+NC-MoM5, 6; TF+NC-MoM9,
 6
 Spanos, G.: MI-WeA8, 57
 Spatz, J.P.: BO+NS+BI+NC-ThA3, 79
 Sperling, B.: TF-TuA11, 38
 Spontak, R.J.: TF+NC-MoM9, 6
 Sprinkle, M.: GR+EM+NC-TuM2, **19**;
 GR+SS+NC-MoA2, 10; GR+SS+NC-MoA5,
 11
 Sprunger, P.T.: SS2+NC-WeM4, 49
 Spycher, P.: BI+NC-TuA5, 25
 Stacchiola, D.J.: SS1+NC-ThA7, **87**
 Stach, E.A.: IS+NS+TR+NC-ThM5, **70**
 Stafford, C.M.: NM+EM+PS+NS+NC-ThM4, 72
 Stafford, L.: PS1-WeA1, **59**; PS1-WeA2, 60
 Stafström, S.: SE+NC-WeA10, 62
 Stair, P.C.: EN+BI+SS+SE-TuM1, 18; TF-MoA1,
 15
 Starke, U.: GR+SS+NC-MoA7, **11**
 Starr, D.E.: SS+NC-MoM11, 5; SS1+NC-ThA10,
 87
 Stavale, F.: SS1+NC-WeM12, **48**
 Steele, J.J.: SE+TF+NC-ThA4, 84
 Steinem, C.: BI+NC-ThM9, **66**
 Steitz, R.: BO+AS+BI+NC-WeM2, **40**
 Stevens, K.: TR+NS+EM+NC-WeA9, 64
 Stoilov, V.: TR+NS+EM+NC-WeA12, 64
 Stokes, D.J.: EN+AS+TF+VT+NC-WeA4, **55**
 Stokes, G.Y.: NS+NC-ThM3, 73
 Stolbov, S.: SS1+NC-TuA5, 35
 Storts, D.: BI+NC-TuA9, 26
 Stout, P.J.: PS-TuM11, 22
 Striccoli, M.: NS+NC-ThM10, 74
 Strobel, S.: NM+EM+PS+NS+NC-ThM3, **71**
 Stroschio, J.A.: GR+SS+NC-MoA8, 11;
 SS+EM+NC-FrM10, 93
 Stuve, E.M.: SS1+NC-ThA4, 86
 Styer, A.L.: BI+NC-TuA12, 26
 Su, J.F.: TR+NS+EM+NC-WeA12, **64**
 Su, J.-J.: NM+MS+NS+NC-WeM5, 44
 Sugimoto, Y.: NS+NC-TuM11, 21
 Sullivan, S.P.: BI+NC-TuA12, 26; BI+NC-TuA4,
25
 Sun, D.: SS2+NC-WeM11, 50
 Sun, X.Y.: TF+NC-MoM9, 6
 Surpi, A.: GR+TF+NC-TuA3, 31
 Sutherland, D.: BI+NC-ThM5, **65**
 Suu, K.: MN+NC-MoA9, 13
 Suzer, S.: AS-MoA3, **8**
 Svedhem, S.: BI+NC-ThM4, **65**; BO+AS+BI-
 WeA10, 54; SS+AS+NC-FrM9, 91
 Swaminathan, P.: SS1-ThM3, **75**
 Swartzentruber, B.S.: SS1+NC-WeM10, **48**
 Sykes, E.C.H.: EN+BI+SS+SE-TuM11, 18;
 NS+NC-TuA9, 34; NS+NC-WeA10, **59**;
 NS+NC-WeM4, 45; SS1+NC-TuA9, 36
 Szymonski, M.: BO+EM+BI+NC-ThM11, **67**
 — **T** —
 Tabari, A.M.: BI+NC-ThM11, 66
 Tachibana, M.: GR+TF+NC-MoM11, 2;
 GR+TF+NC-MoM4, 1
 Tadisina, Z.R.: MI+NC-TuA12, 33
 Tak, Y.: NS+NC-TuA5, **34**
 Takada, N.: PS1-WeA8, 60
 Takahashi, H.: BM+BI+BO+NC-TuA3, 27
 Takahashi, T.: EN+AS+TF+VT+NC-WeA5, **55**;
 EN+EM+NS+P+A+T+V-ThM11, 69
 Takei, H.: BO+NS+BI+NC-ThA2, **78**
 Takeuchi, H.: TF-TuA12, 38
 Takeuchi, M.: NS+NC-ThA11, 84
 Takeuchi, W.: GR+TF+NC-MoM8, **2**
 Tallarico, D.A.: SS+NC-MoM1, 4
 Tan, S.: BI+SS+NC-MoA8, 10
 Tanaïke, O.: GR+TF+NC-MoM4, 1
 Tanaka, H.: NS+NC-ThA11, **84**
 Tang, F.: SE+TF+NC-ThA10, **85**
 Taniguchi, M.: NS+NC-WeM3, 45
 Tao, F.: SS+NC-MoM9, **5**
 Taschuk, M.T.: SE+TF+NC-ThA4, **84**
 Taylor, M.: BO+PS+AS+BI+SS-TuA1, 28
 Tedesco, J.L.: GR+SS+NC-MoA1, 10
 Tegenfeldt, J.: BI+NC-WeM11, 40
 Teki, R.: EN+AS+EM+TF-WeM11, 42
 Tekiel, A.: BO+EM+BI+NC-ThM11, 67
 Tempez, A.: EN+AS+EM+TF-WeM3, 42
 Templier, C.: SE+NC-WeA1, 61
 Tenent, R.C.: NS+NC-FrM8, **89**; NS+NC-WeA4,
 58
 Tepavcevic, S.: EN+EM+NS+P+A+T+V-ThM9,
 69

- Teplyakov, A.V.: BI+NC-TuA4, 25;
 BO+EM+BI+NC-ThM9, 67
 Terfort, A.: BO+AS+BI+NC-WeM1, 40
 Terlinden, N.M.: TF-MoA11, 17
 Teter, M.A.: SS+NC-MoM2, 4
 Textor, M.: BI+NC-ThM11, 66; BI+NC-TuA5, 25;
 BO+NS+BI+NC-ThA8, 79
 Thallapally, P.K.: EN+AS+TF+VT+NC-WeA3, 55
 Theilacker, W.M.: BI+NC-TuA12, 26
 Theisen, J.P.: EN+EM+NS+P+A+T+V-ThM10, 69
 Theodore, D.: AS-MoA11, 9
 Thevuthasan, S.: IS+NS+TR+NC-ThM10, 71
 Thiel, P.A.: SS+NC-MoM3, 4; SS+NC-MoM5, 4;
 SS1+NC-WeM5, 47
 Thomas, H.: BO+AS+BI+NC-WeM1, 40
 Thomas, J.C.: SS+EM+NC-FrM6, 92
 Thompson, P.E.: MI-WeA8, 57
 Thornton, K.: EN+AS+EM+TF-WeM4, 42
 Thürmer, K.: SS1+NC-ThA5, 86
 Thundat, T.G.: TR+MN+NC-WeM10, 51
 Tierney, H.L.: EN+BI+SS+SE-TuM11, 18;
 NS+NC-TuA9, 34; NS+NC-WeA10, 59;
 SS1+NC-TuA9, 36
 Ting, Y.H.: BO+PS+AS+BI+SS-TuA8, 29; PS1-
 WeA12, 61
 Tokuda, Y.: GR+TF+NC-MoM8, 2
 Tolba, M.: NS+NC-WeA11, 59
 Tomanek, D.: BO+EM+BI+NC-ThM12, 68
 Toney, M.: AS-MoA10, 9
 Tornow, M.: NM+EM+PS+NS+NC-ThM3, 71
 Torres, J.: MS+NC-MoM7, 3
 Tosatti, S.: BO+NS+BI+NC-ThA8, 79
 Tratnyek, P.G.: IS+NS+TR-WeA5, 56
 Trigwell, S.: NS+NC-WeM11, 46
 Trinkle, D.R.: SS+NC-MoM4, 4
 Tsai, K.-H.: EN+EM+NS+P+A+T+V-ThM1, 68
 Tsai, S.J.: NS+NC-FrM11, 89
 Tskipuri, L.: SS2+NC-WeM10, 50
 Tuccitto, N.: EN+AS+EM+TF-WeM3, 42
 Turchanin, A.: GR+TF+NC-MoM5, 1
 Turkot, R.: PS-TuM5, 22
 Turley, R.: NS+NC-WeM9, 46
 Turner, H.C.: TF-MoA8, 16
 Twiss, J.L.: BI+NC-TuA12, 26
 Tyler, D.: BM+BI+BO+NC-TuA12, 28
— U —
 Unal, B.: SS+NC-MoM3, 4; SS+NC-MoM5, 4
 Unlu, M.S.: BM+BI+BO+NC-TuA5, 27
 Urgen, M.: SE+NC-WeA8, 62
 Urquhart, A.J.: BO+PS+AS+BI+SS-TuA1, 28
 Uvdal, K.: BO+EM+BI+NC-ThM5, 67; MI+NC-
 WeM11, 44
 Uvdal, P.: SS+AS+NC-FrM8, 91; SS1+NC-ThA8,
 87
— V —
 Vahlberg, C.: BO+EM+BI+NC-ThM5, 67
 Vallett, A.L.: NS+NC-WeA9, 58
 Vallier, L.: PS-TuM9, 22
 Valsesia, A.: BI+TF+MI+NS+NC-ThA5, 77;
 BO+NS+BI+NC-ThA5, 79; BO+NS+BI+NC-
 ThA9, 79; BO+PS+AS+BI+SS-TuA11, 29;
 NM+EM+PS+NS+NC-ThM5, 72
 Valtiner, M.: SS+AS+NC-FrM10, 91
 Van De Keere, I.: SS+AS+NC-FrM9, 91
 van de Sanden, M.C.M.: EN+EM+NS+PS-TuA1,
 30; TF-MoA11, 17; TF-MoA2, 15
 Van Delden, J.: MN+NC-MoA5, 12
 Van der Ven, A.: SS+EM+NC-FrM6, 92
 Van Dorp, W.F.: SS1-ThM11, 76; SS1-ThM12, 76
 Van Haesendonck, C.: GR+TF+NC-TuA9, 31
 Van Keuren, E.: EN+EM+NS+P+A+T+V-ThM3,
 68
 Van Roey, F.: MS+NC-MoM1, 2
 van 't Erve, O.M.J.: MI-WeA8, 57
 Van Tendeloo, G.: GR+TF+NC-TuA9, 31
 Vandervelde, T.E.: EN+EM+NS+PS-TuA4, 30
 Vandervorst, A.: MS+NC-MoM1, 2
 Vanfleet, R.: NS+NC-WeM9, 46
 Vanhulsel, A.: GR+TF+NC-TuA9, 31
 VanMil, B.L.: GR+SS+NC-MoA3, 10
 VanVorouss, D.: SE+NC-WeA12, 63
 Vasudevan, S.: BI+NC-WeM3, 39
 Vaughn, J.M.: IS+NS+TR+NC-ThM2, 70
 Veer, W.V.: NM+MS+NS+NC-ThA9, 82
 Vegh, J.J.: NM+EM+PS+NS+NC-ThM12, 73
 Verbridge, S.S.: MN+NC-MoA7, 13
 Vereecken, J.: SS+AS+NC-FrM9, 91
 Vermande, E.: NM+EM+PS+NS+NC-ThM11, 72
 Veyan, J.-F.: GR+TF+NC-TuA8, 31; MN+NC-
 MoA10, 13
 Vijayaraghavan, S.: EN+AS+EM+TF-WeM3, 42
 Villani, M.L.: NM+EM+PS+NS+NC-ThM11, 72
 Virojanadara, C.: GR+SS+NC-MoA7, 11
 Vitale, S.A.: PS-TuM1, 21
 Vitali, L.: GR+SS+NC-MoA7, 11
 Vitchev, R.G.: GR+TF+NC-TuA9, 31
 Vlahovic, B.: NS+NC-WeM10, 46
 Vlastakis, B.: TR+MN+NC-WeM5, 51
 Voevodin, A.A.: NS+NC-TuA11, 34; SE+NC-
 WeA3, 62; TR+MN+NC-WeM2, 50
 Vogel, E.M.: GR+EM+NC-TuM12, 20; TF-TuA1,
 36
 von Bergmann, K.: MI+NC-TuA8, 33
 von Klitzing, K.: GR+SS+NC-MoA7, 11
 Voorhees, P.W.: EN+AS+EM+TF-WeM4, 42
 Vorburger, T.: MS+NC-MoM11, 3
 Vrancken, C.: MS+NC-MoM1, 2
— W —
 Wahl, K.J.: BO+AS+BI-WeA2, 53;
 TR+NS+EM+NC-WeA11, 64
 Waite, A.R.: SE+NC-WeA3, 62
 Walczak, K.: BI+NC-WeM3, 39
 Walker, A.V.: BO+AS+BI-WeA9, 54
 Walker, M.: TR+MN+NC-WeM1, 50
 Wallace, D.J.: EN+EM+NS+P+A+T+V-ThM6, 69
 Wallace, J.: SE+NC-WeA12, 63
 Wallace, R.M.: GR+EM+NC-TuM12, 20;
 SS+EM+NC-FrM9, 93; TF-TuA1, 36
 Walle, L.E.: SS+AS+NC-FrM8, 91
 Walock, M.J.: MI+NC-WeM12, 44; MI+NC-
 WeM6, 43
 Walsh, M.A.: NS+NC-ThM3, 73
 Walt, D.R.: BI+NC-WeM12, 40
 Walton, S.G.: NM+EM+PS+NS+NC-ThM4, 72
 Wang, B.Y.: MI+NC-WeM2, 43
 Wang, C.M.: IS+NS+TR+NC-ThM10, 71;
 IS+NS+TR-WeA5, 56
 Wang, G.-C.: SE+TF+NC-ThA10, 85
 Wang, H.: GR+TF+NC-MoM1, 1; MS+NC-
 MoM8, 3
 Wang, H.T.: BO+EM+BI+NC-ThM1, 66
 Wang, J.J.: TF-TuA5, 37
 Wang, P.: BO+AS+BI+NC-WeM11, 41
 Wang, Q.H.: NS+NC-WeM5, 45
 Wang, Q.M.: TF-MoA7, 16
 Wang, S.: GR+EM+NC-TuM5, 19
 Wang, Y.: AS-MoA5, 8; SS+NC-MoA2, 14
 Wang, Y.L.: BO+EM+BI+NC-ThM1, 66
 Wang, Z.: GR+SS+NC-MoA1, 10; NS+NC-FrM6,
 88
 Ward, T.Z.: MI+NC-WeM5, 43
 Watt, F.: GR+TF+NC-TuA12, 32
 Watts, J.F.: AS-MoA1, 8
 Weaver, J.F.: SS+AS+NC-FrM11, 91
 Weaver, J.H.: SS+NC-MoM4, 4; SS1-ThM1, 75;
 SS1-ThM3, 75
 Weder, C.: BM+BI+BO+NC-TuA12, 28
 Wee, A.T.S.: GR+TF+NC-TuA12, 32
 Wehner, S.: IS+NS+TR-WeA2, 56
 Wei, D.: PS1-WeA2, 60
 Wei, D.H.: MI+NC-WeM2, 43
 Wei, Z.: GR+TF+NC-TuA5, 31
 Weidner, T.: BO+EM+BI+NC-ThM10, 67
 Weilnboeck, F.: NM+EM+PS+NS+NC-ThM12, 73
 Weis, C.: SS1+NC-ThA9, 87
 Weis, P.: NS+NC-ThM9, 74
 Weishaupt, K.: NS+NC-WeM12, 46
 Wendt, A.E.: BO+PS+AS+BI+SS-TuA8, 29; PS1-
 WeA12, 61
 Wendt, S.: SS+AS+NC-FrM7, 91
 West, K.: MI+NC-WeM1, 42
 Whitman, L.J.: NS+NC-ThA9, 83
 Whitney, E.: EN+AS+EM+TF-WeM1, 41
 Whitty, A.: BI+TF+MI+NS+NC-ThA4, 77
 Widenkvist, E.: GR+EM+NC-TuM6, 20;
 GR+TF+NC-MoM3, 1
 Widenqvist, E.: GR+TF+NC-TuA3, 31
 Wiesendanger, R.: MI+NC-TuA3, 32
 Williams, R.S.: NS+NC-TuM1, 20
 Willis, D.E.: BI+NC-TuA12, 26
 Willis, R.F.: GR+EM+NC-TuM1, 19
 Willson, G.: NM+EM+PS+NS+NC-ThM12, 73
 Wilson, J.R.: EN+AS+EM+TF-WeM4, 42
 Wind, S.J.: BO+NS+BI+NC-ThA1, 78
 Winkler, T.: BO+AS+BI+NC-WeM1, 40
 Witte, G.: NS+NC-FrM6, 88
 Wnuk, J.D.: SS1-ThM10, 76; SS1-ThM11, 76;
 SS1-ThM12, 76
 Woell, C.: SS+NC-MoA2, 14
 Wolf, S.A.: MI+NC-WeM1, 42;
 NM+MS+NS+NC-ThA5, 82
 Wöll, Ch.: NS+NC-FrM6, 88
 Won, Y.D.: TF-MoA10, 17
 Wong, E.: NS+NC-WeA1, 58
 Wong, S.S.: MI+NC-WeM2, 43
 Woo, R.L.: NS+NC-FrM5, 88
 Wormeester, H.: SS1-ThM4, 75
 Wright, P.C.: BO+NS+BI+NC-ThA10, 80;
 BO+PS+AS+BI+SS-TuA5, 28
 Wright, V.A.: NS+NC-TuA4, 34
 Wroble, A.T.: EN+EM+NS+P+A+T+V-ThM6, 69
 Wu, H.H.: SS+NC-MoM4, 4
 Wu, M.H.: NS+NC-WeM10, 46
 Wu, W.: NS+NC-ThA4, 83
 Wu, Y.: GR+TF+NC-MoM1, 1
— X —
 Xu, Q.: IS+NS+TR-WeA8, 56
 Xu, Y.: NS+NC-WeM11, 46
 Xue, J.: EN+EM+NS+P+A+T+V-ThM4, 68
— Y —
 Yagisawa, T.: PS-TuM3, 22
 Yakimova, R.: BO+EM+BI+NC-ThM5, 67
 Yakshinskiy, B.: SS1-ThM12, 76
 Yalcin, A.: BM+BI+BO+NC-TuA5, 27
 Yamada, T.: NS+NC-ThM5, 74
 Yamamoto, S.: SS1+NC-ThA10, 87
 Yan, T.: SS1+NC-TuA2, 35
 Yan, X.-M.: MN+NC-MoA10, 13
 Yang, C.: EN+EM+NS+PS-TuA3, 30
 Yang, F.: MI+NC-WeM4, 43
 Yang, J.C.: IS+NS+TR+NC-ThM11, 71
 Yang, K.: BI+TF+MI+NS+NC-ThA7, 77
 Yang, T.: BO+EM+BI+NC-ThM12, 68
 Yang, Z.G.: IS+NS+TR+NC-ThM10, 71
 Yanina, S.V.: SS+AS+NC-FrM3, 90
 Yarmoff, J.A.: SS1-ThM2, 75
 Yasuda, K.: BO+NS+BI+NC-ThA2, 78
 Yasuno, S.: TF-TuA12, 38
 Yatsuda, K.: PS1-WeA9, 60
 Yellen, B.B.: BI+NC-TuA11, 26
 Yeom, G.Y.: NS+NC-FrM10, 89
 Yin, L.F.: MI+NC-WeM5, 43
 Yokota, Y.: NS+NC-ThM5, 74
 Yong, K.: NS+NC-TuA5, 34
 Yoo, W.J.: EN+EM+NS+PS-TuA3, 30
 Yoon, B.: TF+NC-MoM3, 5; TF+NC-MoM4, 6
 Yoon, Y.K.: MN+NC-MoA8, 13; NS+NC-ThA5,
 83
 Yoshida, K.: BI+NC-TuA8, 26

- Yoshimura, H.: GR+TF+NC-MoM11, **2**;
GR+TF+NC-MoM4, **1**
- Yuan, L.: MI+NC-TuA5, **32**
- Yudasaka, M.: EN+BI+SS+SE-TuM3, **18**
- Yun, Y.: SS2+NC-WeM1, **48**
- **Z** —
- Zachar, V.: BI+NC-TuA8, **26**
- Zachary, A.M.: EN+EM+NS+P+A+T+V-ThM6,
69
- Zakharov, A.: GR+SS+NC-MoA7, **11**
- Zakharov, D.N.: IS+NS+TR+NC-ThM5, **70**
- Zaki, N.: SS1+NC-WeM3, **47**
- Zalkind, S.: SS1-ThM12, **76**
- Zaluzec, N.J.: IS+NC-ThA1, **80**
- Zauscher, S.: BI+NC-TuA11, **26**
- Zhang, A.P.: NS+NC-ThA5, **83**
- Zhang, C.: BI+NC-ThM6, **65**
- Zhang, L.: SY+SS+BI-TuM12, **24**
- Zhang, S.B.: EN+AS+EM+TF-WeM1, **41**
- Zhang, W.H.: SY+SS+BI-TuM12, **24**
- Zhang, X.: BI+NC-TuA4, **25**;
BI+TF+MI+NS+NC-ThA1, **77**;
BO+EM+BI+NC-ThM9, **67**; GR+TF+NC-
MoM5, **1**
- Zhang, X.F.: IS+NC-ThA11, **81**; IS+NC-ThA9, **81**
- Zhang, Y.W.: SS+NC-MoM9, **5**
- Zhang, Z.: BI+NC-TuA12, **26**; SE+TF+NC-ThA5,
85; SS+NC-MoA7, **14**
- Zhao, K.: BI+NC-TuA9, **26**
- Zhao, W.: SY+SS+BI-TuM12, **24**
- Zhao, Y.: SE+TF+NC-ThA1, **84**; SE+TF+NC-
ThA5, **85**
- Zharnikov, M.: BO+AS+BI+NC-WeM1, **40**;
SY+SS+BI-TuM5, **23**
- Zheng, Y.: EN+EM+NS+P+A+T+V-ThM4, **68**
- Zhitenev, N.: SS+EM+NC-FrM10, **93**
- Zhou, C.: BO+AS+BI-WeA9, **54**
- Zhu, J.F.: EN+EM+NS+P+A+T+V-ThM12, **69**;
SY+SS+BI-TuM12, **24**
- Zhu, M.Y.: GR+TF+NC-MoM7, **1**
- Zhu, X.-Y.: BI+NC-ThM3, **65**; SS2+NC-WeM12,
50
- Zhu, Y.: SS2+NC-WeM11, **50**
- Ziemer, K.S.: MI+NC-WeM4, **43**
- Zillner, E.: EN+EM+NS+P+A+T+V-ThM12, **69**
- Zoican, C.: NS+NC-FrM1, **88**
- Zorman, C.A.: BM+BI+BO+NC-TuA12, **28**
- Zubkov, T.: SS1+NC-ThA1, **86**
- Zuercher, S.: BO+NS+BI+NC-ThA8, **79**